Introduction to Adhesive Bonding

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Contents

Preface

Glues or adhesives are known to everybody as superglue. We all remember that man glued upside down in the TV commercial and we use superglue every day to repair small objects. However, we do not imagine that it is used to make cars or airplanes. The truth is that it is, and increasingly so. It is nowadays a joining technology that rivals other conventional methods such as welding or riveting in transport, civil engineering, electronics, packaging, sport equipment, shoes, etc. Surprisingly, adhesive bonding can give joints stronger than bolted or riveted joints despite the apparently weak polymeric material of the glue. That is due to the more even spreading of the load in an adhesive joint.

This book pretends to demystify the erroneous concepts that common people have about adhesives. It is intended to be a simplified guide on how to design and produce adhesive joints. It is an easy-to-read manual with basic knowledge that allows anyone without a background in this area to understand the adhesion phenomena. The writing is very easy and assumes that the reader can come from any background and level of education.

The book starts with a general introduction explaining the benefits and limitations of the technology and with examples of applications. Chapter 2 is on the theory of adhesion that shows in which conditions a good bond can be formed between an adhesive and a material to join. Surface preparation is an essential step to guarantee adhesion, a step that we all apply carefully at home when we use superglue. The main adhesive families are described next with all the tests available to determine their properties. Then comes the manufacture with all the necessary steps. The use of this technology relies on a proper control, especially using nondestructive techniques. One of the weak points is that it is very difficult to detect weak bonds. Environmental issues are also dealt with as we are manipulating chemical products when we use adhesives. The technology is actually also referred to as chemical joining. The important task of designing a joint is discussed in Chapter 8. This is a complex job, but we tried to make it as easy as possible so that every engineer is not afraid of using this technology. Another drawback of adhesive bonding is the durability and ways to predict how the joint strength will evolve with time. However, there are already several techniques in place to deal with that. Finally, several case studies are presented in Chapter 10 related to the transport industry, electronics, packaging, etc. These case studies are good illustrations on how this technology can effectively be applied to improve products normally manufactured with other methods.

At the end of the book, the reader will be able to produce quality adhesive joints in a simple way, without resorting to complex knowledge. The book is useful for the bonder in an industrial context, a design engineer, or a university student.

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1

Benefits, Limitations, and Applications of Adhesive Bonding

Even before reading this book, you probably might already have a general idea of the advantages and capabilities of adhesive bonding, but to deepen your understanding of the subject it is necessary to first precisely define the most important concepts, benefits, and limitations associated to the use of this technique. This will allow you, as a user of this technology, to understand all the subsequent chapters of this book and eventually be able to make informed decisions regarding the usefulness of adhesive bonding and implement it in practice.

Skeist and Miron (adhesive technology scholars) first stated in 1981 that adhesives are the diplomats and the most social members of the polymer world. No other technique of joining materials is so versatile and their transversality lies in the ability to unite different materials, in their capability of remaining permanently in the assembly, in the fact that adhesives are user friendly and their success is measurable by a reduction in production costs while maintaining adequate mechanical properties. Although adhesives have been used for millennia, no other bonding technique meets current demands so successfully.

If we look around, we can easily identify applications of adhesives in numerous items of our daily life, showing how this joining technology is an important, yet somewhat hidden, tool in the way we shape our world. Adhesives are found in cutting-edge applications in the mobility sector, where materials are increasingly more complex, lighter, and the associated designs are increasingly bold. The demands of civil construction have also boosted the application of adhesives, and, in recent decades, we have increasingly seen their application in multi-material structures, something which would be virtually impossible to build using traditional techniques. Nevertheless, we also observe the application of adhesives in less demanding applications, such as small gadgets and household appliances that facilitate our daily life as well as clothes and shoes. And as we will see, adhesive bonding is also prepared to play an important role in a new world, more concerned with sustainability and ecological aspects. Today we already have adhesives that meet strict structural demands but also can be produced from materials of biological origin and with a very small ecological footprint, and the use of these materials is expected to grow significantly in the short term.

Introduction to Adhesive Bonding, First Edition.
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1.1 Definition of Basic Concepts

To truly understand the complexity and versatility of an adhesive, we must first clearly define and understand its role. Kinloch, in 1987, defined adhesives as a material which, when applied to surfaces of other materials, can join them together and resist separation, a very rational and synthetic definition of the capabilities of this material. It is, however, necessary to understand that not all adhesives have the same behaviour, and, therefore, it is imperative to differentiate between structural and non-structural adhesives. Adams, one of the greatest impellers of the study of adhesives in the second half of the twentieth century, stated that a structural adhesive is an adhesive that can resist substantial loads and that is responsible for the strength and stiffness of the structure. It is expected that this joint will be stable over the lifetime of the structure, i.e. that its properties will not degrade, that the joint design will be well executed, and that all necessary steps leading to a high-quality bonding joint will be undertaken.

However, if one wishes to be truly knowledgeable in this subject, it is necessary to keep a set of additional basic concepts in mind. So, let us name things as real experts. The adhesive is the substance that initially fills the gap between the materials to be bonded, adheres to them, and solidifies. The materials to be bonded are called substrates and, after bonding, the term generally used is adherend. Between the adhesive and the adherend, the interface is formed. The interface is also designated as the boundary layer and can be defined as the plane of contact between the surface of the two materials (see Figure 1.1).

Adhesives work by exploring the adhesion phenomena. We will study this subject in detail in the following (Chapter 2 - Principles of adhesion), but for now we can define adhesion as the attraction between two substances resulting from intermolecular forces established between them. A joint is the set formed by the adhesive, adherends (or possible intermediate layers as primers), and the interface. A primer is a substance that is used to inhibit corrosion and to improve the level of adhesion with the adhesive and the adherend. In an ideal and well-designed joint, the adherend should always be the weakest part, which means that the presence of the bonded joint does not reduce the strength of the structure.

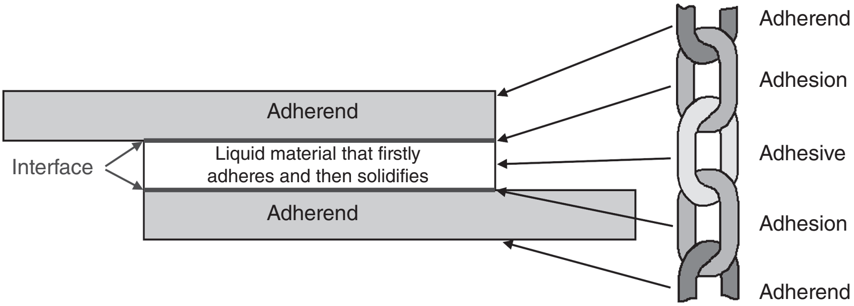


Figure 1.1 Constituents of an adhesive joint.

1.2 Historical Context on Adhesive Bonding

As mentioned before, although the use of adhesives has expanded significantly since the twentieth century, their use actually dates to prehistorical periods. Adhesives extracted from natural sources were used to craft weapons, tools, and decorative objects. Evidence of application of adhesives was found in several excavations, corresponding to quite distinct civilisations (Babylon, Egypt, and the Aztecs), which indicates that the need to join materials was a common necessity for ancient people.

Around 1500 BCE, the Egyptians discovered that tendons, cartilage, and other animal waste could be reused to produce a suitable adhesive for carpentry work. As a testimony to the early historical production of glue and proof of its immense cultural importance, a mural painting was found at the tomb of the vezir Rekhmara in Thebes, which clearly demonstrates men working with this glue. The painting portrays in detail the different aspects of veneer work, including the use of gelatine glue.

The rise of Roman and Greek empires brought about the increased use of adhesives as it was applied in the construction of buildings that are still standing to this day. The art of adhesive boiling was developed further, and the profession of the adhesive cooker was established in Greece at an early stage (and called as Kellopsos). There are several reports in Greek mythology regarding the importance and symbolism given to the adhesives at that time. One of the best-known stories, and with greater emphasis on the strength and weaknesses of adhesives, is the story of Icarus and his father Daedalus using wings built with glued feathers to escape from the Minotaur's maze. Aristotle emphasised in his studies the adhesion properties that can be found in geckos, a very common animal in the Mediterranean. Geckos, like other reptiles, are animals that have the ability to adhere to vertical surfaces.

During this period of history, and due to the geographical proximity to the sea, the techniques for producing adhesives from fish and other animals had become further refined. The Romans were among the first to use beeswax and tar to caulk planking in ships and boats. They extended the range of adhesives in use at that time to include adhesives produced by boiling fish waste. Some of their knowledge has been applied in products used as late as the twentieth century. One example is the application of adhesives extracted from sturgeons in jewellery, where gems were glued to the metal using these adhesives.

However, following the decline of these civilisations and the onset of the Middle Ages, advances in the development of new adhesives halted. Science in general stagnated and the study of adhesives was no exception to this trend. The lifestyle of the populations did not undergo drastic changes until the fifteenth century. Humanity then witnessed a variety of cultural and social revolutions, which would significantly change the course of the study of adhesives, especially during the Renaissance period and the Age of Discovery. At this stage, a widespread use of adhesives in construction work and in the manufacture of furniture emerged, although most applications were still quite conservative in their nature. This period also brought forth some of the first scientific work carried out in this field. Scientists like Galileo Galilei and Isaac Newton were deeply intrigued by adhesives found in nature and attempted to understand how they worked.

Around 1750, the first patent for an adhesive was issued in Britain. This patented adhesive was produced from a fish source, still drawing from centuries-old knowledge. Further patents were then rapidly issued for adhesives derived from natural rubber, animal bones, fish, starch, milk protein or casein. The accelerated development of all these materials was mainly the result of the Industrial Revolution, which triggered technical breakthroughs that saw factories opting for new materials to formulate their adhesives. Cellulose nitrate became the first wood-derived plastic polymer to be synthesised. It was initially used in the manufacture of small items such as ivory billiard balls. Please note that the adhesives created in this era had very limited mechanical strength and were not especially well suited for structural applications. In addition, they were often limited to the geographical availability of some of these raw materials, limiting their globalisation potential.

The first real advances in the drive toward true structural adhesives took place in the late nineteenth century, when the vulcanisation process was patented, and, by 1900, the first adhesives based on synthetic polymers were introduced and quickly became widespread. Creating adhesives from petroleum by-products revolutionised both the versatility and the capabilities of adhesives. Between 1920 and 1940, significant progress was made in this area, but similar to what has been observed to date, structural adhesive applications were still looked upon with some reluctance.

A major revolution in the application and the capabilities of adhesives occurred during the World War II, where new materials were formulated for use in the aeronautical industry. Aircraft and other military equipment were produced at a frenetic pace, and the demands on the components produced reached incomparable requirements. The use of adhesives was expanded to a myriad of structural and non-structural applications, and the rate of creation and manufacture of new adhesives has never slowed down since then. Today, it is unthinkable to conceive our life without using this bonding technology.

1.3 Benefits and Limitations of Adhesive Bonding

You are now aware that the use of adhesive bonding has greatly expanded in the second half of the twentieth century, driven by technological advances in material science and chemistry and gaining popularity due to the important advantages it brings over other well-established joining methods. The most important of these classical joining techniques are based on welding and plastic deformation processes, and to understand why and where adhesives are currently used, we must first discuss a few of the particularities associated with these joining processes.

Let us start by discussing welding, a very efficient and inexpensive technique for joining high-strength metal structures which necessitates the application of large amounts of heat (or energy) to fuse the base and filler materials. It is this heat application that exposes the joined materials to large-temperature gradients, which can change their structure and mechanical properties drastically and severely distort the welded structure. In fact, it is quite difficult to ensure that a welded joint will have strength which is comparable to that of the base material, and furthermore many metallic alloys are simply unsuitable for welding at all. The high temperature also precludes the use of welding in some specific situations, for example in the vicinity of composites or polymers due to the low thermal resistance of these materials. In addition, many welding techniques cannot be used in very limited spaces or for complex geometries and often necessitate additional work to improve the appearance of the welded joint. After welding, the welded joint must be coated by a protective layer (e.g. paint primer or anti-oxidation coating) to avoid corrosion.

Joining via plastic deformation does not require the very high temperatures encountered in welding, as in this case specially designed tools are used to apply large forces that deform metallic sheets and clinch them together in a solid joint. However, the joint geometries that can be created using plastic deformation are quite limited. The large plastic deformations applied to the metal introduce significant stress concentrations on the complete structure, which can lead to early failure. Note that it is also common for plastic deformation techniques to require additional work steps to remove sharp edges that are a by-product of the joining process. Finally, as is the case for the welding technologies, coating with an additional material is often performed to avoid corrosion of the joined materials.

In contrast, adhesive bonding is seen as a more benign joining technique, which does not involve the large temperatures and mechanical loads encountered in welding and plastic deformation joining. This means that adhesive joints allow for more uniform stress distribution. In addition, since this technique relies on an adhesive to establish the connection, it is able to join dissimilar materials, which makes it especially well suited to lightweight, multi-material structures that are now commonly found in vehicle design. Due to the flexibility and excellent damping properties of the adhesive, it is the only joining technique that is capable to bond and ensure the integrity of glass panels (e.g. windshield). Also, it is used in hem-flange to ensure structural integrity and as a waterproof barrier to avoid corrosion.

However, one must never forget the fact that adhesive joining is a relatively new and thus still evolving joining process. New adhesives and bonding technologies are constantly reaching the market and have led to the creation of highly innovative products, with features and capabilities that were unthinkable just a few decades earlier. As an example, we can look into the transportation sector, where designers are always searching for novel joining technologies that enable lightweight construction, essential to meet the challenges posed by the regulatory pressures that demand increased energy efficiency. But the use of adhesives is not limited to transportation industries. Nowadays adhesives are widely used in civil applications, bonding floors and roofs, and in the fixation of structural elements. The flexibility of adhesives absorbs the thermal expansion of the building structures in different seasons, ensuring a durable construction. Even in medicine the use of adhesive is now extensive, where it is used to construct medical devices, used by medical professionals during their interventions, or in products to seal wounds, where bio-adhesives allow for direct contact with human organs. Moreover, adhesives are used in many more applications, joining components in the packaging, electronic, sport, or footwear industries.

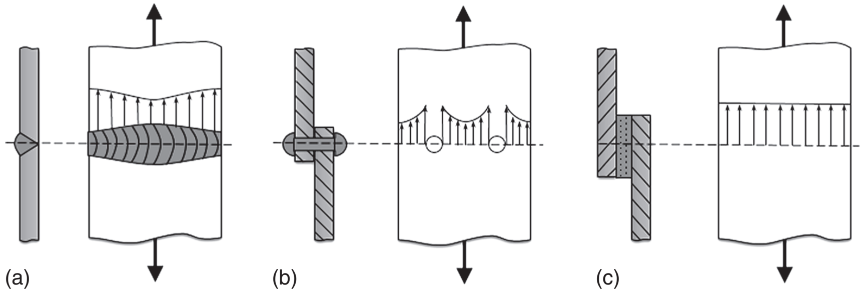


Figure 1.2 Stress distribution as a function of welding (a), riveting (b), and bonding (c) technologies.

Still, please be aware that many in the industrial sector still have some distrust of adhesive bonding, wrongly assuming that this technique cannot provide mechanical performance comparable to other established joining methodologies. This is simply not true as we will repeatedly see in this book.

To summarise, adhesive bonding is a mature, efficient, and unique joining technology that enables the construction of high-performing, highly efficient products. When properly implemented, adhesive joints can:

- Provide a more uniform stress distribution (Figure 1.2);
- Reduce stress concentrations (points which present a high level of stress) as the bond is fully continuous;
- Enable the construction of lighter structures;
- Provide improved fatigue resistance;
- Deliver more flexibility in terms of design and manufacturing processes;
- Allow to join a wide range of materials, including dissimilar materials;
- Be applied over large surfaces, improving the stress distribution and structural stiffness;
- Provide good vibration damping properties;
- Allow for combined joining and sealing properties in one bondline;
- Avoid damaging the fibres in composites with through-holes;
- Ensure no direct contact between the parts to be bonded, avoiding corrosion;
- Provide either electrical/thermal conduction or insulation;
- Be implemented in a fully automated process.

However, some important limitations must be considered when adhesive joints are used, such as:

- The requirement of a careful and suitable selection of surface treatment, especially for polymeric adherends. As we will see, an incorrect surface preparation can have a drastic effect on joint strength;
- Low peel and cleavage strength. Cleavage occurs when load is concentrated at one edge of the joint, while the opposite side remains mostly unstressed. This has the effect of prying the joint open, as if we were inserting a crowbar at the edge of the adhesive layer. Due to this leverage effect, stresses on the adhesive are maximum

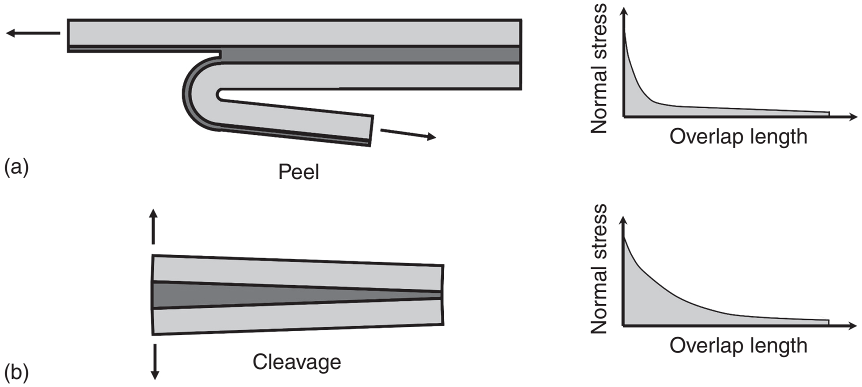


Figure 1.3 (a) Peel and (b) cleavage stresses acting on bonded joints (left) and resultant peel stress distributions (right).

near the area where the cleavage load is being applied and minimal at the opposite end of the joint. It is this concentration of stresses that results in very low cleavage strength. Peel loads are concentrated along a thin line at the edge of the adhesive layer and can only occur where one substrate is flexible.

- The clearest example of the poor peel strength of adhesives is seen in an adhesive tape. If we apply a tape to a flat surface, we will see that it will be very hard to remove if we pull in a direction parallel to the surface. However, should we pull one edge of the tape perpendicular to the surface, we will verify that it is very easy to disbond the tape. In this case, the load we are applying is concentrated just on a very small area. These loading modes are shown schematically in Figure 1.3.
- Limitations with the handling time during manufacturing. This is the time after which the bonded joints can be unclamped and freely moved, as the adhesive has developed enough strength to hold the adherends. In practice, this means that bonded joints are not immediately ready to be handled after manufacturing, which can slow some production processes;
- Special fixture requirements that allow hold together the joined parts during the curing process, also related to the concept of the handling time;
- Difficult disassembly of the bonded parts, which creates challenges both for the repair and the recyclability of bonded parts;
- Low resistance under extreme environmental conditions;
- Wide variation of mechanical properties as a function of environmental conditions exposure.

Due to all these unique characteristics, adhesives are now extensively used in a wide range of industrial sectors, but still it is important to remember that their usage is not only restricted to high-performance structures, such as those in the transportation industry. It is the objective of this chapter to help the reader understand how the use of adhesives has allowed for the growth of new products in these different industries.

1.4 Examples of Current Applications of Adhesive Bonding

1.4.1 Transportation

The constant advances in the highly technological transportation field are usually led by the innovations of road vehicle and aircraft manufacturers. These two industries are the principal promoters behind the development of new manufacturing technologies such as the use of novel high-performance materials (including composite materials) and the practical implementation of highly versatile and high-performance joining technologies. In the last few years, a dramatic reduction of the environmental impact of the transportation industry has been targeted, an effort which necessitates the development of new materials and joining materials. A vehicle, which uses a lightweight construction that employs these techniques, allows for significant weight reduction, decreased energy consumption, and ultimately leads to dramatically reduced emissions. In the following four sections, we will see how adhesive bonding has been adopted by the aeronautical, road transport, and rail industries and the naval industry to achieve these goals.

1.4.1.1 Aeronautical Industry

Before World War II, aircraft were mainly built out of wood, a lightweight, readily available construction material with modest mechanical performance. However, as aircraft performance increased, wood was gradually replaced by aluminium alloys, which was extensively used throughout the second half of the twentieth century. As material science advanced, composites became the new material of choice for these high-performance applications, as they have extremely high specific strength and stiffness, combining low weight with exceptional mechanical performance. However, this transition necessitated the development and adoption of novel joining techniques, as the aluminium structures in aircraft were usually of riveted construction. In the case of composite aircraft, riveting and fastening are problematic and adhesive bonding is preferred. In Figure 1.4, the evolution of the materials used in aircraft construction can be seen. In the last century, aircraft were predominantly built out of metal, but there has been a transition to a structure which is composed of more than 50% of composite materials. And with this dramatic increase in the usage of composite materials, an increase in the use of structural adhesives has also naturally occurred.

The structure of aircraft can be divided into two groups, primary (e.g. fuselage or wings) and secondary (e.g. spoilers or air brakes) structures. The main difference between these two groups is the fact that when a primary structure fails, this will lead to a loss of the aircraft. In contrast, when the secondary structure fails this does not lead to a complete loss and only localised damage occurs. In the first commercial aircraft, the use of composite materials was only possible in secondary structures. However, due to major improvements in manufacturing technologies, new composite materials have been created and are now used in the primary structures of aircraft, supporting the pressurisation loads and the flight cycles (take-off, cruise,

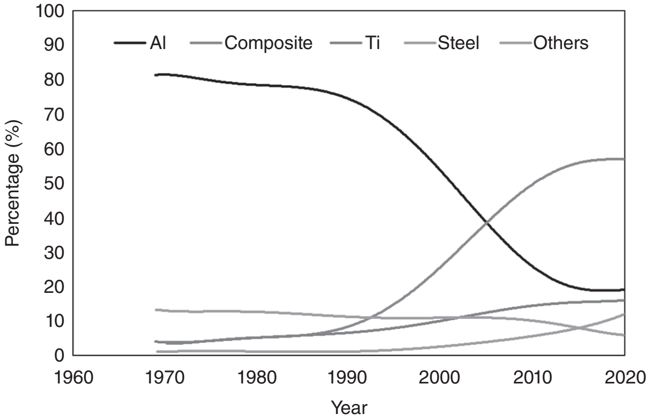


Figure 1.4 Materials used in aircraft construction through the years.

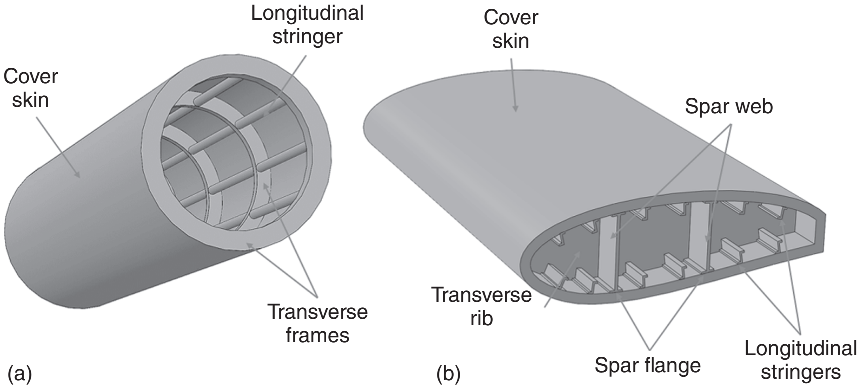


Figure 1.5 An example of a fuselage (a) and wing (b) construction.

and landing loads) and ensuring structural integrity. Adhesive bonding is still mainly used in the secondary structures as the use in primary structures is limited due to the difficulty in detecting weak adhesion using non-destructive tests.

An example of major aircraft structures are the aircraft wings. Here, different adhesive joint configurations can be found, as shown in Figure 1.5. Currently, three different joining techniques are used in aircraft construction (Figure 1.6). These types of joints are mainly used to reinforce the skin of the airplanes, which is achieved by attaching a stringer to a thin sheet of material. In aircraft which use aluminium materials in their construction, riveting is the main joining technology used. However, as stated before, with the increased use of composite materials, adhesive bonding became indispensable to join secondary structures.

In the aeronautical industry, the classical riveting-based joining processes provide a fast inexpensive and effective technique to join materials, with the potential of being easily automated. It is also suitable to join complex dissimilar materials, such as composites and lightweight aluminium alloys. However, riveting requires

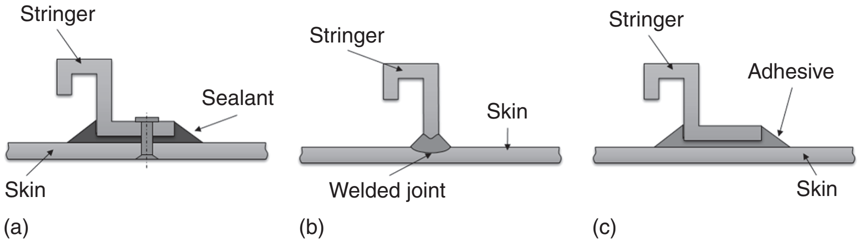


Figure 1.6 Three different joining techniques typically used in aeroplane structures. (riveting (a), welding (b) and adhesive bonding (c)).

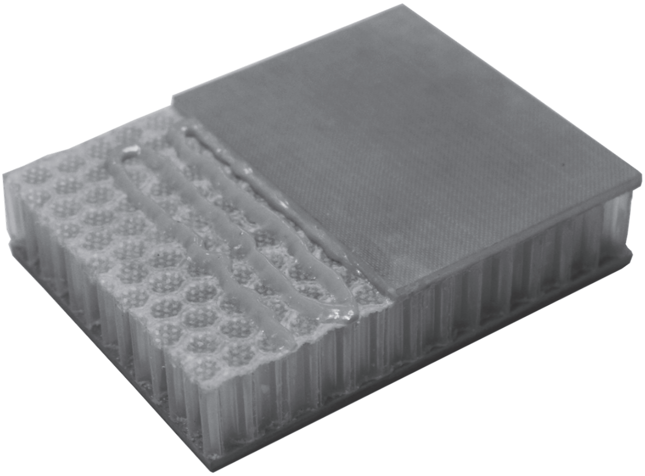
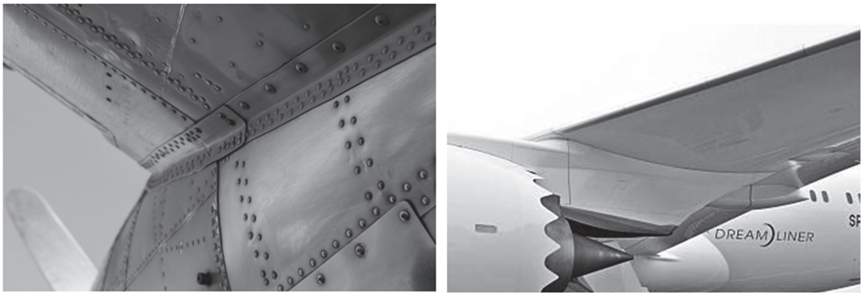


Figure 1.7 A typical sandwich structure used in lightweight composite construction, showing the adhesive used to bond the skin to the core.

drilling many holes, which can be the source of major stress concentrations and require sealants to ensure water tightness. The presence of the exposed rivet heads can also be damaging to the aeronautical qualities of the aircraft, and more expensive flush rivets must be used instead. As a partial alternative, welding is used to join metallic aeronautical components quickly and strongly, although not in the primary flight structures. This is because in these primary structures, many of the lightweight alloys used are in fact very hard to weld. Welding degrades the mechanical properties of the base material, and the large temperatures induced by this process can cause thermally induced distortions in very thin materials typical of structural construction. Thus, adhesive bonding appears as a very powerful alternative for aeronautical applications, allowing to combine dissimilar materials without the introduction of large thermal stresses, free of holes, and other geometrical modifications. It also allows to create innovative materials such as sandwich structures (as shown in Figure 1.7) with a wide range of lightweight core materials and external sheets as well as hybrid laminates, combining metal and composite layers. It also allows to obtain surfaces with good aerodynamic qualities and impermeable to liquids and gases.



(a) (b)

Figure 1.8 Appearance of fuselages constructed using riveting (a) and bonding techniques (b).

However, there are still some limitations in place with the use of adhesives in the aeronautical industry. For example, due to the sensitivity to contamination that this technique has, it is necessary to ensure a clean and inert room during the application of adhesives. There is also a limited understanding by aeronautical designers of adhesive performance in the long term, especially when exposed to service conditions, which include extreme moisture levels and temperature. Lastly, the most important of these limitations for the aeronautical industry is the fact that defects and crack in adhesive joints are very difficult to detect. The available non-destructive testing does not allow to detect certain defects (e.g. weak adhesion), and many regulatory bodies do not allow the use of adhesives in primary flight structures without some sort of additional reinforcement joining method (which can be, for example, rivets).

The performance of aircraft is highly dependent on the aerodynamic efficiency of the fuselage. Figure 1.8 shows the typical appearance of aircraft, which uses mainly riveting and welding techniques in contrast with that of a wing that uses a mainly composite construction. The presence of rivets is quite evident, creating an irregular surface with poor aerodynamic efficiency. In addition, metallic fuselages are also quite susceptible to corrosion and fatigue damage, both of which are potentiated by the holes required by the riveting process. In clear contrast, with a composite construction, the fuselage appearance is visibly much smoother, something which is essential to achieve maximum aerodynamic efficiency. Combined with the low weight of composite materials, this type of construction allows for significant reductions in fuel consumption, which can be up to 25% lower and, consequently, leads to an important reduction of CO_2 emissions.

1.4.1.2 Road Transport and Rail Industry

The reduction of vehicle weight and emissions has been the main goal of the transport industry in the last few decades. The almost exclusive use of steel in transportation structures has now been complemented with the use of lightweight metals (especially aluminium alloys), composites, and polymeric materials. In addition, classical structural joining technologies such as welding or riveting are often replaced or assisted by adhesive bonding technologies. Moreover, given the

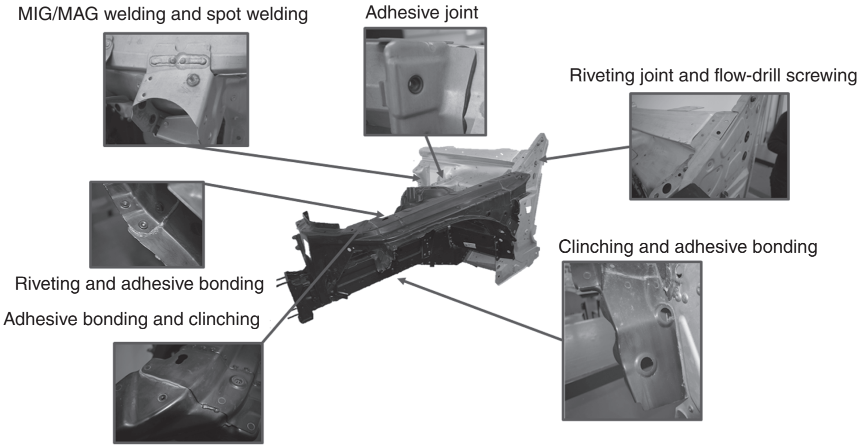


Figure 1.9 Different joining technologies used in some actual body structures.

increased environmental concerns associated with material selection and design, it is now essential to ensure that the end-of-life of vehicle structures has low impact on the environment. This has led to the use of materials with a high level of recyclability and reusability.

Automotive Manufacture The current priority of the automotive industry is to reach major reductions in structural weight, which is only possible with the increased adoption of composite materials. Ultimately, this approach can lead to reductions of up to 70% of the structural weight of the vehicle. If correctly designed, these lighter vehicle structures can have significantly reduced fuel consumption and pollutant emissions, while still ensuring optimal mechanical strength, corrosion, and crash resistance.

The current design trend is to combine different materials in the same structure, such as steel, light metal alloys, composites, or polymers, to create a highly optimised structure. However, this approach necessitates the simultaneous use of many different joining techniques, such as welding, plastic deformation, and bonding (Figure 1.9).

Several welding technologies can be used in a vehicle structure, such as tungsten inert gas (TIG) welding, gas metal arc welding (GMAW), resistance spot welding, laser beam welding, and friction stir welding. Joining techniques based on plastic deformation are also extensively used, such as flow-drill screwing, clinching, grip punch-riveting, semi-hollow punch-riveting, and roller hemming. Often, the roller-hemming procedure is combined with adhesive bonding to avoid corrosion and improve joint appearance and integrity. In this case, besides providing strength to the joint, adhesives act as sealants.

As stated before, there has been also an increase in the use of composite materials in vehicle body structures. A good example of this trend is seen in some electric cars, where the total weight of the body structure is only 150 kg. Two main construction approaches are combined in this structure. The first is the use of lightweight

(a) (b)

Figure 1.10 Two examples of heavyweight public transport ((a) bus and (b) train).

materials to reduce the weight and the second is the use of recycled materials to reduce the ecological footprint. For this type of construction, given the materials being used, the only suitable joining technology is adhesive bonding.

Rail and Bus Manufacture Buses and trains have until recently been exclusively made with steel structures and panels, joined using welding, riveting, and fastening. This has led to heavyweight vehicles with high fuel consumption and with high level of emissions (Figure 1.10). Due to newly imposed environmental regulations and the cost of fuel, combined with the development of new light materials, the materials used in these vehicles have progressively changed to light materials to increase efficiency and decrease the emissions.

Concurrently, there is now an important trend toward the use of electrical propulsion for public transportation, which, due to the weight of the batteries used, is only practical with the extensive use of lightweight materials in the body structure. To reduce the cost of producing these structures, vehicles are constructed in as few steps as possible. For example, the main panels and roof are constructed as individual modules to be integrated in the full structure. To assemble the different parts and elements, which include metals, composite materials, and glass, adhesive bonding is the technology that allows for optimal mechanical performance (good mechanical properties and damping properties) and efficiently join different materials. Adhesives are extensively used to join floor structures, side panels, roof structures, and windows, as can be seen in Figure 1.11.

1.4.1.3 Naval Industry

The ships that are used for fishing and cargo transport are mainly built out of steel components, assembled using welding. The construction of these boats is also modular, divided into smaller subsections that are later joined by welding and fastening in a final assembly step (Figure 1.12). As stated before, when welding is used the high temperature generated causes significant distortion of the pieces to be joined. For

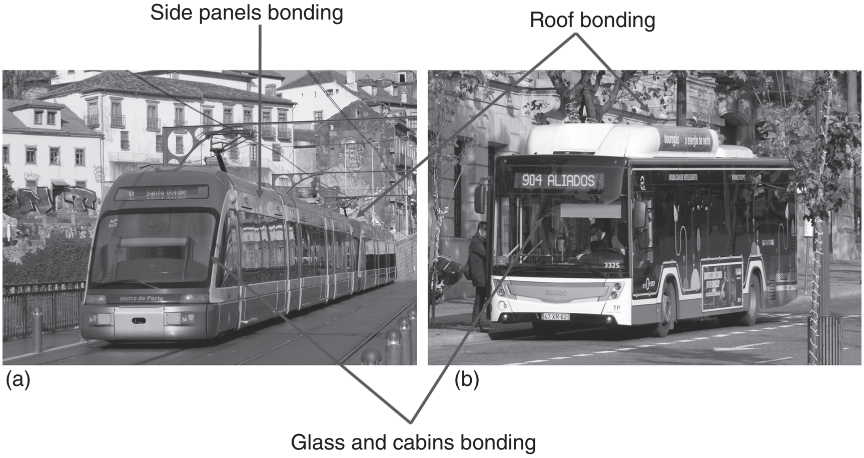


Figure 1.11 Ecological trains (a) and buses (b).

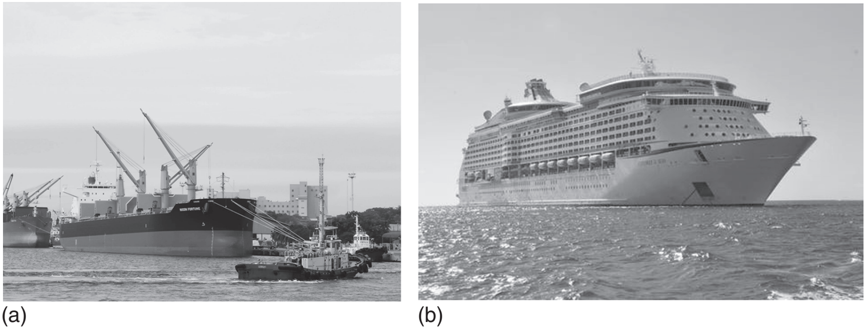
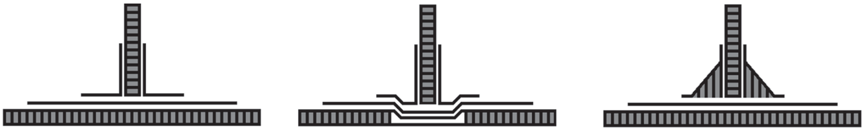


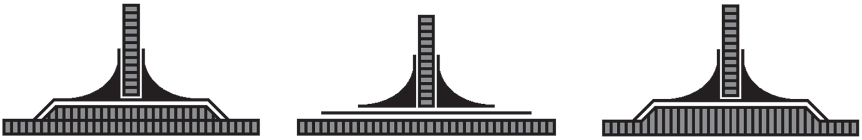
Figure 1.12 Example of large ships (cargo ship (a), cruise ship (b)).

large vessels these distortions are often not critical, but for smaller ships this distortion is usually unacceptable. To improve the quality of construction, performance, and reduce the fuel consumption (and consequent emissions), naval structures generally move away from the metallic construction and opt for a bonded composite construction.

Yachts are an example of a ship where high performance is a crucial design parameter. This type of ship uses complex composite hulls and superstructures, with the aim of attaining maximum performance, while maintaining low weight to minimise fuel consumption. The hull of these ships is typically of a sandwich type of construction, with composite skins and reinforcement bonded by adhesive (Figure 1.13). This construction leads to a structure with high strength and toughness, an aspect which is very important to resist the severe wave motions during storms. Another important property associated to the use of adhesive bonding is the excellent damping and waterproofing characteristics it can confer to the ship structure.



Continuous core in joint Core removed at joint Core with wedge fillet



Core with skin under pad Core with radius fillet Core with skin over pad

Figure 1.13 Example of adhesive joints used in naval industry (honeycomb panel cores shown in light and dark grey).

Regarding the reduction of the ecological footprint, the use of adhesive bonding requires little energy (especially if cured at room temperature) and allows bonding of recycled materials efficiently.

1.4.2 Civil Engineering

Although less visible and publicised, you should be aware that adhesive bonding plays an important role in the building and construction industries, where adhesive materials are found in many different and important applications. The following sections will summarise some of these applications and explain the advantages that the use of adhesive brings to diverse civil engineering applications, such as tiling, floor and wall covering, achoring, facades and wooden construction.

1.4.2.1 Tiling

For tiling purposes, bonding technology using cement-based adhesive mortars (as seen in Figure 1.14) is employed to ensure a flexible and durable bonding. This is a safety critical application, as the bonded joint must ensure integrity under normal utilisation and worst-case scenarios, such as earthquakes. Failure of tiles in tall buildings can be very dangerous, which requires a careful adhesive selection and application process.

1.4.2.2 Floor and Wall Covering

The use of adhesives is one of the most efficient technologies to ensure that walls or floors are waterproof. Adhesive is also used in the construction of wood floors, ensuring the integrity of the wooden parquet. Wallpaper application is also done with adhesives, although in this case high-strength adhesives are not needed.

1.4.2.3 Anchoring Systems

Anchoring systems are perhaps the most demanding application of adhesive bonding in civil engineering applications. Instead of using mechanical fastening to fix

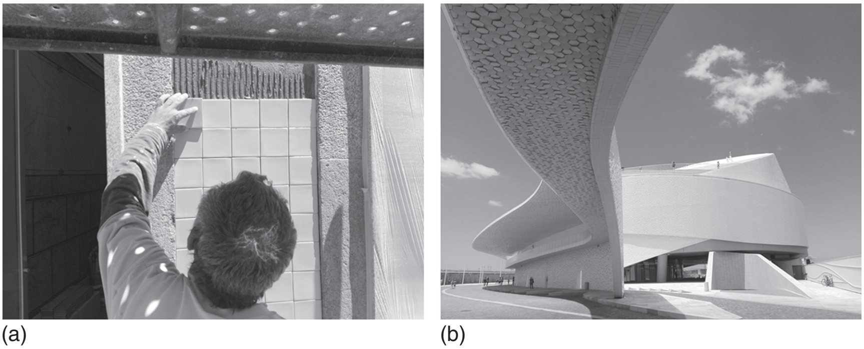


Figure 1.14 Tilling application using cement-based adhesive mortars (a) and example of application of tiles on multiple facades of the Porto Leixões Cruise Terminal (b).

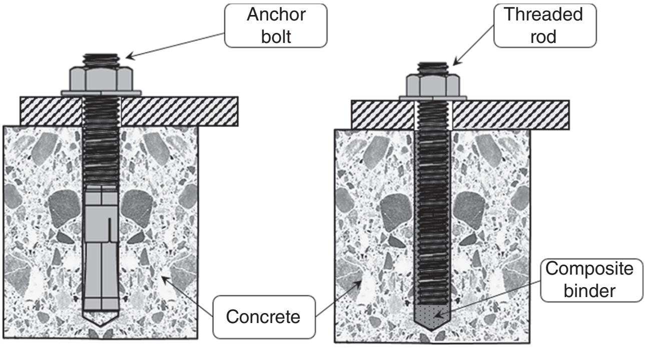


Figure 1.15 Typical anchor systems used in civil engineering applications.

the components (such as threaded rods) to a building structure, adhesive bonding is used (Figure 1.15). The adhesive fills a hole drilled in concrete or the masonry, providing support for a high-strength anchor system via interlocking. It also allows for quick replacement, as the adhesive can be removed if it is subjected to high temperature. When compared to mechanical fastening, this bonding-based technology is vastly superior, as it provides higher strength and is more flexible, not requiring precise drilling of the hole to fit exact threaded rod dimensions.

1.4.2.4 Building Facades

In the last decades, the main materials used in building facades have changed dramatically. Instead of steel, stone, or masonry, which have been historically fixed with riveting, fastening, or assembled with mortar, there is now extensive use of glass facades. The buildings shown in Figure 1.16 are an excellent example of the diversity of materials used in construction today. However, it is hard to join glass safely and effectively, due to the large differences in thermal expansion between the glass and the metal framework which supports it. This difference in thermal expansion can cause large stresses and eventually lead to failure of the glass panes, but it can be almost entirely avoided with the use of flexible and compliant bondlines to support the glass, Figure 1.16. Similarly, the use of solar panels integrated into roofs is

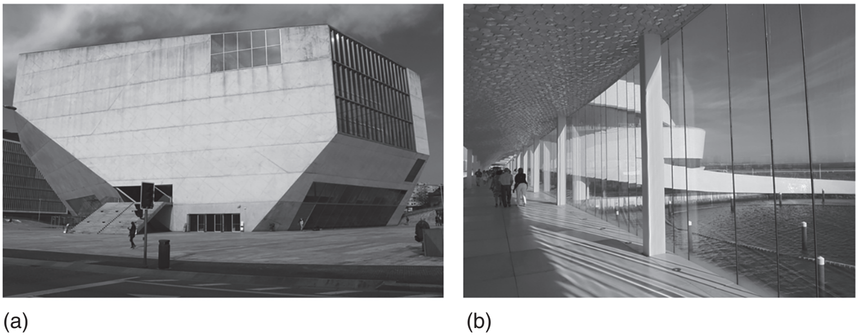

(a) (b)

Figure 1.16 Building facades with adhesive application: (a) application in panels, metallic structures and glass in Casa da Música, concert hall in Porto-Portugal (b) application of adhesives on tiles and glass in Porto Leixões Cruise Terminal.

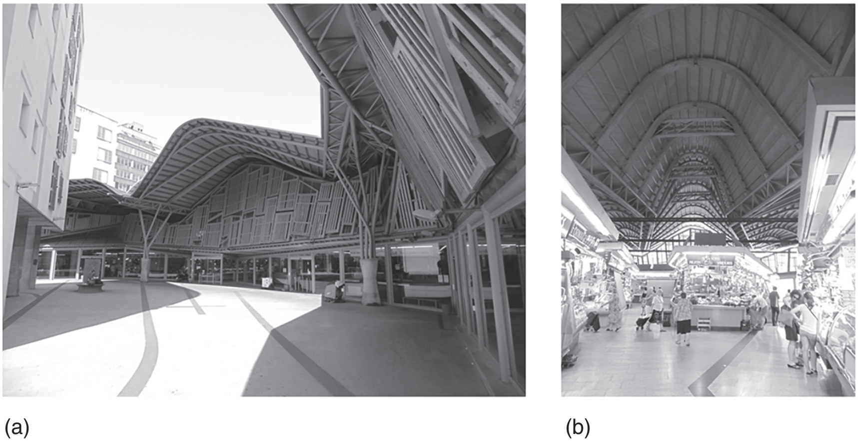

(a) (b)

Figure 1.17 Application of wooden bonded joints in the Santa Caterina market in Barcelona in Spain (a) outside facade and (b) market interior.

only possible with modern adhesive technologies, a further demonstration of how adhesive bonding is a key tool to support the design and construction of sustainable buildings.

1.4.2.5 Wooden Construction

The use of wood in construction has been extensive since the establishment of the first human civilisations, as this is a naturally sourced material, which can easily be obtained and processed. The Santa Caterina market in Barcelona is an excellent example of the application of bonded joints in wood, both outside and inside, as can be seen in Figure 1.17.

There are several methods available to join wood beams and panels, such as fastening and nailing (Figure 1.18). However, these technologies introduce holes in the wood beams, leading to pre-cracks that can promote premature damage. Adhesive bonding is suitable to reduce beam dimensions and consequently the amount of

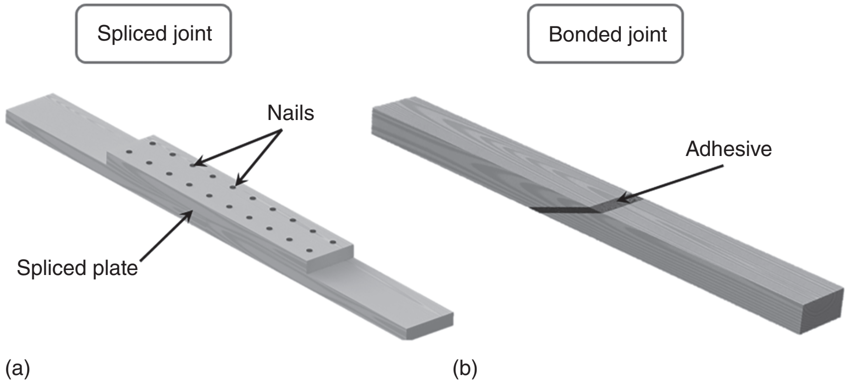


Figure 1.18 Wood beams structures joined by fastening (a) and bonding (b).

wood used, doing so without introducing damage and creating stress distributions that are almost uniform. The amount of material used and weight of the joint can be optimised and reduced while ensuring strength and stiffness that are much higher those than obtained using conventional joining technologies.

1.4.3 Labelling and Packaging Industry

1.4.3.1 Labelling of Consumable Products

The use of labelling is practically ubiquitous in consumer products. Labels are used for attaching barcodes, product identification, and branding tags and warning labels. The first labels used were directly stamped in the product. However, stamping is a technique that only allows to include very limited information, with limited flexibility in the process. Nowadays, the information that must be included in every product is so large, that practically all labelling is done with a paper or polymer label attached to the product with an adhesive. Figure 1.19 shows these two different labelling techniques.

Other types of specific labels were developed to be used as identification systems, for example in automotive licence plates (Figure 1.20) or to be used as security systems for preventing forgeries (for example in wine bottles, passports, and identification documents). The first licence plates used were simply made with polymeric materials in two different colours to ensure visibility. Gradual evolution has led to much more advanced licence plates, which include laminated retroreflecting label tapes to ensure a good visibility in any climatic conditions. This type of security system is only possible with the use of adhesives.

1.4.3.2 Packaging

The packaging industry represents a very large industrial sector that has pioneered many innovative joining techniques. Due to its very large product volumes, any small change in the manufacture process has a huge impact in production costs, and thus this industry is always keen on seeking ways to produce more efficient and cheaper products. The first packages were mainly wooden containers, assembled

Figure 1.19 The evolution of labelling techniques, showing painted labels, moulded shapes, wax seals, and modern adhesive labels.

Figure 1.20 Licence plates with (a) and without (b) retroreflecting tape.

using nails. However, this is a very heavy and expensive solution not compatible with the high volumes and low costs of the modern shipping industry. Modern packaging has mostly veered away from solid wood and employs inexpensive yet very compact and lightweight materials. Perhaps the most successful of these materials is corrugated board, a paper-based product. There is a large variety of corrugated board configurations (shaped as a function of the product to be transported and the travel conditions). Figure 1.21 shows a typical corrugated board construction, where an external paper skin reinforced with a waved core paper sheet is joined with adhesive. The main advantage of this type of material is that it is totally composed of recycled paper and that it can be recycled multiple times.

1.4.4 Medical Applications and Devices

The medical field is a target of intense scientific research, which leads to a constant evolution of the materials being used in medical devices. Due to their inherent advantages, adhesives also play a key role in many healthcare-related products.

Through the years, medical devices have been significantly improved to simplify their use and ensure superior safety. Examples of such medical devices are syringes, catheters, valves, filters, respiratory masks, and endoscopes. Figure 1.22 shows some of the earliest syringe models, which were reusable and made of stainless steel. These

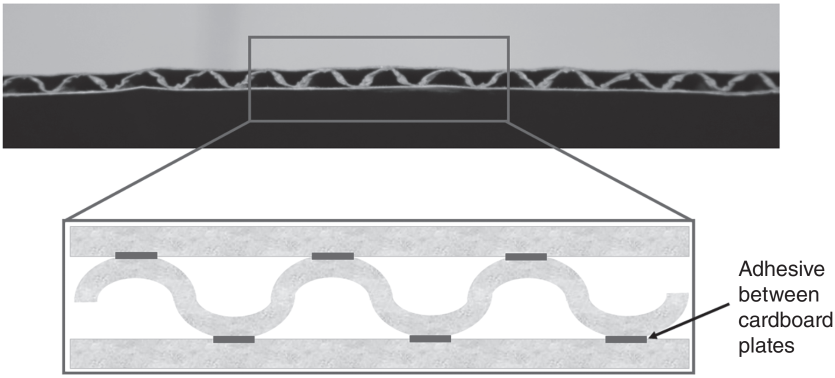


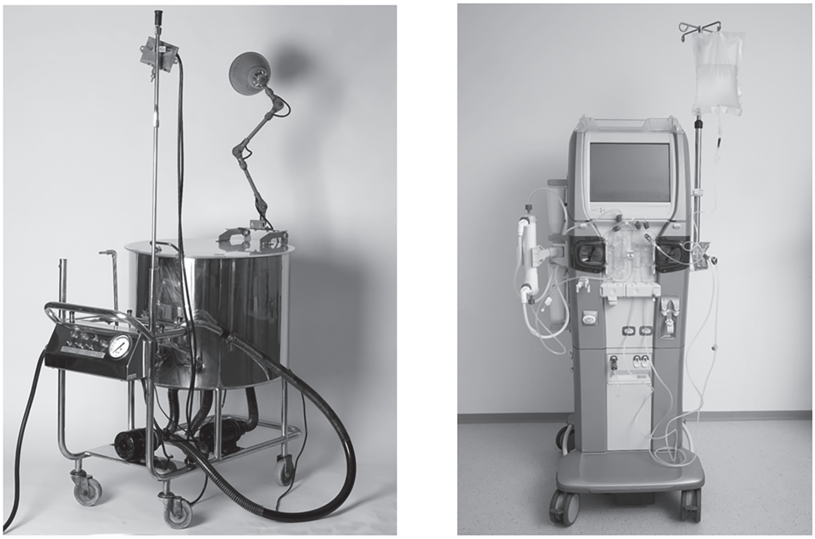
Figure 1.21 Corrugated board.

Figure 1.22 Examples of a few of earliest syringe models. (a) Syringe dated from 1875 to 1900 and (b) syringe dated from 1960 to 1970.

models required sterilisation before use and after many repeated uses often became worn out and developed leaks, creating unsanitary conditions for both the medical professionals and the patients alike. In addition, this basic design does not allow to easily control the amount of liquid inside the syringe or to check if air bubbles are present, which also represents a significant danger for the patient.

Figure 1.23 shows a modern syringe, as currently used in several medical applications. Syringes are now composed of several different components, made of different materials, such as polymers, rubber, and stainless steel. The body of the syringe is now made of a transparent polymer and printed with marks to allow for an easy control of the amount of liquid contained inside. To ensure that leaks do not occur, rubber is used to create a perfect watertight seal. These modern syringes are used only once and are fully recycled after use. The needle, manufactured from stainless steel, is connected to the polymeric body. In the construction of a modern syringe, a consistent and strong bond between these two materials must be ensured. Although

Figure 1.23 A modern syringe design.



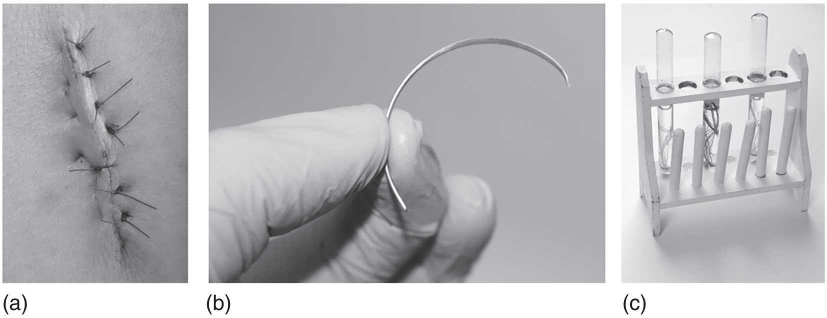
(a) (b)

Figure 1.24 Artificial kidney equipment of 1960s (a) and 2020s (b).

adhesives are not used in this joint, the mechanism of adhesion is explored to ensure a strong and durable connection between the metallic and polymeric parts.

Artificial kidneys or dialysers are equipment used in haemodialysis or renal replacement therapies. Haemodialysis is a method for removing waste products (creatinine and urea), as well as free water from the bloodstream when the kidneys are unable to do so due to pathological causes. Modern dialysers typically consist of a cylindrical rigid casing enclosing hollow fibres, moulded or extruded from a polymeric material. Through the years, the construction of artificial kidneys was optimised, and biomaterial usage was increased, allowing to reduce the dimensions and improve efficiency (Figure 1.24).

For many decades, the default technique for re-joining tissues cut during surgery was to use stitches. However, this technique is strongly dependent on the skill of the medical professional that carries it out. In addition, some scarring due to the stitching remains visible after healing and can only be removed with plastic surgery. This technique ensures the correct position of the two parts to be joined with the tension applied in the line. However, it introduces stress concentrations in the hole created in the tissues, which can lead to failure. In such cases, the patient must return to the hospital to re-stitch the injured part, which can lead to delays in patient recovery and infections. Figure 1.25 shows the stitching technique that is used after surgery



(a) (b) (c)

Figure 1.25 Stitching technique (a), suture needle (b), and threads (c) dated from 1970.

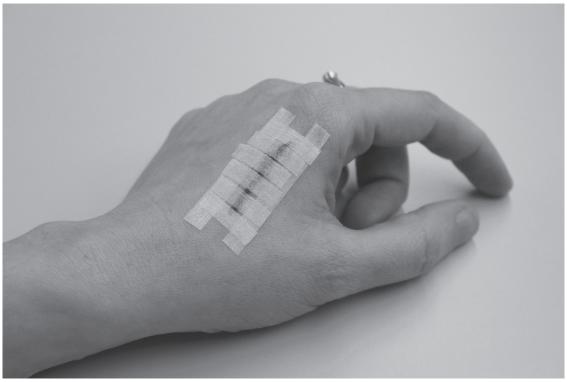


Figure 1.26 Application of an adhesive to join tissues.

and the scarring that remains visible after the tissues heal, which is not acceptable in most cases. In addition, this technique requires the sterilisation of both the wire and needle that are used to avoid infections.

As an alternative to stitching, special adhesives have been developed to join tissues. Using this technique, very little scarring occurs, and the continuously bonded area ensures a well-distributed contact between the joined tissues, drastically reducing the mechanical loads that are transferred to the tissues. The final aspect is not very dependent on the doctor's skill and does not leave any holes. In Figure 1.26, the process of application of an adhesive to join the tissues is shown, evidencing the fact that it not necessary to use any tool on the skin as is the case with stitching.

Some babies are born with defects in the septum of the heart, and their correction implies an invasive surgical intervention. To simplify this method, a team of researchers invented a new method that is much simpler, more effective, and less invasive: the application of an adhesive formed by a new biomaterial. Researchers developed a novel non-toxic adhesive with strong adhesion to the tissue where it is applied and can resist the constant pressure exerted by heartbeats and the presence of blood. It is applied through a small catheter and is quickly activated by light. Figure 1.27 shows an illustration of a defect in the septum of the heart, highlighting how a bio-adhesive can correct the defect. This is an example of a new and much less invasive methodology to correct defects, where adhesives play a key role.

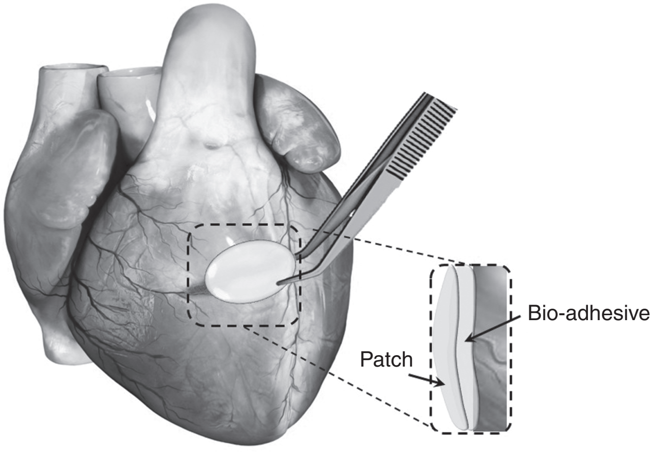


Figure 1.27 The use of bio-adhesive to correct the septum damage of the heart.

In summary, adhesive bonding techniques have been used and developed to create new medical products and techniques that simply would not be possible with traditional joining techniques. In medical applications, the use of the adhesive is growing, being used to simplify the intervention and avoiding the conventional intervention (e.g. organ transplantation), accelerating the healing process.

1.4.5 Electronic Devices

In electronic devices, adhesives are used for attaching and joining of components, allowing to combine many complex parts with different purposes. Electronic devices are constantly evolving to become smaller and more powerful, which is achieved by closely mounting several electronic components without gaps, something only possible with adhesive technology. The adhesives used for this purpose show good thermal conductivity to provide an efficient heat or electrical transfer between the components and high dielectric strength (that is, a high electrically insulating capacity) to avoid undesired current flows or short circuits. The use of adhesive permits greater flexibility in design and allows for a streamlined product assembly process. These are key aspects that have played a role in the development of mobile devices with powerful computational capabilities, improved efficiency while remaining relatively compact (Figure 1.28).

1.4.6 Sport Equipment

The use of adhesives is widespread in many different types of sport equipment, and this is especially true in sports where high performance and efficiency is of the utmost importance, demanding sporting equipment to be built with the lightest materials and manufactured using highly efficient joining techniques. Adhesive bonding again appears as the most suitable technique to join light materials. Sporting equipment is optimised according to the type of use or the

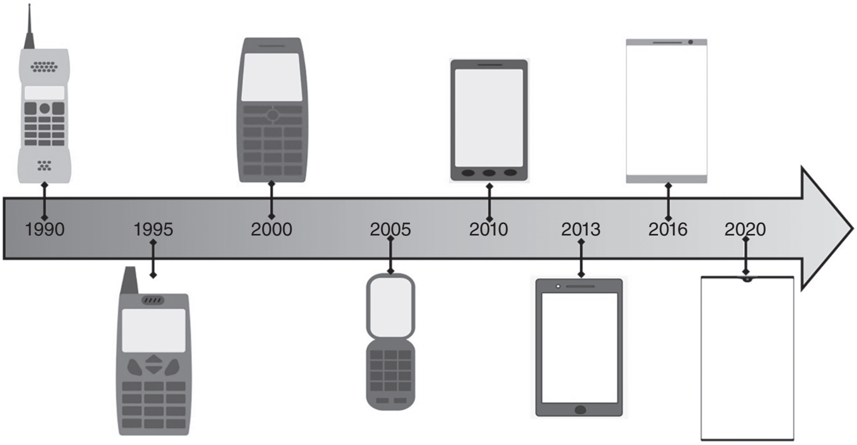


Figure 1.28 Evolution of mobile phones.


(a)
(b)

Figure 1.29 Bicycle evolution, bicycle with metal frame (a) and with composite frame (b).

performance of the athlete who will use the equipment. One good example of a high-performance equipment that is only possible with the use of adhesives is bicycles, where aluminium, titanium, and fibre composites are combined in a single product. Adhesives are used to join these materials with highly dissimilar thermal coefficients leading to strong and stiff joints. In Figure 1.29, a comparison is made between a classic metal framed bicycle and a modern composite framed equivalent.

1.4.7 Footwear

The footwear industry is one the most important sectors of the Portuguese economy, as Portugal is one of three main shoe-manufacturing countries in the world. In the last 20 years, the footwear industry has completely changed from traditional methods of production (almost purely handmade) to much more modern methods of production (becoming almost fully automatized). In the traditional methods, the main materials used were limited to rubber and leather, joined by sewing processes (Figure 1.30). Nowadays, there is a much wider range of materials that are used in the shoe construction, such as textiles or foams, which have led to more comfortable

(a) (b)

Figure 1.30 Shoes manufacturing, (a) sewing technique and (b) bonding technique.

shoe designs. However, these softer, more compliant materials cannot be stitched, as they become easily damaged by the holes, which are essential to the stitching process. For these new materials, only adhesive joining can ensure a strong and durable joint. Adhesives are also used efficiently in more specific applications, such as baby shoes and fireman boots, maintaining the integrity, safety, and strength necessary in these conditions.

2

Principles of Adhesion

In Chapter 1, we have seen that the aim of an adhesive is to create a strong connection between two separate parts, but to do so, an adhesive joint must rely on perfect adhesion between the adhesive and the adherents. We have seen that understanding exactly how and why adhesion exists was for long a mystery to those who first studied bonded connections. However, rest assured that modern science is now able to fully explain the principles behind the process of adhesion. The aim of this chapter is to provide a brief but complete explanation of the theories of adhesion and the main factors influencing it. This is a very important chapter, as through this book, we will see that many of the concepts covered here will serve as the fundamental basis that allows us to understand many different aspects of the adhesive bonding process, from surface preparation to long-term durability.

At a first glance, the bonding process seems quite simple and straightforward. We apply an adhesive, allow it to set, and then it creates a perfect connection between the adhesive and the adherend. However, if this does not occur and incorrect joint preparation is carried out, there is a high likelihood that premature joint failure will occur. However, this ideal situation not only occurs, and an incorrectly prepared joint will often result in premature failure. The adhesion phenomena involved in the bonding process are quite complex and it is important to have at least a basic understanding of mechanisms involved if one wishes to create strong and durable joints.

Starting with a very simplistic view, we suggest you visualise adhesives as bridges between the surfaces of the adherends. There are two essential types of forces involved in this simplified bond. The first is adhesion – the connection force between the adhesive and the adherend. The second is cohesion – the internal strength of the adhesive.

Thus, failure of an adhesive joint can occur in three possible ways, as illustrated in Figure 2.1. These are adhesive failure (failure at the interface), cohesive failure (which can occur in the adhesive or the adherend), and mixed failure, where there is a combination of adhesive and cohesive failure in the same fracture surface.

There are several mechanical tests that can evaluate the behaviour of adhesives and adhesive joints, which will be discussed in greater depth in Chapters 4 and 8.

Introduction to Adhesive Bonding, First Edition.
Eduardo André Sousa Marques, Ana Sofia Queirós Ferreira Barbosa, Ricardo Joao Camilo Carbas, Alireza Akhavan-Safar, and Lucas Filipe Martins da Silva.

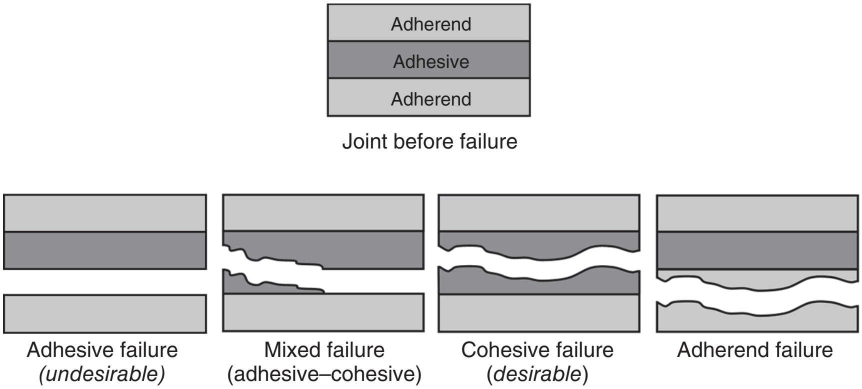


Figure 2.1 Examples of failures that may occur in an adhesive joint.

Although Isaac Newton was mostly known for his studies in mathematics and astronomy, he was an avid observer of nature and made some important contributions to the theory of adhesion. He wrote: ‘There are therefore agents in nature able to make the particles of bodies stick together by very strong attractions. And it is the business of experimental philosophy to find them out’. Newton has realised that there are two fundamental questions to be asked about the phenomenon of adhesion. He inquired about the forces involved in the adhesion and about the internal forces that hold materials together.

To answer Sir Isaac Newton’s questions and to understand in a holistic way how adhesion occurs between the adhesive and the adherend, it is necessary to understand a set of six different factors: the roughness of the surfaces, the wetting of the surface by the adhesive, the phase change of the adhesive, the work of adhesion, the process of spreading the adhesive, and lastly the theoretical framework behind the process of adhesion. We will analyse in detail each of these factors in the following sections of this chapter.

2.1 Forces Associated with Adhesion

Adhesive joints, as is also the case for other conventional joining methods, are able to resist external loads that attempt to separate them. This is achieved because there are several internal forces that allow the joint to remain cohesive (see Figures 2.2 and 2.3). Adhesives adhere to adherends via chemical bonds and the types of forces involved are dependent on the chemical nature of the surfaces of the materials concerned. As shown in Figure 2.3, the strongest of these chemical bonds are very short distance forces, only effective over a few angstroms of distance (10^{-10} m). The dispersive forces, such as the van der Waals forces, can act over longer distances but are very weak.

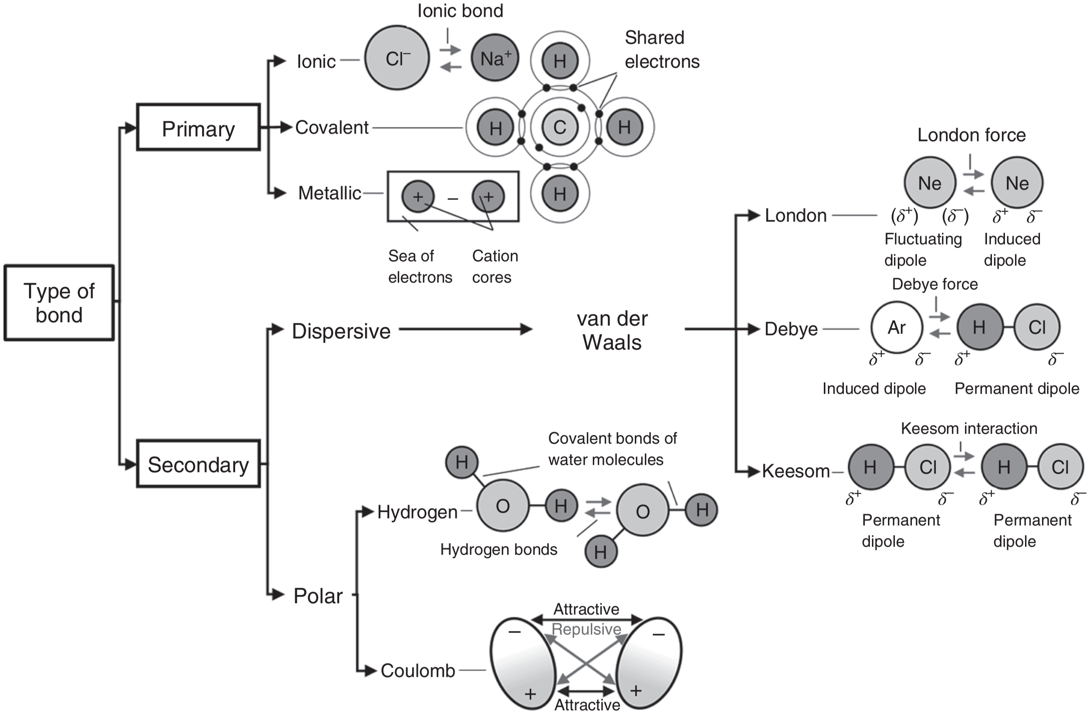
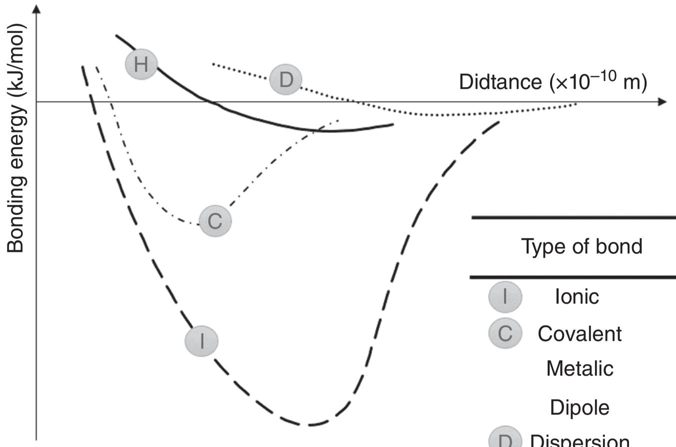


Figure 2.2 Types of bonds that can occur in an adhesive joint.



Type of bond	Bonding energy (kJ/mol)	Bonding distance ($\times 10^{-10}$m)
I Ionic	60–1200	2–4
C Covalent	60–800	1–2
Metalic	100–350	2–6
Dipole	~20	2–4
D Dispersion	~40	4–6
H Hydrogen	~60	~3

Figure 2.3 Comparison of energy and chemical bonding distances.

2.2 Surface Roughness

The roughness of a surface greatly depends on the degree of its preparation. There is no universal optimum value, and consequently, one must adapt the surface preparation to suit the material that will be bonded while also considering the type of adhesive that will be applied.

At this stage, it is important to draw attention to the difference of scale between the roughness and the chemical forces involved. The difference is so large that the roughness profiles are as tall as mountains when compared to the minuscule distances chemical bonds operate on. Even the smallest value of roughness is a thousand times more impactful than the level of action of the bonding forces. Figure 2.4 illustrates this hypothetical case, making it evident that if it were possible to unite two mountains as schematically presented, there would be very few points of contact.

However, how do these two opposite mountains connect? In a first analysis, it is easy to think that the chemical forces could only act on the roughness peaks. However, this is the role that the adhesive must fulfil. If it spreads perfectly on the surface and there is an intimate contact between the whole surface and the adhesive, a good degree of bonding will be possible. This ideal spreading can be obtained if the adhesive is liquid and can flow along the entire rough surface, as depicted in Figure 2.5.

Afterwards, a phase change will occur through a hardening process and the bond between the adherends and the adhesive takes place. Increasing surface roughness influences the wettability and should be well understood to ensure bond quality.

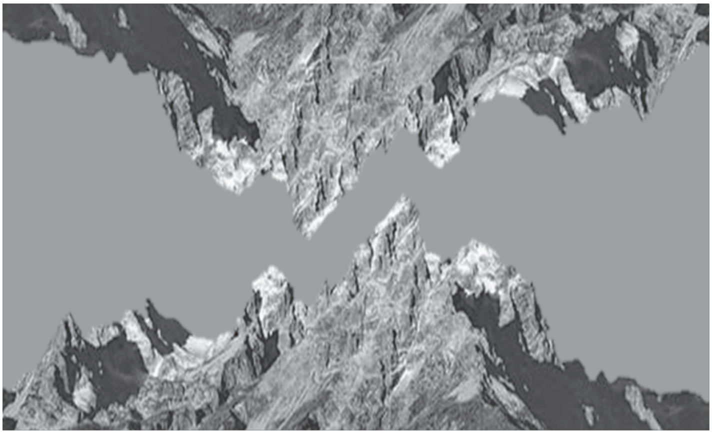


Figure 2.4 Schematic representation of the influence of surface roughness in the direct contact between two surfaces.

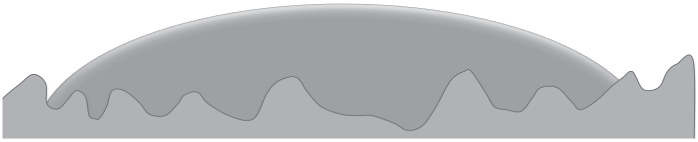


Figure 2.5 Schematic representation of a liquid wetting a rough surface.

The change of surface roughness can be achieved through surface preparation methods, which is one of the most delicate and important operations in joint manufacturing. This topic will be discussed in greater depth in Chapter 3.

However, changing the roughness of a surface might influence the local chemistry. For example, if some superficial layers are removed, this will affect the adsorption properties of the surface. As it will be explained in more detail later in this chapter, adsorption is related to the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. The scale of surface roughness encountered in adhesive joints varies from the macroscopic scale all the way to the nanoscale and a surface roughness measurement looks at the height, depth, and interval of ridges. There is an ideal surface roughness for each type of material represented by the variable R_a. What R_a captures is in fact the average roughness (the arithmetic average value of the degree to which the surface deviates above and below what is considered flat). The larger an R_a number, the rougher the surface. Another way to measure the surface roughness is R_z, which is the maximum height of a surface profile. The different ways of measuring surface roughness are discussed in more detail in Chapter 6.

2.3 Wettability

In an ideal scenario, liquids would be able to fully wet all surfaces, but this is not always true. We can learn this just by observing leaves when they become wet by the effect of dew or rain. Water drops assume the shape of a sphere, instead of forming a uniform film on the surface of the leaves, as shown in Figure 2.6. This phenomenon occurs because the surface is hydrophobic, repelling water molecules.

As we have seen, wetting a solid surface with a liquid is essential for ensuring good adhesion by completely filling the gaps between the surfaces of the adherends.

Figure 2.6 Image of a water drop being repelled by a leaf.

Per definition, wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when both substances are brought together. The degree of wetting (or the wettability) is determined by a balance of forces between the adhesive and cohesive forces. Adhesive forces between a liquid and solid cause a liquid drop to spread across the surface. Cohesive forces within the liquid cause the drop to ball up and reduce its contact with the surface. The contact angle between the liquid drop and the solid surface provides an inverse measure of wettability.

The contact angle and its physical properties of interaction between solids and liquids provide valuable information for determining the optimal adhesion bonding surface wettability conditions. The angle formed by the solid surface and the tangent line to the upper surface at the end point is called the contact angle, corresponding to the angle between the tangent line at the contact point and the horizontal line of the solid surface. These concepts are schematically represented in Figure 2.7.

One of the fundamental concepts associated with wetting is that of surface tension. When the molecules inside a liquid are analysed, it can be observed that the forces of attraction are in equilibrium in all directions. However, the same is not observed at the surface, simply because there are no neighbouring molecules on the outside of the fluid (at the interface with air/vapour). As such, the molecules on the border are exposed to a force that pulls them into the liquid. To bring new molecules to the surface, it is necessary to provide energy to counteract the inertia of molecules that are ‘very comfortable’ in equilibrium inside the liquid (see Figure 2.8). This extra energy is called surface free energy (mJ m^2).

At the beginning of the nineteenth century, an English polymath called Thomas Young was the first to study the phenomenon of wetting, equating the surface tension vectors at the contact point of the three phases: solid, liquid, and vapour, postulating the well-known Young’s equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\,\theta \tag{2.1}$$

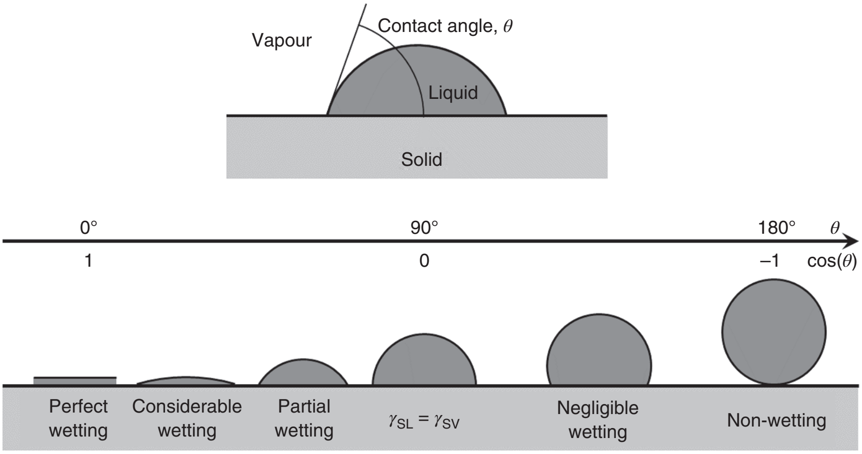


Figure 2.7 Range of possible contact angle between a liquid and a solid and its variations.

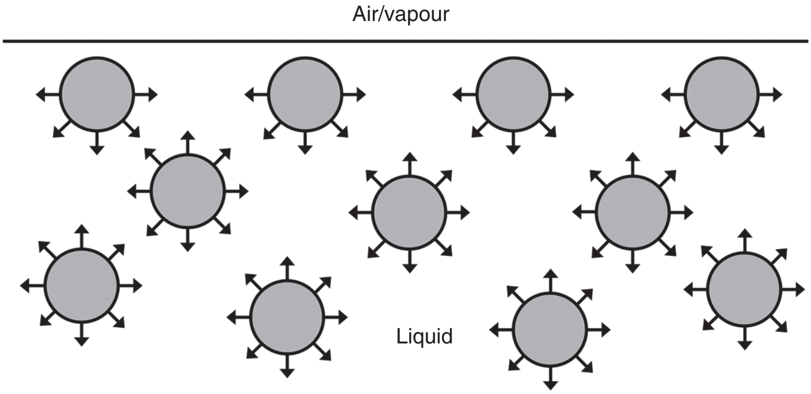


Figure 2.8 The unbalance of attraction forces to the liquid surface gives rise to surface tension and surface energy.

In Eq. (2.1), γ_{LV} corresponds to liquid surface tension in equilibrium with the vapour, γ_{SV} , relates to the surface tension equilibrium between the solid and the vapour, and γ_{SL} is the interfacial tension between the solid and the liquid. Although this equation pioneered the study of wetting, it has little practical interest because the measurement of the surface tension for solids is a very complex issue. Different approaches of assessing the wettability of a surface will be presented in detail in Chapter 6. These include quick and economical techniques such as the use of dyne pens or even water break tests and more elaborate procedures such as measuring the contact angle formed by a drop of calibrated liquids in precise optical equipment.

Surface energy can be defined as the energy required to create an area unit on a surface and different materials have different surface energy values. The higher the surface energy, the higher the wettability and the lower the contact angle. The molecular force of attraction between different materials determines their adhesion. The strength of attraction depends on the surface energy of the substrate. High surface energy means strong molecular attraction, while low surface energy means weaker attractive forces. Liquid adhesives applied in a surface with a high surface energy flow easily and fully wet the surface. Wetting out is necessary to maximise the attractive forces between the adhesive and the surface.

Many adhesives are specifically formulated for use in low surface energy surfaces, but whatever the surface energy of a given substrate may be, the area of attachment must be solid, dry, and clean to maximise adhesive contact.

Surface tension and surface energy are key concepts related to wettability. Thus, before we discuss wettability, it is necessary to clearly define these two concepts. The surface tension of a liquid is defined as the energy needed to create a new liquid–gas interfacial area, i.e. the interfacial tension of a liquid–gas interface. On the other hand, the surface energy is a property of the adherend, i.e. the interfacial tension of a solid–gas interface.

When we walk near a clean river, pond, or lake, we can easily find insects walking on water, for example, the Gerridae, commonly known as water striders. At first glance, it looks like a miraculous walk, contrary to all the laws of physics.

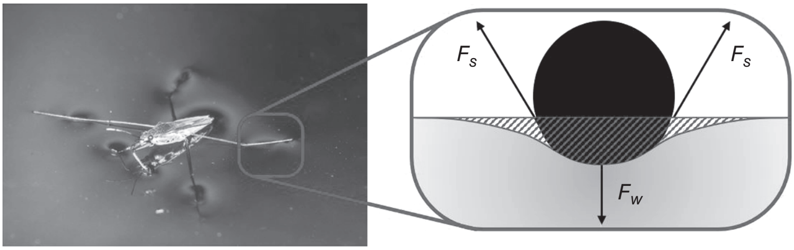


Figure 2.9 Example of forces involved in a body touching the surface of a liquid. F_w, weight of the body; F_s, surface tension.

Nevertheless, there is a very simple explanation (see Figure 2.9). These insects are anatomically built to spread their weight over the water surface and able to move on top of this layer. The higher energy state on the surface of a liquid makes it behave as if it were under tension, that is, as if there was an elastic membrane on the liquid/gas border.

Measuring the surface energy of a liquid is a relatively easy procedure and can be done using a capillarity test, for example. However, when solid surfaces are analysed, the complexity of the analysis increases. The techniques most commonly used for measuring this property on solid surfaces will be discussed in more detail in Chapter 6.

2.4 Adhesion and Cohesion Work

Still during the nineteenth century, Anthanase and Paul Dupré carried out a study of surfaces. They considered the work involved in separating a layer of liquid from a solid surface and as a result were the first to establish the concept of adhesion work (W_a), the difference between the energy of new surfaces created, and the energy of the interface that was destroyed (see Figure 2.10). This theory is represented by Eq. (2.2):

$$W_a = \gamma_S + \gamma_L - \gamma_{\text{SL}} \tag{2.2}$$

There are significant differences between the equations proposed by Young and Dupré. In Young's equation, the solid surface is balanced with vapour, where the

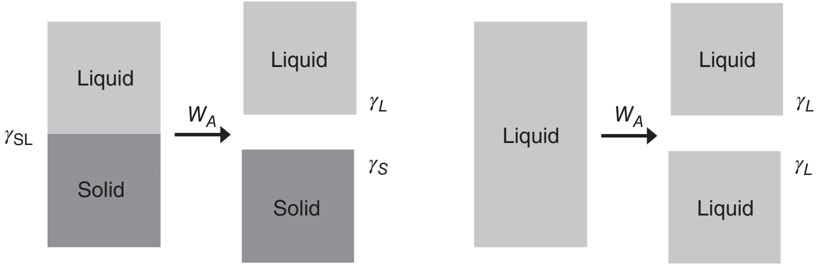


Figure 2.10 Physical representation of the Dupré analysis.

corresponding energy is γ_{SV}. When liquid separation occurs, only one solid surface is considered, so the energy is γ_S. When analysing the liquid, there are also changes in Dupré's equation as γ_L does not vary with the environment.

The surface energy of a solid covered by a layer of adsorbed steam is less than a surface in the vacuum. The difference is known as the spreading pressure, π.

Thus, it is possible to combine the two previously proposed equations to obtain a more reliable and accurate mathematical equation (see Eq. (2.3)):

$$W_A = \gamma_{\mathrm{LV}}(1 + \cos\,\theta) + \pi \tag{2.3}$$

In this way, it is possible to combine the two previously proposed equations and therefore represent more precisely and accurately the case of a drop of liquid adhesive on a solid surface. As the relevant energies do not vary much during the solidification of the adhesive, this represents reasonably well its behaviour in the solid state. The spreading energy is always positive but, depending on the nature of the vapour and liquid, it can vary from very low and negligible values for polymeric surfaces (oil in polyethylene) to considerably high values (water over metal oxides).

If we focus or analysis on a liquid, the work to divide it and create two new liquid bodies (consequently creating two new surfaces) is called the cohesion work, W_c, which is equal to $2\gamma_{\mathrm{LV}}$. For a perfect wetting to occur, i.e. achieving a contact angle of zero, Eq. (2.4) must be followed:

$$W_A = 2\gamma_{\mathrm{LV}} + \pi = W_C + \pi \tag{2.4}$$

Ideally, all fractures should be cohesive in the adhesive, rather than occurring at the interface (adhesive breakage), because the energy associated with adhesive fracture is greater than that of cohesive fracture. This topic is discussed in more depth in Chapter 8.

2.5 Spreading

The ease of spreading a liquid on a surface is related to the contact angle between the liquid and solid surface. When the value of the contact angle is greater than zero, we have a clear indication that the liquid will not fully spread. However, when the angle is zero or very close to it, the liquid will wet the surface completely, spreading freely and spontaneously, at a speed that will depend on the viscosity of the adhesive and the roughness of the substrate.

In another way, when the surface tension of a liquid is lower than that of a solid, the liquid spreads. However, when the opposite occurs, with the surface tension of the liquid being higher than that of the solid, full spreading of the liquid is not possible. The minimum energy principle defines this concept and states that:

$\gamma_L < \gamma_S$, the liquid will spread
$\gamma_L > \gamma_S$, the liquid will not spread

If our aim is to ensure maximum adhesion in a bonded joint, we must assess the superficial of the materials and then implement methods that reverse unsuitable surface energy conditions. In this case, it is possible to intervene in the surface preparation, increasing the surface energy of the solid. To ensure good bonding and that any fracture that may occur is cohesive, surface treatments should be applied to the adherends. Each material class, application, or even geometry of the adherends has optimum treatment methods. This aspect, so crucial in the preparation of adhesive joints, is detailed in Chapter 3.

2.6 Adhesion Theories

With the knowledge obtained so far, you might have already figured that the process of adhesion does not occur always in the same way. In fact, there are several different ways in which an adhesive adheres to the substrate, and it is necessary to understand the different possible mechanisms, one or more, that act during the adhesion. The literature describes four theories or mechanisms, which are particularly useful for explaining certain phenomena associated with adhesive bonding. These key theories are based on adsorption, mechanical interlocking, diffusion, and electrostatic forces. The mechanism underlying each of these theories is schematically represented in Figure 2.11.

It should be noted that the theory of adsorption (in particular, physical adsorption) is always applicable whenever there is a bond between materials, which is not true for the other theories. For example, mechanisms based on the theory of diffusion occur mostly in polymeric materials, and those represented by the mechanical theory occur when there is a certain degree of roughness. Lastly, the electrostatic theory is especially applicable to pressure-sensitive adhesives (usually called PSAs).

2.6.1 Adsorption Theory

To adhesively bond, the adhesive and substrate must inevitably come into close and intimate contact. As we have seen, in many cases, a liquid adhesive comes in

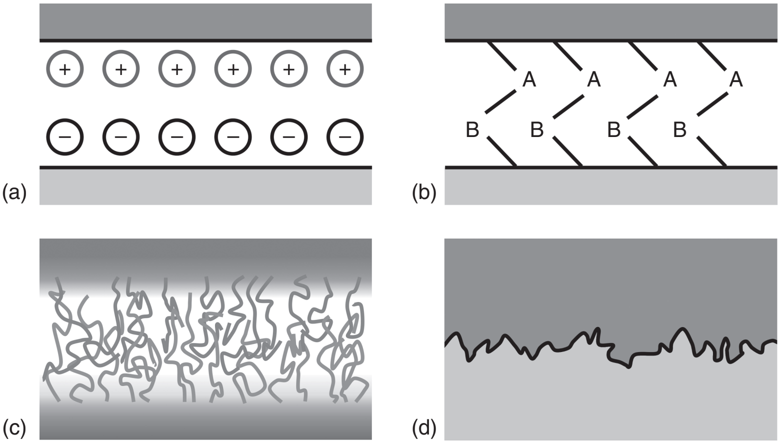


Figure 2.11 Mechanisms of bonding: electrostatic attraction (a), physical/chemical bond (b), interdiffusion bond (c), and mechanical bond (d).

contact with a solid substrate and, after a hardening process (i.e. solidification of the adhesive), the two components bond. However, there are several factors that can affect the nature of this contact, such as the adhesive viscosity, the surface energy of the substrate, and the adhesive and kinetic properties of the adhesive, all of which will influence how the adhesive spreads and wets the surface of the substrate. These issues should be carefully considered when the adsorption theory is described. Concisely, there will be adhesion whenever there is contact between two materials at the molecular level, and when two materials come into contact, there will be forces of attraction between them. Different types of bonds present different bond dissociation energies. Therefore, the theory of adsorption considers both physical and chemical adsorption (also known as chemisorption, as represented in Figure 2.11). Physical adsorption contributes to the strength of all structural adhesive joints and is the most important adhesion mechanism, mainly due to van der Waals forces, hydrogen bonds, and acid–base interactions, as represented in Figure 2.11. However, primary connections can also occur at the interface, constituting what is commonly referred to as chemisorption. For example, we have seen that van der Waals bonds operate in longer distances but are weaker than primary bonds, so the type of bond established will influence the strength of the adhesive bond.

In general, adhesives are at first supplied in a liquid or viscous state and only solidify after application to the substrate. However, there is no guarantee that the substrate will always be wetted before the adhesive sets. Whether the wetting equilibrium will be reached, or not, will depend on the relation between the forces responsible for spreading the adhesive and variation of adhesive viscosity over time, as suggested by Figure 2.12.

Moreover, the surface energy of the solidified adhesive will be different when compared to the liquid one, changing the equilibrium conditions. Considering the application of the adsorption theory of adhesion, these concerns are relevant.

Although roughness is one of the main aspects of mechanical theory of adhesion, it also exerts a very important influence within the adsorption theory. The effect of substrate roughness on adhesive wettability can be assessed, and there is a direct relationship between these two properties, i.e. if the roughness of the substrate is small, its effect on wettability is small. On the other hand, extremely rough surfaces (at the macro or microscale) can drastically reduce the ability of the adhesive to wet the substrate surface, changing the balance. If a decrease in wettability is observed, the adsorption will also consequently reduce.

2.6.2 Mechanical Theory

Mechanical theory is the oldest theory forwarded to explain the adhesion between the adhesive and the substrate. According to the mechanical theory, successful adhesion will occur if there is a certain degree of irregularities on the surface that could be roughness or porosity. An interlocking effect will occur when the liquid adhesive penetrates and fills all the cavities and irregularities of the substrate, and later, when it cures and solidifies, a key lock effect is obtained, impeding separation as the result of re-entrant angles and tortuous flow passages, leading to a considerable load transfer capability (see Figure 2.13).

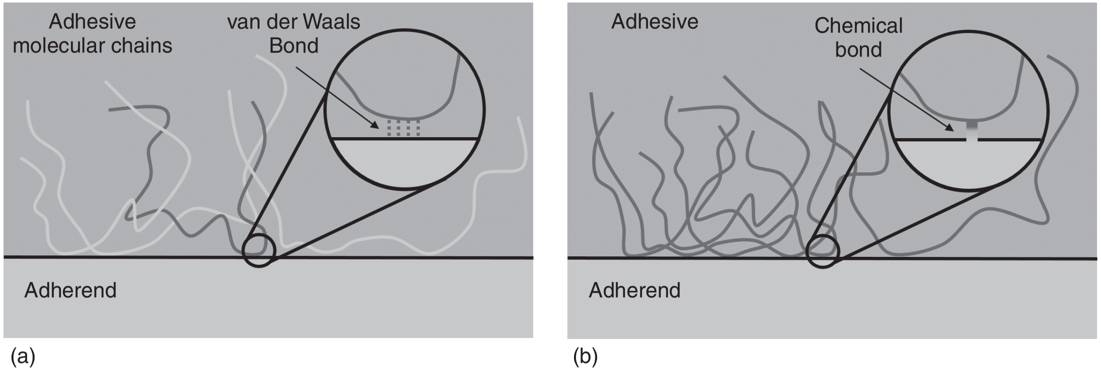


Figure 2.12 Schematic representation of the theory of adsorption. (a) Physical adsorption and (b) chemical adsorption.

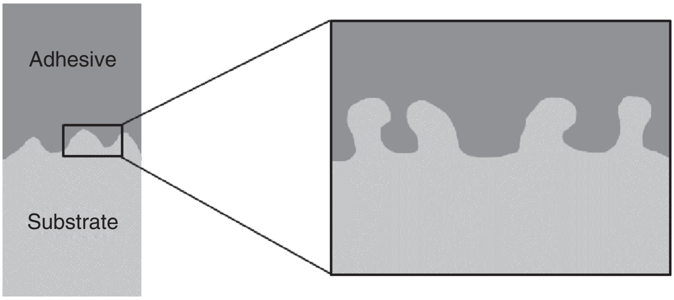


Figure 2.13 Schematic representation of the mechanical theory with the adhesive interlocking or 'hooking'.

A mechanical bond is usually characterised as a low energy bond when compared to a physical/chemical bond, with lower load transferring capabilities than the strength of a physical/chemical bond. In most cases, purely mechanical bonding is not enough to obtain a good quality joint. Nonetheless, the presence of mechanical interlocking in a bond can be a significant advantage when combined with other mechanisms. There are countless successful pre-bonding treatments which allow to obtain rough, microfibrous, or microporous surfaces.

As you might already have realised so far, when an adhesive is applied to a substrate, the adhesion process cannot be satisfactorily explained by a single theory. Thus, to better explain this idea, in Figure 2.14, two types of surface preparations are presented. In the first case, the adherends present high roughness and the adhesive flows along the surface, filling each irregularity. This surface preparation will provide mechanical interlocking, ensuring ideal adhesion between the substrate and the adhesive. On the other hand, when the surface does not present any irregularities, mechanical interlocking cannot occur. Comparing the two types of bond, the one with the highest degree of superficial irregularities will be more likely to present more satisfactory results. However, this phenomenon is not linear, as the increase in roughness may not lead to an increase in the strength of the bond. It is necessary to evaluate the type of substrate and that of the adhesive. In fact, for very viscous adhesives, the increase in roughness can lead to manufacturing defects. As a rule of thumb, for θ lower than 90°, the roughness can be considered to be good. However, if the θ is higher than 90°, then the roughness is often not satisfactory.

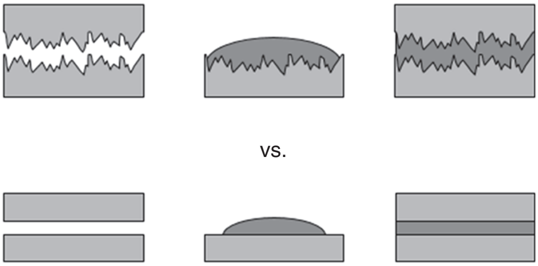


Figure 2.14 Influence of surface preparation on mechanical adhesion.

2.6.3 Diffusion Theory

In the 1960s, Voyutskii and Vasenin formulated what it would be known as the theory of diffusion. This theory is quite particular and is valid for explaining the adhesion mechanism in polymeric materials, not being applicable joints with metal adherends. Its basic concept is quite simple and relates to the welding of thermoplastics by the application of a solvent or heat. In this process, the end of a polymeric chain of one surface diffuses in the structure of the second surface. The bonding occurs by the formation of bridges or chemical bonds at the interface, as suggested in Figure 2.15. Although its concept is quite simple, it has some particularities, since the two polymers must be chemically compatible and miscible.

In this theory, two types of diffusion-based adhesion can be considered depending on the adherends. If one wishes to join similar materials, then this process is called self-adhesion, and when the materials are dissimilar, it is called heteroadhesion.

This theory also does not apply to unsolvable materials or when the movement of each polymeric chain is highly restricted by its reticulated or crystalline structure, or when the polymer is below its glass transition temperature (T_g). T_g can be defined as the gradual and reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a stiff state into a rubbery state, as the temperature is increased. This concept will be discussed in greater depth in Chapters 4 and 6.

2.6.4 Electrostatic Theory

Like the diffusion theory, the electrostatic theory was also developed in Russia in the middle of the twentieth century by Deryagin. This theory describes what happens in PSA . PSAs are adhesives usually supplied in tape form that will adhere to an adherend with the application of pressure, without the need for a solvent (such as water) or heat for activation. This type of adhesive will be addressed in greater depth in Chapter 4.

The adhesive and the adherend are considered to act as two plates of a condenser (a device that stores electrical energy in an electric field) and the separation work corresponds to the work required to separate the two charged plates (see Figure 2.16). In this theory, the forces of the electrons are involved all throughout the interface

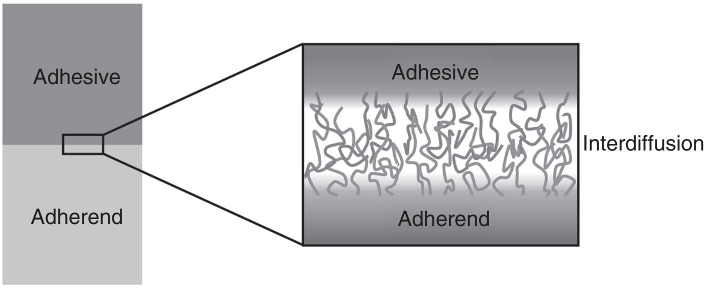


Figure 2.15 Schematic representation of the diffusion theory.

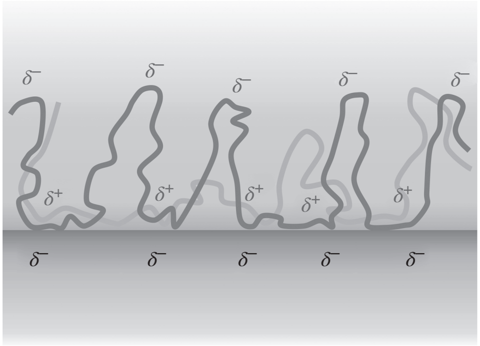


Figure 2.16 Schematic representation of the electrostatic theory.

where negative and positive charges are created that attract each other. This theory is somewhat controversial, as some consider that these forces may not be the cause, but only the result of a truly resistant joint.

2.7 Defects and Weak Spots in Adhesive Joints

At this stage, you have so far learned the main concepts and theories that serve as a basis for designing a perfect joint, but real joints are sometimes far from being as perfect as the theory suggests, and there are discrepancies between the two. Three main justifications can be proposed for this phenomenon, as can be schematically seen from Figure 2.17:

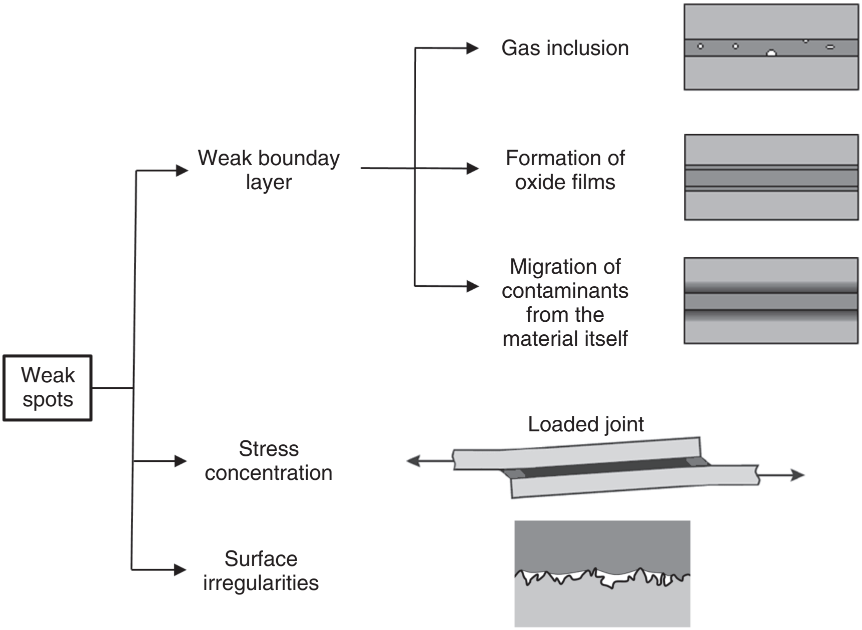


Figure 2.17 Possible weak spots in adhesive joints.

Each of these effects may explain cases where real-world joints are not as strong as those theoretically predicted. Still, it is possible to minimise this discrepancy by using a more careful joint design and an optimised surface preparation, which takes into account the materials that will be bonded and the final application. In general terms, it can be said that there are five common reasons for the failure of an adhesive joint:

- Inappropriate adhesive selection – When selecting an adhesive, the bonder has to consider (at least) the adherends being joined, the environment it will be suggested to, and how long will the joint lifetime be.
- Unaccounted for environmental factors – Even if the type of adhesive is appropriate for the application, an unplanned or unexpected change in the environment can cause the adhesive to fail. Heat, cold, moisture, and the introduction of chemicals are all potential culprits.
- Incorrect surface preparation – Careful consideration must be given to the cleanliness of the adherends. Grease, oil, dust, and dirt are a few examples that can cause poor bonding.
- Improper curing of the adhesive – Adhesives require specific actions in order to fully cure. Some of those include time, air flow, and the amount of pressure used during application. If any or all of these requirements are not followed, failure is possible.
- Lack of elasticity and strength – Flexibility and adhesion levels are critical components to think about when selecting an adhesive. The specific type and amount of stress on the joint must be accounted for.

These topics are covered in detail in Chapters 3 and 4, where surface preparation techniques are described in detail and the specific characteristics and needs of each adhesive formulation are described.

3

Surface Preparation

The surface preparation of a substrate is a fundamental task in the creation of a strong and durable adhesive joint, which should never by carried out lightly. In fact, when we are faced with the necessity to design a bonded joint, the selection of the most suitable treatment for the joint in question is undoubtedly one the most critical steps, as an incorrect or insufficient surface preparation will almost always result in very weak joints. This chapter has been written to ensure that those who are interested in manufacturing good performing joints can fully understand the purpose and capabilities of surface preparation methodologies. To do so, the characteristics of different substrate materials and surface treatment methods are described in detail, establishing a direct link with the theories of adhesion described in Chapter 2.

3.1 Objectives of Surface Preparation

Wolfgang Pauli, a well-known physicist, amusingly stated that ‘God made solids, but surfaces were the work of the devil’. This expression allegorically exemplifies the complexity of surface treatments. As we have seen in Chapter 2, some degree of modification to the surface properties of the substrates is often necessary to ensure maximum adhesion to the adhesive. This operation is one of the most important steps in the manufacture of a bonded joint since the mechanical performance of the joint is greatly dependent on the preparation of the surface.

The aim of surface preparation is to optimise the adhesion forces between the substrate surface and the adhesive layer. For this purpose, a compromise must be made between wettability, adhesive viscosity, and substrate roughness. Ideally, the adhesive should spread across the surface, indicating that the chosen adhesive must wet the surface of the substrate. Chemical compatibility (intermolecular and chemical interactions) between the adhesive and the surface layer of the substrate must be ensured.

In addition, it should be ensured that there is no ‘weak layer’ between the adhesive and the substrate. This layer can be the result of several factors such as contaminant films, oxide layers, rust, corrosion, scale, loose particles, dust, or even grease. The surface preparation should be tightly controlled, as the substrate’s surface should not

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Eduardo André Sousa Marques, Ana Sofia Queirós Ferreira Barbosa, Ricardo Joao Camilo Carbas, Alireza Akhavan-Safar, and Lucas Filipe Martins da Silva.

be damaged, no weak oxide layers shall be formed and the residual deposition and migration of solvents from the interior to the substrate surface should be controlled.

As we will see, there are many types of surface preparations, and some of them are quite complex. It is up to the designer of the joint to understand and identify the best treatments given the intended application.

For the surface treatment to be successful, it must be ensured that environmental conditions are controlled, guaranteeing the reproducibility of the quality of the joints. An effective and successful surface preparation will be the one than can improve wettability and bonding properties, enhance adhesion, improve long-term joint stability, and lead to increased process reproducibility.

To select the optimal surface treatment, one must first identify which material class will be used and what are the specifications of the selected materials. In fact, this is one of the key challenges associated with surface preparation activities, as adhesive bonding works with a wide range of materials and each class of materials has a set of adequate techniques, requiring a careful analysis. The type of surface preparation will unequivocally determine the behaviour of the joint, and this effect can be easily observed in Figure 3.1. Three different types of surface preparations have been used, and it is evident that the type of fracture obtained and the mechanical behaviour change significantly with the type of preparation chosen. The specifications of each type of surface preparation will be elaborated in detail throughout this chapter.

Considering the factors stated above, the selection process of a surface treatment must consider the initial strength, durability, initial condition of the substrates, type of the substrate, and nature of the surface and production factors (cost, time, etc.). Predicting the environmental and loading conditions that the joint will be subjected to is also of major importance. The surface treatment should be adjusted appropriately, ensuring the durability of the adhesive joint. In addition, the current state of the surface of the substrate and any additional limitations associated with production process should also be considered, which can include cycle times and applicable health and safety regulations. In industrial applications, one of the main factors

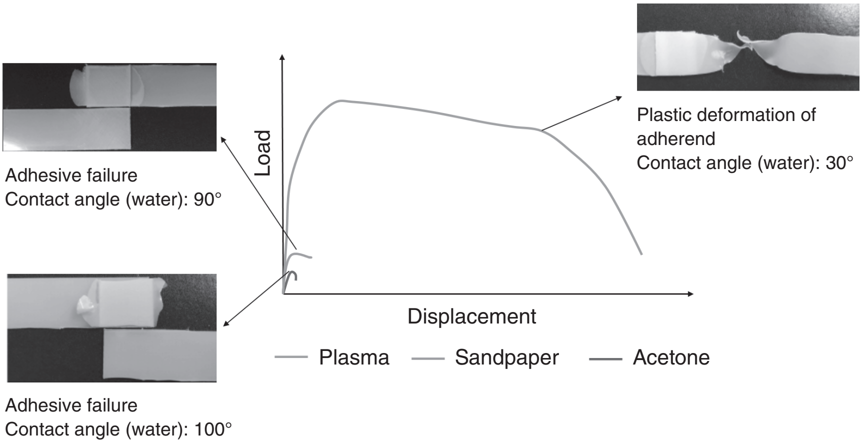


Figure 3.1 Effect of surface preparation on the mechanical behaviour of an adhesive joint.

behind the selection of a treatment is its cost, requiring an analysis of the cost of the treatment against the value of the bonded component. Sometimes, the best surface preparation may not be the most suitable for the joint component (considering the application). Overevaluation of the surface preparation should be avoided, as it can entail unnecessary costs.

There are several methods suitable to conduct the evaluation of surface preparation, with different degrees of complexity. This can be the simple application of a dyne pen or the use of contact angle measurement equipment. This topic is presented in detail in Chapter 6.

In the following sections of this chapter, you will find considerations on materials commonly used as substrates in bonded joints, describing the surface conditions they often exhibit and how adhesion can be improved. The following classes of materials are discussed: metals, polymers, composites, and other materials (wood, ceramics, and concrete).

3.2 Classes of Substrate Materials

3.2.1 Metals

Metals are materials composed of a crystalline structure, possessing surfaces formed by several regions that usually do not have well-defined boundaries but are well clearly demarcated in Figure 3.2 for better understanding. The surface treatments suitable for metals depend on many factors. The most important of these factors is whether the metal has a strongly adhered oxide on its surface or not. Typically, the nature of the oxides is not well known, so it is advisable to remove them and replace them with a stable and well-controlled oxide. Ideally, the surface preparation should remove all layers until the base metal is exposed. The segregation layer is a metallic surface but has a different chemical composition due to segregation phenomena of alloy elements and impurities.

3.2.2 Polymers

When compared to metals, the preparation of polymeric materials is more complicated. As we have seen in Chapter 2, these materials have a low surface energy, and above all, their surfaces are more dynamic and change more easily than metals.

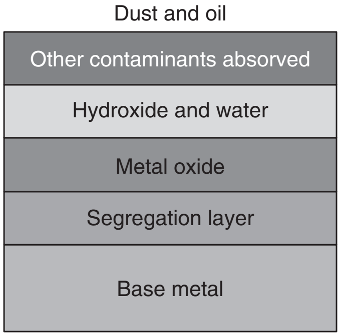


Figure 3.2 Possible surface layers that can be observed in a metal.

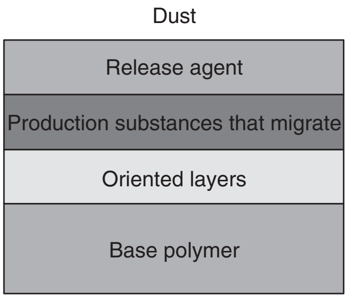


Figure 3.3 Possible surface layers that can be observed in a polymer.

Migrating production substances and oriented layers can greatly influence the joint strength without influencing the properties of the base polymer. The surfaces of the plastics give rise to very dynamic regions that continually establish new internal balances with the interior of the polymer and external balances with the environment (see Figure 3.3). In the case of elastomers, the more fluid nature of the molecules allows for an easier diffusion of the contaminants, which can weaken the surface.

There are many contaminants that can be present on polymer surfaces, which include plasticisers, lubricants, release agents and hydrophobic agents, antistatic agents. In addition, handling the materials with bare hands will generate fingerprints, which are rich in chloride ions, amino acids, urea, ammonia, grease and some magnesium, calcium, and sodium ions.

As we have discussed in the introductory section of this chapter, the selection of an optimal surface treatment is a challenging proposal for any kind of material. However, in polymers, it can be even more so. For instance, a simple cleaning with organic solvents may entail some issues because polymers present little to no resistance to solvents and there is a risk of irreversible changes in properties (dissolution, swelling, morphology changes, and stress crack formation). Despite these shortcomings, solvents are used for cleaning and degreasing because of their low costs and the ease of use. When aqueous cleaning agents are employed, in general, plastics are resistant to aqueous cleaning agents. However, many polymers have poor resistance to concentrated acids and bases (especially at high temperatures). The use of surfactants (molecules that spontaneously bond to each other to form closed bubbles) to ensure that adequate wetting could also promote stress cracking and plastics absorb water to differing extents; thus, drying again can be very difficult.

3.2.3 Composites

Many different types of composite materials exist because they are made by combining different materials in order to obtain a synergistic product with improved performance. As multiphase materials, composites not only exhibit some of the inherent properties of each constituent but also a new set of intermediate properties that arise from the formation of an interfacial region. In structural applications, adhesives are almost always selected for joining fibre-reinforced composites with polymeric matrices, as they do not necessitate holes or other modifications to be made in the composite material. However, ensuring optimal adhesion to composites is difficult, as the surfaces of these materials are usually covered with silicone or fluorocarbon-based release agents as a result of their manufacturing processes. As a result, surface energies are often very low, especially in composites with thermoplastic matrices, and it is essential to remove these agents before applying the adhesive. However, one must be aware that the use of intensive abrasive treatments can cause surface damage and even damage the reinforcement that provides strength to the composite, so a careful selection of the best procedures to treat the surface should be made.

3.2.4 Other Materials

In this section, a set of diverse materials that are commonly bonded with adhesives are described. We will start our analysis by focusing on wood.

The application of adhesives in wood is a millenary technique, but to obtain good quality joints, it is necessary to fully understand the particular characteristics of this material. Wood changes with ageing, its properties degrade, and undergoes major contraction or expansion because of exposure to the environmental conditions. Because of the intrinsic characteristics of a natural material, it presents ample porosity, which can be beneficial to the joining process. However, in order to obtain durable wood joints, it is necessary to remove any remaining dust on the surface and to pay special attention to the resins present on the surface.

Adhesion technology is also increasingly used to bond ceramic materials in a diverse set of applications, ranging from civil construction to aerospace vehicles. Ceramic materials are easily bonded because their surface energy is naturally high. However, ceramics are highly likely to contain a layer of adsorbed water and hydrogen ions, which is very difficult to permanently remove. Thus, the adhesive suitable for bonding ceramic materials must be compatible with this layer.

Bonding concrete has some similarities to bonding ceramic, but some additional considerations should be made, as the surface of concretes is even more affected by the environment. In addition, the surface of concrete is porous and weak, so sealants should be used to waterproof and harden the surface before any bonding takes places.

3.3 Surface Preparation Processes

Until now, we have clearly established that the main function of any surface treatment is to promote desirable physical and/or chemical properties to the surface with the objective of improving adhesion between the substrate and the adhesive. However, this might be achieved in several different forms. We can use a surface treatment to remove and/or prevent the formation of any weak layer at the interface adherend/adhesive. We can also act on the chemical side to maximise the degree of molecular intimacy between the adhesive or primary agent and the adherend during the adhesion and hardening/curing process. Often, a surface treatment will generate a specific surface structure, or texture, on the surface of the adherend. Such complex structure can help increase the fracture energy of the joint, redistributing stresses away from the interface zone. Many treatments rely on the passivation of the surface of the adherend before applying the adhesive, i.e. creation of an outer layer of material by a micro-coating, created by chemical reaction with the adherend base material, or by spontaneous oxidation in the air. Passivation lends itself to ensuring the corrosion resistance of the component or part and, consequently, its durability.

Although the processes employed in surface treatment can be very different and lead to distinct surface morphologies and conditions, the end result of a surface treatment should always be the same: an increase in the joint strength, achieved by promoting adhesion between the materials to be bonded and the adhesive. This is the final goal of surface treatment, regardless of the procedure used to achieve it.

Thus, we can state that surface preparation can act via material removal processes, chemical modifications of the surface or induce important changes in the topography of the surface. The objective of these activities is to remove or prevent the posterior formation of a weak layer on the surface, maximise the degree of molecular interaction between the adhesive and the adherend, optimise the adhesion forces to ensure adequate joint strength, and to create a specific surface microstructure on the substrate.

Despite this variety in actuation mechanisms, surface treatments are classified into two major groups: passive treatments and active treatments. When a passive treatment is applied, there is no modification of the chemical nature of the adherend surface. Such treatments are only able to clean and remove the weak layers on the surface, which is an important contribution to improving adhesion, but in many cases, this is not sufficient. Nonetheless, passive treatments are almost always used as an initial step in the surface preparation, exposing unblemished material which, if necessary, can then be processed using an active treatment.

Active processes can also be used for cleaning and removing the weak layers, but their main characteristic is the fact that they change the chemical nature of the surface, this being the reason for the ‘active’ denomination. These processes can further be divided into physical or chemical treatments, depending on the way they modify the surface in order to improve adhesion. Figure 3.4 shows how surface preparation can be classified.

Before we advance to a detailed description of the most important surface treatments, we should discuss in more detail the nature of surface contamination. In fact, pre-existing contamination is one of the main problems that must be solved when designing a surface preparation procedure, so it is necessary to understand well its possible origins. The source of the contamination can be the material itself or be external to it. In polymeric materials, it is possible that the internal migration of low-molecular-weight substances, often used as processing aids, can occur and create a highly modified surface layer. This layer might be composed of internal contaminants and be responsible for poor self-adhesion between substrates, creating weak boundary layers. External contaminants may be organic or inorganic in nature. The removal of organic contaminants is commonly achieved using simple degreasing processes, whereas the removal of inorganic contaminants might entail a combination of degrease, removal of contaminants resulting from the treatment process, and, in extreme cases, deoxidising solutions. It should be emphasised that the

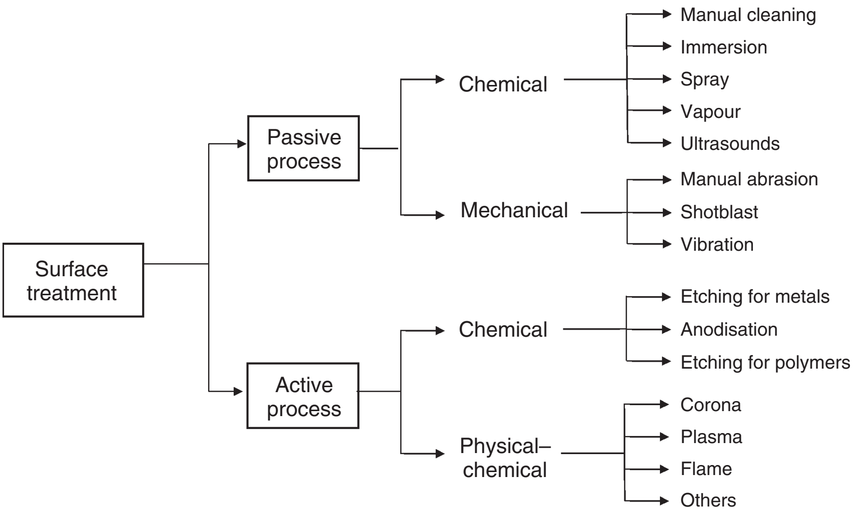


Figure 3.4 Classification of surface preparation.

role of surface contamination and its effects on the mechanical performance of the joint is complex. This has been the subject of several studies aimed primarily at applications in the aeronautical and automotive industries. In order to avoid renewed surface contamination, the adhesive application should be carried out directly after surface treatment. The process steps for pre-treatment and surface preparation are all extremely important and must therefore be carefully considered during the planning and the execution of the bonding process.

3.3.1 Passive Processes

It is common to find surface preparation processes that consist in several distinct steps, i.e. using multiple techniques. In most cases, a passive surface treatment process on the surface is first required. These treatments can be carried out by chemical or mechanical passive mechanisms but, as mentioned above, they do not alter the chemical structure of the material being treated.

3.3.1.1 Passive Chemical Processes

Chemical processes aim to remove oily or greasy areas, which are the sources of very low wetting and adhesion. In many non-structural bonding applications, these processes are often sufficient, but they are often the first step of a more complex surface treatment process in high-responsibility structural applications. Degreasing is the simplest possible method suitable for obtaining a clean surface and thereby increases its surface free energy and spreading coefficient. This process can be obtained by manual cleaning, immersion, spray, vapour, or ultrasound exposure. The first three of these methods are simple and easy to implement but are also difficult to control as their effectiveness depends almost entirely on the skill of the operator who performs the task.

Nonetheless, in general terms, mechanical, chemical, electrochemical, and some other alternative treatments tend to give much improved levels of adhesion and durability when compared to a simple degreasing process.

The cleaning agents used to perform the passive surface treatment should remove all soluble contaminants from the substrate surface. Polar agents dissolve polar contaminants, while non-polar agents show better performance on surfaces with non-polar contaminants. In order for the reader to better understand this concept, let us do a short review of the relevant chemical processes. You might already be aware that in chemistry and physics, polarity relates to the electric charge distribution around atoms, chemical groups, or molecules. Molecules are known as polar agents when there is an electronegativity difference between the bonded atoms. Water (H_2O), ammonia (NH_3), and ethanol (C_2H_6O) are good examples of polar agents. On the other hand, in non-polar agents, electrons are shared equally between atoms of a diatomic molecule or when polar bonds in a larger molecule cancel each other out. The homonuclear diatomic elements (H_2, N_2, O_2, and Cl_2), carbon dioxide (CO_2), ethylene (C_2H_4), hydrocarbon liquids, and most organic molecules are good examples of non-polar agents.

When we select a cleaning agent, we must ensure that the cleaning agent does not swell, dissolve, or degrade the substrate. The cleaning agent should evaporate in a residue-free manner and must meet safety regulations and environmental protection regulations. Most of these agents are used in industrial applications and should be available and reasonably priced, as these steps, although essential, will make the final product more expensive.

There are several cleaning agents that can be used to prepare the surface; they are usually grouped into three main groups: organic solvents, aqueous cleaning agents, and compressed gases, as synthesised in Figure 3.5.

Cleaning agents based on organic solvents can be applied in wiping, dipping, and in vapour degreasing processes. Halogenated hydrocarbons are an attractive option within organic solvents as they present excellent ability to dissolve oil and grease and dry rapidly. Pure hydrocarbons distinguish themselves from halogenated hydrocarbons because of a considerably lower ability to dissolve grease, although this can be somewhat improved by adding aromatics or oxygen-containing hydrocarbons.

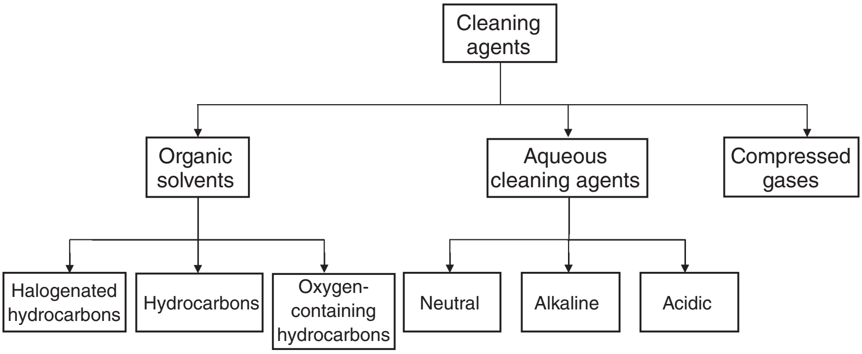


Figure 3.5 Classification cleaning agents.

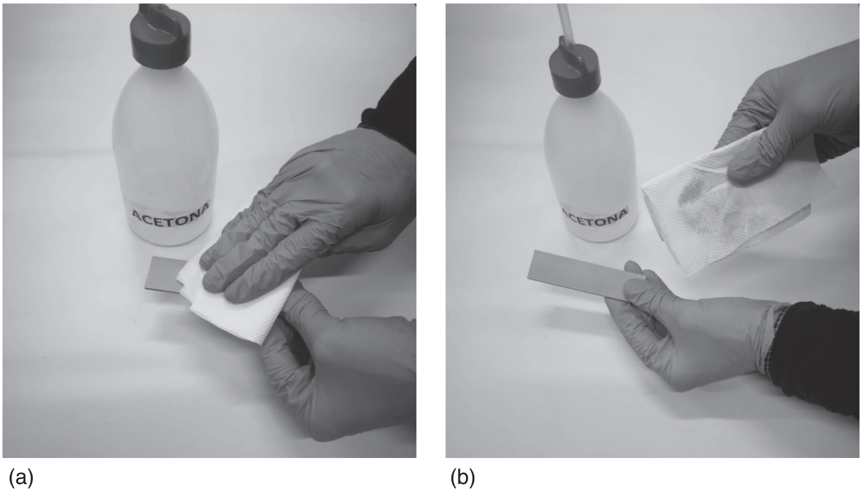
They have the disadvantage of drying slowly and usually are not residue-free, making fine cleaning impossible. The oxygen-containing hydrocarbons are the most popular group of cleaning agents (for example, isopropanol, ethanol, and acetone). They are, in general, effective for polar and, in some cases, ionic contaminants (fingerprints, some salts, etc.), drying at a faster rate than hydrocarbons.

Aqueous cleaning agents can also be employed in wiping and dipping cleaning processes. However, this type of agents is also suitable for use in spray form. As their main solvent is water, its effectiveness is not very high, but the relatively weak cleaning action can be improved by increasing the temperature (30–90 °C) and using high pressure during the spraying process. Alkaline aqueous cleaning agents, as suggested by the name, present a pH higher than 10. They are very effective at degrading oils and greases and are mostly used at higher temperatures (60–90 °C). As in neutral cleaning agents, rinsing with demineralised water is highly recommended after cleaning. Acid aqueous cleaning agents present a pH less than 5 and are used at 50–80 °C in spray or immersion methods. The use of these agents follows the same recommendations as those described before and the treated surfaces should be rinsed with demineralised water after cleaning.

Lastly, cleaning is also possible using highly pressurised gases directed at the surface. In practise, this is usually achieved with highly compressed carbon dioxide (CO_2). This method is very effective at removing oil, grease, and polar contaminants. This method mainly relies on the peeling forces generated by the pressurised gas and thus presents low toxicity. It is also sustainable, since, when operated in closed circuit, a simple separation of the CO_2 from the contaminants can recycle the gas back into the process.

Manual Cleaning Manual cleaning, also known as wiping, requires the use of a paper or cloth impregnated with a suitable solvent to clean the surface, as depicted in Figure 3.6. The most commonly employed solvents include isopropyl alcohol, acetone, methyl ethyl ketone, perchloroethylene, trichloroethylene, or 1,1,1-trichloroethane. However, because of increasingly stricter environmental and occupational safety legislation, there is a trend for this list to be gradually reduced as organic solvents are replaced by aqueous solvents. In this operation, care must be taken to ensure that the solvent is not contaminated. This operation is very effective when it comes to preparing the surface of metals as they suffer no degradation of its properties when exposed to most solvents. For some polymers, a cloth soaked with solvent is sufficient to remove, for example, the grease and/or plasticisers that have migrated to the surface interface. However, one must be aware that some powerful solvents can even dissolve the polymers being treated, which mandates that extra care should be taken when selecting the most suitable solvent. The selection of the cloths, tissues, or paper used in this operation is also critical, as it must be ensured that they do not release solid residues that compromise the surface.

Immersion Methods The immersion process is a very effective method for surface degreasing. Whenever possible, it is advisable to use pressure washers because, given their efficiency, all corners of the part will be reached. For better effectiveness, the



(a) (b)

Figure 3.6 Surface preparation using acetone impregnated paper. (a) substrate cleaning and (b) observation of the clean substrate and of residue on the acetone-impregnated paper.

cleaning agent must be replaced frequently, and the cleaning action can be further aided by rinse washing, ultrasound action (cooling may be required), or manual brushing. This method is quite advantageous as its effectiveness does not depend on the operator but the size of the components that can be handled is limited by the capacity of the immersion vat. However, for specific, large volume applications, there are industrial solutions that use large-scale tunnels. Another significant disadvantage of this process is the fact that when flammable solvents are used, costly explosion-proof facilities are almost always required. This is valid when solvents with flash points below 55 °C are used, with the flash point being the lowest temperature at which its vapours ignite if given an ignition source.

Spray Methods This method employs low-pressure spraying (3–6 bar) and high-pressure liquid jets (especially with neutral cleaning agents, hot water, and steam, pressurised up to 2000 bar). In this method, flammable solvents can only be used under an inert gas atmosphere because highly explosive aerosols are easily produced.

Vapour The vapour degreasing method can dissolve oils, greases, solid paraffins, and other substances present on the substrate. It is used for very cleaning delicate components with intricate shapes as it is a fine-cleaning method with excellent cleaning action and penetration capabilities. Again, when flammable solvents are used, it is essential to provide for an explosion proof. This is not necessary for aqueous cleaning agents, which, although generally less effective, might represent a less costly proposition.

To implement, this method requires a heated vat containing a high-temperature solvent bath and a cooled condensation zone. The part being treated travels along the top of the vat, being subjected to steam, resulting from the evaporation of the solvent. A highly pure solvent vapour continuously condenses on the surface and washes contaminants away. Eventually, the components warm up and condensation no longer takes place (drying stage).

Ultrasound With the ultrasound degreasing process, pores, which would otherwise be inaccessible, are easily cleaned, and particles that are strongly bonded to the substrate can be removed. Ultrasonic waves generated by a specialised apparatus vibrate the solvent and the particles in the component are effectively dissolved. The solvent used must meet certain requirements to ensure the effectiveness of the process. The first of these requirements is to ensure that the solvent is neutral to the material being treated and does attack or etch it. In addition, the solvent being used must not produce any type of foam, which would impede the cleaning process, and it must cavitate in an adequate manner. Cavitation means the formation of bubbles in the liquid because of the pressure changes induced by the ultrasonic waves. In some liquids, these bubbles have the potential to be highly destructive and erode the surface being cleaned.

This treatment is necessarily restricted to components with relatively reduced dimensions, as the working space afforded by the ultrasound cleaning equipment is limited. In addition, this process is not very well suited for large-scale manufacturing as it requires operation in batches, difficult to include in an assembling line.

3.3.1.2 Passive Mechanical Processes

Passive mechanical processes usually remove friable surface layers as they are very effective for removing thick layers of oxides and other weak surface layers and generate a macro-rough surface texture on surfaces.

In simple words, the creation of these rough surfaces provides the possibility of redistributing stresses on the superficial layers of the treated materials and the new topography creates a larger surface area for adhesive interaction with a topography suitable for mechanical interlocking, characteristics that are highly advantageous for promoting adhesion. However, a cleaning process must always be conducted before and after this step to remove contamination and debris present in the surface. It is also a very economical technique suitable for application to most materials.

In this type of treatment, it is very important to precisely evaluate the level of erosion needed to remove the oxide layer and not to damage the base material. Several key points and parameters should be the target of study before industrial implementation on a large scale. The first important parameter is the kinetics of the treatment, requiring an optimisation of the material removal rate. The depth of the removed material should also be tightly controlled. For example, in a shot blasting process, the air pressure, the distance between the substrate and the applicator gun, and the incidence angle should all be precisely controlled to avoid excessive abrasion. Furthermore, one must ensure that no permanent deformation of the surface occurs which, as we will see, is highly likely to occur due to the release of stresses locked in the surface. There is also the possibility of performing these processes using a supporting fluid, such as water to aid in cooling and partially lubricate the abrasion process.

Abrasion Manual abrasion, or in some cases, machine-aided abrasion (as achieved, for example, using belt grinders), is usually employed to prepare the surface of a substrate, given its practicality and the fact that it does not require large investments in specialised equipment. Abrasion is ideal when small-scale work is to be done in a workshop or at home.

Manual abrasion processes, using sandpaper, brushes, and metal wool, strongly rely on the experience of the operator. If performed incorrectly, they often give inconsistent results and should only be used if no other method is possible. When a dry abrasion process is employed, a prior degreasing is strongly recommended, as otherwise the surface residues can become embedded in the surface being treated or are transferred to other areas of the surface. Abrasive materials are usually categorised according to a grain size-based ISO designation, representative of the amount of the abrasive material that can fit through a square inch filter. Thus, the higher the ‘P-grade’, the smaller the grain size. A ‘P’ in front of the grit size implies that the product is graded in accordance with the European Federation of European Producers of Abrasives (FEPA) standard. When preparing surfaces for bonding, a grain size of P120–P180 is often considered optimal. However, when compared to coarser grain sizes (P80–P100), smearing and contamination of the abrasive material can easily occur during the abrasion of non-ferrous metal. Table 3.1 provides more detailed information on the ISO designation for each particle type and its respective average size. It is recommended to abrade the surface in a cross hatch pattern in order to ensure that no preferred direction exists on the treated surface. After the process is concluded, particles and dust must be thoroughly cleaned from the surface, which can be achieved by using an oil-free compressed air blast, a wet cleaning process.

Shot Blasting Shot blasting is a process widely used in surface preparation, particularly when working with metal substrates. Shot blasting allows for a very effective removal of contaminants and oxide layers. This method requires investment in specialised equipment, although the cost of shot blasting cabinets is not very high because of their relatively simple construction, as presented in Figure 3.7. It should be noted that each substrate requires a different blasting procedure using different particle shapes, sizes, and pressures. For many materials, shot-blasted surfaces are

Table 3.1 Grain size for abrasion particles, with ISO designation and average particle diameter.

Grain size	ISO designation	Average particle diameter (μm)
Medium	P60	269
	P80	201
Fine	P100	162
	P120	125
Very fine	P150	100
	P180	82

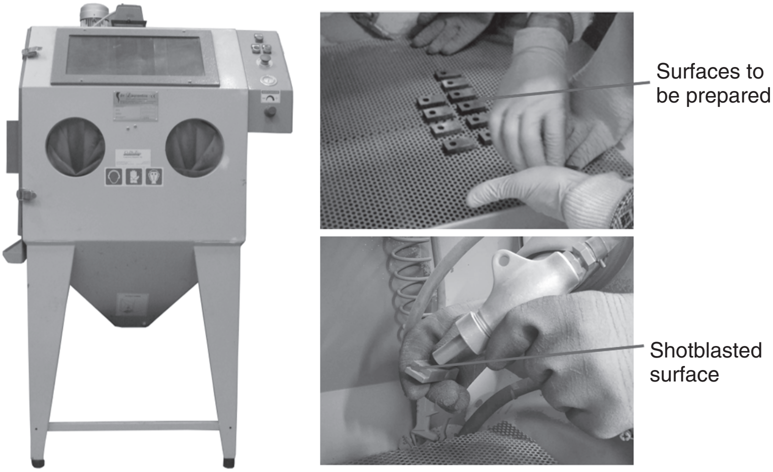


Figure 3.7 Surface preparation using shot blasting.

capable of greatly increasing the adhesion level. However, excessive roughness can cause a decrease in strength because of the formation of pores on the surface, which may be the source of cracks under service.

A successful shot blasting process will lead to increased surface roughness, increasing it by a factor that reaches 100, as well as greater microroughness (<0.1 mm) and macroroughness (>1 mm). It will lead to complete removal of oxides and other contaminants from the surface. Thus, a shot blasting process will simultaneously increase mechanical adhesion and allow for a stronger chemical bond between the adhesive and the substrate material, increasing the adhesion between the adhesive and the substrate. Figure 3.8 shows the condition of a steel surface after shot blasting.

Several parameters must be monitored in order to ensure reproducibility of the treatment, such as the abrasive material used (material composition, size, shape, and purity), the air pressure (restricted to a few bar of pressure to avoid damage), the

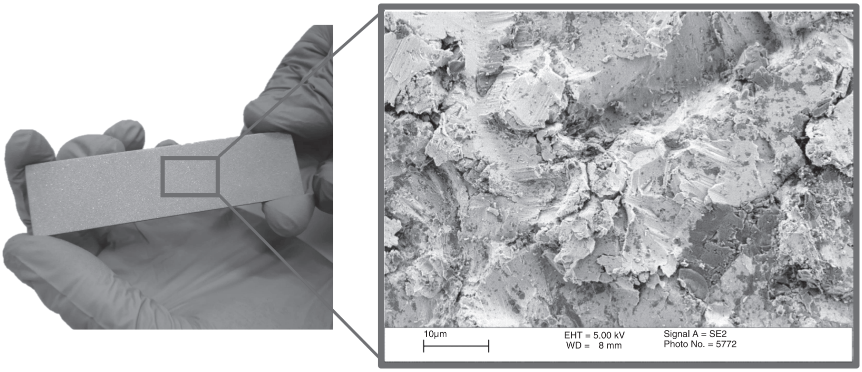


Figure 3.8 Condition of a steel surface after shot blasting.

particle incidence angle (usually 45°–60°), process time, and the substrate material and geometry.

The abrasive particles used in this process are composed of high hardness oxides such as Al_2O_3 (corundum), carbides (such as SiC), glass powder, boron nitride, abrasive steel, or even frozen liquids or gases (dry ice). Generally, these particles have sharp edges that will be responsible for removing the material from the substrate.

The type of the material and the geometry of the substrates must be considered when using this type of surface preparation as there is the potential to plastically deform the materials during this process. In the case of very thin sheets, the compressive stresses generated from the impact of the particles can cause an imbalance in the stresses acting on both sides of the sheet material and cause it to bend. The higher the pressure of the shot blasting, the larger these stresses become and the more significant the bending. To counterbalance this effect, the easiest solution is often to blast the opposite surface, returning the part to a balanced state. The surface preparation time should also be controlled, as a prolonged shot blasting process can lead to defects such as cracks or incorporation of abrasive particles into the substrate surface.

This technique can adopt a wet or dry procedure. Wet blasting is more versatile than dry blasting and can adapt to a wider range of abrasive particles. Wet blasting consists of three parts of water (in volume) for one part of abrasive. Again, it should be noted that the larger the index, the thicker the grain. For example, an abrasive with a particle size index of 325 corresponds to an actual particle size of 45 μm and an abrasive with a particle size index of 80 corresponds to an actual size of 192 μm.

As usual, it is recommended to clean the surfaces after the blasting process is completed. This is achieved by first blowing the surface with oil-free compressed air, and then adopting a wet cleaning process, using a solvent.

Vibration In a vibration surface treatment process, the substrates are placed in a container together with the abrasive and are subjected to vibration. The relative movement of the substrates and the abrasive particles creates friction, which will grind, polish, and brighten the materials being treated. The abrasives can be varied and include sintered ceramics, plastic composites reinforced with abrasive powders, and steel or glass beads with different shapes. As with many other processes, vibration can be carried out dry or assisted with a fluid (wet process). Traditionally, the process uses water mixed with a few additional chemical compounds used for different purposes. This includes the lubrification of the contact between the part to be treated and the abrasive and ensuring that the mixture of the lubricant and the abrasive remain clean and without the formation of sediments.

However, the wet vibration treatment process also has some disadvantages, the most important of which is the formation of muddy residues that require complex and expensive treatments in order to be correctly disposed of. This disadvantage can be overcome by using more environmentally friendly abrasives that are available on the market. Eco-friendly abrasives are those that have the greatest capacity to be recycled or those who generate by-products that can be reused in other applications.

3.3.2 Active Processes

As it has already been pointed out, passive treatments might not always be sufficient to prepare a surface to be bonded. There are a plethora of active treatments that can be applied, which are divided into two major groups: chemical active processes and physical active processes. These treatments aim at different results depending on the material being treated. When used in metals, the objective is often to remove a detrimental oxide and other types of weak layers and protect the surface from corrosion. Surface roughness of interest may range in scale from hundreds of microns to nanometres. In polymers, the target is usually to activate the surface and create reactive areas in the surface to promote the adhesion. Adhesion to surfaces with some degree of roughness may be effective because of the intrinsically high surface energy of atoms on a rough surface. Another explanation is that the increase in surface area (by a very high factor) also increases the surface energy.

3.3.2.1 Active Chemical Processes

Active chemical processes are quite diverse and highly specialised to the target materials. Treatments applied to metals differ greatly from those applied to polymers since the purpose is different. In metals, the oxide layers and other weak layers are removed, promoting an increase in roughness and leading to an improvement in mechanical adhesion. Thus, the chemical method is based on the principle of solubility of oxides, hydroxides, and other surface compounds in the pickling agent. Figure 3.9 depicts the main types of active chemical processes. The pickling agent can be an acid (H_2SO_4, HCl, HNO_3, or HF) or a base (NaOH), and all products of the reaction are generally soluble in an aqueous media.

Phosphatisation is especially suitable for use with iron and zinc alloys. The agents consist of acid alkali phosphates, phosphoric acid, metal salts, additives, and water. In these etching processes, the metallic ions initially dissolve, and there is an increase in pH on the surface of the metallic substrate. Subsequently, a moderately soluble metal phosphate layer crystallises on the surface. The formed layer will have a thickness in the range of micrometres. For aluminium alloys, phosphatisation (chemoxal and phosphoric acid methods) can also be used. For the chemoxal method, substrates are immersed in a 6% solution of phosphoric acid salts

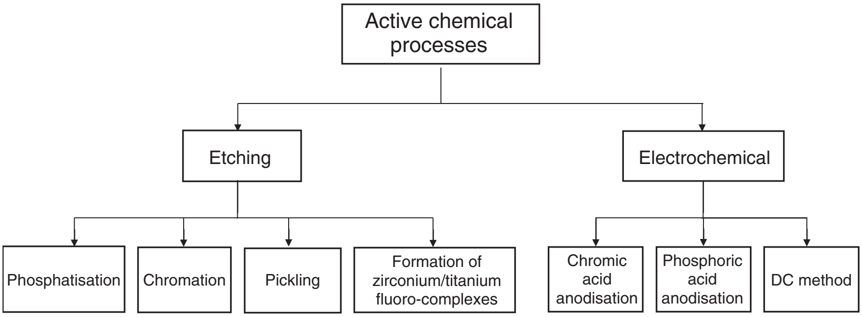


Figure 3.9 Classification of active chemical processes.

for one minute at 80 °C. For phosphoric acid methods, substrates are immersed for three minutes in a mixture of H_3PO_4, alcohols, and water. The formation of a phosphate-containing Al-hydroxide layer occurs, where the layer has a thickness in the micrometre range. Chromation is especially suitable for aluminium and magnesium alloys, as it promotes a powerful oxidising effect. However, extreme care must be taken with the effect of chromium ions on acid solutions. The most dangerous form is chromium VI, which is a known carcinogen. It is produced by industrial processes and affects the immune system of humans. Therefore, its use is often not recommended, despite being able to achieve good results. The corrosion-resistant layer formed has a thickness of 0.1–0.5 μm.

The pickling and Forest Products Laboratories methods (sodium dichromate /sulphuric acid) can be used as an alternative to chromation, especially for aluminium alloys, where an intense oxidising effect with a production of an acicular /honeycomb-shaped oxide structure occurs. This method is extensively used in the aircraft manufacturing industry.

The formation of zirconium/titanium fluoro-complexes is commonly used to process aluminium alloys but also suitable for high-purity magnesium alloys. In this method, the alkali/acid-cleaned surface is immersed in a solution that contains zirconium and/or titanium fluoro-complexes and organic components. Consequently, formation of highly insoluble aluminium–zirconium (or titanium) mixed oxides on the surface is observed, also with the organic component being incorporated as a complex ligand. This layer blocks the active centres of the metal to oxygen (corrosion protection) and acts as an adhesion promoter for adhesives.

Electrochemical treatments are especially used for aluminium and titanium alloys in the aircraft industry. In this treatment, the formation and growth of an oxide layer with a well-defined cellular structure occurs. The differences between a treated and untreated aluminium alloy surface are depicted in Figure 3.10. These

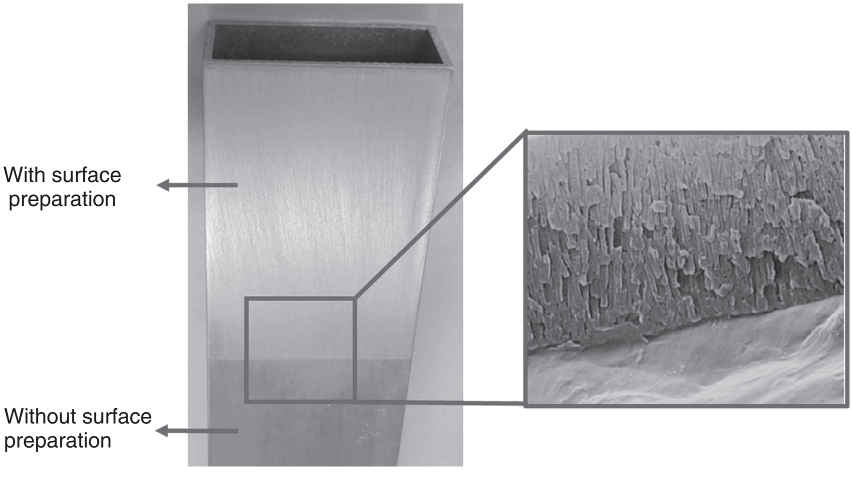


Figure 3.10 Surface modifications in an aluminium alloy before and after surface preparation.

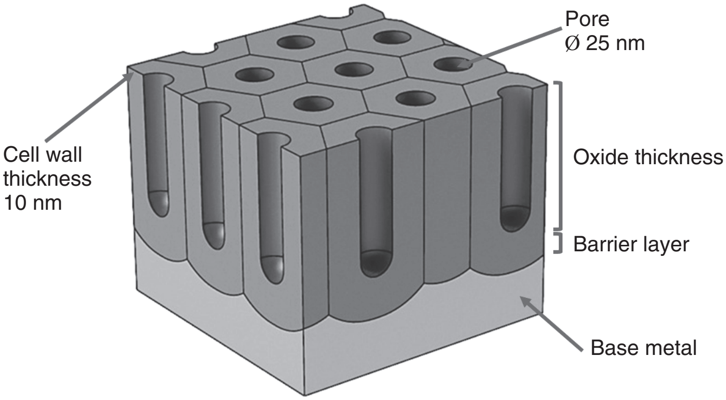


Figure 3.11 An idealised cell structure for the growth of an oxide after anodisation surface preparation (typical cell wall thickness and pore diameters for aluminium shown).

changes are easily observed with the naked eye but are especially obvious when observed under a scanning electron microscope. In electrochemical treatments, only ion-conducting oxides (e.g. Al_2O_3 and TiO_2) can be built up into thicker layers by anodisation, and Figure 3.11 schematically represents the oxide layer formed on the surface of a metal. Electron-conducting oxides (e.g. Fe_xO_y and Cr_2O_3) cannot be used for this purpose. The treatment takes place in acid anodising baths, where the substrate to be treated acts as an anode (with positive charge). Substrates treated with electrochemical methods present particularly good results with regard to adhesion, long-term stability, and corrosion resistance.

Polymers are considered a as class of materials that are quite difficult to bond, mainly because of their low surface energy and great chemical inertia. Chemical treatment of polymers is generally more difficult than that of metals and requires special care. The purpose of activating a surface is to create reactive locations on the surfaces intended for bonding. These reactive locations will generate strong van der Waals, hydrogen, and chemical bonds and can also provide a limited contribution to mechanical interlocking.

It should be noted that polymeric surfaces also contain pigments, antioxidants, and release agents, all of which can migrate to the surface and interfere or alter treatments. Thus, small changes in the formulation, or in its manufacturing process, can alter the surface condition of the polymer and jeopardise the quality of the surface preparation. It should be pointed out that polymeric surfaces are very active and thus can change rapidly with the handling conditions or temperature changes before bonding. Therefore, it must be ensured that the bonding process is fast and that the storage life will depend on the type of the polymer, the storage conditions, and the type of treatment applied.

Generally speaking, the chemical preparation (etching) of surfaces should follow a seven-step procedure. Initially, the surface must be cleaned, degreased, and dried. Subsequently, the bath should be prepared, considering the material-specific formulations and processes. Only then can the etching agent be applied (using a brush and a roller) or parts immersed in an etching bath. During etching, there should be a strict control of the process parameters (temperature and time). Afterwards, the treated surface should be rinsed with water, followed by another rinse with distilled water. At the end of this stage, the treated surface should be dried, which finally leaves the material ready to receive the adhesive application.

3.3.2.2 Physical–Chemical Processes

Physical–chemical processes can be applied to metals but are particularly effective in treating polymeric and composite materials. These processes are responsible for changing the texture of the surface to be treated and act by a diverse set of mechanisms. They can perform surface cleaning, where the surface is excited with enough energy to remove superficial contaminants or break fragile layers on the surface.

In essence, this type of surface preparation modifies the surface by its oxidation, removal weak layers, increase of surface functionality or free energy, and enhanced roughness. The oxidation of the surface is responsible for increased crosslinking and the subsequent introduction of functional groups that lead to the increase of surface energy.

One important note to remember is that the results obtained by these treatments can decrease with time, as the surface becomes highly reactive and can create bonds with compounds present in the atmosphere. Thus, it is highly advisable to perform the treatments with a short time window before the adhesive application.

Flame Flame treatment is a very simple and inexpensive polymer surface treatment that is carried out by exposing the surface of the substrates to an oxidising flame. The objective of this treatment is the oxidation of the polymer surface. This will lead to the formation of chemical complexes that are favourable to the establishment of desired bonds (thickness ≈ 5–10 nm). The phenomena intervening on the surface are of the same type as those that occur in alternative methods such as plasma treatment or corona discharge, but because this is a more energetic and energy dense method, it has more potential to damage the substrates.

Its effects quickly deteriorate with time, as the now highly chemically active treated material reacts with the atmosphere. Consequently, adhesive bonding should be performed immediately after treatment or within a short period of time. In some situations, where it is not possible to bond immediately after the treatment, a second treatment can be done to ensure good adhesion with the adhesive. Figure 3.12 schematically shows a flame treatment.

The main advantages of this methodology are related to its low cost and equipment requirements. It can be easily done manually and in on-site conditions and it is well suited for use in automated assembly lines. It is also suitable for large components and does not produce significant hazardous waste.

As the flame must reach all parts of the surface for the treatment to be successful, it has important limitations with regard to the geometry being processed, especially for thin components and complex shapes with many undercuts. In addition, it is also only suitable for processing polymers or composites with the polymeric matrix.

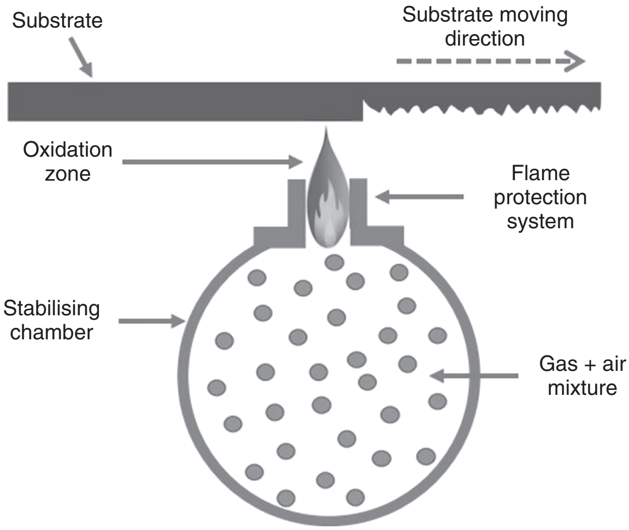


Figure 3.12 Schematic representation of flame treatment.

Plasma Plasma is one of the four main physical states of matter corresponding to a gas in which a certain portion of the particles is ionised. The basic premise is that the heating of a gas causes the dissociation of its molecular bonds, converting it into its constituent atoms. In addition, this additional heating may lead to the ionisation (gain or loss of electrons) of these molecules and the atoms of the gas, transforming it into a plasma containing charged particles (electrons and positive ions). Most polymeric materials present chemically inert and nonporous surfaces with low surface energy, non-receptive to adhesive bonding, and a plasma-based surface treatment modifies changes this by creating a chemically active surface, which adheres readily to adhesives.

Plasma treatment can be carried out with ionised air (atmospheric plasma) or with a specific gas, contained and ionised within a chamber (low-pressure plasma). In the low-pressure plasma process, the effectiveness of the treatment may change depending on the gases employed. For example, gases such as oxygen, helium, nitrogen, or carbon dioxide increase the surface energy of polymers, but when CF_4 is applied, the surface energy decreases instead.

Plasma treatment is probably the most versatile surface preparation technique. Generally speaking, plasma treatment is very effective, highly flexible, and quite inexpensive to use. In theory, it can replace practically all other active physical treatments. As shown in Figure 3.13, good wettability results are achieved by applying a plasma-based surface preparation. However, we must be aware that its equipment is quite costly and investment is only justified if there is a large series production or if the manufacture process relies on a wide range of different polymeric materials with different shapes, necessitating the flexibility offered by this process. Figure 3.14 shows the surface modifications that occur when a composite material is superficially prepared using atmospheric plasma.

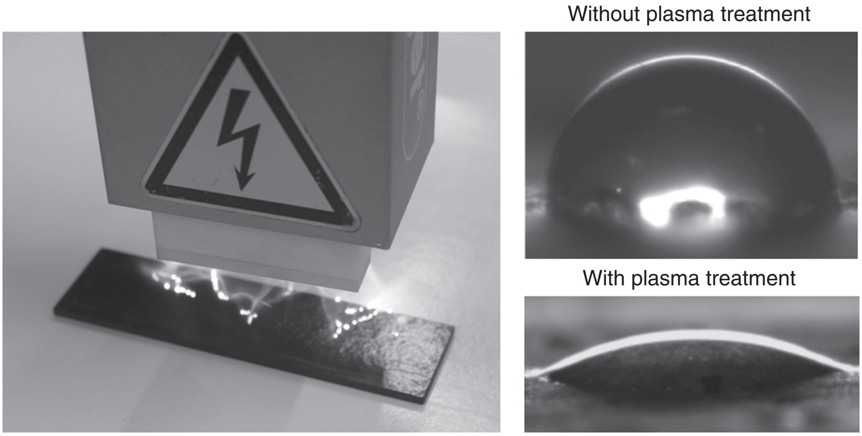
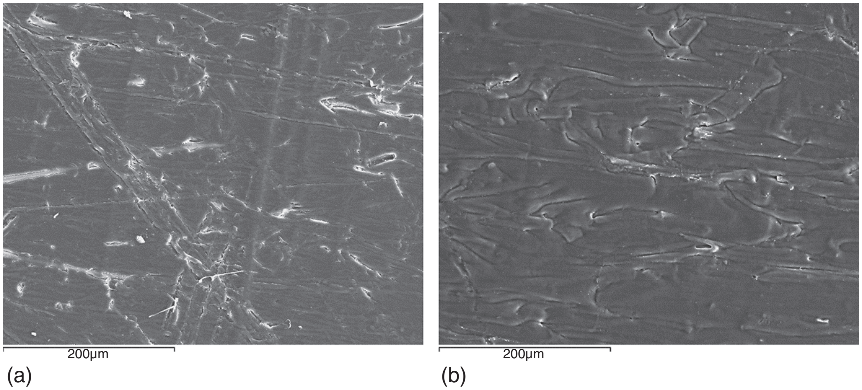


Figure 3.13 Atmospheric pressure plasma treatment (APPT) and its effects on the contact angle of a surface with and without surface treatment.



(a) (b)

Figure 3.14 Composite material without (a) and with (b) atmospheric pressure plasma surface preparation.

Corona Discharge Corona discharge treatment (CDT) is a surface modification technique that applies a low-temperature corona discharge plasma to promote modifications in the surface properties. A corona discharge plasma is simply the highly ionised air that surrounds an electrically charged conductive material, which is exposed to the atmosphere. This technique was first developed in 1951 by the Danish engineer Verner Eisby.

This treatment was initially developed to prepare the surface of polymeric films for the adhesion of paints and coatings, but its potential for adhesive joints was quickly noticed. This type of equipment is ideal for treating flat shapes such as films, allowing both sides to be treated simultaneously (see Figure 3.15). Usually, the equipment consists of a high-frequency generator, a high-voltage transformer, a fixed electrode, and an electrode formed by a roller, whose peripheral layer is a dielectric material.

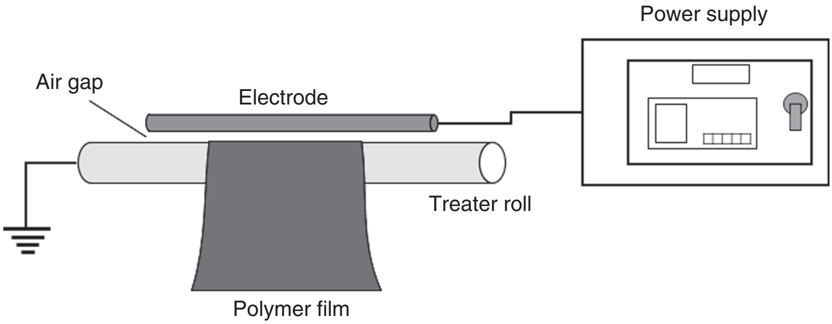


Figure 3.15 Schematic representation of corona treatment.

As is the case for plasma and flame treatment, the effects of the corona discharge greatly treatment diminish over time and thus also requires a minimal period between treatment and bonding.

This process is remarkable for its very high treatment speed and its ability to handle large surfaces, features which make it especially well suitable for use in industrial applications. However, the geometries it can process are quite limited, being almost exclusively used for treating films or plates. In addition, as with any treatment that relies on plasma, it is only suited for treating polymeric materials or composites with a polymer matrix.

Other Treatments In addition to the treatments already presented above, it is possible to treat surfaces to be bonded with alternative methods such as ultra-violet radiation or electronic bombardment. However, the industrial use of these methods is very limited, mainly because of difficulties in their implementation and the high associated costs, especially when compared to the methods already presented.

3.3.3 Primers and Adhesion Promoters

Primers and adhesion promoters are often used in industrial applications to improve the strength and durability of adhesive joints. Adhesive manufacturers have made an effort to innovate in this sector, creating surface preparation solutions suitable for use with the adhesive they market, creating complex product systems that include not only the adhesive components but also other substances intended to increase the adhesion level. Primers are often seen as a type of highly diluted adhesive to be applied like a paint to the surface to be bonded. Primers can fully wet the surface and establish a bridge between the surface of the material and the adhesive, having characteristics that enhance chemical bonding for improved adhesion (Figure 3.16). Its function is to mainly provide additional chemical bonding in a very thin film form, exploring physical effects such as surface tension and dipole interactions. It is also recommended to ensure that chemical compatibility exists between the adhesive and the primer.

Adhesion promoters serve as chemical adapters, changing the nature of the interactions that exist at the interface, as shown in Figure 3.17. Primers and adhesion

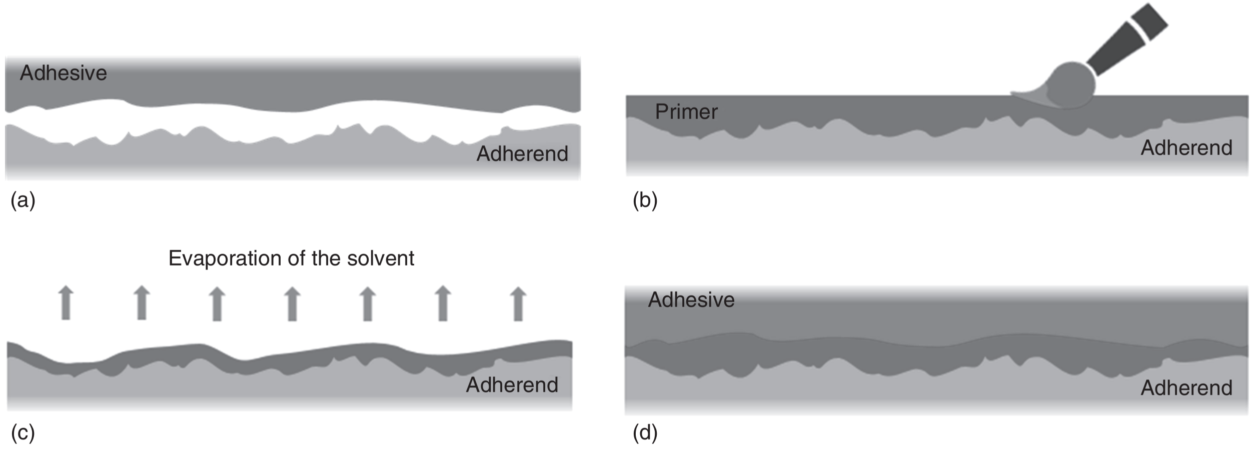


Figure 3.16 Application of primer and its principle of function. Application of adhesive without primer (a); application of a thin layer of primer (b); evaporation of the primer solvent (c); and application of adhesive with primer (d).

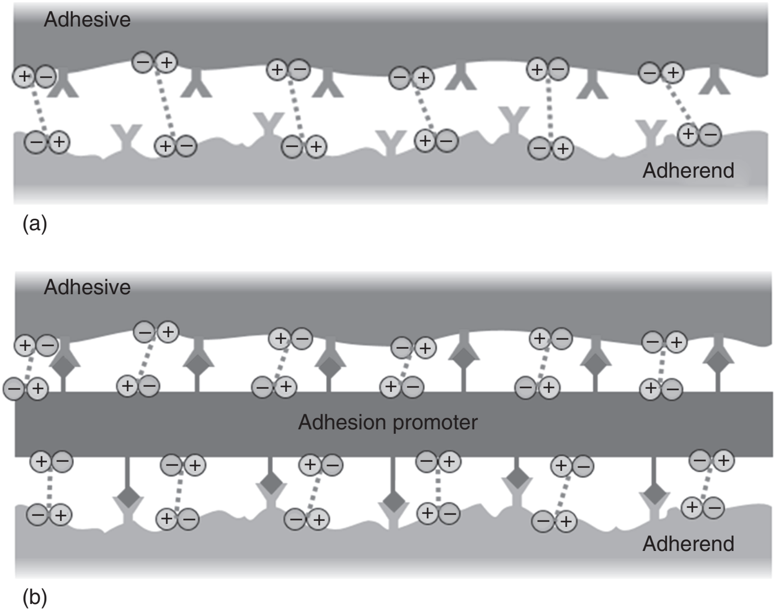


Figure 3.17 Application of adhesion promoters and its principle of function. Physical interactions between the adhesive and the substrate (a) and physical–chemical interactions between the adhesive and the substrate with an adhesion promoter (b).

promoters are applied uniformly, usually in a single thin layer. During application, it is necessary to consider their evaporation and opening time, and special care must be taken in order to avoid contamination while these materials cure.

3.4 Conservation of the Post-treatment Surface

As we have seen in the description of the physical treatments, in an ideal situation, treated surfaces should be bonded practically immediately after the completion of the treatment. Yet, as you might imagine, this is not always possible in practice. In industrial environments, because of practical and logistical issues associated with the production lines, the treated components might be stored until the bonding stage begins. This interval between surface treatment and the actual bonding can have detrimental effects on the joint strength if the ideal conditions of conditioning and preservation of the surface are not guaranteed. Therefore, depending on the treatment, conditioning and preservation actions should be taken. This usually indicates that the components should be stored under well-controlled humidity and temperature conditions and that, if possible, a protective film should be applied. This film has the objective of covering the surface to avoid the deposition of dust and dirt and isolating it from the atmosphere, minimising undesirable chemical reactions.

In fact, even when no surface preparation is carried out or only solvent degreasing is applied, the bonding process should not take more than one to two hours.

When applying shotblasting, the maximum exposure time will depend on the type of abrasion applied (wet or dry) and the susceptibility of the material to oxidation. For example, dry shotblasting applied on a steel surface has a maximum exposure time of four hours. If wet blasting is applied to the same material, the maximum allowable exposure time increases to eight hours. However, if the material to be treated is aluminium, the maximum exposure time increases to 72 hours.

Plasma surface preparation, a physical active process, provides maximum improvement in the surface energy for a short period of time after the treatment is concluded. From then on, there is a gradual decrease of surface energy, until the preparation becomes inactive. It is therefore advisable to bond the materials during this short interval of time. Please note that the duration of this period may vary as a function of the material treated and the parameters chosen for the surface preparation, as in some cases, it might last for a maximum of eight days.

Chemical active processes are known to remain active for longer periods of time. Etchings can be active from 6 to 30 days depending on the solution applied and the material to be prepared. Anodising, a process extensively applied to aluminium and titanium, not only significantly improves the stability of the surface of these materials but is also able to improve the adhesion for periods of up to 30 days.

As you might have understood, there is no single clear rule regarding the surface preparation and its conservation until the moment of bonding. Instead, you are advised to be fully aware of the various details that lead to development of a surface suitable for bonding, with a high surface energy, taking into account the concepts described by the adhesion theories in Chapter 2.

4

Main Families of Adhesives and Adhesive Selection

If you have decided to use adhesive bonding to build a new structure or repair something important that is broken, it is very likely that the first question that you will have will be: What adhesive should I use?

Even if you do not know anything about adhesives, you might know some of its most common designations, such as contact glue, superglue, epoxies, hot glues, and silicones, but the world of adhesives is vast and full of nuances. In fact, the selection of a correct adhesive is a problem that challenges even the largest companies when they decide to implement adhesive bonding in a production process. In addition, it is also important to stress that this selection process is exclusively related not only to the chemistry of the adhesive material itself but also to a wide variety of other factors, such as the adhesives viscosity, how it cures, etc.

In light of these difficulties, the aim of this chapter is to first provide a concise description of the adhesives available on the market, their advantages, limitations, and typical uses, allowing it to be used as a reference in a material selection process. However, to do so, it is important to first classify adhesives into well-defined categories. Therefore, we will start this chapter by analysing the ways we can use to characterise adhesives. Then, using these categories to guide us, a procedure for adhesive selection will be proposed, allowing a simple and direct process for adhesive selection.

4.1 Typical Composition of a Modern Adhesive

Adhesives are mostly polymeric materials and include in their composition several different chemical compounds with different functions. As an example, the most commonly used structural adhesives are the epoxy adhesives, which have in their base an epoxy resin. Before hardening takes place, this resin is not polymerised, which indicates that the material has not yet polymerised. To provide for this, adhesives often include a hardener compound, which can be supplied by already mixing in the resin or can be supplied separately in a different container, as a part of an adhesive system. The hardener is often supplemented with accelerators, substances that further promote the hardening process. A modern trend in adhesive formulation,

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Eduardo André Sousa Marques, Ana Sofia Queirós Ferreira Barbosa, Ricardo Joao Camilo Carbas, Alireza Akhavan-Safar, and Lucas Filipe Martins da Silva.

as we will see in more detail further along this chapter, is to include more than one resin type in a single adhesive, creating hybrid formulations with enhanced mechanical properties. For example, an hybrid adhesive can include a strong and stiff resin to provide strength and a more flexible and ductile material, providing toughness.

However, many high-strength adhesives, as is the case of an epoxy, are quite stiff and naturally brittle, which make them quite unsuitable for use in demanding applications. Adhesive manufacturers solve this issue by introducing additional compounds in the adhesive mixture, known as tougheners and flexibilisers. Tougheners increase the capability of the adhesive to absorb energy and allow adhesives to resist to crack propagations. Rubber particles are perhaps the most famous toughener material, being extensively used to toughen highly brittle epoxies. Flexibilisers also improve the peel and impact strength by allowing the adhesive to deform under the application of stress.

Adhesives are often charged with filler materials, which can be used to reduce costs but also improve some of the adhesive properties. For example, certain fillers facilitate the processability of the adhesive, while others are able to enhance their mechanical performance. However, a balance often must be struck because the use of fillers might have negative effects in other characteristics of the adhesive.

Adhesive formulations can also include solvents and diluents, with the express objective of lowering the viscosity of the uncured adhesive. This can have two objectives. The first is to allow for a better mixing of the diverse adhesive components during the manufacture or between the resin and the hardener and the second is to make the adhesive more fluid so that it wets the surface better. Solvents and diluents are typically liquid compounds that are chemically and physically compatible with the adhesive resins.

4.2 Methods for Adhesive Classification

Adhesives are a diverse set of materials and can be classified in many ways, but five classification methods are the most important for material selection purposes. These are the molecular structure, the chemical composition, the physical form, the mechanical performance, and lastly the hardening method.

4.2.1 Molecular Structure

Most adhesives are polymers, sharing their basic chemistry with the common plastics that we use extensively in our everyday life. These materials have large molecules composed of many repeated subunits which are called monomers. The monomers are joined in a process we call polymerisation, a process shown in Figure 4.1.

In polymerisation, monomer molecules react together in a chemical reaction, forming polymer chains or more complex three-dimensional networks. These polymeric chains can be organised into four different ways, which gives rise to the four categories in the molecular structure general classification. These are the thermosets, thermoplastics, elastomers, and the hybrid materials.

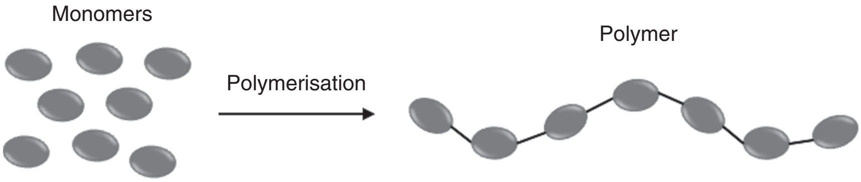


Figure 4.1 The polymerisation process.

4.2.1.1 Thermosets

Thermosets have tightly packed polymeric chains, which, because of their closeness, are interconnected by many chemical bonds (known as a highly reticulated structure), which are shown in Figure 4.2. Thermosets are also impossible to melt, which indicates that they can operate at relatively high temperatures without damage. This strong structure indicates that if you are seeking a very strong material for using in an important structure, you should use thermoset adhesives, as these include the stiffest and strongest adhesive formulations.

4.2.1.2 Thermoplastics

In contrast to thermosets, thermoplastics present a much more open molecular structure, with less connections between the different polymeric chains. The polymeric chains are thus freer to move and slide relative to each other, and the main consequence of this freedom is the fact that they can melt and become liquid above a given temperature (the fusion temperature). Thermoplastic adhesives have relatively low strength and are highly flexible, not being especially well suited for structural applications. Thermoplastic adhesives find extensive use in the assembly of non-structural panels, liners, and cables. Hot glues are an excellent example of thermoplastic materials, as they are melted during the application process to fill gaps and provide bonding strength when solidified. Figure 4.3 shows examples of the typical polymeric chains present in thermoplastic adhesives, demonstrating their restrictive and poorly reticulated nature.

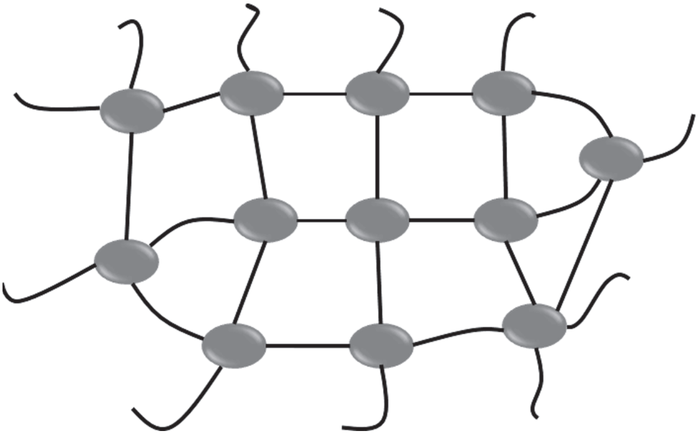


Figure 4.2 Highly reticulated structure of a thermoset adhesive.

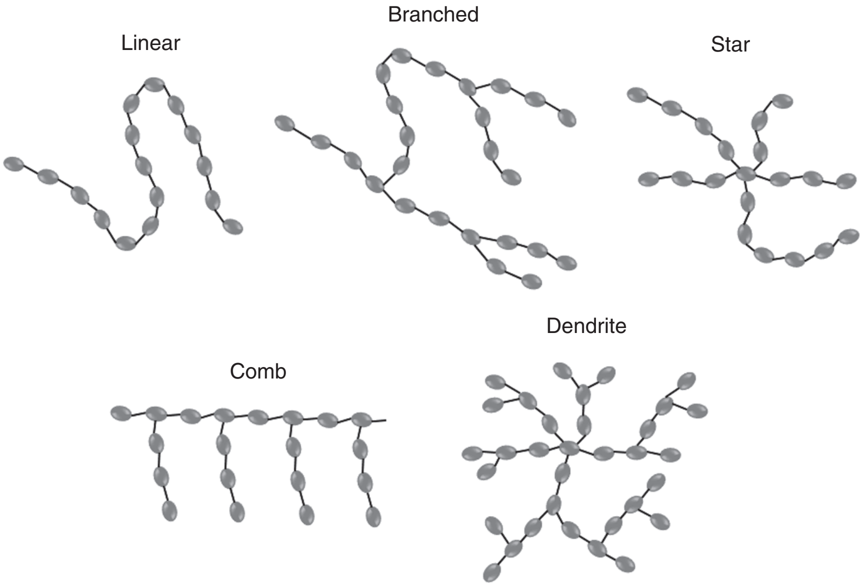


Figure 4.3 Different polymeric chains present in thermoplastic adhesives.

4.2.1.3 Elastomers

Elastomers are polymers with the highest degree of freedom in their molecular structure, having long polymeric chains that are only interconnected by widely spaced crosslinking connections. As a result, an elastomer adhesive is very flexible and can stretch to become several times longer that its initial length. The strength of these adhesives is quite low, but the extremely low stiffness is very useful for many applications where we wish to be able to absorb vibration or large relative movements. Figure 4.4 shows a typical structure of an elastomer, showing the sparse connections between multiple chains.

4.2.1.4 Hybrid Materials

Hybrid materials are those that do not necessarily conform to a single of the three groups presented before. This indicates that they are composed of a combination of substances with distinct molecular structures. An important example of this group is the toughened thermoset adhesives, which we have already touched when describing the typical composition of an adhesive. Why is this type of combination necessary? The reason is usually the search for increased toughness. Thermoset adhesives, as described above, are stiff and strong but come at a cost of a fragile behaviour similar to that of a glass. Fragile materials break suddenly because cracks progress through the material very quickly. However, if a fragile material, such as a highly reticulated thermoset, is reinforced with elastomer particles, the movement of the crack will be slowed when they reach these particles. The crack will have to move around the particle and energy will be consumed by separating the particle from the adhesive matrix. This process is usually known as cavitation, representing the formation of voids around the rubber particle, as shown in Figure 4.5.

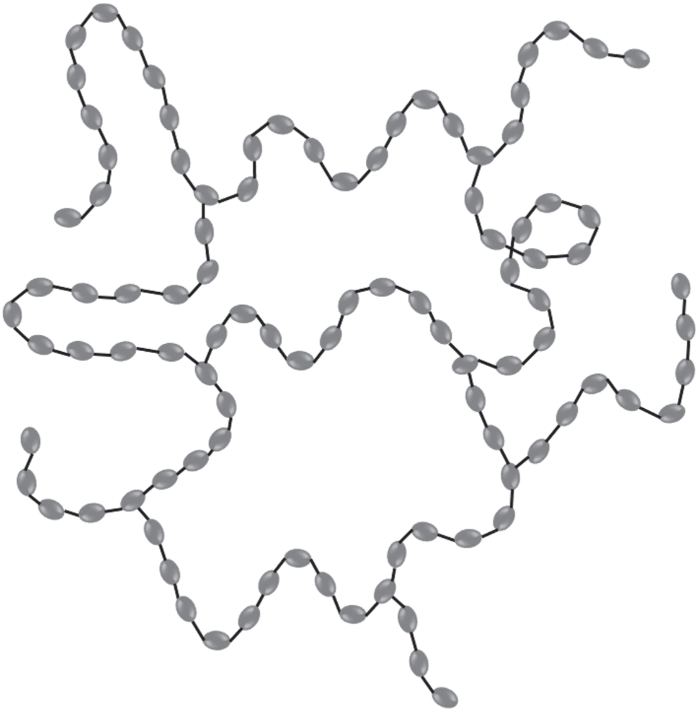


Figure 4.4 Molecular structure of an elastomeric adhesive, showing the widely spaced crosslinks between the polymeric chains.

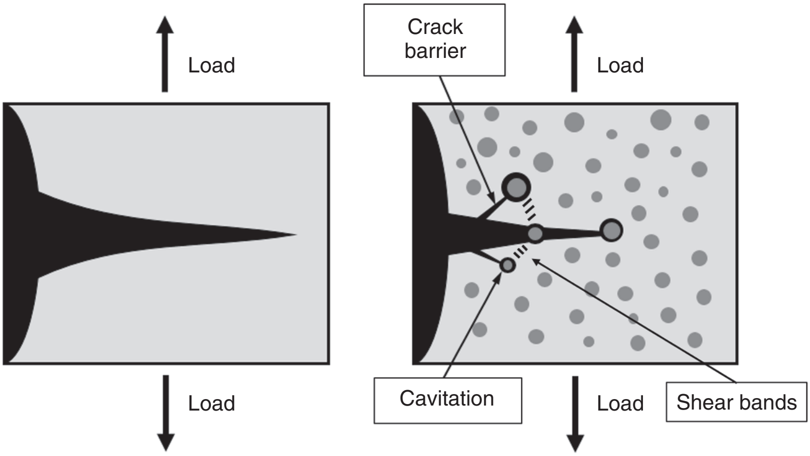


Figure 4.5 Arrest of crack propagation in a thermoset adhesive reinforced with rubber particles.

In addition, there is also the formation of shear bands around the particles, which consume energy as the material yields. These reinforced adhesives thus combine the high strength of the thermoset adhesives with the incredibly high toughness of the elastomeric materials. In fact, many adhesives available on the market explore some type of reinforcement of this type, as it enables great improvement of the mechanical behaviour at a low cost.

4.2.2 Physical Form

The physical form of an adhesive is a major factor in its selection process, as it will determine if an adhesive is suitable for use in a given application. As an example, if one must apply an adhesive to a tight, relatively inaccessible gap, only a liquid adhesive can be used. In contrast, if one wishes to fill a gap thicker than 0.2 mm, only a paste adhesive will be suitable, as it has the necessary viscosity to remain in place and not flow out of the bond line. Therefore, it is highly important to be aware of the different physical forms that adhesives can present. Adhesives can be obtained in liquid form, as pastes, films, and tapes.

Figure 4.6 shows these adhesive forms, highlighting the diversity of the adhesives available in the market in this regard.

In general, paste adhesives find extensive use in the automotive industry, where good gap filling capabilities are crucial. In contrast, film adhesives are commonly found in aeronautical applications, as they provide a very precise way to metre the adhesive and to control the adhesive layer shape. More detail on the different adhesive forms and the way they influence the manufacturing process of a bonded joint is presented in Chapter 5.

4.2.3 Mechanical Properties

It is common to see high-performance adhesives being referred to as structural adhesives. However, what are these structural adhesives and what distinguishes them

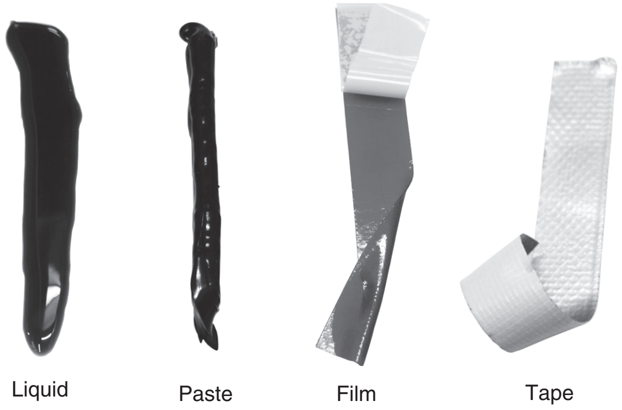


Figure 4.6 Examples of the four main forms of adhesives.

from a non-structural adhesive? Well, the difference is somewhat arbitrary, but most authors agree that the difference between them is the tensile strength. Structural adhesives have a tensile strength above 7 N of force for each square millimetre of bonded area (or 7 MPa). This value shows the remarkable load carrying ability of structural adhesives, as even the weakest structural adhesive can support a kilogram (which exerts 9.8 N of force) with a very limited bonded area, slightly larger than 1 by 1 mm. High-performance structural adhesives can go up to 40 or even 50 MPa, which is more than enough to manufacture a high-performance racing car, an airplane or a spaceship.

4.2.4 Hardening and Implementation Method

The hardening method of an adhesive is an extremely important parameter, especially for industrial applications. Although you and I can live with an adhesive that takes 24 hours to cure if we need to repair something in our homes, an engineer creating a bonded vehicle structure knows that the lengthier manufacturing processes will lead to higher costs. Thus, if the adhesive can be made to handle loads faster, this indicates that the factory can manufacture more cars per day. Consequentially, industrial users highly value adhesives that cure in minutes or even in seconds, although with these rapid hardening times, other challenges arise (such as a very low pot life, a term indicating that they must be used almost immediately after their preparation).

The hardening method, also called as curing method, is mainly related to the method by which the adhesive becomes solid enough to carry a load. However, please note that not all adhesives undergo a phase transition and a traditional hardening process. Some, known as pressure-sensitive adhesives (PSAs), never really undergo any phase change. Considering this fact, it is more correct to divide adhesives into three distinct implementation methods. Two of these involve phase changes and hardening and the other relies only on the application of pressure to the adhesive (PSAs). We will start our analysis with the study of chemical reaction hardening, advance to those that use a physical process and lastly analyse the particularities of the PSAs.

4.2.4.1 Hardening by Chemical Reaction

Although many different adhesives cure via a chemical reaction process, there are many different ways to do so. First, we need to remember that when uncured, most adhesives exhibit a non-reticulated structure, often in a non-polymerised state. Thus, we need to supply some sort of stimuli to ensure that the adhesive will polymerise and reticulate, providing the necessary mechanical cohesion to create a strong bond.

We already know that many adhesives are composed of two different components that, when mixed, react to create a solid, cured adhesive, one of which is the resin, the main component of the polymer, and the other is the hardener, a chemical compound that will react with the resin (often releasing significant heat in an exothermal reaction) and cause it to polymerise and reticulate. Before the mixture is complete, these components are very stable, but when they are mixed, they strongly react and the cure can be quite fast, although the curing speed depends on the amount of hardener used.

Alternatively, some adhesives are supplied with the resin and the hardener already mixed in a single container and are known as one-part adhesives. However, why there is no cure inside the containers? The trick is ensuring storage at low temperatures. The polymerisation and reticulation processes are, as many chemical processes, strongly accelerated by heat. By storing a pre-mixed adhesive at low temperatures, it is possible to greatly delay the hardening process.

Other one-part adhesives do not require the existence of a separate hardener and resin and cure instead via the application of an external energy source or in the presence of a catalyst. For example, many adhesives and pastes used in dentistry start to cure when exposed to ultraviolet (UV) light. This light will provide the necessary energy to start the reticulation process. Other sources of radiation, such as visible light or electron beams, can also be used to cure adhesives.

A catalyst material can also be used to promote the curing of one-part adhesives. Well-known examples are the thread locking adhesives, which are adhesives that are used to provide additional strength to threaded connections. These adhesives have their cure initiated by the contact with the metal that is used in the fasteners. Silicones, on the other hand, cure in the presence of water. Water vapour present in the environment will serve as a catalyst to initiate the curing of these materials, which is quite practical as these adhesives often find use as sealants.

4.2.4.2 Hardening via Physical Processes

Many low-strength adhesives are provided as a suspension within a liquid solvent or in water. The most famous of these are the contact adhesives, which find extensive use to bond fabric or shoe components. With the use of a heat source, the solvent will evaporate and only the dry adhesive will remain in the surface. The surfaces to be bonded should then be forced into contact, generating a strong bond. These adhesives never undergo a chemical change, and their operation is similar to that of PSAs but supplied in a liquid solution. The use of highly volatile solvents has been gradually reduced, and the use of water-based solutions is now preferred instead, as this reduces the health hazards and the pollution associated with these materials.

Another common type of adhesive that is implemented via a physical process is hot melts, also known as hot glues. These thermoplastic-based adhesives do not undergo any type of chemical change during their application. They are simply heated up to a temperature above their fusion temperature, become liquids, and flow and wet the surface to be bonded. As the source of heat is removed, they cool down and solidify, creating the desired bonded connection.

4.2.4.3 Pressure-Sensitive Adhesives

PSAs are a particular subset of adhesives that do not undergo any type of change in their application process. These soft, visco-elastic solids are completely non-reactive and form a bond because of the pressure applied between the adhesive and the substrate. The adhesive adheres to the surface because of its tackiness, achieved with special compounds known as tackifiers, of which rosin ester is an example.

Tackifier compounds lower the surface energy (which enhances wetting) and improve the adhesion, which is attained via van der Waals forces. The molecules of PSAs exhibit dipole moments, and they induce dipole moments in the surface molecules of the substrate. The oppositely charged molecules of the adhesive and the substrate form physical bonds whose strength is related to the effectiveness of the wetting (the closeness between the adhesive and the substrates). If pressure is applied, the adhesive will penetrate further into the surface and increase the strength of this attraction. As they rely solely on van der Waals forces, PSAs are always low-strength adhesives, but, unlike most adhesives, they are easily removable, reusable, and highly flexible, which allows them to find use in diverse applications, such as tapes, labels, stickers, and automotive trims.

4.2.5 Chemical Composition

The chemical composition of an adhesive refers to the identity of the chemical compounds that makes it up. This is a very common way to classify adhesives; in fact, most adhesive manufacturers will divide their product line into the different chemical families of adhesives. If you ever heard about an epoxy adhesive or a silicone adhesive, these names refer exactly to the chemical composition. Sections 4.3 and 4.4 provide a list of the main families of adhesives and non-structural adhesives, divided according to their chemical composition.

4.3 Main Structural Adhesives

4.3.1 Epoxy Adhesives

Epoxy-based adhesives are known as the king of adhesives, as these are quite strong and stiff materials, which find extensive use in structural applications. If you are considering an application where maximum mechanical performance is necessary, epoxy adhesives will often be the only choice available. You will find epoxy adhesives in many cutting-edge aerospace applications, where they are used to bond sandwich panels, advanced composites, and exotic metal alloys. Epoxy adhesives are very important industrially and cure exothermically (that is, they release heat during the curing process). They are also dimensionally very stable, which indicates that they will not shrink significantly during the curing process, an essential feature for high precision applications that ensures stress-free joints. In general, cured epoxies are very stable and durable and are not damaged by contact with water, solvents, or oils. Going back to the example of the aeronautical industry, it is now common to see that an epoxy-bonded aircraft structure remains in service for several decades. Epoxies are available in one-part or two-part formulations, with both finding extensive use. One-part epoxy adhesives cure with high temperature. However, they cannot be stored for long periods of time, as they become damaged, especially if they are not kept refrigerated. For two-part adhesives, curing can be done at room temperature and with relatively low shrinkage. Shrinkage is the reduction of volume that adhesives undergo while curing, which can be detrimental for the geometrical characteristics of the joint and can also stress the adhesive layer. More details on shrinkage are given in Chapter 5.

As highly crosslinked thermosets, they are strong and stiff but fragile, so commercial versions of epoxies are usually hybrids, reinforced with small amounts of rubber or other tough material. In the unreinforced epoxies, cracks can progress relatively unimpeded, but the presence of small rubber particles will hinder this free crack propagation. This will greatly increase the toughness of the adhesive at the cost of a slightly reduced mechanical strength and lower resistance to high temperatures.

Besides rubber, it is very common to see epoxy adhesives reinforced with other materials to attain a specific property improvement. For example, epoxy–polyurethane hybrids are extremely popular in the automotive industry, combining the stiffness and strength of the epoxy resin with the toughness of the polyurethane, which gives them excellent impact absorbing capabilities. These very tough and ductile materials, known as crash-resistant adhesives, can bond surfaces that have not been previously prepared (which are, for example, contaminated with oil), all of which are features that make them especially well suited for joining vehicle bodies.

If instead we are searching for an epoxy adhesive that performs well at high temperature, we can choose one reinforced with a phenolic resin. Phenolic materials are known to exhibit high thermal resistance, so the resulting hybrid adhesive will excel at high temperatures, providing a significant strength at up to 175 °C. However, these materials have a significant drawback, which is their low toughness. These are relatively fragile materials that must not be exposed to impacts. The main use of these materials is in aeronautical applications, bonding sandwich structures that operate at high temperatures, caused by the friction generated in high speeds or heat from the motors.

4.3.2 Polyurethane Adhesives

Polyurethanes are part of another very important adhesive family, as they can easily be formulated with a wide range of mechanical properties. They can be made very flexible and tough, distributing stresses evenly along a bondline or they can be formulated to be stiff and strong, rivalling epoxies in sheer mechanical performance.

Polyurethanes are available in one- and two-part formulations. The one-component variants (sometimes referred to as 1C or 1K PUR) are those that exhibit higher flexible and cure by reaction with water from the surroundings. The cure process is generally very slow (lasts multiple days) and dependent on a minimum air moisture content (approximately 40% relative humidity), although temperature can be used to accelerate the curing process. These materials are known for their excellent strength at low temperatures, although their mechanical performance drops quickly at high temperatures. They are also able to bond substrates with low adhesion (low surface energy) such as glass or plastics, for example, although the use of primers is often recommended to achieve maximum durability. One-component polyurethane adhesives are typically found in applications where both sealing and flexibility of the bondline are necessary, the main example of which is the windscreen in a vehicle. In this application, the flexible bondline can isolate the glass from the deformations that occur in the vehicle structure, while providing a very durable, waterproof joint.

In contrast, two-part systems (also called 2C or 2K PUR) are now more widely used in structural applications because they have very high strength to both shear and peel loads. In addition, these materials still retain the capability to absorb impacts and vibrations, the capability to bond to difficult substrates, and durability under very adverse environmental conditions. The two-part formulation enables them to cure more quickly, without being dependent on moisture or heat application. One key application of two-part polyurethanes is to bond panels in vehicle structures. In this application, the polyurethane adhesive plays a key role in vehicle safety, as the use of a tough and flexible adhesive ensures that the vehicle structure is compliant but remains unbroken during a crash, leading to maximum energy absorption.

4.3.3 Acrylic Adhesives

When an application demands a very fast curing adhesive, acrylics are usually the right answer. These adhesives, while not as strong and stiff as epoxies, still find extensive use in structural applications because of their extremely fast cure, which can greatly accelerate the production processes of bonded components. Less time spent on manufacturing usually means reduced product cost, which is why these adhesives have become increasingly popular in the past few years. They can also bond to very poorly prepared surfaces, even those that are contaminated, allowing to eliminate additional costly surface preparation steps.

Acrylic-based adhesives are typically divided into three major groups. These are the anaerobic adhesives, the cyanoacrylates, and finally the modified acrylics. Let us start with the anaerobic adhesives.

The expression ‘anaerobic adhesive’ indicates an adhesive that does not require air to cure. These are more widely known as threadlocking adhesives because of their most famous applications. In this case, a one-component adhesive is used to ensure that a fastener will not come loose during service. The curing process of these adhesives requires two conditions: the first is the previously discussed lack of air, a condition that is created when the adhesive is applied inside a thread. The second is the presence of a catalyst, which is usually the metal that forms the thread and the fastener. In this case, the cure will be generally fast, within a few minutes or hours. Because of the peculiar curing process, this adhesive can only be cured in thin layers (less than a tenth of a millimetre); however, it retains its strength under a wide range of temperatures (−55 to 150 °C) and does not require any type of surface preparation.

The second major group of acrylic-based adhesives are the cyanoacrylates. You might already know these materials by their popular name of ‘superglue’. As you might have experienced first-hand, they are one-component liquid adhesives that cure in minutes, catalysed by the presence of moisture. They are relatively fragile materials, which have found use in very specific applications where small components must be precisely and quickly bonded. Note that large areas cannot be bonded with these materials because the curing process starts almost immediately after application. These materials thus have a very short pot life. Although they are resistant to oil, they are not very durable to moisture. The main users of these materials are the optical and electronical industries.

Finally, the strongest of the acrylic-based adhesives are the modified acrylics. The most important of these are the methyl methacrylate adhesives. These are the two-component adhesives that can challenge epoxies and polyurethanes in major structural applications. Although their strength and stiffness are below that of epoxies, they are among the fastest curing structural adhesives, not necessitating long curing times or controlled temperature ovens for completing the curing processes. They often contain rubber and additional strengthening agents to ensure maximum toughness. Methyl methacrylates are widely used in highly technological applications such as the aerospace, automotive, and marine industries. Their fast cure makes them especially well suited for high-volume production lines. Their service temperature is usually limited between −40 and 120 °C, which is sufficient for automotive applications. One final characteristic of these adhesives that is worth mentioning is their very strong odour, which can make working with these adhesives a very uncomfortable proposition. Efficient ventilation systems are indispensable when these adhesives are used.

4.3.4 Phenolic Adhesives

Phenolic adhesives are relatively inexpensive adhesives that are usually provided in liquid or film forms. These are thermosetting resins (they do not melt with temperature) that can withstand high temperatures (up to 180 °C) and harsh environmental conditions (high moisture and exposure to oil and solvents). They are relatively fragile and exhibit low peel strength. Nonetheless, they are quite creep resistant. A major disadvantage of phenolic structural adhesives is the fact that the cure process requires both heat and pressure. These adhesives cure via a condensation process (described in more detail in Chapter 5), which indicates that during cure, water molecules are generated and released into the adhesive. Because of the high cure temperature (of more than 100 °C), vapour bubbles are formed and become trapped, which can lead to a highly porous adhesive layer. To avoid this effect, phenolic resins must be always cured under constant pressure.

Phenolic resins readily penetrate and adhere to many organic and inorganic fillers and reinforcements. They are highly compatible with cellulose fillers, which make them an ideal binder for particleboard, plywood, and other processed wood products. Liquid phenolic resins are also used to penetrate and saturate paper.

As is the case for the other adhesives presented in this section, phenolics often are supplied as modified adhesives. The most common among these are nitrile-phenolic, vinyl-phenolic, and neoprene-phenolic adhesives. They are manufactured in solvent solutions and as supported and unsupported films. In the case of the solvent-based adhesives, an evaporation cure is employed. An important historical note is the fact that the first truly structural adhesive used in the aeronautical industry was a vinyl-phenolic formulation (of the Redux series), developed in the United Kingdom during the early stages of World War II.

4.3.5 Aromatic Adhesives

The last major group of structural adhesives is the aromatic adhesives, which are the most temperature-resistant structural adhesives in existence, able to sustain temperatures up to 280 °C, almost 100 °C above all other major structural adhesives. Almost exclusively supplied in film form, these are of high cost and difficult to process materials that are specifically formulated for joining components that will be subjected to intense temperatures, finding use almost exclusively in aerospace applications.

Although extremely resistant to harsh environments, they are quite limited in their mechanical behaviour, being fragile and having low resistance to peel forces. In addition, their toughness cannot be easily increased by adding other materials as is the case for other adhesives. They are available in different formulations, the most common of which are the polyamides, bismaleimides, and polybenzimidazoles. As described for the phenolic adhesives, the processing of aromatic adhesives is only possible with the application of pressure to avoid excessive porosity.

4.4 Main Non-structural Adhesives

4.4.1 Elastomeric Adhesives

Elastomeric adhesives are very flexible adhesives based on natural or synthetic rubber-based materials. These adhesives have excellent peel strength and toughness but low shear strength. Their extreme elasticity and toughness lead to good fatigue and impact properties. Elastomeric adhesives are used in applications where the joint is subjected to large movements, impact, or any other conditions where there is a significantly relative movement of the bonded substrates, such as, displacements caused by thermal expansion. Being relatively inexpensive, these adhesives are also widely used as sealants, as they can fill large gaps effectively. They also find use in instrumentation and electronics, construction of optical components, and thermal protection panels.

There are many different elastomeric materials that can be used for non-structural applications. These are natural rubbers, styrene-butadiene rubber, polyurethanes, butyl rubbers, polysulfides, polyisobutylenes, silicone, nitrile rubber, and neoprene.

Silicone rubbers have extremely high temperature resistance, which allows them to be used in extreme applications such as thermal protection systems for aerospace applications. However, most elastomeric adhesives react poorly to high temperatures and cannot be used above 100 °C. In addition, another important disadvantage associated with these adhesives is the fact that a significant amount of creep. Creep is the slow and gradual adhesive displacement that occurs under relatively low mechanical loads, much lower than those necessary to break the adhesive. If left unchecked for long periods of time, an adhesive joint can fail because of excessive creep. For most adhesives, creep is only significant at high temperature, but in some cases, it might easily occur at room temperature. This means that a relatively unloaded joint held together by these adhesives can easily deform if not designed to account for creep.

4.4.2 Polyester Adhesives

Polyester adhesives are non-structural and relatively inexpensive materials. Generally, polyesters have high peel strength and are used to join materials that are usually difficult to bond, such as glass, plastics, rubber, and wood. Polyesters are resistant to solvents, water oils, and even some acids. Polyesters are available in two main types: saturated polyesters and unsaturated polyesters. While saturated polyester adhesives have no double bonds (a covalent bond between two atoms involving four bonding electrons) in their main chain, unsaturated polyester resins have double bonds in their main polymeric chain. This chemical particularity is the root of a significant difference between the two types of polyesters: while the saturated polyesters are thermoplastics, the unsaturated polyesters are in fact thermosetting resins.

Saturated thermoplastic polyester adhesives exhibit high peel strength for a non-structural adhesive and are mainly used to laminate plastic films, such as polyethylene terephthalate (PET) and bond fabrics. These materials have the particularity of being perfectly transparent, which makes them useful for the assembly of high-quality optical components (camera lenses, for example). This type of polyester adhesive is available in solution or as solid films.

Unsaturated polyester adhesives are supplied in two-part systems that harden when a catalyst is introduced, with an exothermal cure. Unsaturated polyester resins are of low cost, low-strength alternatives to epoxy resins applied to the surfaces to be bonded with a brush or a roller or by spraying. They are usually applied in the production of glass fibre laminates, optical products, and in the repair of composite panels.

4.4.3 Hot Melt Adhesives

Commonly known as hot melts, these are cheap and easy-to-use thermoplastic adhesives. These adhesives are heated and melted to fill a bondline and, upon cooling, solidify and form a strong bond. They are quite flexible, possess low mechanical strength and low temperature resistance. Hot melts are extensively used for carrying out small repairs, fixing wiring and panels and sealing packaging, among many other applications. Hot melt adhesives are also used to replace solvent-based adhesives, as they provide some important advantages over these materials. For example, the emission of volatile organic compounds is greatly reduced and no drying or curing steps are necessary. Also, as they are stable in the solid form, with extremely long shelf lives. A long shelf life indicates that the adhesive can be stored for long periods of time while it awaits use, without any significant degradation of its properties. In addition, these materials are also very safe to handle, with generally low toxicity.

Among the main disadvantages of this type of adhesives are the fact that they cannot be used to bond substrates that are temperature sensitive and that the adhesive itself has a very low high-temperature resistance. If the melting point of the adhesive is exceeded, the adhesive will melt, flow out of the bondline, and the joint will fail.

The temperature resistance can be increased by combining a hot melt with an adhesive that cures after the hot melt has solidified. For example, a polyurethane or silicone will continue to cure as it is being catalysed by humidity or an ultraviolet curing resin can be used instead.

4.4.4 Inorganic Adhesives

All the adhesives described up to this point possess what is called an organic chemistry. That is, they are all organic based compounds, which contain carbon connected with covalent bonds in their structure. However, there is a specific type of adhesive that does not rely on this type of chemistry but instead uses solely inorganic compounds. These are the inorganic or ceramic adhesives. This chemistry makes them extremely resistant to high temperatures, able to operate over 600 °C. Although they can be likened to conventional cements used in civil engineering, ceramic adhesives are based on alkali silicates and various metal phosphates, usually filled with a ceramic powder. During the curing process, a combination of dehydration and chemical reactions occur within the adhesive, creating a solid refractory layer.

It must be noted that the high temperature capabilities of these materials come with several important drawbacks such as their high cost and complex curing process. The curing temperature depends on the binder being used and can range from a minimum of 250 °C, up to 1000 °C, very far from the temperatures used to cure organic adhesives.

However, the most important challenge associated with the use of these adhesives is the fact that they are extremely fragile, possessing very low resistance to peel and shear. Because of the inherent fragility and generally low mechanical performance of inorganic adhesives, their use is strictly restricted to low stress, high temperature, or corrosive environments, usually bonding ceramic or metal substrates.

4.5 How to Select an Adhesive

The process behind the selection of an adhesive is quite complex and requires exact knowledge of different aspects related to the joint configuration, manufacture, and its service conditions.

We can begin our analysis by looking at the joint geometry. This is a complex subject and will be better addressed in the chapter related to adhesive joint design (Chapter 8). Nonetheless, it is still possible to illustrate how the joint design will affect material selection. For example, will our joint load the adhesive mainly under shear or will large peel forces exist? Can we use a large adhesive layer to reduce the stresses acting on the adhesive layer or are we restricted to very small adhesive layers? All this directly influences the adhesive selection, as we often do not require the best performing (and most expensive adhesives) if we correctly design a joint. A second aspect associated with the joint configuration is the nature of the substrate materials. In practice, many adhesives are incompatible with some types of substrates, requiring severe and expensive surface treatments to provide some degree of adhesion. By selecting an adhesive that meets the necessary performance specifications and easily adheres to intended substrates, one can avoid additional costly steps.

The subject of surface treatments leads to the discussion of another important adhesive selection criterion, which are the constraints associated with the existing or planned manufacturing process. We must always remember that adhesive bonding is often an important yet small part of larger manufacturing process. Thus, industrial users often seek to ensure that application of the adhesive is well integrated in an efficient manufacturing process, and this is reflected in different aspects of the adhesive selection process. For example, in the automotive industry, the adhesives used in the vehicle frame must cure with the exact same conditions found in the electrostatic zinc coating process (e-coat) as the inclusion of an additional stage just for curing the adhesive would be prohibitively expensive. The form of the adhesive also plays a key role in this use, as these adhesives, in the uncured state, must have wash-off strength to avoid being removed during immersion in the e-coat tanks. In another example, if a two-part adhesive is to be applied with a robotic arm, it must remain viscous enough to be pumped to the applicator gun. All these criteria lead to very strict adhesive selection guidelines, which greatly restrict the available material and often can only be met with adhesives specifically formulated for a given application. More specifically, in an industrial application, one should take into account the adhesive form, method of application, curing conditions (temperature, pressure, and time), application time (working time or pot life), time from which the joint can be handled (holding time), shelf life, safety concerns, and, of course, the cost.

Lastly, it is imperative to discuss one of the most critical, yet less understood adhesive selection constraint, which is the durability of the adhesive under the expected service conditions. As we will see later during this book, designing for static loads and short-term conditions is well understood, but the same is not true for the long term. Under fatigue and creep conditions, in humid environments and even under large impact loads, adhesives often behave quite differently from what is stated in the manufacturer datasheets, which use test data obtained under well-controlled, static conditions. In many cases, correct adhesive selection is only possible if the actual long-term testing is carried out, allowing to compare the performance of different adhesives and to better understand how they react to these extreme conditions.

To highlight how all these aspects can interrelate, a schematic example of an adhesive selection process is shown in Figure 4.7.

To better aid in the comprehension of the adhesive selection process, Section 4.5.1 will give a practical example related to the selection of an adhesive for the automotive industry.

4.5.1 Case Study: Adhesive Selection for the Automotive Industry

As stated frequently throughout this book, the automotive industry is a major user of adhesives. Adhesives are used in the structure of the vehicle, providing high strength, stiffness, and impact resistance to the vehicle frame, in the windshield, where they provide a durable, flexible, and waterproof method to connect the fragile glass to the vehicle frame and in the interior, where they are used to bond the trim parts, textiles, and insets.

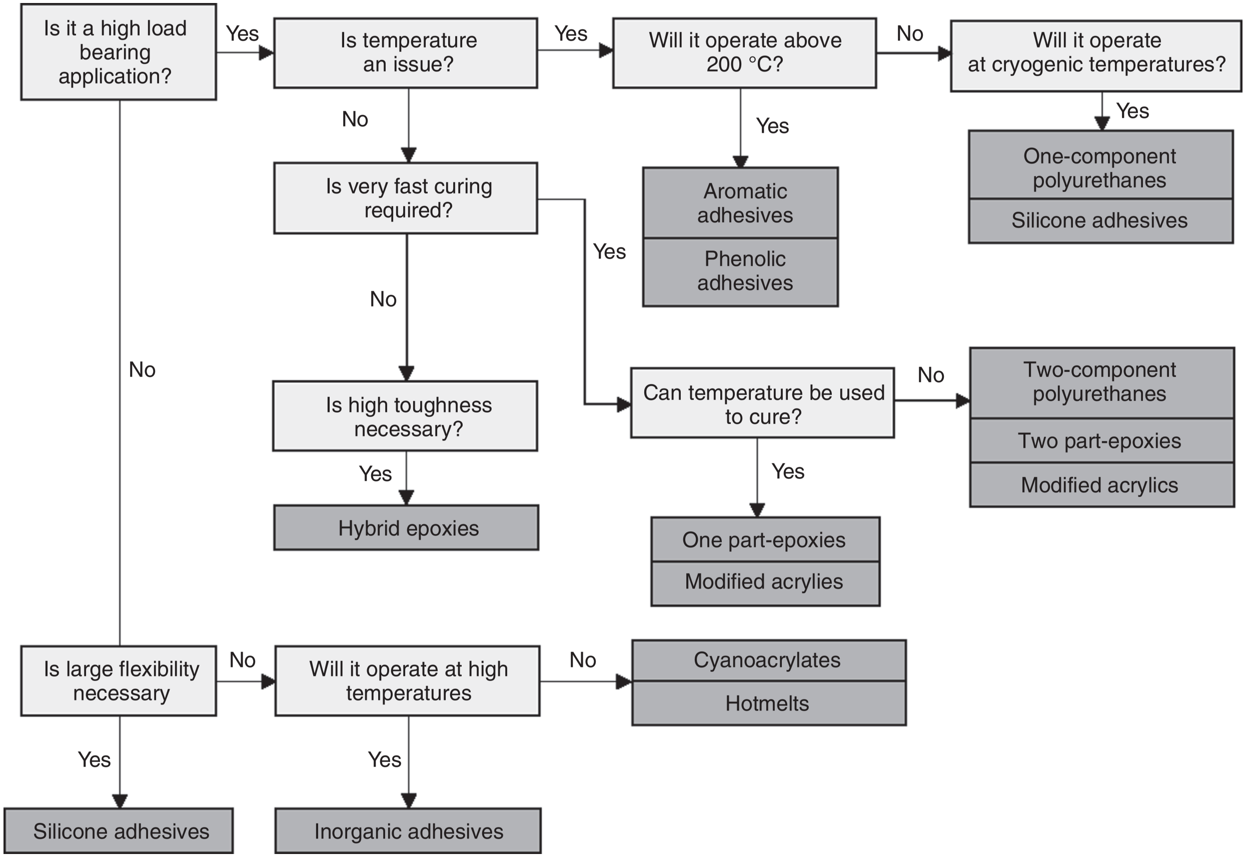


Figure 4.7 Example of an adhesive selection flowchart.

In this case, we are going to take a look into an adhesive for structural assembly of an aluminium-framed vehicle. Generally speaking, the automotive industry will have the following demands for an adhesive:

- Excellent mechanical strength;
- Should maintain strength between −40 to 80 °C;
- Good ductility and toughness, especially under impact conditions and crash tests;
- Relative humidity: 0–100%;
- Bonded joint lifetime: 15 years;
- Fast cure up to a temperature of 180 °C;
- Good gap filling capabilities and wash-off strength;
- Fatigue resistant.

Although there are many adhesive formulations available, for this application, the following four adhesive formulations are typically used:

- Two-part acrylic (methyl methacrylate);
- Conventional one-part epoxy;
- Two-part, stiff polyurethane;
- Crash-resistant, hybrid epoxy adhesive.

As stated above, methyl methacrylates have, as advantages, high cure through depth, room temperature cure, high peel and impact strength, good environmental resistance, and bond to moderately contaminated surfaces, and their cure can be accelerated with heat. However, their use is hampered by the slow fixture times (5–30 minutes), the generation of waste associated with the static mix process, the strong odour they emit, and the low strength and stiffness when compared with epoxy-based adhesives. For automotive industry applications, the key advantage of this adhesive is the very fast curing process, which has the potential to greatly accelerate the manufacture process. However, the relatively low strength and stiffness are somewhat undesirable for automotive applications.

One-part epoxies are often highly specialised adhesives with a wide range of formulations available. These are known for their high level of adhesion to many substrates as well as their unrivalled strength, durability, and environmental resistance, all highly desirable features for the automotive structural construction. The cure process is generally fast if heat can be used, quickly achieving a large depth of cure. Fixturing systems are essential. The factor that most limits the use of epoxy adhesive in modern structural use is the fact that they are quite brittle, especially in an unmodified state. This raises some concerns regarding impact strength.

Two-part polyurethanes are known for their flexibility and very high toughness. They are quite strong, especially under impact and withstand well very low temperatures. As is the case for the two-part epoxies, some sort of mixing system is essential. The cure is not very fast, especially for very large adhesive thicknesses such as those that are usually found in automotive structures. Lastly, the use of primer on the surfaces to be bonded is often recommended as they might have low adhesion to

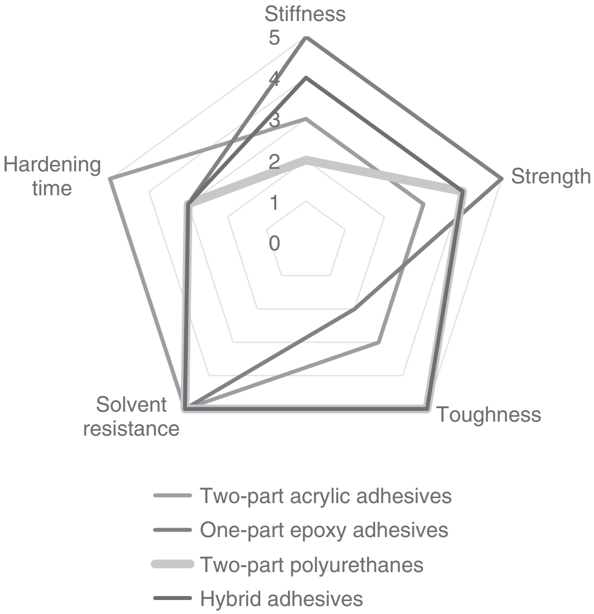


Figure 4.8 Comparative analysis of adhesives suitable for joining a vehicle body with different characteristics ranked from 0 (poor) to 5 (excellent).

some substrates, including aluminium. This additional step is highly undesirable, as it requires additional stages in the manufacturing process.

Finally, the last adhesives under consideration are the modified epoxies. Combining different chemical formulations in the same product, these are extremely tough and very strong. They combine the strength of the epoxies with the ductility of the polyurethanes while retaining good solvent and environmental conditions. They excel under impact conditions. The use of these materials is somewhat limited by their high temperature of cure and high cost.

These relative advantages and disadvantages can be plotted graphically using a suitable radar plot, as shown in Figure 4.8.

For the intended application, a high-ductility, modified epoxy is the most well-suited adhesive type. With a hybrid formulation, it retains the strength, low curing time, and high solvent resistance of epoxies with the extremely high toughness of the polyurethanes. Although costly and requiring a curing stage at high temperatures, the advantages it brings for structural bonding are undeniable.

An example of such adhesive is the crash-resistant adhesive. These adhesives have high failure load but also fail in a safer fashion, deforming plastically before joint separation occurs, redistributing and reducing peaks in the shear stress distribution. This is very evident when analysing the load–displacement curves (Figure 4.9), when compared with a stiff and strong epoxy.

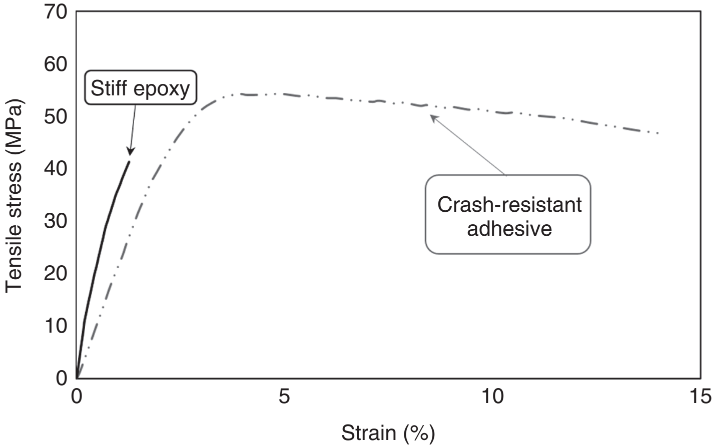


Figure 4.9 Comparison between the behaviour of a crash-resistant adhesive and a high-strength, unreinforced epoxy adhesive.

4.6 How to Test and Characterise an Adhesive

As we have seen in this chapter, the mechanical properties of an adhesive must be well known both to ensure that an adhesive selection process is successful and to support the joint design process. It is therefore very important to understand the methods that are most widely used for adhesive characterisation. We will start by analysing quasi-static mechanical characterisation methods, which allow to study the response of an adhesive to different mechanical loads at relatively low testing speeds, which approximate a static load. Lastly, Section 4.6.1.3 will give a short description of some of the procedures that can be employed to characterise adhesives under more demanding conditions, such as moisture, fatigue, and impact. A subsequent chapter on the durability of adhesive joints (Chapter 9) will greatly expand on this subject.

4.6.1 Mechanical Testing

Mechanical testing of adhesives is achieved with a wide variety of tests, which are used to determine parameters such as strength, stiffness, and critical fracture energy. This data is crucial for design purposes which, as we will later see in detail in Chapter 8, requires some or all these properties to create powerful material models. Some models rely only on the elasto-plastic properties of the adhesive (stiffness, plasticity, and strength), while more sophisticated models take into account the critical fracture energy of the materials to accurately model damage onset and propagation.

It is also important to mention that adhesive characterisation for design purposes almost always requires testing in at least two different loading modes. This is because, unlike metals, there is a large discrepancy between the yielding and shear strength of polymers caused by a difference in the principal stresses acting on the material (known as a deviatoric stress condition). Thus, most adhesive characterisation processes include methodologies for testing in mode I (a tensile load, which pulls the adhesive material apart) and mode II (a shear load, in which the material is forced to move in parallel but opposite directions). Furthermore, it is even possible to test adhesives under mixed-mode conditions, that is, in a loading condition that includes both tensile and shear loads and is more representative of what occurs in practice, although much more complex to test and analyse.

It is also important to note that adhesive testing is rarely conducted under compression loadings because of the propensity of the relatively soft adhesive material to buckle. It is possible to create special testing jigs that support the specimens during the compression testing process, but this often leads to excessive friction between the jig and the specimen, providing erroneous results. Accordingly, all material characterisation techniques shown in Sections 4.6.1.1 and 4.6.1.2 are based on tensile or shear loadings.

4.6.1.1 Strength Tests

Tensile Testing Tensile testing allows determining how an adhesive will behave when loaded under tension. In this case, a sample of the material will be stretched and will attempt to resist this load until it eventually fails. The specimens used in tensile testing are usually manufactured in a ‘dogbone’ or ‘dumbbell’ shape. Why is this peculiar shape used? Why is a single rectangular plate of material not used instead? Well, the dogbone shape is used because it provides two large surfaces for gripping in the testing machine and smoothly tapers into a central, less wide section, relatively far from the grips and where the load is applied evenly along the resistant section of the material (a uniform stress distribution). Two key stresses can be identified in this testing procedure. The first is called the yield stress, which corresponds to a stress at which the material starts to undergo plastic deformation. It is quite useful for design purposes because although the material can withstand higher loads before it fails, once it passes this point, it becomes damaged and cannot be restored to its original strength. The failure stress is the second of these key stresses, corresponding exactly to the stress at which the material ruptures or loses all its load-bearing capacity. The process of tensile testing an adhesive is shown Figure 4.10.

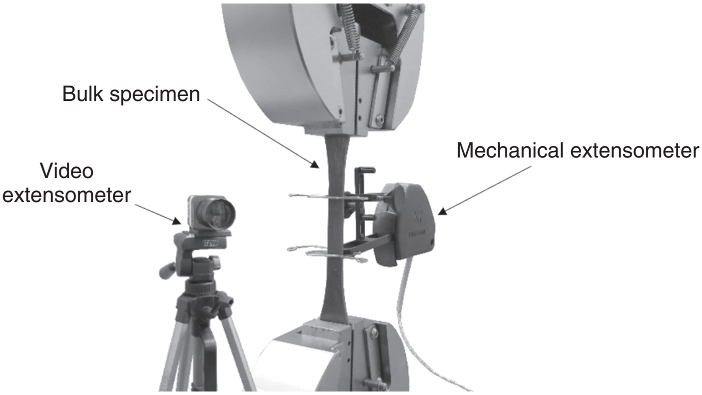


Figure 4.10 Tensile testing of adhesives.

If the length of the specimen is measured during the test, it becomes possible to relate its deformation to the stress. This can be achieved by precisely measuring the displacement on the material using a mechanical extensometer or an optical extensometer, using calibrated video or still images (as shown in Figure 4.10). The use of optical methods is quite useful when characterising very flexible adhesives, as it can read larger displacement easily. With this data, it becomes possible to create a stress–strain curve and thus characterise the material behaviour under tensile loads. An example of a stress curve is shown in Figure 4.11. The tensile stiffness (Young's modulus) of the material is a very important property that can be extracted from this curve. There are different methodologies available for extracting Young's modulus from the curve, but they all determine the slope of the initial elastic portion of the curve. It is also possible to determine the yield strength of the material and the elastic and plastic components of strain and the strain at failure.

One important note regarding tensile testing of adhesives is the fact that the strain at failure registered during these tests can provide a rough idea of the total elasticity and ductility of the material (how good it is at deforming before suffering failure). However, tensile testing should never be considered as an effective method for determining the maximum deformation supported by an adhesive because even the presence of very small defects on the central portion of the tensile specimen will be greatly reflected in the strain at failure, while having minimal impact on the material strength and stiffness. In fact, the manufacture of these specimens is a highly critical process. The best practice to obtain these specimens recommends the use of steel mould with a silicone rubber frame, according to the French standard NF 76-142 (1988). The mould should be placed in a hot plate press for adhesive curing. The pressure applied by the press will compress the silicone rubber frame and cause it to expand sideways towards the adhesive. This will in effect introduce a hydrostatic stress on the adhesive. This means that the adhesive will be pressurised from all directions simultaneously while it cures, which greatly reduces the appearance of voids and bubbles on the resultant specimen.

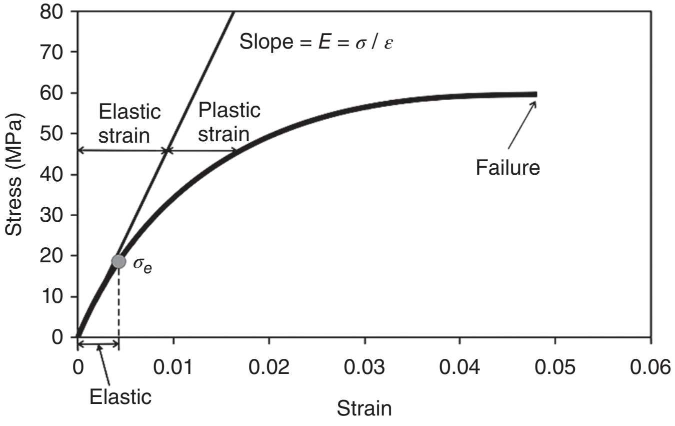


Figure 4.11 Key data that can be derived from tensile testing of adhesives.

Shear Testing Shear testing of adhesives is similar in principle to tensile testing, but in this case, the material is being sheared by two parallel, yet opposite loads. In fact, shear testing is more relevant for testing adhesives than tensile testing because this is the preferable loading mode for adhesive joints. A shear condition distributes the load more evenly across all the adhesive layer in a joint, leading to much lower peeling loads, which are the Achilles heel of adhesive layers.

There are several alternative testing methodologies suitable to perform shear testing, each with its different characteristics. The first method we will discuss is the thick adherend shear test (TAST) . This test uses a specimen that closely resembles a single lap joint but, as the name implies, the adherends used in this case are much thicker than the adhesive layer. This is done to ensure minimum rotation of the joint during the test, ensuring that the tensile load applied to the ends of the adherends is translated into an almost pure shear load on the adhesive layer. The TAST specimen geometry and an example of a successfully tested specimen are shown in Figure 4.12.

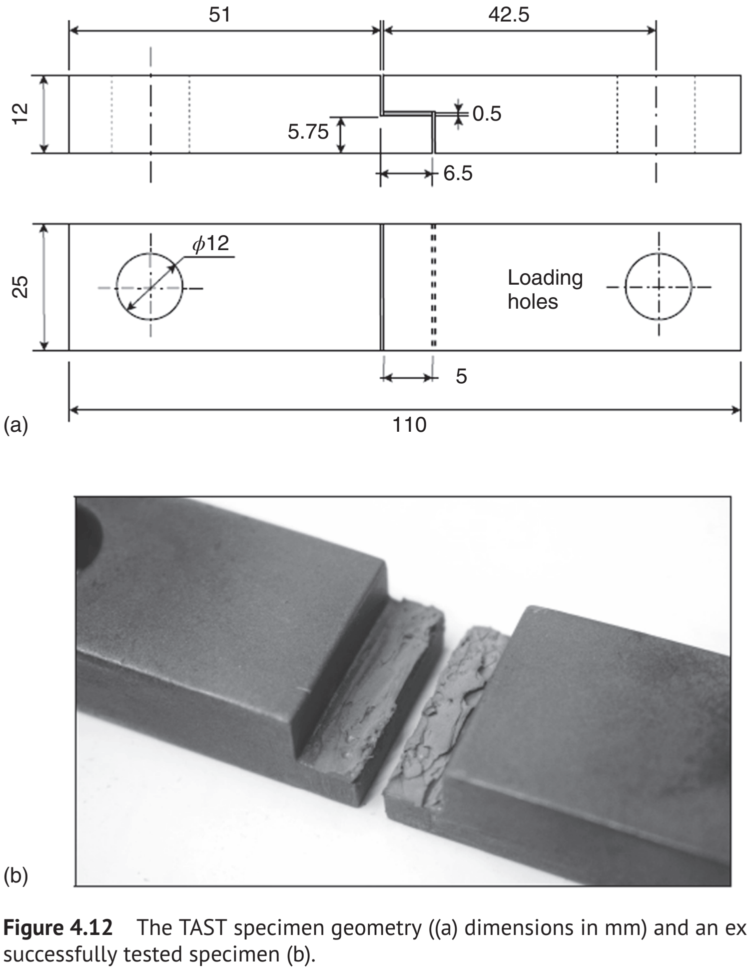


Figure 4.12 The TAST specimen geometry ((a) dimensions in mm) and an example of a successfully tested specimen (b).

Using a load cell and a special extensometer, it is possible to extract data similar to that obtained in the bulk tensile test, but for mode II, that is, for shear. It is possible to obtain the shear yield stress, the shear failure stress, and the shear stiffness of the material.

The key disadvantage of using TAST is the difficulty associated with precisely measuring the displacement of the very thin and difficulty to reach adhesive layer, which necessitates the use of the special extensometer referred above or the use of a methodology that can separate the displacement of the steel specimens from that of the adhesive. In addition, although thick adherends are used, TAST specimens do not have an exactly uniform shear stress distribution, with stress concentration peaks occurring near the edges of the overlap length, which further reduces the accuracy of the shear stress measurements being carried out.

An alternative to the TAST methodology is the use of ARCAN specimens, as shown in Figure 4.13. This specimen is also known as a butterfly specimen, which is shaped like two triangles joined together by adhesive. By pulling the edges of this specimen in two different directions, an almost pure shear state is obtained in the adhesive layers. However, ARCAN is able to do much more than test under shear conditions. By rotating the ARCAN testing fixture, one can introduce any type of mixed-mode loading into the specimen, from pure shear to pure tension, as well as a large number of mixed-mode angles.

Note that the ARCAN specimen can be solely made out of adhesive or it can be composed of two substrates (for example, made of metal) joined by the adhesive layer. The use of a complete bulk specimen of adhesive facilitates the measurement of the strain in the adhesive layer, which is especially useful when optical methods are employed. The second configuration (two bonded adherends) is more practical to manufacture but again introduces difficulties in extracting the actual displacement of the adhesive layer and can have adhesion issues between the substrates and the

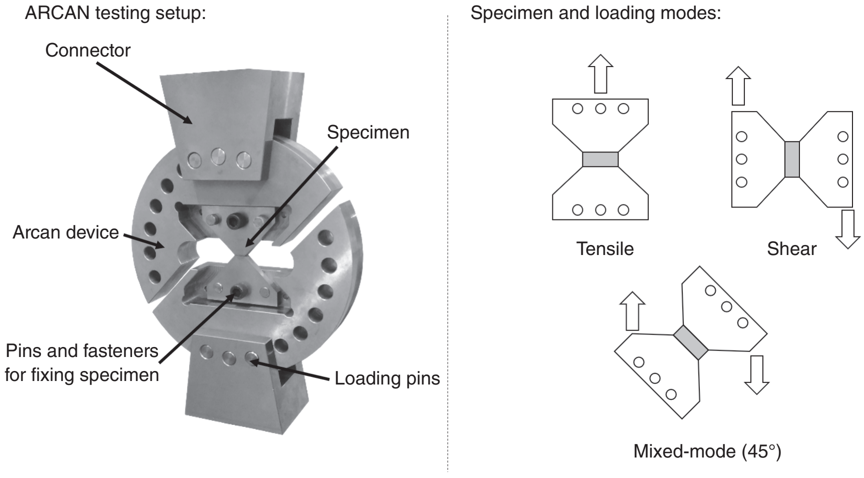


Figure 4.13 Configuration of an ARCAN testing device and examples of three different specimen loading modes.

adhesive. The specimens must be manufactured with an appropriate surface treatment that avoids interfacial failure and allows for a complete test of the adhesive.

As was described for the TAST methodology, the basic ARCAN specimen geometry generates shear stress distributions that are not exactly constant because of the material discontinuities at the edges of the overlap area and the associated stress concentrations that arise at these locations. Some authors have proposed ARCAN specimen designs that are modified with notches at the edges of the overlap length to minimise these stress concentrations, but this comes at the cost of greatly increased complexity in the joint manufacture process.

The data that can be extracted from the test is practically the same that can be extracted from the TAST procedure, although measurement of strain is slightly different. Ideally, optical methods should be employed to ensure maximum accuracy in strain measurement.

Torsion testing can also be used to determine the shear properties of adhesives. In fact, this is perhaps the most effective shear testing method as all the adhesive layer is being sheared uniformly during the test because of the uniform twisting motion. Because stresses are not localised, even the presence of small defects cannot significantly influence the performance of the full adhesive layer. The main drawback associated with this technique is the fact that torsion testing equipment is much less common than tensile testing equipment. One final note regarding this technique is the fact that a correction must be applied to the results because the resulting data is non-linear because of torsional load. The Nadai correction can be used for this purpose suitable for either tubular or butt joints. An example of a butt joint geometry used for torsion testing is shown Figure 4.14.

4.6.1.2 Fracture Tests

Linear elastic fracture mechanics (LEFM) analysis has long been an important design tool for high-performance components, allowing to use fracture toughness (such as the critical stress intensity factor – K_{Ic}) and the critical stress energy release rate or fracture energy (G_{Ic}) to understand when and how easily can cracks propagate through the adhesive layer. However, these approaches based on LEFM are limited, as they assume plastic deformation to be negligible and to occur solely at the crack tip. Nowadays, design processes often rely on damage mechanics approaches, which consider both the material damage and plasticity characteristics and use this data to accurately determine the locations where cracks form and then use the principles of LEFM to understand how these cracks will propagate. These approaches require the elasto-plastic data obtained with tensile and shear testing

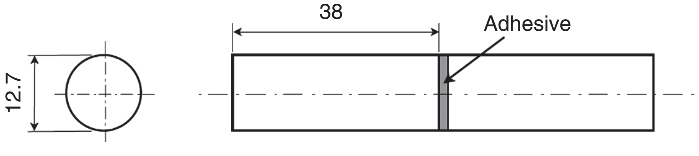


Figure 4.14 Butt joint specimen geometry for torsion testing (dimensions in mm).

as well as the fracture energy measurements obtained with appropriate fracture testing procedures.

When a crack grows, it generates new surfaces exposing new atoms, and these atoms possess a potential energy that is greater than that of atoms that are undisturbed inside the bulk material. The greater potential energy is due to the fact that the surface atoms are not joined together to other atoms, creating a more unstable condition. Thus, a crack will only propagate if the reduction in the potential energy is higher than the energy necessary to create the new crack surface. Using the Griffith theory, one can define the critical energy release rate, or the fracture energy that corresponds to the minimum energy that must be supplied to the material so that the crack will start to propagate.

Using an adhesive with large fracture energy will ensure that the bonded joint is able to resist significant damage before failure, leading to a joint that is not only strong but also fails in a very safe and predictable manner. If a brittle adhesive is used instead, the joint might be able to sustain large forces, but it will fail suddenly and without warning, something that is undesirable in a structure such as a car body.

Mode I Experimental techniques for the determination of the fracture energy of adhesives are varied, as this has been the target of intensive research during the past few decades. The most common method used for this purpose is the use of the double cantilever beam (DCB) test (Figure 4.15). In this test, two parallel beams are bonded together with an adhesive layer. The beams are pulled apart in a peel type of loading, a crack will form and propagate along the adhesive layer. As this is a tensile loading, using this technique, it is possible to determine the fracture energy of an adhesive in mode I. The extraction of the fracture energy can be done using different methodologies, known as data reduction schemes, that seek to understand how the crack propagation occurs as a function of the load applied to the specimen and convert this into a fracture energy value.

Initially, fracture energy determination could only be achieved with direct measurement of the crack location as the test progresses. This would be often performed by loading and unloading the specimen repeatedly and registering the load and the crack location for each of these cycles. Alternatively, the test can be performed in a single action, and the crack location can be monitored with an optical method.

The compliance calibration method (CCM) is perhaps the simplest method that can be used to calculate the critical fracture energy. This method is based on the use of the Irwin Kies equation.

The determination of critical fracture energy starts with the definition of the total potential energy of the system (Π). This energy is the difference between the elastic energy stored by the body (U) and the potential energy of the external force applied to the body. The potential energy is of the external force obtained by multiplying the displacement (δ) and the load (P). This is shown in Eq. (4.1), and this relationship is schematically represented in Figure 4.16.

$$\Pi = U - P\delta \tag{4.1}$$

According to Figure 4.16, we can write the total potential energy of the system as shown in Eq. (4.2).

$$\Pi = -\frac{1}{2}P\delta \tag{4.2}$$

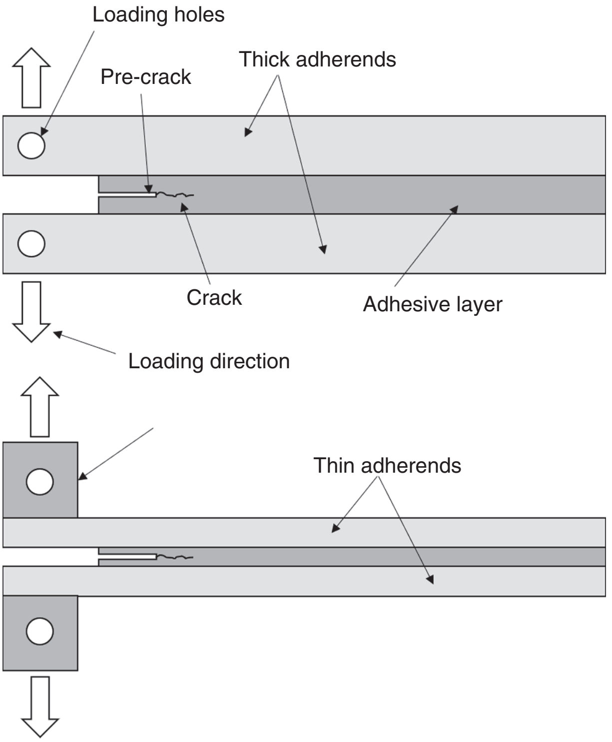
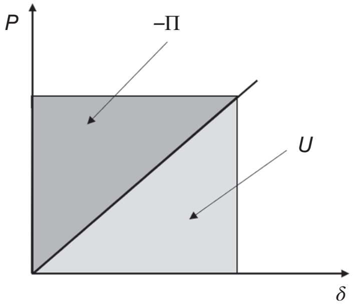


Figure 4.15 Typical examples of the DCB specimen configuration, suitable for thick and thin adherends.

Figure 4.16 Relationship between the total potential energy of the system (Π) and the elastic energy stored by the body (*U*).



Additionally, the compliance of the specimen being tested (C) is obtained by simply relating the displacement and the load acting on the specimen (Eq. (4.3)).

$$\delta = CP \tag{4.3}$$

However, the compliance will evidently be dependent on the crack length (a). The longer the crack in the specimen, the more it will flex for a given load. However, how can we quantify this relationship? We have a powerful tool to help us solve this problem, which is the classical beam theory developed by Euler and Bernoulli. This is a simplification of the linear theory of elasticity that provides a means of calculating the deflection characteristics of beams as a function of its properties and the load applied to them.

We can use the beam theory to define the displacement as a function of the crack length, the load applied to the specimen, the stiffness (E), and the moment of inertia (I). The moment of inertia is purely geometrical property that measures the ability of a beam to resist bending. This allows us to rewrite Eq. (4.3) solely as a function of geometrical parameters such as the width (b) and the thickness (h) of the beams that compose the DCB specimen (Eq. (4.4)).

$$\delta = 2\frac{Pa^3}{3EI} = P\frac{8a^3}{Ebh^3} \tag{4.4}$$

We can then define the compliance as a function of crack length (Eq. (4.5)).

$$C(a) = \frac{8a^3}{Ebh^3} \tag{4.5}$$

Taking this into account, the total potential energy in the system can be written simply as a function of the load acting on the specimen, the crack length, and the dimensions of the specimen (Eq. (4.6)).

$$\Pi = -\frac{1}{2}P^2C(a) = -\frac{1}{2}P^2\frac{8a^3}{Ebh^3} \tag{4.6}$$

As the potential energy equation can be used to determine the fracture energy, we finally obtain the Irwin Kies equation by considering the variation of the potential energy ($d\Pi$) per unit of area (bda). This is Eq. (4.7), which is suitable for the calculation of the critical fracture energy (G).

$$G = -\frac{d\Pi}{bda} = \frac{P^2}{2b}\frac{dC}{da} = 12\left(\frac{P}{bh}\right)^2\frac{a^2}{Eh} \tag{4.7}$$

In simple words, to determine the critical fracture energy in a DCB specimen, it is necessary to obtain the load and displacement curve of the test, provide the specimen width, and control the evolution of the crack length during the test.

Other methods are also available to process the DCB testing data, such as the direct beam theory (DBT), which only relies on the beam theory proposed by Timoshenko and the correct beam theory (CBT), which evolved from DBT by also including the effects of rotation and deflection at the crack tip.

However, as they all rely on visual identification of the crack location, these methods are highly dependent on the test operator and the quality of the optical equipment available. This has led to the emergence of novel methodologies, which do not require the direct measurement of the crack location as they can provide an accurate estimate of its location based only on P–δ data. One of the most important of these is the compliance-based beam method (CBBM) that considers the deflection of the DCB specimens and uses this data to determine the effective location of the crack tip. More precisely, CBBM considers the compliance of the complete DCB specimen and uses this information to determine the crack length (using an approach that is also based on the classical beam equations). This method is quite powerful because it also accounts for the damaged area immediately ahead of the crack tip, known as the fracture process zone, which cannot be visually detected.

Mode II For mode II testing, the end notch flexure (ENF) is also widely used. The geometry of the specimen used is practically the same of the DCB specimen. What differs is the loading conditions, as in this case, the specimen is loaded in a three-point bending configuration. With this load, the upper and the bottom substrates follow different curvatures, which causes a relative movement between them. This relative movement shears the adhesive layer and causes the initiation and propagation of a crack. As this a mode II test, it is used to extract the fracture energy in mode II. As is the case for the DCB test, both the load and the location of the crack tip are necessary to extract the fracture energy. The CBBM method can again be used effectively to determine the crack location without direct measurement. Besides the ENF specimen, there are also other configurations that can effectively be used for mode II fracture toughness testing, such as the four ENF, an ENF specimen loaded under four-point bending, and the end loaded split (ELS) test. These tests are schematically shown in Figure 4.17.

Mixed Mode Lastly, it is also possible to carry out fracture energy testing under mixed-mode conditions. This can be achieved in several different ways. For example,

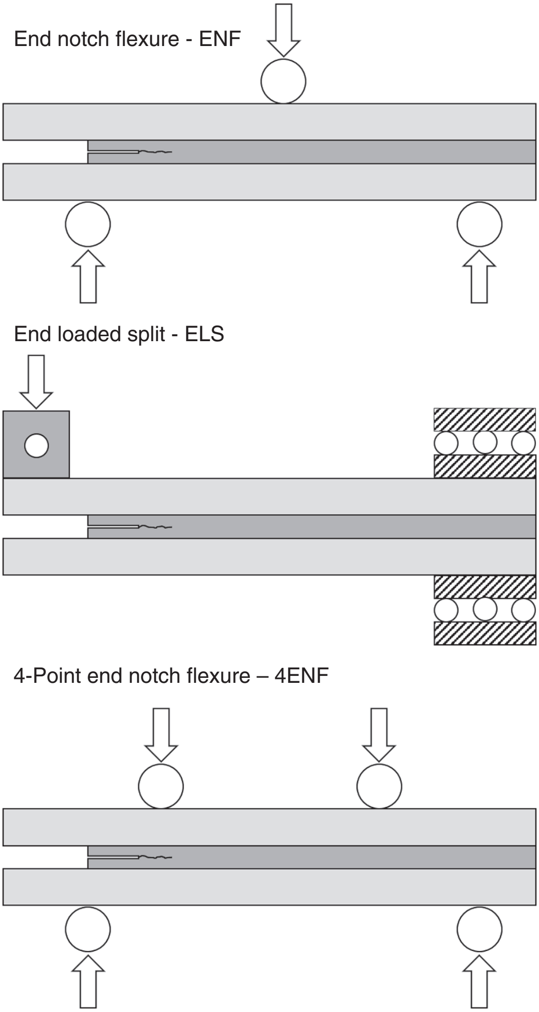


Figure 4.17 Mode II fracture testing configurations.

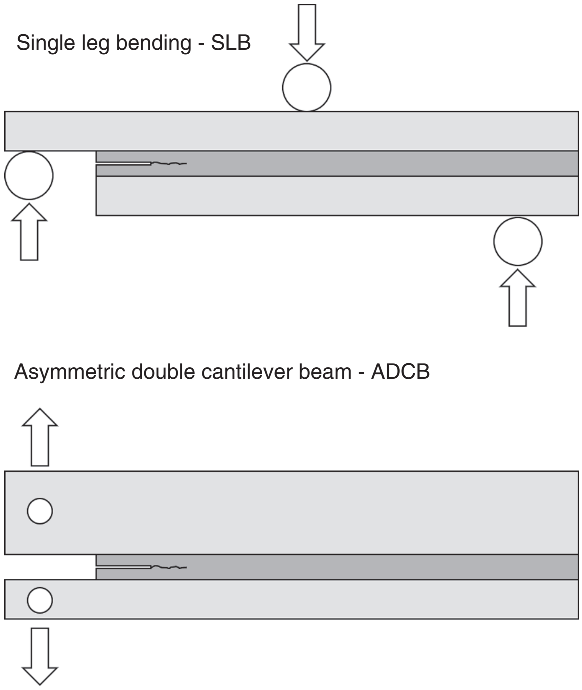


Figure 4.18 Examples of mixed-mode testing configurations.

it is possible to modify the classical DCB specimen geometry to have some degree of asymmetry in the adherends. The asymmetry will cause a load imbalance that will simultaneously generate peel and shear forces on the adhesive layer. For example, the single leg bending (SLB) specimen achieves this by using adherents with different lengths, while the asymmetric double cantilever beam (ADCB) specimen does so by using substrates of different thicknesses. Alternatively, special testing devices can be constructed that are able to load standard DCB specimens with different ratios of mode I and mode II loads. These are known as mixed-mode bending (MMB) apparatuses, which achieve this controllability by having a variable geometry. Figure 4.18 shows special specimens suitable for mixed-mode fractures, which combine adherends with different degrees of stiffness to achieve an unbalance of stresses acting on the adhesive layer, creating the desired mixed-mode conditions.

Recent advances in mixed-mode testing procedures have led to the development of mixed-mode testing apparatus, which use symmetrical specimens (often the DCB specimen) but assembled in a special jig that is able to provide for distinct loading conditions in each of the substrates. These apparatuses are often highly reconfigurable, with simple geometrical changes being able to alter the balance of loads acting on the specimen and thus the mixed-mode condition. An example of this equipment is shown in Figure 4.19.

4.6.1.3 Testing Under Severe Environmental and Loading Conditions

All the tests referred in Sections 4.6.1.1 and 4.6.1.2 are those that are carried out under room conditions, at very low testing velocities, which approximate a static loading (known in practice as quasi-static testing conditions). The specimens are

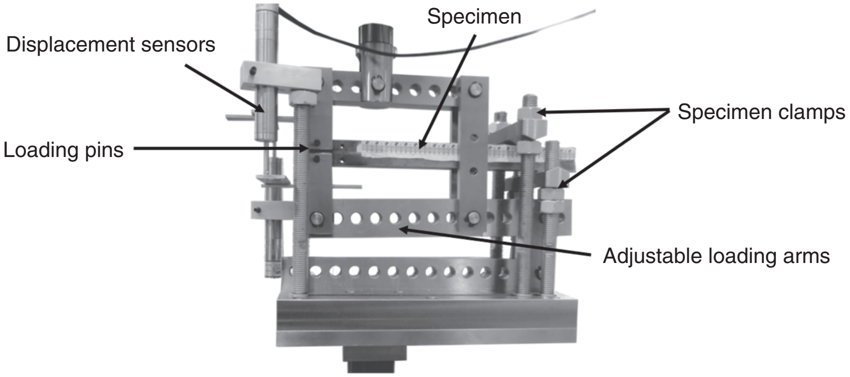


Figure 4.19 Apparatus for mixed-mode testing of DCB specimens.

kept at ambient temperature, there are no cyclic loads, and no moisture is present in the adhesive layer.

However, in practical applications, adhesives are often loaded under very severe environmental and loading conditions. For example, when used in a vehicle body, an adhesive might be subjected to large temperature gradients and harsh vibrations and even suffer strong impacts under a crash event. Such conditions might be highly damaging because adhesives, which as we have seen are mostly polymeric materials, are very sensitive to environmental conditions and their properties can vary drastically with these factors.

Therefore, if one wishes to design a joint to operate under these conditions, it is important to precisely understand how the properties of the adhesive will vary and use this data to create suitable material models. This section highlights a set of key adhesive testing procedures that are suitable for determining the behaviour of adhesives under severe environmental and loading conditions. Please note that Chapter 9 is also devoted to the durability of bonded joints and will demonstrate in detail how adhesives behave under these conditions.

Extreme Temperature Testing Let us start by looking at temperature testing. In this case, the same test methodologies that are used at room temperature can be employed, but the tests are carried out inside temperature-controlled chambers. The main difficulty associated with these tests is ensuring that the appropriate measurements can be done inside the chambers. For example, if one wishes to perform tensile testing inside a controlled temperature chamber, it might not be possible to use an optical system to measure the strain, as the door of the chamber might not have a sighting glass or restrict the line of sight. The temperatures at which adhesives are tested mainly depend on the intended application. For adhesives to be used in the automotive industry, testing is usually performed at −20 and +80 °C, temperatures that match those encountered by a road vehicle during service. In aeronautical applications, the temperature ranges from −55 °C, found in the outer layers of the atmosphere, up to 100 °C near motor components. In the case of high-speed, supersonic aircraft, frictional heating can lead to even higher temperatures, close to +200 °C in the skin of the vehicle. For space, in-orbit applications, we can expect a range of temperatures between −170 and 123 °C, alternating between these two temperatures as the satellite or aerospace vehicle transitions from being exposed to the sun to being shielded by the earth. Testing under these wide temperature ranges is achievable using liquid nitrogen injection (for cold testing) and powerful electrical heating elements (for high-temperature testing).

Temperature testing of adhesives is fundamental because of the existence of the glass transition temperature (T_g). T_g is the temperature at which a polymer will change from a stiff and brittle, glassy behaviour to a viscous and rubbery state. Above the glass transition temperature, the stiffness and strength will drop, but adhesives will gain toughness. The determination of T_g of an adhesive can be achieved with different methodologies, but the most effective relies in the use of a dynamical mechanical analysis (DMA) equipment. This equipment takes a sample of adhesive and loads it mechanically, at a frequency that matches the natural frequency of the material. By doing this, the vibration generated on the specimen is greatly amplified, as the material enters a resonant behaviour. The vibrating material is then heated up gradually. When it reaches T_g, the material will suddenly exhibit a severe drop in the amplitude of its oscillatory movement, as the transition from the glassy to the rubbery state causes a significant increase in the damping of the material. By detecting the temperature at which this drop in amplitude occurs, one can identify the T_g of the adhesive.

Tests of Aged Adhesive An aged adhesive is one that has gradually absorbed moisture during service. There are diverse applications where adhesives are exposed to ambient moisture and even in direct contact with liquid water, especially in bonded structures for the marine, offshore, and wind power industries. Ageing is likely to occur in the automotive and aerospace fields, as vehicles must operate under highly diverse meteorological conditions.

Ageing can have some drastic consequences on the mechanical performance of an adhesive and this necessitates the establishment of testing methods that are able to assess the effect of the absorbed moisture on the adhesive and in bonded joints. Testing the performance of adhesives and bonded joints in these conditions is usually performed in two steps. The first step consists in ageing a specimen up to a desired saturation level by immersing it in water at a controlled temperature. Higher temperatures will accelerate water absorption. This can be done until full saturation is reached (the maximum amount of water that the adhesive can absorb) or until a partial level of saturation is reached. Determining the ageing time necessary to attain a given saturation level requires knowledge of the water diffusion rate in the adhesive (which can be determined using bulk adhesive specimens and the appropriate Fick's law). This diffusion rate can then be implemented in a model that will show how water will ingress in the adhesive layer as a function of time. After a specimen is aged, it can then be tested exactly as is done in quasi-static conditions, as it is assumed that the water content will not change much during the relatively short test duration. Typically, adhesives will become weaker, less stiff, and more ductile when aged with water. However, these effects are typically reversible, as the original adhesive properties are mostly restored when the adhesive is dried.

Impact Testing Impact testing is essential in applications where the adhesive layer is expected to sustain impact loads. This is done because adhesives are visco-elastic and visco-plastic materials, which indicates that their mechanical properties, either in the elastic and the plastic domain, are sensitive to rate at which they are loaded (the strain rate). This means that an adhesive tested at low speeds will have drastically different behaviour from one tested under impact. Bonded joint designers working in the automotive industry are especially concerned with impact behaviour of adhesives and bonded joints, as they must create multi-material structures that are able to withstand impact loads and absorb large amounts of energy. This is only possible with impact testing data, which allows determining material properties that are dependent on the testing rate.

It is important to ensure that under impact testing, the adhesive layer is loaded as uniformly as possible at high velocity. Again, the specimen configurations are generally like those used in quasi-static testing, but the testing machines are quite different. Servo-hydraulic, drop weight, and split Hopkinson pressure bar (SHPB) testing machines can be used for this purpose. Servo-hydraulic testing machines use a pressurised oil source to drive a piston, which allows for relatively high testing speeds. Highly specialised impact testing models can reach up to 5 m/s while more universal equipment can reach only 0.5 m/s. Drop weight testing machines attain similar speeds but are much cheaper, as they rely only on gravity to accelerate an impactor that will load an adhesive joint. Lastly, SHPB equipment is used to attain very large speeds (more than 10 m/s). SHPB tests use highly pressurised air to drive an impactor bar towards a specimen fixed in an output bar. The incident, transmitted, and reflected stress waves can be measured and allowed to precisely determine the load sustained by the specimen during testing. Typically, adhesives will show increased strength under impact loads and, for modern structural adhesives, increases in adhesive toughness have also been reported.

Fatigue Testing Fatigue testing of adhesive joints is highly important for many practical applications, especially those concerned with transport applications. For example, in aircraft fuselages, the bonded joints are subjected to repeated pressurisation cycles, as the aircraft climbs and descends in its flight, creating highly variable stress conditions that can cause premature failure. Although adhesive joints are naturally quite durable under fatigue conditions, adhesives are still susceptible to becoming damaged by the effect of cyclic loads. To design joints that will withstand a given fatigue life (for example, last a set number of loading cycles before failure), proper fatigue testing of adhesives is essential. Two different approaches can be followed for this purpose. One approach is the stress–life (S–N) approach and the other is the fracture crack growth (FCG) approach, also known as the Paris' law approach. The S–N approach is more limited, as it is concerned with the identification of the total life of the joint, which in most cases corresponds to the elapsed number of cycles sustained until a fatigue crack appears in the adhesive layer. However, there are many applications where appearance of fatigue cracks does not necessarily indicate that the structure has failed or will fail soon. In these cases, the FCG approach is better suited, as it is able to predict how the crack progresses along the adhesive layer and permits the definition of a maximum limit to this propagation. This type of approach is typical of aeronautical structures, where cracks are allowed, provided that they are within well-defined limits. Both approaches require the use of fatigue testing machines, which are testing machines that use hydraulic cylinders or piezoelectric actuators to impose sinusoidal load or displacement curves. These tests are controlled by defining a frequency (the number of times that this curve is repeated within a second of time), the peak value of the curve (maximum load or displacement), and the *R*-ratio (the ratio between the highest and the lowest values of the curve).

In the S–N approach, a specimen is fatigue tested under a given stress level. For example, a DCB specimen can be loaded, cyclically, to a load level that reaches 60% of its quasi-static strength. The specimen is fatigue tested until it fails and the number of cycles it sustained is registered. This process can be repeated for different load levels (for example, 40% or 80% of its quasi-static strength), allowing us to understand how the stress level in the adhesive influences its service life.

In the FCG or Paris' law approach, the aim is to characterise the crack initiation and propagation process within the adhesive layer. While S–N testing can be carried out with practically any type of bonded specimen, FCG testing demands the use of suitable fracture mechanics specimens such as the DCB or ENF specimen. In this case, the crack propagation must be monitored during the test, allowing to understand how the adhesive becomes damaged as a crack progresses and to monitor the rate of crack propagation. Detailed information on the effect of fatigue on bonded joints and adhesives is present in Chapter 9.

4.7 Mechanical Properties of Adhesives

To conclude this chapter, this section provides a summary and data on the basic mechanical properties of different commercially available adhesives. We will start this section by analysing Figure 4.20, which roughly shows some of the most

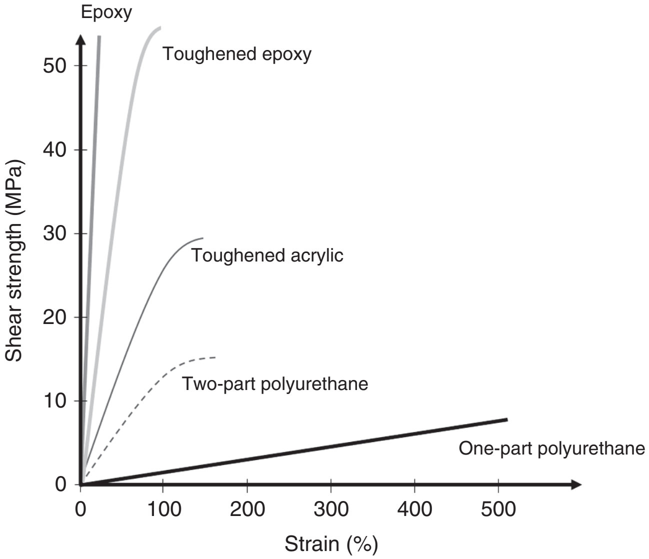


Figure 4.20 Typical shear stress–strain curves of different types of structural adhesives.

Table 4.1 Mechanical properties of various adhesives at room temperature.

Adhesive	Manufacturer	Tension				Shear				G_{Ic} (N/mm)	G_{IIc} (N/mm)
		E (MPa)	σ_y (MPa)	σ_r (MPa)	ε_r (%)	G (MPa)	τ_y (MPa)	τ_r (MPa)	γ_r (%)		
Epoxides											
02 Rapid	Delo	1000		24	20						
AF 163-2K	3M	1522	46.9				46.9			4.05	9.77
Araldite 2015	Huntsman	1850		22.5	4.4	560	14	20	40.3	0.43	4.70
Araldite 2020	Huntsman	2400	44		4.8					0.51	
Araldite 2021	Huntsman	1130	26.5			404		18.4		1.6	3.7
Araldite 420	Huntsman	1850	30				35			3	12.5
Araldite AV 119	Huntsman	3450	67.1	67.1	4.1	1260	47	47	50.7		
Araldite AV138	Huntsman	4590	41	41	1.3	1559	25	30.2	5.5	0.35	4.91
Betamate 2090	DuPont	2580	41.7		4						
Betamate UN3077	DuPont	3483	57.8		2.33						
Hysol EA 9150	Loctite	2852		79	5	1056				0.35	
Hysol EA 9321	Loctite	3870	22	46	3.8	1030	20	33	6.35	0.45	
Hysol EA 9330	Loctite	2646		38.6	2.4	965				0.37	
Hysol EA 9359.3	Loctite	2650	42.5	42.5	4.5	660	35.3	35.3	63		
Hysol EA 9361	Loctite	670		7.99	44					2.61	
Hysol EA 9394	Loctite	4420	31	59.8	4.64	1140	25	40.4	8.36		
Hysol EA 9628	Loctite	2377		51.7	7.5	624					
Terokal 5089	Loctite	1159		31.5		440		23.1		2.2	
Redux 810	Hexcel Comp.	1730		40	5.53						
SikaPower 4720	Sika	2171	25.8		3.4					1.15	4.15

(*continued*)

Table 4.1 (Continued)

Adhesive	Manufacturer	Tension				Shear				G_{Ic} (N/mm)	G_{IIc} (N/mm)
		E (MPa)	σ_y (MPa)	σ_r (MPa)	ε_r (%)	G (MPa)	τ_y (MPa)	τ_r (MPa)	γ_r (%)		
Supreme 10HT	Master Bond	3240	25	45.5	2	1460	37.1	37.1	16.1	0.3	
T-836/R-810	Nagase Chemtex	855	49.6							4.9	15
T-836/R-820	Nagase Chemtex	846	47							2.3	7
XN1244	Nagase Chemtex	5872	68.2		8.05	2150	32			0.47	2.20
XNR6852	Nagase Chemtex	1176	59.9		100						
XNR6852-3	Nagase Chemtex	1870	48.3		15	665	45			6.4	51
Polyurethanes											
Araldite 2026	Huntsman	200		18	50						
Sikaflex 256	Sika					1.351	8.26	8.26	330		
Bismaleimides											
Redux HP655	Hexcel Comp.	3620	80.7	80.7	2.39						
Redux 326	Hexcel Comp.	4850	50.9	50.9	1.28	1615	37.9	37.9	3.7		
Modified acrylics											
Araldite 2024	Huntsman	760		20	42.5						
DP-8005	3M	590	6.3	13	5.3	178.6	5.3	8.4	180	1.1	6
SikaFast 5211 NT	Sika	260	5.06								
Silicones											
RTV 106	Momentive	1.6		2.3		0.86		1.97		2.73	5
SI 5699	Loctite	2.4		2.4		0.91		1.8		2.2	5

E, the Young's modulus; σ_y, the yield strength; σ_r, the strength; ε_r, the tensile failure strain; τ_y, the shear yield strength; τ_r, the shear strength; γ_y, the shear failure strain; G_{Ic}, the critical fracture energy in mode I; and G_{IIc} the critical fracture energy in mode II.

The tensile and compressive properties shown were obtained in the bulk form, and the shear properties were obtained with the thick adherend shear test (TAST) and the critical fracture energies were determined with the double cantilever beam (DCB) and end notch flexure (ENF) test.

important structural adhesives and typical shear strain curves they exhibit. It clearly shows the huge variety that exists in structural adhesives, which can exhibit extreme stiffness and strength.

Table 4.1 provides the mechanical properties of several structural adhesives, including stiffness, strength, and critical fracture energy. This data can be used in suitable analytical and numerical models such as those that are presented in Chapter 8.

5

Manufacture

Chapters 2–4 have shown that many different factors are related to the quality and performance of a bonded joint. The proper selection of the adhesive and the quality of the surface preparation are perhaps the key aspects in this regard. However, these considerations are of limited importance if the bonded joint is not correctly manufactured. Simply put, we can select materials and design the joint as well as we can, but in the end, it is the quality of the practical implementation that will result in a successful joint.

This practical implementation of an adhesive joint, that is, the manufacture of the joint, can be done in many ways. It can be done manually, in a low series production, or it can be performed by automated machines, working at a high rate of speed in large-scale assembly lines. Regardless, it should always be carried out in a logical manner, with a well-defined sequence and procedures, respecting the knowledge and experience that has been gathered during the past few decades in research and application of adhesive joining.

In this chapter, we will see that the manufacturing procedure of a bonded joint consists of several sub-steps joined together to form a coherent procedure. This procedure includes substrate surface preparation, adhesive metering and mixing, adhesive application, assembly of the joint, adhesive hardening, and finally any necessary joint finishing activities. The different steps of the joint manufacture process are shown in Figure 5.1, and it is the purpose of this chapter to discuss all these steps in detail and to fully understand how they relate with what has been debated in Chapters 2–4.

As Figure 5.1 shows, this process is considered to start with the surface preparation of the substrates to be bonded. We have already discussed this procedure in detail in Chapter 3, so in this chapter, we will focus our discussion on all subsequent steps.

5.1 Adhesive Storage

Although not directly related with the act of manufacturing a bonded joint, adhesive storage is an unavoidable step of the manufacturing process that might result in serious issues if not carried out correctly. One must be aware that many adhesives

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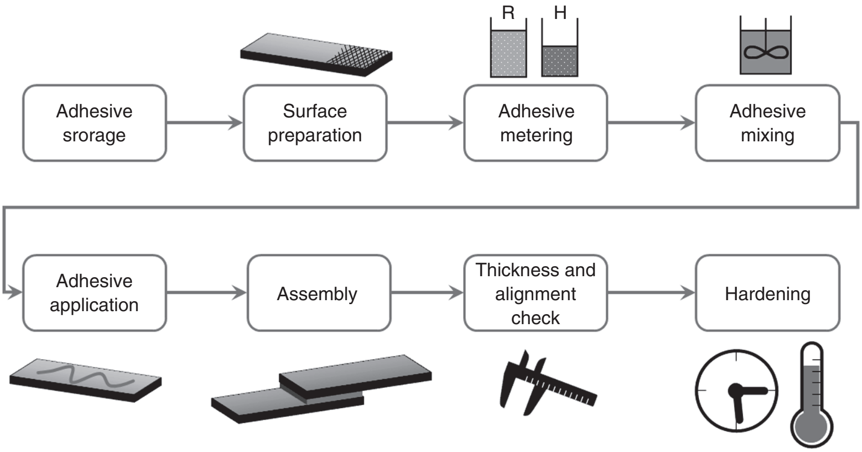


Figure 5.1 Procedure of adhesive joint manufacturing.

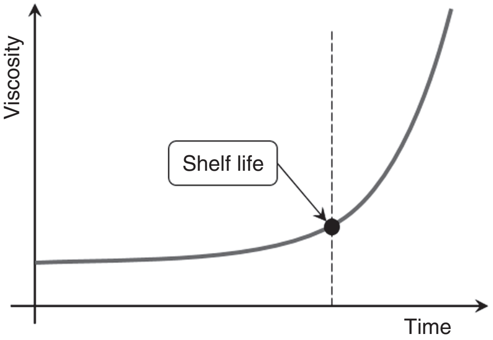
are reactive compounds that can easily degrade and become unusable if not stored under optimal conditions and this can greatly affect not only the final strength of the joint but also the reliability of the manufacturing process. For example, experimental work has shown that if an epoxy film adhesive is stored at elevated temperature, its shear strength can drop around 20%. Furthermore, the same research has shown that if the same adhesive is stored in an environment statured with water vapour, the damaging effect is even more pronounced, leading to a drop of almost 40% in the tensile shear strength.

There are many different aspects that must be considered when storing an adhesive, most of which are related to the environmental conditions faced by the adhesive during storage. The most important of these are the storage time, the moisture level, the temperature, the exposure to light and ultraviolet (UV) radiation, and the presence of contamination. Sections 5.1.1–5.1.4 explain the influence of each of these aspects on the stored adhesive and suggest optimal storage conditions that should be ensured.

5.1.1 Storage Time

The concept of ‘shelf life’ is extremely important for adhesive storage, indicating the maximum time that an adhesive may be stored, under specified conditions, with no significant changes in properties. These changes in properties are usually directly related to the increase in adhesive viscosity. For high-temperature curing, one-component adhesives, which include the resin and the catalyser or curing agent in a single container, the curing reaction is always occurring, even at room temperature. The longer the adhesive remains stored, the more this hardening process progresses, until a point is reached where the adhesive is excessively viscous and cannot be used to create a durable bond. This process is shown in Figure 5.2. Some adhesives (such as solvent-based adhesives) are chemically more stable

Figure 5.2 Viscosity of an adhesive as a function of time.



during the shelf time. For this type of adhesives, provided that they are kept in a sealed package, the permissible storage time can reach up to two years.

This is true even for two-component adhesives, where other secondary chemical reactions might occur within the resin or the hardener. It is important to note that the definition of shelf life can only be made under a specified set of storage conditions (for example, within a given range of temperatures and moisture levels).

5.1.2 Humidity

Moisture is generally harmful for stored adhesives, and this damage can occur via two distinct mechanisms. The first of these mechanisms is direct moisture absorption by the adhesive. In this case, the presence of water will change the adhesive properties, significantly reducing adhesive strength and increasing its ductility.

The other damage mechanism is associated with the fact that many adhesives rely on moisture as a catalyser for the curing reaction, such as some single-component polyurethanes adhesives. In this case, if moisture is allowed to reach the stored adhesive, the adhesive will increase its viscosity faster and become unusable in a shorter period of time. Regardless of the hardening mechanism, excessive humidity should always be avoided during storage for most adhesive formulations.

5.1.3 Temperature

Storage temperature has an effect which is somewhat similar to storage time. In a stored one-component adhesive, the curing reaction is always occurring at a rate that is directly proportional to the storage temperature. In this case, storage at low temperatures is highly advisable, as it will allow us to reduce the rate of this curing process and slow down the increase in viscosity. Many one-component adhesives require storage at temperatures well below ambient temperature. In these conditions, it is recommended to hold the container at room temperature for some time before using the adhesive. This is done so that the condensation can be avoided, as the water vapour present in the atmosphere tends to naturally condense in the surface of a very cold adhesive. This process helps the adhesive to reach room temperature before it is applied. The specific time that the adhesive should be kept at room temperature is usually provided by the manufacturer.

However, note that not all one-component adhesives are sensitive to storage temperature. A moisture curing polyurethane, for example, cures in the presence of moisture and ambient temperature only has a limited effect on its hardening. As long as the container remains sealed and kept in a dry place, increased temperatures will not cause any degradation of the adhesive.

5.1.4 Light and UV Radiation

Adhesives, as polymers, are highly susceptible to degradation by UV radiation present in sunlight. UV rays interact with the molecular bonds of these materials and form free radicals, which then react further with the oxygen present in the atmosphere. The exposed surfaces of the adhesives will discolour, lose strength, and crack. In extreme cases, the adhesive can even completely disintegrate. Uncured adhesives must be stored in containers that do not allow for UV light to penetrate and ensure that no degradation can occur before application.

After the application is carried out, adhesives are typically installed in joint configurations that shield them from direct sunlight. In cases where this is not possible, the adhesives are pigmented with particles (UV stabilisers) that will absorb the incident UV radiation and avoid its penetration into the adhesive layer. One classical example is the polyurethanes that are used to bond windscreens in cars. These adhesives are exposed to sunlight behind the windscreen but are filled with UV stabilisers that will absorb sunlight and provide them with the characteristic black colour.

In addition, if an adhesive is curable via exposure to UV radiation, storage in a container permeable to UV radiation will lead to a gradual increase in viscosity until the adhesive is not usable, similar to what occurs to a heat curing adhesive stored at high temperatures.

5.2 Adhesive Metering and Mixing

Measuring and mixing a precise quantity of the adhesive to be applied in a joint is very important, especially when we are considering the use of an adhesive which has two separate parts (resin and hardener). In this case, an incorrect ratio between the weight of the resin and the hardener can significantly alter the properties of the adhesive. In low-volume applications, precision scales are usually employed to measure the amount of the adhesive. In large-scale manufacturing processes, this is usually achieved by measuring the volume of each component being pumped. In addition, even if the adhesive only has one component, it is still highly important to apply the right amount of adhesive to the joint, as one must both minimise waste (adhesive overflow) and avoid situations where insufficient adhesive is present in the joint, leading to the appearance of major defects. In this section, we will discuss all the aspects related to the procedures and the equipment used to precisely meter the adhesive using in the joint and its mixing. Because of the emphasis on mixing, this section will mostly be devoted to the handling of two-part adhesives, which are fully reliant on this process to initiate hardening.

5.2.1 Adhesive Metering

As mentioned above, for two-component adhesives, not only the amount of the adhesive but also the weight (or volume) ratio of the resin and the hardener should be precisely measured. Some adhesives are provided in containers or cans and some others are in the form of cartridges. Examples of different cartridge shapes are shown in Figure 5.3. Because of their geometry, the cartridges are designed to dispense the correct ratio of resin and hardener to the joint and thus, when the adhesive is provided in cartridges, usually, there is no need to measure the weight ratio of the two parts of the adhesive as a separate step. Still, it is fundamental to control the amount of adhesive being applied to the joint, which can be done by weighing the complete mixture or metering the volume being pumped by an automated application system.

5.2.2 Adhesive Mixing

After metering of two-component adhesives is complete, the resin and hardener should be mixed as uniformly as possible and without introducing air into the mixture. Different techniques are suitable for mixing the resin and hardener and its selection depends mainly on the scale or the manufacture process. Smaller manufacturing operations will rely on manual or unpowered methods while larger operations will often employ powered machinery, able to process larger amounts of adhesive.

In low-scale manufacturing, mixing of adhesives is often achieved manually. The bonder will, as described above, weigh the two components of the adhesive mixture and manually mix them together using a spatula or an equivalent manual tool. This process requires a good degree of skill on part of the bonder, as it is quite hard to avoid the introduction of air bubbles in this mixture.

If the resin and hardener are provided in cartridges, mixing the adhesive is usually carried out using a special nozzle provided by the manufacturer, attached to

Figure 5.3 Examples of different adhesive cartridges and containers.

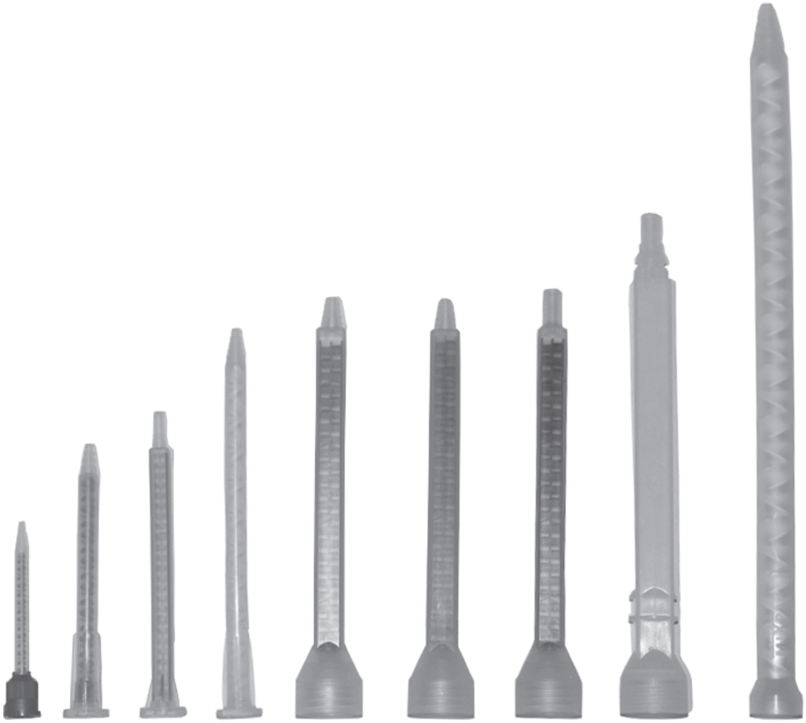


Figure 5.4 Different types of the nozzles used to mix the adhesive contained in cartridges.

the end of the cartridge. The adhesive components are squeezed from the container using manual force or air pressure and then forced through the nozzle, which provides a labyrinthic or helicoidal path for the adhesive components to follow. As they traverse these nozzles, the initially separate parts will gradually combine until they completely mix. Figure 5.4 shows different types of nozzles used for mixing the two parts of adhesives.

Another approach for mixing the resin and hardener is to use specially designed mixing machines. These machines subject the two parts of the adhesive to a rapid rotational movement, which uses large centrifugal forces to mix the adhesive together. These are usually expensive machines but are very effective at mixing the material, so they are often found in laboratories and manufacturing operations where the joints must be completely defect free.

Another type of mixing machine that finds extensive use in industrial applications is the screw type mixer/pump combination. These machines are large-scale powered versions of the mixing nozzles used with cartridges. These machines use an Archimedes-type screw to pump the two adhesive components from separate barrels. As these components traverse the screw, they become mixed and are also pressurised. This pressure removes voids and allows the mixed adhesive to be fed to a nozzle via a tube. This nozzle is often attached to a programmable robot, and these machines are commonly found in applications where very large volumes of adhesive must be applied very quickly, such as the automotive industry and wind turbine

(a) (b)

Figure 5.5 Different adhesive mixing techniques: high-speed mixer (a) and screw mixing method (b).

manufacture. Ultimately, the use of powered mixers is highly recommended in most cases, as the resultant mixture of the resin and hardener will be much more uniform, and the process time will be greatly reduced. Figure 5.5 shows diverse examples of adhesive mixing equipment.

The speed of the mixing process and the mixing time are the two parameters that should be carefully controlled in mixing procedures that use automated processes, especially if adhesives with low pot life are considered. The pot life of different adhesives is quite varied and can vary drastically (from just a few seconds to several hours), thus greatly affecting the maximum duration of the mixing process. For example, an adhesive with a very long pot life (such as the Master Bond EP21ND-LP that is a two-part epoxy-based adhesive with a pot life of two to four hours) can be easily mixed using a manual method, but the one with a very short pot life (for example, Henkel H8003 that is a two-component acrylic adhesive with the pot life of seven minutes) must use a process that allows it to be applied almost instantly after the mixture. This can be achieved, for example, with a mixing nozzle tip, which allows us to quickly apply the adhesive to the joint after mixture.

However, the mixing process of two-component adhesives often generates heat (it is an exothermal reaction), and this can be exacerbated with the use of a fast and aggressive mixing procedure. In fact, an automated mixing equipment operating at large speeds will heat up the adhesive mixture considerably, and this can have the undesirable effect of accelerating the curing process and drastically reducing the pot life of the adhesive. This can even ultimately lead to the adhesive curing within the mixing equipment itself, blocking the system and leading to costly repairs and delays. It should also be noted that using thin bondline generates less heat, as there is significantly less material available to take part in this exothermal reaction. However, the mixing procedure must thus be designed to consider the effect of temperature on the pot life and set the mixing time and mixing speed accordingly.

As it has been repeatedly mentioned during this chapter, one of the main concerns associated with the mixing process is the introduction of voids into the adhesive mixture during the mixing process. Voids can drastically decrease the strength of the joint if they are not removed before the bonding process takes place. There are some techniques to remove the voids. A rough manual approach is using a simple sharp tool (such as a toothpick) to burst the visible bubbles. However, this is not very effective, as many smaller bubbles are often hidden within the bulk of the adhesive material. A much more efficient method is the use of a vacuum machine. In this method, the mixture is inserted in a vacuum chamber where the air pressure is decreased to near zero. The low pressure applied on the mixture surface causes the bubbles to move up to the surface and then burst. To speed up the process, the temperature can be increased during the vacuum process. However, again it should be noted that the pot life of the adhesive must be respected, especially if the temperature is also increased during the vacuum process. Another important aspect is the fact that, during the vacuum process, the volume of the adhesive increases slightly because of the reduction in surface pressure acting on the adhesive. Accordingly, the adhesive container should have enough space for this expanded volume of the adhesive. Among all the mixing techniques described, the use of a high-speed mixer is generally considered to be the most effective at mixing the adhesives, although it can only operate with limited adhesive quantities at a time.

5.3 Adhesive Forms and Application

After the adhesive is removed from storage and, if necessary, metered and mixed, it should be applied on the surface of the substrates that are to be bonded. As was the case for the mixing procedure, the process of adhesive application can be performed manually by the bonder or it can be an automated procedure using robots. For industrial applications, manufacturing a reliable and consistent adhesive joint is an important challenge, which is often hard to set up correctly even for simple joint geometries. Manual application of adhesives, performed by bonders who may dispense an incorrect amount of adhesive or may apply the adhesive with an inaccurate geometry, cannot fully guarantee the strength and durability of the bonded structures. Using an automated procedure will greatly improve the production process and will significantly increase the mechanical performance of the joints.

Regardless of the application mode (manual or automated), the adhesive application process is in fact highly dependent on the form of the adhesive. In terms of the viscosity, adhesives can be categorised into four groups including the paste (high viscosity), liquid (low viscosity), tape, and film adhesives. Each of these forms has vastly different application processes and capabilities. We will start by analysing the characteristics and the application process of liquid adhesives.

5.3.1 Liquid Adhesives

If an adhesive is supplied in a liquid form, then it easily flows and covers the substrate surface when it is applied (good wetting). They are suitable for use in hard-to-reach locations and can wet the substrates very well. However, because of the low viscosity, they are more appropriate for use in thin bondlines, especially those whose adhesive thickness is lower than 0.1 mm. Using liquid adhesives, the excess adhesive flows out very easily, leading to significant waste. Because of the same reason, it is also quite difficult to create thick adhesive layers using a liquid adhesive. We often find these adhesives being used in low-strength, manual applications. A manual application process will usually rely on brushes, simple rollers, syringes, tubes, or pressurised applicators. As they flow very easily, low power is required to automate the application of these adhesives, but special care must be taken to ensure that the applied adhesive does not flow out of the joint. This is usually achieved by introducing grooves in the substrate geometry, which will contain the adhesive, often held in place by surface tension.

5.3.2 Paste Adhesives

Paste adhesives are much more viscous than liquid adhesives and thus rely on an application process that can provide a force or pressure to transfer it to the surface of the substrate. The application can be achieved manually, with spatulas, blades, or scrapers or by using speciality equipment, such as mechanical or pneumatic applicator guns. In fact, the use of powered application equipment is usually unavoidable when a bonder must apply high viscous paste adhesives, especially those that are formulated to be thixotropic. What are thixotropic adhesives? These are paste adhesives that are sufficiently viscous to flow and form a uniform layer but, when left by themselves, do not flow out of the joint. This is very useful when the adhesive is applied to a vertical surface. The automotive industry often prefers thixotropic adhesives because they can remain in place while the unfinished vehicle frames are immersed in the electrostatic coating tanks. Paste adhesives are generally preferred by industries that manufacture components where large gaps exist. For example, paste adhesives allow to safely bond wind turbine components in which the adhesive layer is up to 10 mm thick or automotive frame panels in which adhesive thicknesses of up to 1 mm are used to account for small misalignments in the vehicle frames.

Figure 5.6 shows different types of manual applicators that are suitable for use with paste adhesives. This type of material generates low waste, can be applied with precision, and is effective for any adhesive layer thickness.

An important note related to the application of paste adhesives is the fact that the adhesive bead shape is highly important to ensure minimal potential for air entrapment. Good paste adhesive application practice must ensure that the bead shape provides a path for the air to escape the joint during the joint assembly process. This is easily illustrated in Figure 5.7. The upper images (Figure 5.7a,b) show beads of adhesive which, when the substrates are closed, do not generate closed spaces that preclude the movement of the air. In contrast, the lower shapes provide clearly contained areas (Figure 5.7c,d), where the air becomes trapped. However, the optimal geometry should be one depicted in Figure 5.7b, as it strikes a balance between providing paths for adhesive flow and covering the bonded surface quite effectively.

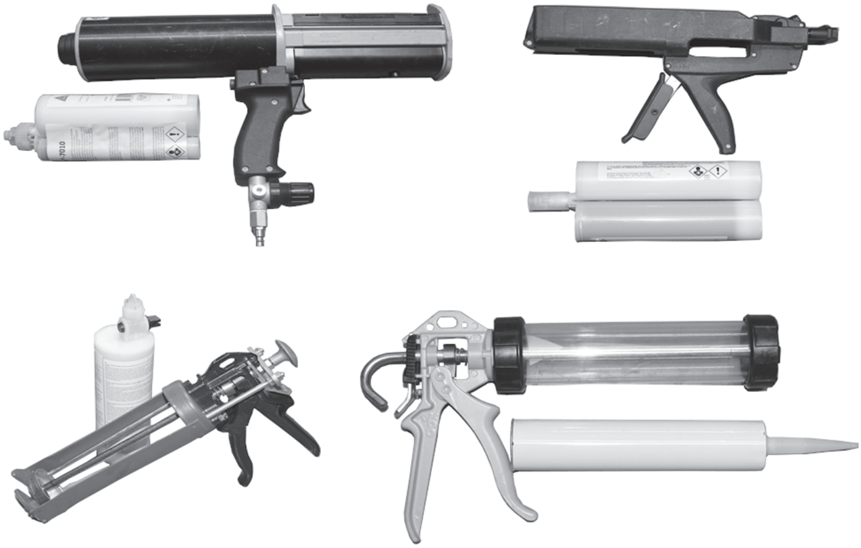


Figure 5.6 Different types of manual adhesive applicator guns and respective adhesive cartridges.

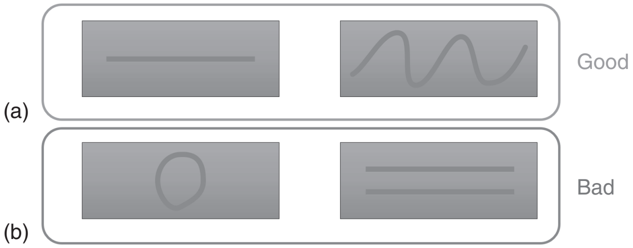


Figure 5.7 Different paste adhesive application patterns: good patterns (a) vs. bad patterns (b).

5.3.3 Film Adhesives

Film adhesives are commonly found in highly technological applications such as the construction of airframes in the aeronautical and aerospace industries where there is a very thin bondline between the bonded components. In these materials, a heat-curable adhesive is generally held in a carrier material, which can be, for example, a woven cotton layer. They allow for minimal waste, do not require mixing, and are easy to process. Their application process is very different from that found for liquid and paste adhesives because they can be cut and applied very precisely to the bondline. This allows their application to be carried out with excellent repeatability and leads to highly consistent adhesive layer thicknesses. However, they have two major drawbacks. The first is the fact that they are usually limited to flat or slightly curved surfaces and the second is related to its cost, as these materials are quite expensive because of their manufacture process.

5.3.4 Tapes

Tapes are somewhat similar to film adhesives, but the main difference is related to the fact that most adhesive tapes do not contain heat-curable adhesives but use pressure-sensitive adhesives instead (PSAs). PSAs are adhesives that always operate in a solid phase (they do not require a cure process). Instead, PSAs are tacky and must be pressed against the substrate to develop a bonding force. The form factor is also usually different. While film adhesives are supplied in wide rolls that allow them to cover large surfaces, tape adhesives are much less wide and intended for more localised applications.

5.4 Joint Assembly and Fixturing

The act of assembling a joint is one of the most critical steps of the joint manufacturing process, for it is at this stage where the two substrates and the adhesive are finally brought together. Obviously, any defect or misstep during this process will lead to an unsatisfactory joint with geometrical issues and other defects. In this section, we will discuss the tools and techniques that should be used to ensure the correct geometry of a bonded joint during the assembly (and later hardening) process and learn about the methods that can be used to avoid the entrapment of air as the substrates are brought together in a single joint.

5.4.1 Moulds and Fixtures

If you have ever bonded something by yourself, maybe when repairing a component or fixing a broken part, you probably have already noticed that it is quite challenging to ensure proper alignment of the parts during the bonding process just with your hands as the substrates will easily slide over the uncured adhesive. The same is true for any adhesive joint, even those used in industrial applications. The solution for this issue is to use a device or tool that can ensure that the adhesive and the substrates remain still and precisely located during the hardening process that will follow. These tools are usually called moulds, jigs, or fixtures. An example of a simple mould and technique for manufacturing adhesive bulk samples is explained in Chapter 4. Moulds usually have a simple but smart construction, using positioner blocks and pins to restrict the lateral and vertical movement of the parts to be bonded. In fact, moulds are the most effective way we have available to precisely define the geometry of a bonded joint. Using moulds, we can fix the overlap length, the adhesive thickness, and even create special features, such as fillets in the overflow of the adhesive at the edges of the bonded area.

An example of a mould for the manufacture of single lap joint (SLJ) specimens is shown in Figure 5.8. Note the presence of pins to ensure that the substrates remain perfectly aligned and of the positioner blocks that allow to precisely define the intended overlap length by adjusting set screws.

A mould for the design of butt joints is shown in Figure 5.9. This mould design uses a set of clamps, tightened by small fasteners whose task is to ensure that both

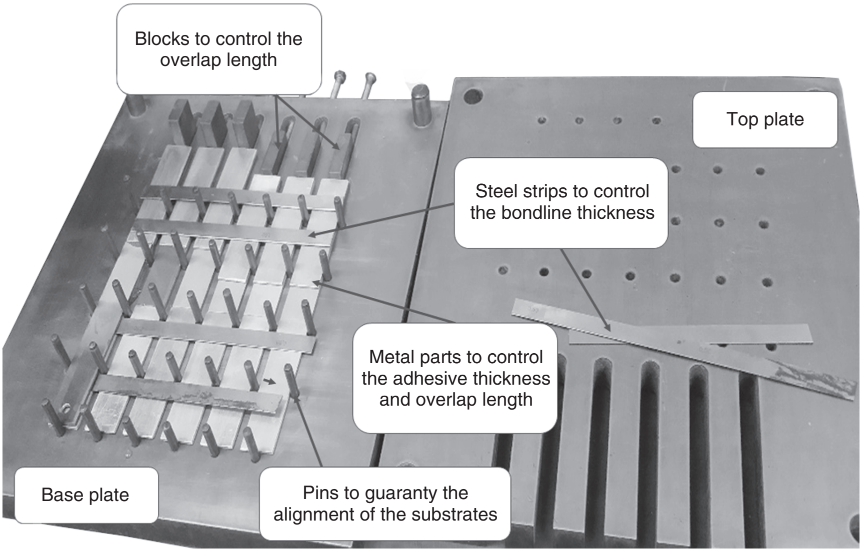


Figure 5.8 Mould for the manufacture of SLJ specimens.

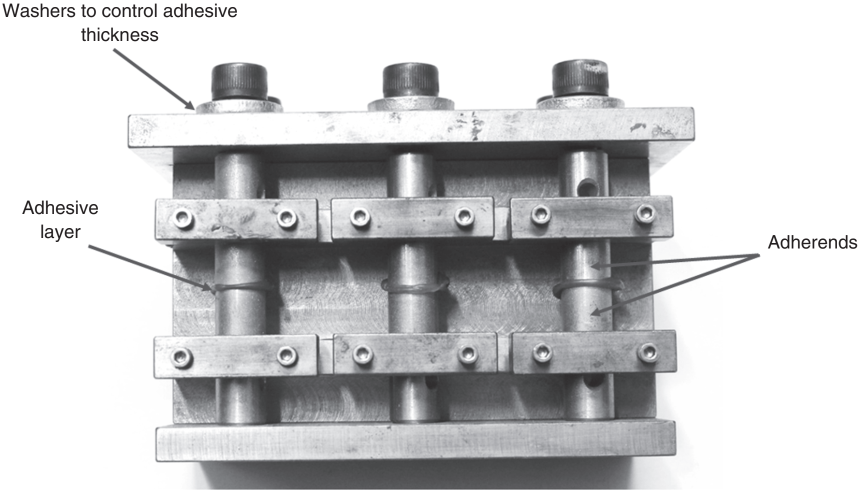


Figure 5.9 Mould for the manufacture of butt joint specimens.

the upper and lower substrates of the butt joint are in perfect alignment. On top of the mould, there is a set of adjustment screws whose task is to precisely define the adhesive layer thickness.

Fixtures or moulds should also guarantee that a uniform pressure is applied to the bonded area during the hardening process. The applied pressure helps the adhesive to better spread on the substrate surface. For use with adhesives that are cured at high temperature, the mould should be preferably made with the same material as the substrates. This is to ensure that there is no difference in the coefficients of thermal expansion between the mould and the substrates, which would otherwise introduce large thermal stresses to the joint as the materials expand with temperature.

When using a mould for processing adhesive joints, it is fundamental to ensure that it is coated with a material that will preclude the adhesive from bonding to the mould itself. For metallic moulds, this usually is achieved with the use of a mould release agent, a material that offers very low surface energy and thus does not adhere strongly to the adhesive. Alternatively, the mould can also be manufactured directly with a low surface energy polymer, such as a polytetrafluoroethylene (Teflon), although this usually leads to a very fast mould wear rate.

The procedure explained above is mainly used at the laboratory level where standard or routinely manufactured adhesive joints are tested. However, for real components, such as the components of a vehicle body or the airframe of an aircraft, where the size is much larger and the geometry is complex, it is not possible to use the common laboratory techniques to fix the joints during the curing process. In this condition, other techniques such as the use of clamps and using localised weld points to hold the parts together, etc., are commonly employed, providing a way to restrict the movement of the joint while the adhesive hardens.

5.4.2 Adhesive Thickness Control

The definition of the adhesive thickness is perhaps one of the most important geometrical parameters that must be controlled during the manufacture and, as we will later see in Chapter 8, has a major influence on joint performance. For this purpose, moulds are used in conjunction with other components, such as shims, wires, or plates with calibrated thickness equal to the desired adhesive thickness. However, other approaches can also be considered such as the introduction of glass spheres on the adhesive (hard sphere particles) to control the thickness (see Figure 5.10). The diameter of the spheres is almost equal to the thickness of the adhesive. However, it should be noted that spheres may affect the joint strength as they may act as a defect within the adhesive layer.

5.4.3 Joint Assembly

With one of the substrates located in the mould or fixture, all that remains is to apply the other substrate to the joint, completing the joint assembly. However, it is at this

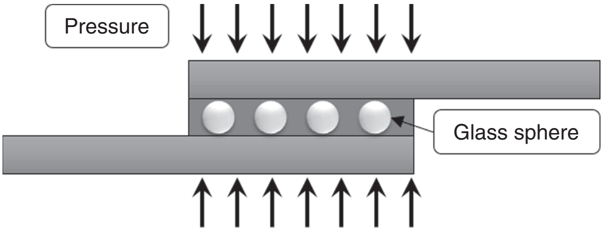


Figure 5.10 Glass spheres used to set the adhesive thickness.

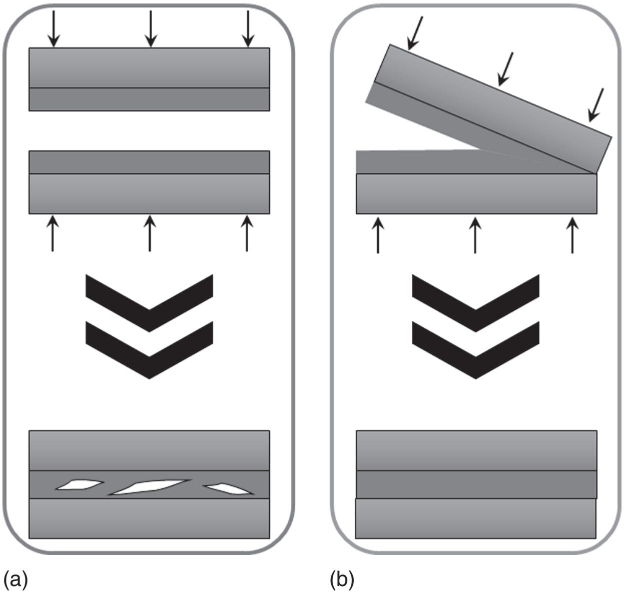


Figure 5.11 Parallel application of the top substrate (a), vs. progressive and pivoted application of the top substrate to avoid air entrapment (b).

stage that air can easily become trapped in the adhesive layer. Thus, the application of the substrates should be conducted in a way as to decrease the possibility of void creation within the bond layer. Accordingly, it is recommended to apply the upper substrate in a progressive movement, in which one of the ends of the substrate contacts first with the adhesive, followed by a pivoting movement until both substrates are parallel, as shown in Figure 5.11.

Of course, this largely manual procedure is only suitable for small-scale components or specimens and may be difficult to implement in large-scale structures. In many larger applications, the components to be bonded are clamped together using manually or pneumatically operated clamps. In this case, the application of the clamping pressure can be locally controlled to ensure that the closing force is first increased in one of the ends of the component, providing a way for air to escape, followed by a closing force on the opposite end, finally assembling the joint. Figure 5.12 shows an automotive component bonded using manually actuated clamps that allow for gradual application of pressure in the adhesive layer during joint closure.

5.5 Adhesive Hardening

A major step in the joint manufacturing procedure is the hardening process where the adhesive is finally converted to a solid state and can support mechanical loads. As we have seen in Chapter 4, adhesives can harden in diverse ways, such as chemical reaction, loss of the solvent, and simply by changing phases. There even are adhesives (PSAs) that simply do not undergo any significant physical or chemical

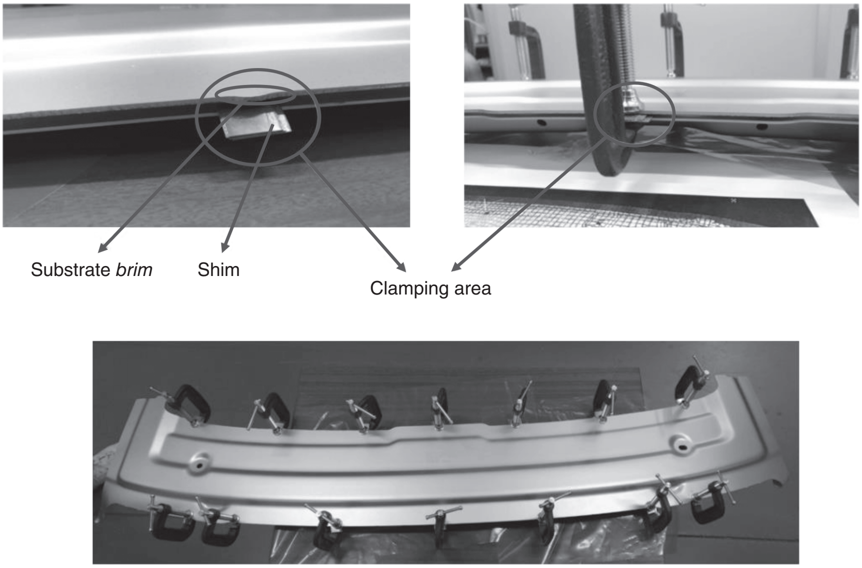


Figure 5.12 Assembly of a large bonded component for the automotive industry using clamps.

change. This section will describe the particularities associated with the manufacturing of bonded joints that use heat-curable adhesives and adhesives that cure via solvent loss.

5.5.1 Heat Curing Processes

Most adhesives used in high-strength, structural applications will usually harden following a chemical process, which can be initiated by the mixture of a hardener or, in the case of a one-part adhesive, this can be achieved by exposing the adhesive to heat, moisture, or radiation. During the hardening process, time and temperature are the two main factors that influence the rate of reticulation of the cured adhesive, which is an indication on how effective the curing process was in converting the monomers into the desired strong and highly reticulated polymer.

In heat curing adhesives, the hardening time is a function of the hardening temperature (see Figure 5.13). Usually, the higher the temperature, the lower the time required for the hardening. If the temperature is not correctly set, then the adhesive will not be completely hardened (too low temperature) or it can be burnt (too high temperature). Both conditions will greatly decrease the performance of the joint and defining a suitable curing cycle can be quite challenging for those starting to implement adhesive bonding in their processes. The heat curing equipment should provide a stable uniform temperature during the curing process. Using a ventilated oven for hot curing the adhesive is highly recommended, as the air circulation can provide a uniform and stable temperature during the curing time. However, there are many other options for curing equipment, which can be better suited for specific applications and component geometries. For example, while the use of hot plates

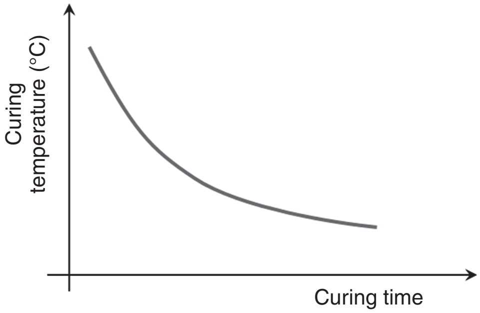


Figure 5.13 Effects of curing temperature on curing time.

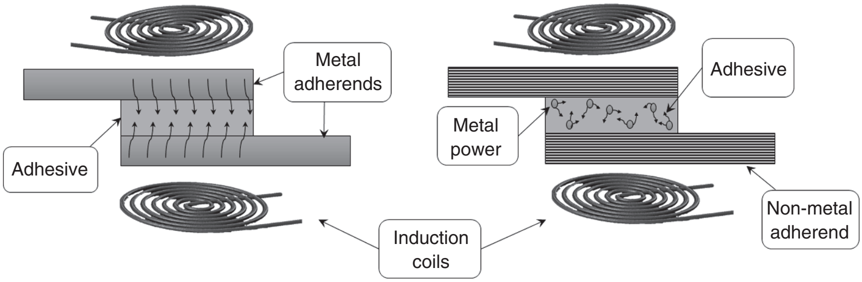


Figure 5.14 Induction technique to heat up the adhesive during the hardening process.

can quite localise the temperature at the external surfaces of the component to be bonded, they work quite well for curing very thin bonded components, where thin sheets of materials are bonded together.

Hardening techniques based on induction and dielectric heating can be used to locally heat and cure the adhesive. As schematically shown in Figure 5.14, by passing an electric current through an induction element, eddy currents will be induced on conductive parts because of interactions with the magnetic field. These currents flow in conductive parts, which will heat up quickly. However, it should be noted that using this approach requires a conductive material to be in contact with the bondline so that heat can be transferred to the non-conductive adhesives. When the adherends are metallic, they can play this role. However, what should we do if the adherends are non-metallic, as in the case of joints with polymeric or composite adherends? In this case, we can add some magnetic particles to the adhesive layer. These particles will allow for the formation of eddy currents and will heat up. This heat will then be transferred to the adhesive material.

Induction heating is a technique that well suited for manufacturing operations where heat must be applied directly to the joint, without heating the complete structure. In these local heating techniques, it is also possible to harden the adhesive in situ, which is very useful for large structures such as aircraft fuselages.

Another local heating method is called the dielectric heating technique, which is based on microwave irradiation. Microwaves pass through the material to be heated and interact with its molecules, causing them to vibrate. Because of these vibrations, increased molecule collisions occur, which generates heat. Figure 5.15 shows a

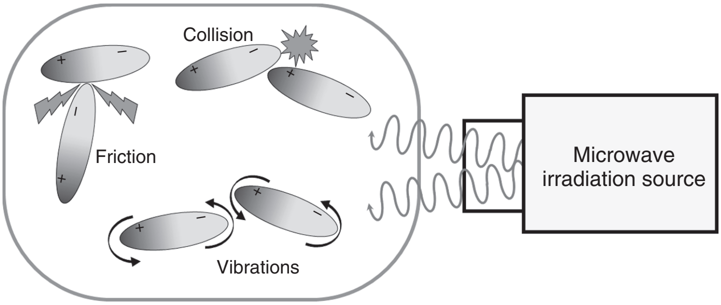


Figure 5.15 Dielectric approach for heating adhesives during the hardening process.

scheme of a dielectric technique. This approach is only applicable to dielectric materials (electrical insulators that can be polarised by an applied electric field), which makes it suitable for plastics. If the adhesive is not dielectric, then it is not possible to heat up the adhesive directly using the dielectric method. However, dielectric particles can be added to the adhesive to enable the use of this technique.

Heated blankets are also a local heating technique. Heated blankets are mobile instruments usually used for local heating of large structures. Using this approach, a blanket that is heated up using electricity power covers the bonded area. Then, the heat is transferred to the joint to harden the adhesive. As the blankets are flexible, they are suitable for curved structures, for example, for repairing large pipes and aircraft fuselage. Figure 5.16 schematically shows a heating blanket used for local heating of an airframe.

Nevertheless, please note that datasheets provided by the manufacturers contain all the necessary information about the hardening conditions.

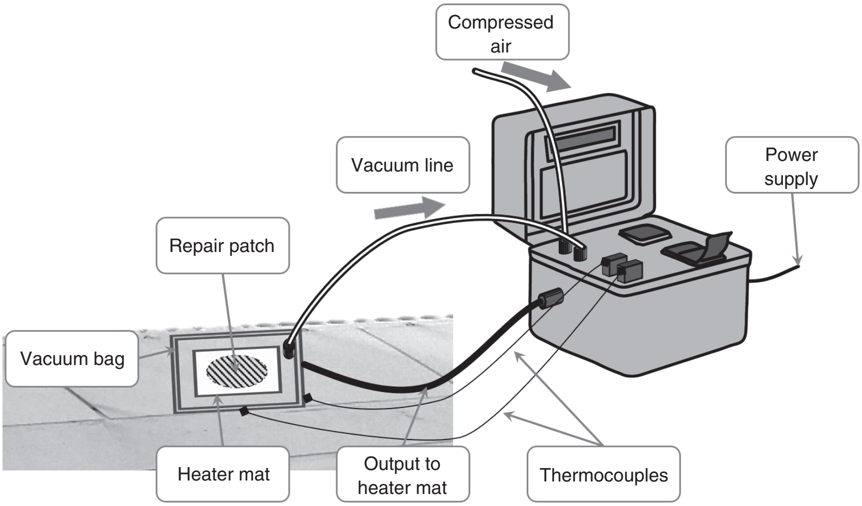


Figure 5.16 Schematic showing a heating blanket and vacuum bag used for local heating of an airframe.

The bonder tasked with carrying out this process should strictly follow procedures recommended by the manufacturer regarding the curing cycle, but while doing this, it should never trust the temperature readings provided by the controller of the equipment used to perform the hardening. This is crucial because what truly matters in the control of a hardening process is the temperature inside the adhesive layer, not the temperature of the air inside the oven or its casing. Thus, when implementing a curing procedure, it is indispensable to embed thermocouples inside the adhesive layer, so that one can fully understand the actual temperature of the adhesive. It is common to see differences of tens of degrees between the temperature shown in the controllers and the actual temperature of the adhesive layer. Because of slow heat conduction, the temperature in the adhesive layer is often the lowest of these two, which has obvious implications in the degree of cure that can be attained.

The heat curing of the adhesives is governed by two distinct reactions. These are the condensation reactions and the addition reactions. In condensation reaction, which is schematically shown in Figure 5.17, hardening takes place and generates a water molecule. The created water molecule can evaporate because of the heat provided during curing. The resultant water vapour will expand within the bulk of the adhesive and will very likely generate porosity. Thus, pressure should be applied to the joints where the adhesive used cures by condensation to avoid porosity within the adhesive. Phenolic resins are cured by the condensation reaction.

In the addition reaction, no water molecule is released, and no porosity appears during the curing process. In this procedure, the two molecules are bonded together and form a new bigger molecule.

Shrinkage is another important effect that adhesives experience during the curing process. Shrinkage can be caused by a chemical reaction (such as the condensation reaction previously described) or it can be caused by the difference between the thermal expansion coefficients of the adhesive and that of the bonded adherends.

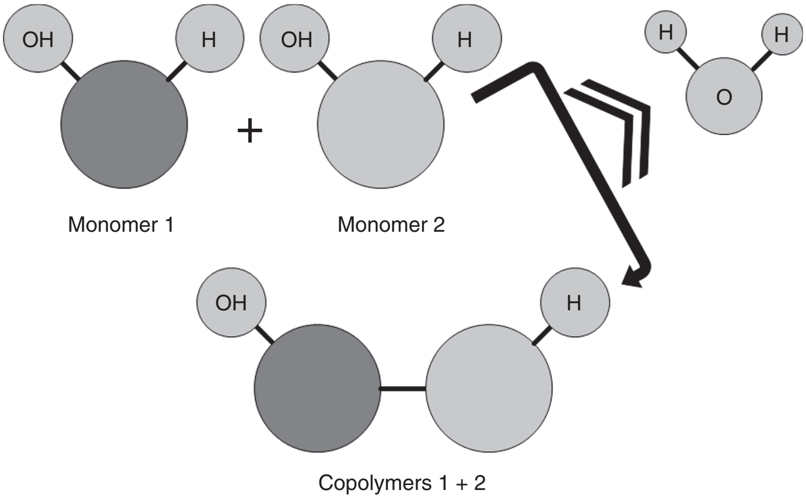


Figure 5.17 Condensation reaction.

Shrinkage can introduce significant residual stresses within the adhesive layer, which, in some cases, can cause a drastic reduction in durability of the bonded joints. Different adhesives have distinct shrinkage characteristics. For example, epoxies are known for their low shrinkage, while acrylics are much more sensitive to this phenomenon. Chapter 8 provides an example of the effect of thermal contraction on the performance of the bonded joints. It has been found that controlling the pressure instead of the displacing can effectively decrease the shrinkage of the adhesive.

5.5.2 Evaporation-Based Processes

Solvent-based adhesives are low-strength adhesives, where the polymeric material that does the actual bonding is dispersed in a solvent or water solution, which must be removed to allow the adhesive to set. This process has several specificities that pose important challenges to the manufacturing process.

When volatile solvents are used, these materials often have a short time window for proper bonding, which requires striking a balance between having some degree of solvent evaporation and ensuring that the adhesive remains tacky. In bonding procedures that use solvent-based adhesives, the adhesive is usually applied by first coating both substrates and waiting until the adhesive reaches the optimal tackiness before bonding. After bonding, the adhesive will continue to gradually lose solvent, until it reaches its peak strength. Note that if the assembly process requires longer open times or higher initial strength, the adhesive can be applied to the substrate, fully dried, and then reactivated by manually reapplying solvent, which will increase the tackiness on the adhesive.

A very practical aspect of the use of solvent-based adhesives is the fact that, even after drying, they remain fully soluble in the solvent that initially carried them. Clean-up applications are simplified, and any assembly mistakes can be easily and cheaply corrected. However, the major drawback associated with these processes is the fact that large amounts of solvents are released to the air. This necessitates special safety equipment and has led to strict regulatory changes, which have severely restricted the use of these materials.

Considering these issues, water-based adhesives have been growing in use. These adhesives follow a similar concept to that of solvent-based adhesive but use water instead of a volatile solvent. As they only release water vapour to the atmosphere, these adhesives obviously result in a safer and greener bonding procedure, but this comes at the cost of more complex processes and important limitations in mechanical performance of the joint.

Maximum strength of a water-based adhesive is reached when all water is removed from the adhesive, and this can be achieved via an evaporation or absorption process. However, in a closed joint, water has limited paths to travel away from the adhesive layer, and thus these, adhesives are better suited for use in applications where one or both substrates are permeable to water.

However, if the use of permeable substrates is not possible, a thin coat of adhesive can be applied to the surface and allowed to fully dry. The adhesive should then be reactivated by applying a precisely controlled amount of water to the adhesive, returning tackiness to the adhesive. It is fundamental to ensure that the amount of water applied is as minimal as possible, so that it can be removed from the adhesive layer even in a closed joint.

Although the materials used are relatively inexpensive, processes that use water-based adhesives can be costly to implement, as they require fine control of the ambient temperatures to ensure that the moisture content in the adhesive later is precisely as needed. An additional drawback of this process is related to the fact that the joints created using water-based adhesives have extremely poor water resistance, as ambient moisture can easily dissolve the adhesive.

5.6 Finishing Steps

After the hardening process completes and the adhesive becomes a solid, load-bearing material, the joint is almost ready for service. However, additional steps are required in many applications before the joint can be used. Initially, all fixtures and grips surrounding the joint should be removed, and if a mould is used to control the joint geometry during the hardening process, the joint should be removed from the mould after the hardening process. However, one must be careful to avoid damage to the joint by applying high loads during this process. To facilitate this process, the mould should be coated with an appropriate release agent and special holes can be included in the mould design, providing a safe location to apply forces and extract the bonded component.

Removing the excess of adhesive is another common part of the finishing step. Although some excess adhesive, such as the fillets at the edges of the bondline, is known to improve the joint strength, many applications require a smooth and polished surface, with the adhesive layer being barely visible. This can be the case, for example, of aeronautical industry applications, where a smooth surface is necessary for aerodynamic purposes, or in the consumer electronics industries, where the aesthetics of the bonded component are highly sought. Nonetheless, the excess adhesive should only be removed when the hardening process is completed. This can be achieved manually using sandpaper or assisted with powered tools such as grinders and polishing machines.

Finally, the manufacture process should conclude with an inspection procedure, where the bonder should check the quality of the bonded structure. As we will see in Chapter 6, there are many different technologies and processes available for controlling the quality of a bonded joint, but a simple visual inspection should always be a part of the process, allowing the identification of issues such as the misalignment of the substrates, non-uniform or incorrect adhesive thickness, areas without adhesives, cracks, uneven fillets, among many others.

6

Quality Control

Throughout this book, we have already repeatedly seen that adhesive bonding is an effective and powerful joining method suitable for use in high-performance bonded structures such as aircraft and automobiles. However, a strong and durable joint is only possible if the adhesive layer behaves exactly as we have designed it to. In high-responsibility applications, it is imperative to ensure that the adhesive is evenly applied through the bonded area, that the adhesion level is adequate, and that the materials of the adhesive and the adherend have not become damaged or degraded. Therefore, how can we make sure that an adhesive layer will in fact perform as expected? This is an undoubtedly difficult task, but it has been the subject of extensive research, which resulted in a variety of different methods suitable to assess the state of a bonded joint. These quality control processes aim to ensure that the finished joint fulfils all the necessary quality requirements.

The quality of the joints is the product of several different factors. Quality assessment of the incoming materials is the first step for controlling the performance of the final product. The next step is controlling the storage conditions. Quality assessment of the manufacturing process is the third step in quality assessment of an adhesive joint, where the hardening and post-hardening processes must be controlled based on strict requirements with regard to time, temperature, and pressure. Adherend alignment, the shape and size of the fillets, and the thickness of the adhesive layer are also important parts of the quality control of the joints during the manufacturing procedure. Lastly, after manufacturing, we can use different testing methodologies to assess the quality of the finished joint. These are divided into destructive testing, where it is necessary to sacrifice a component or structure and non-destructive tests, which can be performed on the actual part that will undergo service.

To summarise, quality control of adhesive joints can be divided into three main steps. The first is quality control of the incoming materials, the second step is the quality control of the manufacturing procedure, and the third stage is quality assessment of the adhesive joints that can be performed using destructive or non-destructive tests. Simply put, the main objective of these quality assessment procedures is to ensure that the bonded structure can safely perform its mission during service. Furthermore, a complete and exhaustive quality control procedure

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Eduardo André Sousa Marques, Ana Sofia Queirós Ferreira Barbosa, Ricardo Joao Camilo Carbas, Alireza Akhavan-Safar, and Lucas Filipe Martins da Silva.

will guarantee that all the produced batches are similar and qualified to perform their tasks. The mentioned three-quality control steps are described in detail in this chapter.

6.1 Quality Control of the Incoming Materials

The first step to control the quality of a bonded joint is to ensure that the materials used in the joint are in accordance with what is specified in the design phase. Both the adhesives and the adherend materials should be assessed to ensure that they meet all the quality requirements. This step consists of different sub-steps as explained in Sections 6.1.1 and 6.1.2.

6.1.1 Control of Adhesive Quality

6.1.1.1 Mechanical Properties

The mechanical properties of the incoming adhesive should be analysed using standard test approaches. In general, tensile and shear strength is a good control parameter because these properties are often critical during design phases. This can be obtained using dogbone shape bulk specimens and shear tests are performed using the thick adherend shear test (TAST) technique. Both test procedures have been already discussed in Chapter 4. Adhesives from different cartridges or batches (randomly selected) should be used in this quality control step. If the adhesive passes the quality control tests, then it can be used for joint manufacturing or can be stored to be used later. As we have already seen, correct storage conditions play a key role in minimising adhesive degradation and should be met based on the recommendations of the manufacturer.

In some advanced applications, control using strength tests is not enough, and more advanced tests are required for quality assessment of the incoming adhesives. These might include fracture energy tests, fatigue tests, impact tests, and creep tests. Fracture mechanics tests are explained in Chapters 4 and 8. Most of the bonded structures usually experience time-dependent loading conditions (e.g. fatigue, creep, and impact) during service, where the mechanical response of the joint changes with time while the loading conditions do not change.

6.1.1.2 Viscosity

Viscosity is an important physical property of the adhesives that is usually measured as part of the quality control procedure. During storage of the adhesive, viscosity changes are usually indicative of important changes in the mechanical properties of the adhesive. Besides, the viscosity of an adhesive directly influences its wettability, so an improperly stored adhesive can lead to adhesive failure of a joint.

Several methods have been employed and proposed for measuring the viscosity of the adhesives. The rotational viscometer is the most common viscosity measurement device based on the measurement of the torque required to rotate a blade within the adhesive.

6.1.2 Control of Adherend Quality

As in the case of the adhesive, the quality of the adherend material should also be controlled before joining. This quality assessment consists of several steps, described next.

6.1.2.1 Mechanical Properties

Tensile testing using dogbone shape specimens is a common approach for the analysis of the quality of the incoming adherend materials. For more critical structures, the quality assessment of adherends in terms of fatigue, impact, and creep is highly recommended and should be adjusted to be representative of the expected service loads. If the incoming materials are composites, more experiments (in terms of the number of tests and test types) are needed to assess the quality of these materials. Composite materials usually show larger scatter in the mechanical performance data, when compared with metallic adherends, which necessitates a larger number of tests for each condition. To further complicate matters, the properties of composite materials are usually different along different directions. Thus, different test types are required to assess the quality of these materials. For example, both tensile and compressive tests should be conducted in different directions. Three-point bending test is also performed to obtain the flexural properties of composites.

6.1.2.2 Wettability, Contact Angle, and Surface Energy

As already discussed in Chapters 2 and 3, the wettability and surface energy of the adherends play key roles in the quality of the manufactured joints. There are several approaches for measuring these parameters. Dyne pens is a common technique that can be used for quality assessment of the surface energy. This technique is a simple and fast method. In this approach, the marker should be used to draw a line along the surface of the adherend. The bonder should visually check the line created by the pen. The line should not break into several small islands as shown in Figure 6.1. If the line is broken with a specific grade of marker, then another marker with a

Figure 6.1 Dyne pen test used for quality analysis of the surface energy.

lower number (grade) should be used. This procedure should be continued until the solid line does not break after a specific time. The number of the corresponding marker using which the line is not broken will determine the surface energy of the adherend. Then, based on the grade of the marker with no broken line, the bonder should decide if the surface has passed the quality control test or not. It should be noted that the marker tip can be contaminated after several uses, which will influence the obtained results.

The water break test is a simple and cheap non-destructive technique suitable for assessing the surface energy of adherends. Using this technique, one can quickly determine if a surface was contaminated, avoiding dangerous situations. The water break test starts by spraying water on the surface. If broken water drops are visible on the surface, this is a sign of the presence of hydrophobic contaminants. Figure 6.2 shows two water break test results on two vastly different surfaces.

Based on ASTM F22, the water break test can be employed for hydrophobic surface films. However, this technique is not appropriate for a precise assessment of the surface energy of the adherends.

Another technique used to control the quality of the adherend surface in terms of the surface energy is to measure the contact angle of a drop on the surface. Figure 6.3

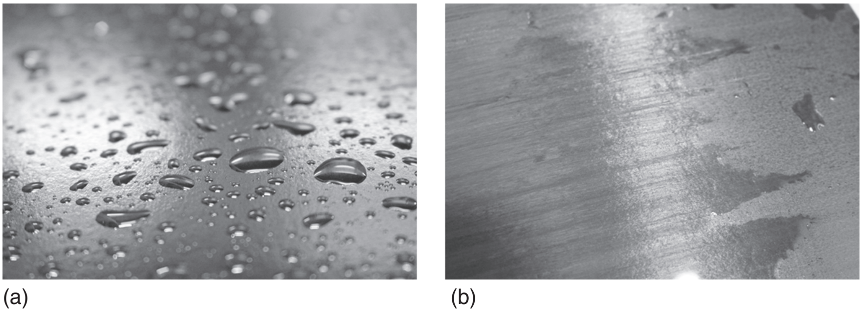


Figure 6.2 Water break test for two different composite surfaces: (a) water droplet formation due to low surface energy or the surface contamination; (b) good wetting, with no clear water droplet formation.

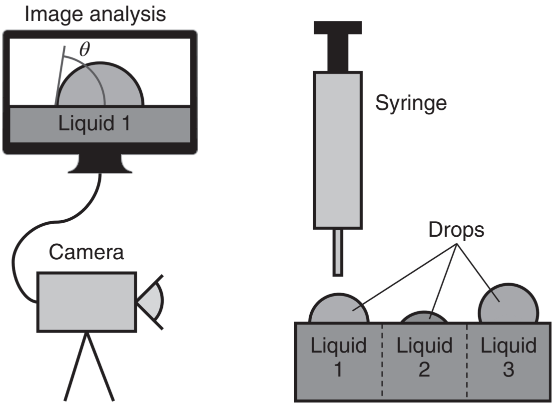


Figure 6.3 A schematic representation of the equipment used for measuring the contact angle of a drop on an adherend surface.

shows a scheme of a device used for measuring the contact angle of a drop on the surface of an adherend.

To perform this quality control test, a drop should be released by a syringe on the adherend surface. Then, using a specific camera, this process is recorded. Using image processing, the contact angle between the drop and the adherend surface is precisely measured.

To calculate the surface free energy from the contact angle (see Chapter 2 for more details), the contact angle of at least two liquids should be analysed. However, knowing the contact angles is still not enough to obtain the unknown values. To solve this issue, we need an auxiliary relation. Several auxiliary relations have been proposed so far. One of these relations is based on the polar (γ^p) and the dispersive (γ^d) parts of the surface energy of the materials. The surface energy (γ) of each material is the summation of the polar part and the dispersive part, as shown in Eq. (6.1). All materials have a dispersive part (γ^d) greater than zero, but for some substances, the polar part (γ^p) is zero.

$$\gamma = \gamma^d + \gamma^p \tag{6.1}$$

Using this concept, some models have been developed to relate the interfacial solid/liquid energy (γ_{SL}) to the surface energies of the liquid (γ_L) and the solid (γ_S). By combining this equation with the Young's equation (Eq. (2.1)), a new relation is obtained (see Eq. (6.2)), which has two unknown parameters that are the dispersive and polar components of the surface energy of the solid (γ_S^d and γ_S^p, respectively). Accordingly, at least two liquids should be tested to obtain the unknown values. By testing the two liquids, the contact angles are measured and substituted in Eq. (6.2). As the dispersive and polar components of the liquids are already known, the unknown variable (γ_S^d and γ_S^p) can be obtained.

$$\frac{\gamma_L(1+\cos\,\theta)}{2(\gamma_L^d)^{1/2}} = (\gamma_S^p)^{1/2}\left[\frac{(\gamma_L^p)^{1/2}}{(\gamma_L^d)^{1/2}}\right] + (\gamma_S^d)^{1/2} \tag{6.2}$$

It should be noted that the wettability quality control should be performed both in the arriving materials and when the adherends are ready for bonding, immediately after the surface preparation.

6.1.2.3 Surface Roughness

As it was already discussed in Chapters 2 and 3, surface roughness plays a major role in the quality of the adhesion between the adhesive and adherends. Accordingly, it is very important to measure the surface roughness of the adherend in order to ensure that it meets the design specifications. The roughness of the surface is a function of the material type, manufacturing process of the adherends, and also the surface preparation technique. Accordingly, to ensure that the surface roughness condition meets all the requirements, it is necessary to control its quality after receiving the adherends and immediately after the surface treatment is applied. An effective surface roughness measurement looks at height, depth, and interval of the ridges, and there is an ideal surface roughness for each type of material. Any process that changes the roughness of a surface should be controlled considering

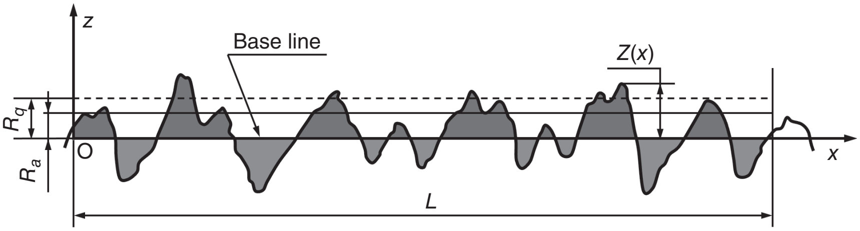


Figure 6.4 Key parameters of the roughness profile.

different variables such as R_a or the average roughness where the average of the roughness of surface is measured based on a base line (see Figure 6.4), and the R_q (root mean square deviation of the profile) in which the roughness is measured based on root mean square low, all serving as benchmarks to decide whether to accept or reject the material and/or the treatment process. Figure 6.4 shows how these parameters are related to the measured roughness profile.

To measure the roughness, two different methodologies can be employed, divided into contact and non-contact technologies. The contact method is perhaps the most common and practical approach for measuring the surface roughness of adherends, although some applications are better suited with the use of non-contact techniques. Profiling the surface using stylus profilers is a typical example of a contact method. As it shown in Figure 6.5, this is achieved by moving the stylus on the surface. The diamond tip of the stylus follows the roughness of the surface.

In this approach, there is a contact between the stylus tip and the adherend surface, which can cause the stylus to wear out (see Figure 6.6). This can introduce errors in the measurement, which will thus differ from the actual surface roughness. The stylus tip should be measured and controlled before the roughness assessment of the surface is initiated. Furthermore, as different levels of surface roughness require different stylus tips, it is important to select the suitable stylus for a given application.

In some materials and for some geometries, the contact-type approach is not satisfactory and might be difficult to implement. Thus, some processes are better suited with a non-contact technique for roughness assessment of the adherend surfaces,

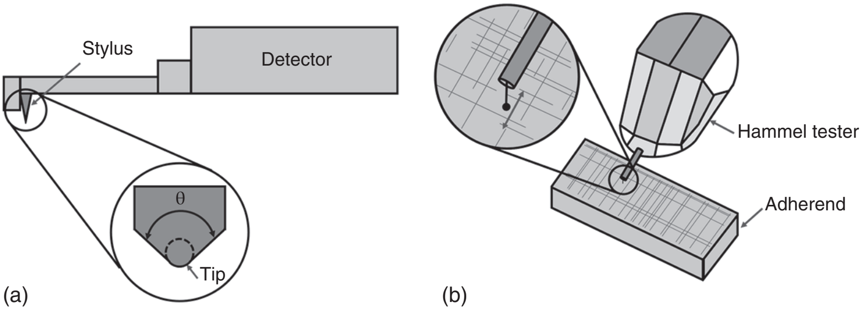


Figure 6.5 Contact-type surface roughness/profile measuring instruments. Stylus and detector configuration (a) and position of the tester over the adherend (b).

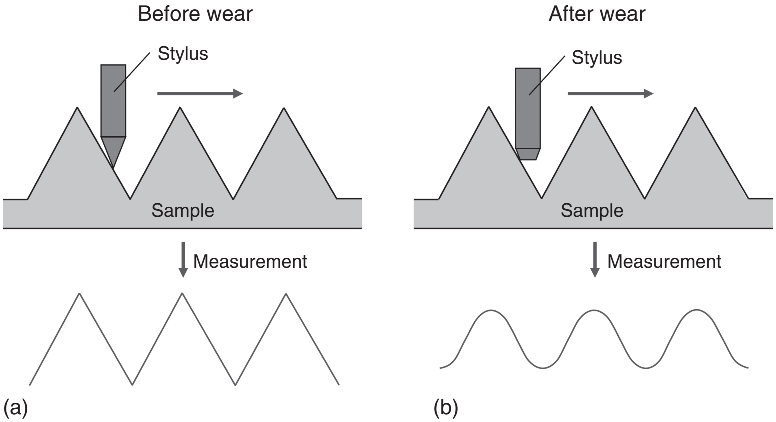


Figure 6.6 Wear of the stylus tip due to the direct contact with the adherend surface and its influence on the measured profile. (a) New stylus and (b) worn stylus.

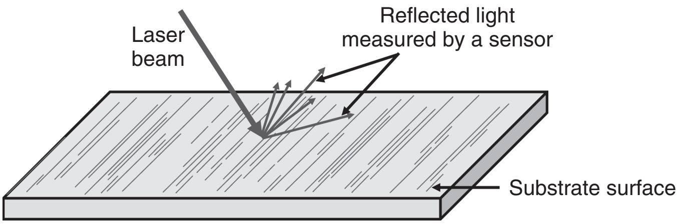


Figure 6.7 Schematic representation of a laser-based, non-contact approach for surface roughness measurement.

making use of an optical method. In this approach, the wavelengths of the light reflected from the surface are measured to analyse the surface roughness. Figure 6.7 schematically shows a non-contact (laser based) approach used for roughness measurement.

Atomic force microscopy (AFM) is a very-high-resolution type of scanning probe microscopy that can also be used for the analysis of adherend surface roughness. AFM employs a cantilever arm with a tip at its end to scan the surface. The tip travels along the surface. The tip will travel vertically because of the roughness of the surface, and this movement is registered to create the roughness profile. The resolution obtainable with AFM is usually less than 10 nm.

However, as you might expect, this requires highly expensive equipment, and its use is mostly limited to the analysis of surfaces with extremely low roughness, where other approaches (optical method and the stylus tool) fail.

6.2 Quality Control of the Manufacturing Process

As we have seen, manufacturing processes of bonded joints consist of three essential sub-steps, comprising adhesive application, the assembly of the joint, and adhesive hardening. Each of these three phases has its particularities, which indicates that the quality of each step should be controlled separately. For example, for the adhesive application, stage one should check if the amount of the applied adhesive is enough to cover all the bonded area and if it is sufficient to form the fillets at the edges of the overlap. Temperature and humidity are also important parameters that should be controlled during the adhesive preparation and its application on the surface. Controlling the adhesive viscosity, which is a function of ambient temperature, is also part of the quality control of the manufacturing process. Shelf time and storage conditions (the relative humidity and temperature) are important parameters that may affect the viscosity of the adhesive. Adhesive thickness is another influencing factor that can significantly change the strength of the joint. During the bonding process, adhesive thickness should be controlled precisely (see Chapters 5 and 8 for more details on the control of adhesive thickness and its effect on joint performance).

Perhaps the most important step in the joint manufacturing procedure is the hardening process where the adhesive is converted to a solid state. Time, temperature, and pressure are three factors that influence the hardening quality. The hardening time is a function of the temperature, and if it is incorrectly set, hardening might be incomplete (if the temperature is lower than the recommended hardening temperature), or the adhesive might become burnt (for temperatures much higher than what is specified by the manufacturer). As you might suspect, both conditions result in very poor joint performance. Datasheets provided by the manufacturer contain all the necessary information about the hardening conditions and control of the adhesive layer temperature during the hardening process is an essential step to ensure that the cure process is carried as intended. One common method for controlling the temperature of the adhesive layer during the hardening process is the use of thermocouples or temperature sensors integrated in the heating setup (for example, an oven). However, this is not a recommended control approach as the nominal temperature shown by the heating equipment is usually higher than what the adhesive really experiences. In this case, some contact or non-contact devices, as shown in Figure 6.8, can be employed to precisely check the temperature of the adhesive layer. The contact method uses a thermocouple sensor. The sensor should be in contact with the object where the temperature is being measured. For the non-contact technique, thermometers that analyse the emitted infrared radiation (IR) should be used. Non-contact thermometers can measure the temperature of the joint from a distance. When the object is hard to access, a non-contact thermometer is preferable.

The evolution of the hardening process of an adhesive can also be analysed using differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), and dynamic mechanical analysis (DMA) techniques, although not directly during the curing process. DSC and DMA can be used to measure the T_g of the adhesive at different hardening steps. The final T_g of the adhesive can be considered as a key parameter to control the quality of the adhesive hardening process.

DSC indicates the degree of adhesive cure by measuring the heat flow of the test specimen. In the DSC method, a small piece of the material is slowly and linearly

Figure 6.8 Hand-held thermocouple thermometer (a) and an infrared-based thermometer (b).

heated up. The absorbed heat and the amount of the emitted heat are measured. In this technique, two samples of the material are needed. One of them is the test sample and the other should be considered as the reference. Test results show the heat flow that is measured as a function of time and temperature. Figure 6.9 shows schematic DSC curves for an adhesive for different times and temperatures. Using the DSC results, it is possible to analyse the quality of the adhesive hardening.

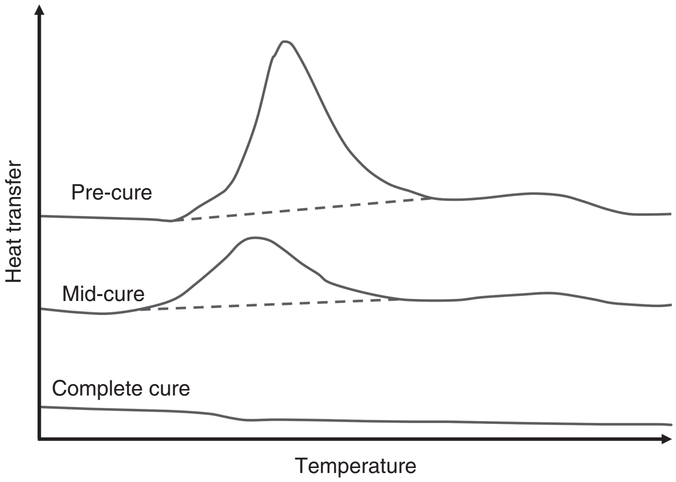


Figure 6.9 Representative DSC curves showing different curves as a function of curing level.

DMA is a thermo-mechanical test where the sample is subjected to a load at a specific frequency and the response to the viscoelastic behaviour of the material is measured. To allow for mechanical loading, the sample should be mounted on the testing machine between a moveable and a fixed plate and within a chamber.

DMA can be a time control test where the temperature is constant or a temperature control test where temperature changes at a specific rate during the test. Three main parameters that are measured by the DMA approach are the storage modulus, loss modulus, and the ratio of these two parameters, which is called the damping factor. These parameters are measured as a function of temperature or time. The values of these parameters change significantly during the hardening process. Figure 6.10 schematically shows the variation of the DMA parameters as a function of temperature. Compared to the DSC method, DMA is more precise, but it is much longer. ASTM D4473 has standardised the test method for analysis of the hardening of thermoset resins based on the DMA technique.

Using the FTIR technique, the hardening mechanisms can be precisely tracked and controlled. To achieve this, the FTIR spectra of the adhesive during the hardening process should be obtained and compared with the reference spectra. Any deviation should be analysed as it is a sign of the deviation from an acceptable condition. Figure 6.11 shows a typical spectrum where different peaks are observed. Each peak corresponds to a specific group of materials. The *x* axis in FTIR analysis results shown in Figure 6.11 corresponds to the wave number of the IR radiation. Each wave number in *x* axis corresponds to a specific group of material compounds. The vertical axis in Figure 6.11 shows the level of IR radiation absorbed by the tested sample. The higher the level of absorbance, the higher the amount of material compound that exists within the test sample.

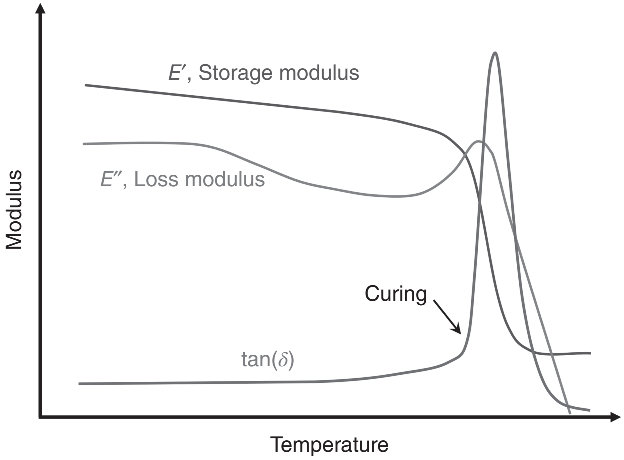


Figure 6.10 Representative DMA curves showing storage and loss modulus, as well as the glass transition peak.

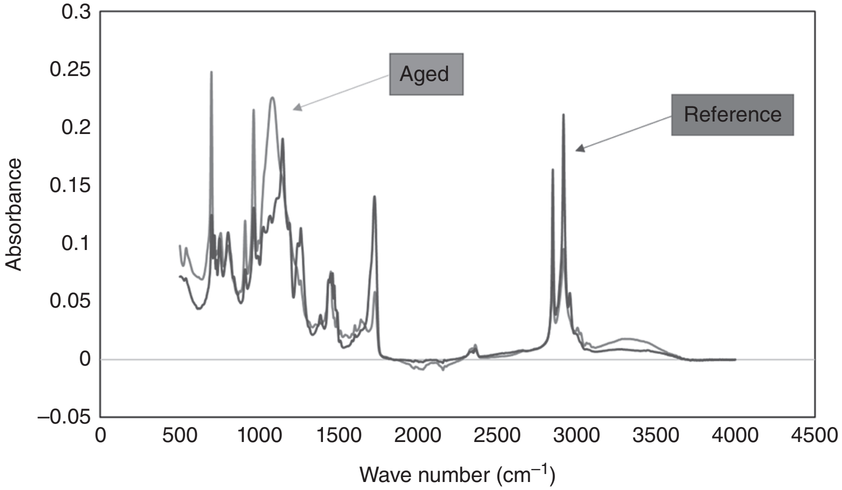


Figure 6.11 A typical FTIR spectrum.

6.3 Quality Control on Bonded Structures

6.3.1 Types of Defects Present in Bonded Joints

Because of manufacturing issues, poor storage conditions, large internal stresses, or unexpected service loads, defects may be introduced into the adhesive layer or at the interfaces. The presence of defects should be detected whenever it is possible, as they can significantly change the joint strength and lead to premature failure. Although ideally there should be a quantitative relation between defects and the strength of joints, in practice, it is not always possible to make this direct relation. The defect type, size, and location are three important factors that affect the strength of the joint and must be determined using the quality control methods.

Porosities, cracks, voids, disbonding, presence of a foreign object, poor cure, and weak adhesion are some of the defects that can be observed in a manufactured joint (see Figure 6.12). To qualify for use in critical applications, such as for example in an aircraft structure, bonded joints must be analysed using destructive and (or) non-destructive approaches. In this section, different quality control methods are described, categorised into non-destructive and destructive tests.

Among the mentioned defects, weak adhesion is perhaps the most concerning, as its detection using the available destructive and non-destructive techniques is almost impossible. In weak adhesion, there is a complete but weak contact between the adhesive and the adherends. No discontinuity is observed, but there is no load carrying capability. Surface treatments, which as we have seen are an important part of the manufacturing procedure, play a key role in the avoidance of weak adhesion,

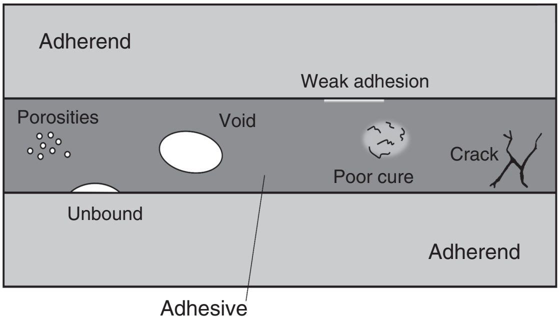


Figure 6.12 Typical defects of the adhesive layer in an adhesive joint.

ensuring that contaminants are removed from the surface and that there is a strong chemical bond between the surface of the adherend and the adhesive material.

During the manufacturing process, the thermal shrinkage associated with the hardening might lead to the appearance of cracks within the adhesive layer. However, the main source of cracks in the adhesive is the service loads, especially if the applied loads are cyclic in nature (fatigue cracks).

As it was discussed in Chapter 5, for some adhesives (such as phenolic adhesives), curing takes place because of the condensation reaction where water molecules are released. In these conditions, voids are usually created because of the presence of trapped gas bubbles in the adhesive mixture, even before the application of adhesive on the surface. Voids in the adhesive layer can also be a product of an incorrect pattern for adhesive application on the adherend surface, which may cause the air to be trapped within the adhesive layer. Voids decrease joint strength by decreasing the bonded area and by increasing the stress level within the adhesive layer. They can also speed up the ageing process by increasing the rate of water uptake, as water can more easily fill the voids. Thus, a suitable quality control procedure will analyse the presence of voids in adhesive layers. If air is trapped at the interface between the adhesive and the adherend, an unbound region will be created. Some porosities in the adhesive layer are the product of the chemical reaction associated with the hardening process, which releases volatiles that can be trapped in the adhesive layer. Other volatile components present in the environment, such as water, can also form porosities, especially if hardening occurs at high temperatures where the water vapour can enter the adhesive layer.

An improper hardening procedure or an incorrect mixing ratio for the two-part adhesives can lead to bonded areas where the adhesive is not fully cured. In these regions, the adhesive is simply not strong enough to support significant loads. As we have seen above, this type of defect can be avoided by carefully controlling the hardening process, including its temperature.

6.3.2 Destructive Tests

Many destructive testing procedures are available for the determination of the performance of bonded joints and structures and identification of defects. Some are standardised and to be carried out in well-defined specimens, while others are more flexible, intended to assess the performance of actual components and structures (proof tests). Since we have devoted a section of Chapter 4 to the study of standardised tests to characterise adhesives and bonded joints, in this section, we will only analyse in detail the proof tests and the analysis of fracture surfaces.

6.3.2.1 Proof Tests

As we will later see in detail, non-destructive testing methods are quite powerful but still not sufficiently developed to allow for the detection of all types of defects that might exist in bonded structures. Thus, destructive tests, known as proof tests, are often used to validate, without margin of doubt, the quality control assessment procedures implemented in previous steps of a manufacturing process. In critical, high-responsibility applications, before series manufacturing begins, it is usual (and sometimes even mandatory) to perform a proof test on a representative structure. This section focuses on this type of tests.

Proof tests are usually a mechanical loading test in which the applied load is higher than the working load limit of the component. Proof tests are categorised as destructive tests as they may result in the failure of the bonded assembly. However, a bonded component can still pass these tests if it withstands the applied proof loads with no failure. Rollover tests in buses or crash tests in cars are good examples of proof tests. Another example is the proof tests carried in aircraft wings, where the test wing must withstand loads up to 150% of the expected service loads.

One of the main issues associated with the proof test is its low sensitivity to very small defects, which do not affect the test results but might have an impact under other types of loads such as fatigue, for example. Also, some long-term degradation phenomena such as ageing that can significantly decrease the durability of the joints are usually not taken into account in this test, which is carried out almost immediately after manufacture. To overcome these issues, a periodic proof test should be performed on joints representative of the bonded structure. Periodic proof test indicates that the joints should be tested during the service at specific time intervals. However, it should be noted that periodic testing of complex-bonded structures is highly expensive and time-consuming. It is almost exclusively used in critical structures where the failure of the bonded assembly leads to a catastrophic failure.

6.3.2.2 Fractography Analysis

The analysis of the fracture surface (Fractography) is a destructive testing approach for quality assessment of adhesive joints. The presence of voids, weak adhesion, contaminations, and insufficient cure are some of the issues that can be detected through fractography. Fractography analysis can take the form of a visual check using aided or naked eyes, or it can be an advanced quality control procedure supported by advanced equipment, such as energy-dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM) analysis, and AFM. The use of the EDS technique together with SEM is an extremely powerful tool to assess the quality of the fracture surface, allowing to clearly identify the chemical compositions of the materials involved. Using SEM, it is also possible to analyse the failure mechanisms. Using a nanoscale scanning tip, AFM is able to analyse the fracture surfaces in extreme resolution. However, it can only scan very small areas, with limited roughness.

Different damage mechanisms create vastly different surface morphologies, which can be identified with some practice by a skilled operator. Type of the defect, its size, and the density of the defects are three parameters that should be analysed. Some applications provide reference tables in which the allowances found for each type of defect are given.

Fractography can also give information about the failure mode (adhesive failure vs. cohesive failure). As we have seen in Chapter 2, when the crack propagates through the interface, the failure is called adhesive failure. Contaminated surface, ageing, inadequate surface treatment, hardening of the adhesive before the bond is formed, among others, are all possible reasons behind an interfacial failure. A visual check with naked eye can give some information about the failure mode. However, for a precise surface analysis, usually advanced techniques such as SEM should be employed.

Figure 6.13 shows an example of an SEM image, showing the fracture surface of an single lap joint (SLJ) subjected to quasi static loading conditions.

Although an analysis with the naked eye can many times suggest the presence of an adhesive failure, the use of high-resolution inspection techniques such as SEM can often show the presence of a very thin layer of adhesive on the adherend surface. In this case, the failure can be considered as cohesive but close to the interface, as schematically shown in Figure 6.14.

Not only the failure mode (adhesive vs. cohesive) but also the fracture type (brittle vs. ductile) can be determined in fractography. For brittle fractures, the crack usually tends to propagate perpendicularly to the direction of the maximum principal stress. Several micro-cracks can be observed on the fracture surface and the distance

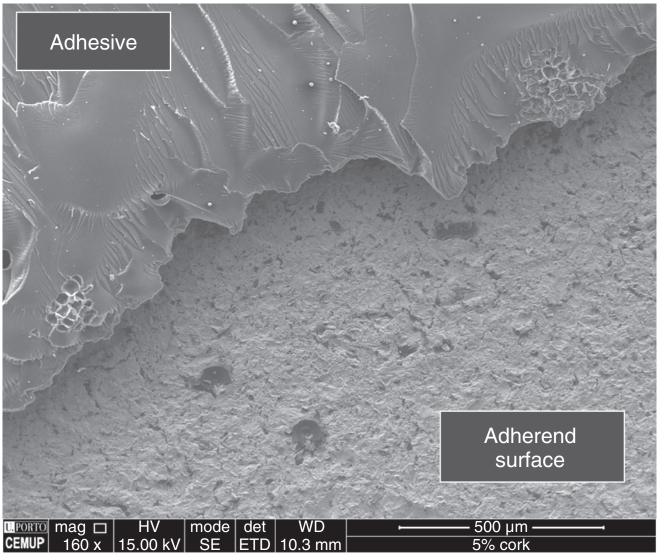


Figure 6.13 An example SEM image depicting the fracture surface of an SLJ.

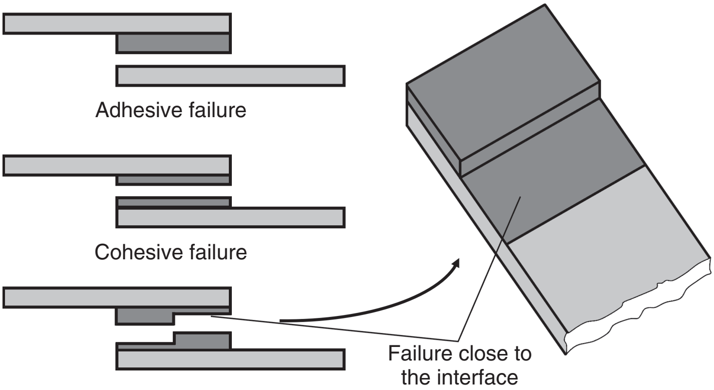


Figure 6.14 Example of a fractographic analysis showing the presence of a thin layer of adhesive typical of a cohesive failure close to the interface.

between the micro-cracks is usually smaller than a ductile fracture. Less deformation on the voids (if there are voids on the fracture surface) is usually observed in a brittle fracture while in a ductile fracture, an SEM analysis allows us to identify that the voids (or porosities) are deformed along the loading direction. Using a microscopy analysis, or even in some cases by a visual check using the naked eye, whitening bands can be observed on the fracture surface in a ductile fracture.

6.3.3 Non-destructive Tests

6.3.3.1 Visual Inspection

When the bonder is visually checking the manufactured joints in terms of defects, he/she is doing a visual quality control check. A visual check can be performed with naked or with the aid of a simple instrument (for example, using a magnifying glass). As shown in Figure 6.15, visual checks are appropriate for the identification of defects or flaws that are noticeable at the joint surface. In addition, geometrical faults such as misalignment, non-uniform adhesive thickness, incorrectly shaped fillets, etc., can also be determined in a visual check. The lack of adhesive overflow

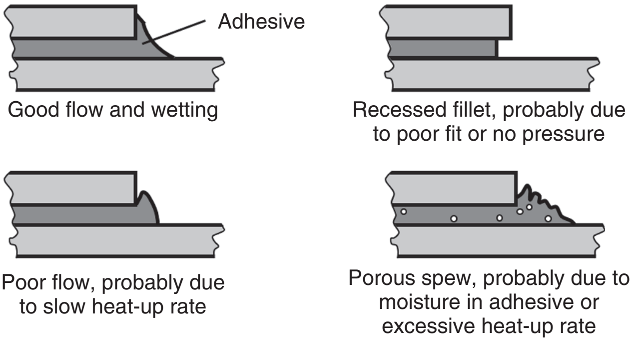


Figure 6.15 Defects in bonded joints identifiable with a visual inspection process.

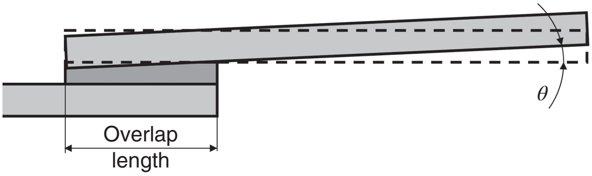


Figure 6.16 Visual inspection using a geometrical analysis achievable using measurement tools.

or fillet at edges of the bondline after manufacturing can be a sign of insufficient adhesive between the adherends or an incorrectly set bondline (thicker bondline).

Visual inspection can act as an initial step for quality assessment of bonded assemblies. Based on this analysis, the joint can be released for service or can be subjected to further advanced NDTs. Although the visual inspection method is a simple approach for quality control of the joints, the operator performing the inspection should be highly skilled and experienced. In addition, it is crucial to provide an appropriate luminous intensity, ensure the correct viewing angle, and use the most adequate tools. The effectiveness of this technique is highly dependent on the quality of the supporting setup. The visible defects and flaws should be compared with reference images in inspection manuals to ensure that they are within an acceptable range. It is also possible to use simple tools to check for misalignments and deviations, which can easily identify significant defects in the geometrical configuration of the joint (Figure 6.16).

6.3.3.2 Tap Test

Like the visual inspection, the tap test (Figure 6.17) is among the simplest NDT approaches used in practice. In this test, a hammer is used to tap the surfaces of the joint. An operator will listen to the reflected sound wave to determine if the joint is qualified or not. Large unbound areas between the adherend and the adhesive or presence of significant voids will noticeably change the reflected sound. The presence of voids or defects generates a resonant sound, while when no defect exists, the sound is usually dull. Although effective at detecting the existence of many defects, this approach is unable to provide information on the size or the type of the defects. Also, if the defect is far from the surface, it will be hard to detect using the tap test. The tap test can be automated to make it more reliable and its results more consistent. The concept of the automated tap test is pretty similar to the

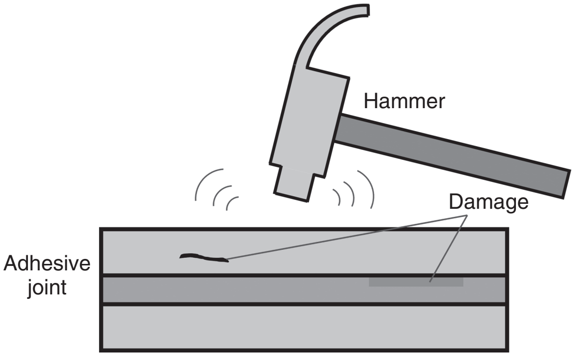


Figure 6.17 Tap test.

manual one, but the hand-held hammer is no longer used. Instead of the hammer, a solenoid is employed to apply multiple and consistent impacts to the same area. Using the automated version of the tap test, it is possible to obtain more information such as the applied load as a function of time and the applied energy that help to assess the quality of the bonded structure more precisely.

6.3.3.3 Ultrasonic Test

Many non-destructive inspection techniques are based on the analysis of mechanical waves travelling through the material. The simplest one is the tap test, which is described above, where sound waves are produced and analysed. Ultrasonic testing is another mechanical wave-based NDT used for inspection of adhesive joints. In this technique, mechanical waves in the ultrasonic frequency range propagate through the joint. When these waves reach a defect (for example, a void or a crack), the reflected waves will be different from the transmitted one. The difference between the two waves (reflected and transmitted) can be interpreted as the presence of a defect. Figure 6.18 shows a schematic of an ultrasonic inspection of an adhesive joint. Voids, porosities, cracks, and disbonding are different defects that can be detected by this technique. However, determining the type and size of defect is quite difficult using this approach.

6.3.3.4 Acoustic Emission Test

The acoustic emission test is also a sound-based test method. In this method, acoustic multiple sensors should be placed on the surface of the joint. During the test or service, any damage-related event within the sample, such as crack propagation, debonding, etc., will lead to the generation of sound waves that will be detected by the acoustic sensors. Although the acoustic emission test is categorised as an NDT test, the specimens must still be mechanically loaded and some damage should propagate during the test. Thus, some authors classify acoustic emission as

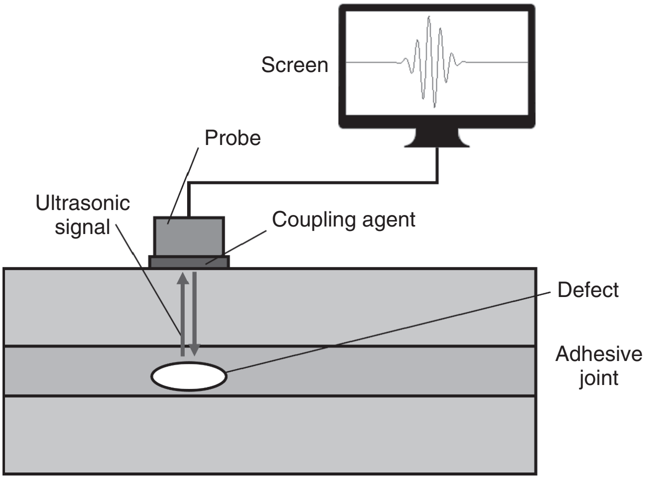


Figure 6.18 A schematic of the ultrasonic test.

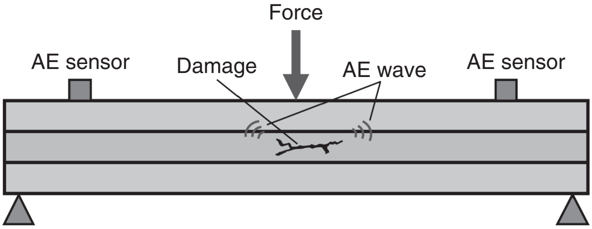


Figure 6.19 A schematic of the acoustic emission NDT procedure.

a destructive test as well, even though the analysed structure is still expected to be fit for service. Similar to other NDT approaches, acoustic emission employs a data acquisition system to record the detected waves.

This technique is especially well suited to detect the delamination or fibre breakage in composite adherends, as well as crack propagation within the adhesive layer. The exact size or type of defect is usually difficult to be detected using this technique, but the initial growth of defects can be accurately detected using this method. Acoustic emission has been shown to be able to detect weak adhesion between the adhesive and the interface. However, this technique is not well suited for ensuring the quality of a bonded structure before it enters service. Although it can detect many types of defects, acoustic emission cannot be really considered as an NDT method as the sample should be loaded until a crack propagation event is generated and detected, making it more useful to monitor structures that are already in service. In fact, just the act of acoustic emission testing has the potential to introduce damage in the bonded structure and can even be the cause of joint failure. Figure 6.19 shows a schematic setup of an acoustic emission test.

6.3.3.5 Radiography Test

As shown in Figure 6.20, in this method, bonded components are exposed to a source of radiation, which passes through them. Two different electromagnetic waves called

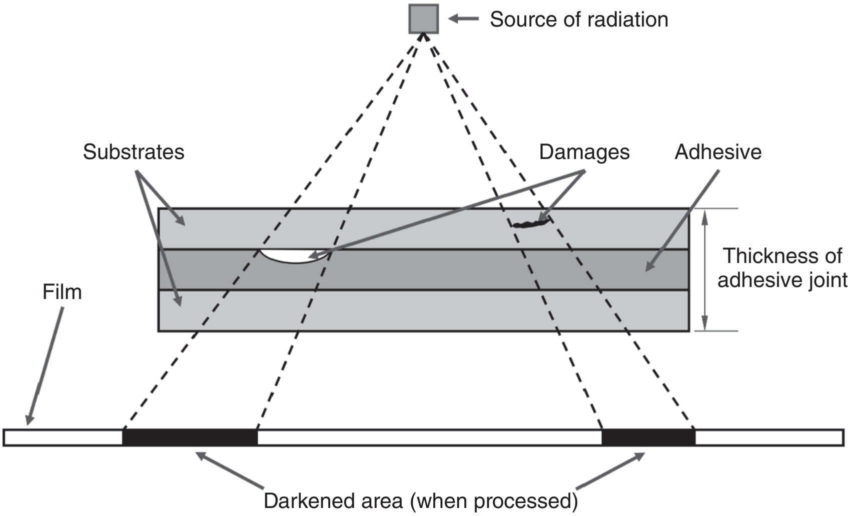


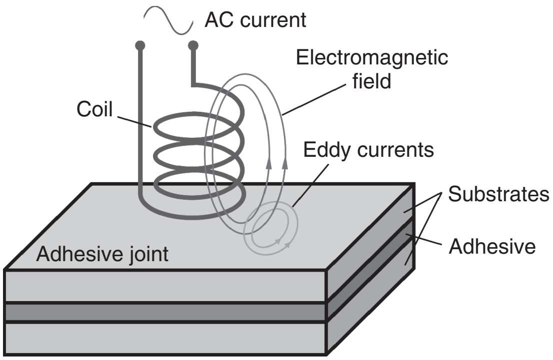
Figure 6.20 A schematic of the radiography inspection procedure.

X-ray and γ-ray can be used in this technique. γ-Ray has a higher frequency compared with the X-ray and their sources are also different. X-ray is produced artificially using a generator while the γ-ray radiation is emitted by radioactive materials. However, both are short-wavelength, high-energy waves able to pass through the components. During testing, as the radiation passes through the joint, part of it is absorbed by the joint and the remaining part is transmitted through the bonded structure. A detector on the other side of the component receives the transmitted part of the radiation, which can be used to create an image. The created image will show defects that are located deep inside the adhesive and the adherend materials and that otherwise would be impossible to visually detect. Defects change the ratio of absorbed and transmitted X-rays. Electrically conductive particles can be added to the adhesive to create better contrast if the obtained images are not sufficiently clear. Crack, disbonding, and voids are the defects that can be detected using the radiography test.

6.3.3.6 Eddy Current Test

The basic principles of magnetism state that when a current is passed through a conductor, it will generate a magnetic field. The opposite is also true, and if a body is under the influence of a magnetic field, currents will be generated in it, known as eddy currents. Eddy current testing explores this principle. In this technique, alternating current is fed to a wire coil, generating an oscillating magnetic field near the component to be tested (see Figure 6.21). The electromagnetic field causes a flow of electrons in the component, and internal defects such as voids and cracks can be detected, as defects change the eddy current pattern. One important limitation of the eddy current test is the fact that the component under test must be conductive, to allow for the formation of the eddy currents. As the intensity of the eddy current at the joint surface is maximum, higher resolution is available for detecting the defects at bonded surfaces. For defects far from the surface, the intensity of the eddy current is inevitably lower, and this leads to low analysis resolution and reduced sensitivity to the defects. Accordingly, the eddy current testing method is most appropriate for detecting surface and near the surface defects. By changing the coil type and the test frequency, the efficiency of the eddy current can increase with regard to the conductivity of the test samples.

Figure 6.21 A schematic of the eddy current test principle.



6.3.3.7 Thermal Infrared Method

In this technique, a source of energy such as a photographic flash or a halogen lamp is used to induce a heat pulse into the joint. As a result of this pulse, the temperature of the tested joint will instantly increase. The distribution of the temperature on the joint surface can then be measured and analysed using an infrared imaging device. The detection of defects is possible because after the heating of the joint, the joint will immediately start to cool down. However, in the presence of a defect, this cooling process will not be uniform because the defects will conduct heat differently from the bulk, non-defective material, as it is schematically shown in Figure 6.22. The images collected by the infrared imaging device should be analysed to decide if the joint is qualified for the service or not. Thermal infrared or thermography method or thermography method is a non-contact NDT approach that is especially useful to test joints that are hard to access. Cracks, void, insufficient hardening, adhesion issues, etc., are some defects that can be detected using the thermographic method.

6.3.3.8 Lamb Wave-Based Testing

Inspection technique based on lamb waves uses the same concepts of the ultrasonic testing method described above but differ in the type of wave being generated. While ultrasonic waves travel uniformly through the material (and thus create particle movement in all directions), in lamb waves, the particle motion is restricted to a single direction, corresponding to the direction of the wave propagation. In these tests, a signal generator and an actuator are used to introduce a lamb wave in the material. Piezoelectric transducers are usually employed as they are able to receive the electrical signals and can also convert them to mechanical waves. Another piezoelectric transducer that acts as a sensor should be employed to receive the waves. The sensor converts the receiving waves into electrical signals and sends it to a data acquisition system. This procedure is schematically shown in Figure 6.23. Although in theory this method may be able to detect any kind of damage, its ability to identify weak adhesion still requires further investigation. However, interpreting the received signals is quite complex, which needs a special data processing algorithm.

6.3.3.9 Electromechanical Impedance Spectroscopy

Electromechanical impedance spectroscopy (EMIS), as an NDT approach, uses both the mechanical and electrical concepts to detect defects in bonded structures. Similar to the lamb wave method, EMIS also employs piezoelectric sensors, which can act both as an actuator and as a signal receiver (sensor). However, in contrast with the lamb waves where a set of waves is generated only for a given excitation frequency, EMIS excites the joint in a much wider range of frequencies. In EMIS approach, first, an AC voltage is generated using a generator. Then, the voltage is delivered to a piezoelectric component that acts as an actuator. Piezoelectric materials can convert electrical signals into a mechanical excitation and vice versa because these sensors have a coupled electromechanical behaviour. This indicates that they can also receive the mechanical response and convert it to electrical signals. The obtained

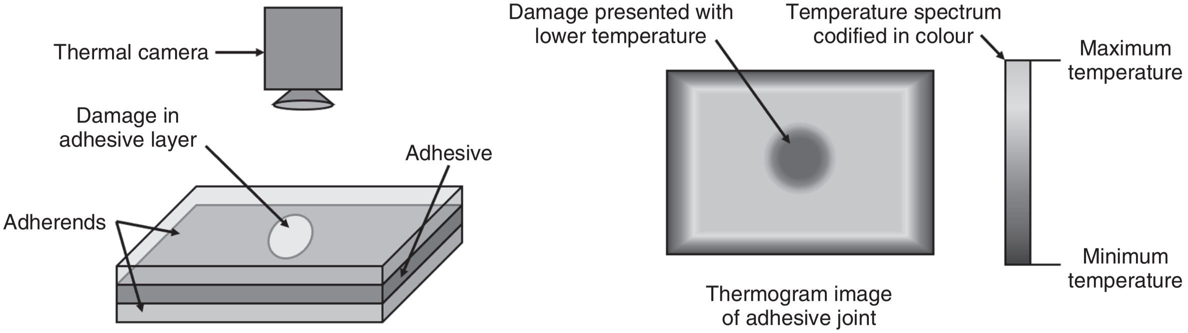


Figure 6.22 Thermal infrared method for NDT of the joints.

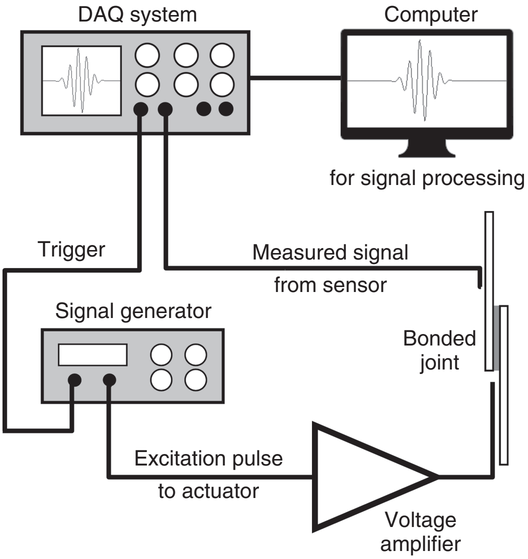


Figure 6.23 Schematic representation of the procedure used for NDT of joints using a lamb wave-based method.

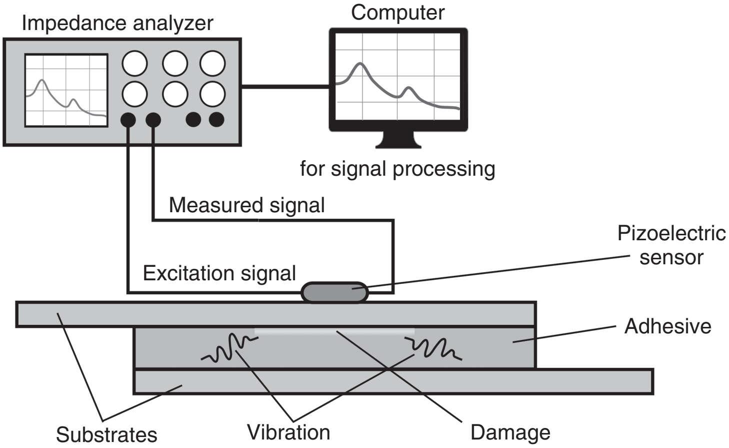


Figure 6.24 Schematic representation of the procedure used for NDT of joints using an EMIS-based method.

electrical signals are sent to a data acquisition system where the response signals are recorded and processed. The scheme of the EMIS set up is shown in Figure 6.24. The piezoelectric sensor can be permanently bonded to the structure for a continuous health monitoring of the bonded structure in service. Compared to other NDT techniques, EMIS is a lightweight and an inexpensive approach with a wider range of frequencies than can be used in this method. Using the EMIS technique, it is possible to detect adhesive disbonding and cracks in adhesive joints. As we have seen, weak adhesion between the adhesive and the adherend is a defect that is quite difficult to detect. Recently, EMIS technique has been considered by researchers to detect the weak adhesion in adhesive joints.

6.3.3.10 Laser-Based Testing

The laser test is an advanced technique for non-destructive inspection of adhesive joints. It combines both concepts of the fibre-optic and the ultrasonic method. Because of the flexibility of the fibre-optic system, using the laser method, the inspection can be performed remotely where the joints are hardly accessible. In this technique, a laser generates and sends one or more laser pulses to the bonded structures. The joint surface is then heated up because of the absorption of the laser pulses. This phenomenon generates ultrasonic waves on the surface of the joint and produces some signals. Detecting the interfacial disbonding is possible through the analysis of the received signals. Laser test is mainly used for testing aeronautical structures. The Boeing company uses this technique to detect weak adhesion in components of the aircraft it manufactures. However, it should be noted that the loads generated by the laser may be strong enough to damage defect-free areas and cause immediate joint failure in bondlines where some defects are already present. Figure 6.25 schematically shows the process of laser testing of an adhesive joint.

To summarise this chapter, we have seen that quality assessment of the joints should be performed whenever possible to ensure the optimal performance of the adhesive joints during service. Several parameters can influence the quality of a bonded component, such as the condition of the incoming materials, manufacturing procedure, service loading, and the environmental conditions. To analyse the quality of a bonded structure, several destructive and non-destructive techniques have been developed.

The application of each quality control method is limited to the specific conditions. Some of them are limited for specific adherend materials (e.g. the eddy current approach) while some others are limited to the specific size of the joint (e.g. the radiography method). In some techniques, advanced equipment is required, while in some others, the quality control can be performed without any advanced tool. However, it should be noted that detecting the size of the damage and the location of the defect is still a big challenge for adhesive joints. Almost none of the quality control procedures cannot precisely detect the location and type of the defect. On

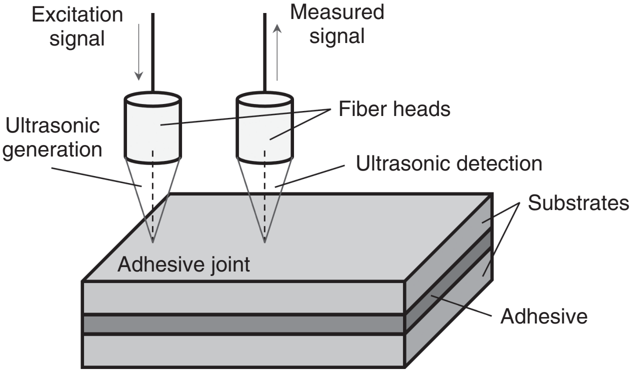


Figure 6.25 Schematic representation of a laser-based NDT inspection procedure.

the other hand, each quality assessment method is limited to specific types and sizes of defects. Also important is the fact that weak adhesion is a highly damaging defect that is very hard to detect by the current DT and NDT techniques. To find a solution for detecting the weak adhesion, further research is needed. In practice, using a combination of different quality assessment techniques is usually recommended to guarantee the mechanical performance of the adhesively bonded structure during the service.

7

Environment, Health, and Safety

The use of adhesives in industrial applications has greatly expanded in recent times, but this also indicates that those who operate with these materials can now be exposed to a variety of possibly hazardous materials and conditions and that resultant waste must now be properly disposed. It is therefore highly important for those who operate with these materials to be familiar with the safe procedures for handling them.

A sustainable application of adhesives in the world economy must inevitably be based on the three dimensions of sustainable development: social, economic, and environmental. The world history of the past century has been an excellent teacher in this respect, showing that the economies solely based on economic profits quickly face difficulties associated with social and environmental problems. Thus, there is a need for an increased awareness on how to achieve sustainable growth, providing for each of the three dimensions. Sustainable product development should be a constant process of continuous improvement, fostering the common good for global growth while respecting the responsibility and efficiency of the planet finite resources.

In European Union member countries and the United States, the production and development of adhesives and sealants is certified by the guidelines established by Responsible Care®, promulgated by chemical trade associations worldwide, including the REACH – Registration, Evaluation, Authorisation and Restriction of Chemicals, Adhesive and Sealant Council and FEICA – Association of the European Adhesive & Sealant Industry. Responsible Care is a global initiative that began in 1984, by and for the chemical industry, which calls upon companies to demonstrate commitment to the highest standards of health, safety, and environmental performance. Today, largely because of the restriction in CO_2 emissions imposed by the European Union and other governmental entities, there has been an additional effort to defossilise and replace solvents with water-based ones, ensure low-hazardous vapours, and develop methods to reuse and recycle adhesive joints, both for the wellbeing of workers operating with adhesives and the environment. The work of these international organisations with local stakeholders, through their national associations, is focused on continuously improving health, safety, and environmental performance and to communicate with stakeholders about their products and processes. For the application of adhesives to have a sustainable

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Eduardo André Sousa Marques, Ana Sofia Queirós Ferreira Barbosa, Ricardo Joao Camilo Carbas, Alireza Akhavan-Safar, and Lucas Filipe Martins da Silva.

growth, it is necessary to consider the following aspects: energy savings, material efficiency, durability, repairability, and recycling.

One important key point to begin this discussion is that adhesive bonding is more attractive than other joining techniques in terms of energy saving because its environmental load is small. Nevertheless, adhesive consumption has been increasing massively because of industrial globalisation and the fast growth of many emerging countries, leading to an increase of the total environmental load associated with adhesive bonding. To address the environmental issues, this total environmental load, albeit small, has to be reduced by all means possible.

As has been further explained in Chapter 4, adhesion technology is a relatively new and constantly expanding field. The aim of the whole scientific and industrial community is to develop more efficient, durable, and sustainable materials.

Repairability and recycling are also particularly sensitive issues within the technology of adhesion. As you know, adhesive joints are not particularly easy to separate, especially if they are bonded with high-performance adhesives or applied to large, bonded areas. Therefore, easy dismantlability of the joints is rarely desired unlike what is requested from other joining methods, such as mechanical fastening. This leads to a limited use of adhesives for substrates that have to be separated. For example, the most widely used adhesives in the transport sector are epoxy based and, as already explained in Chapter 4, these are thermosetting materials, i.e. incapable of being remelted and easily recycled. Given the international guidelines regulating the percentage of recyclability of materials in the transport sector, this feature could be an obstacle to a wider application of adhesives. However, the study of adhesives has not stagnated in the face of these challenges and new formulations are constantly being created to mitigate these problems. In fact, the development of innovative technologies and processes for easy recycling and repair of bonded structures is currently being pursed in the industrial sector.

If an adhesive bond can be reversed without damaging the components, recycling is made significantly easier, allowing us to reuse these materials at a high-quality level. A technique that can achieve this aim is the use of adhesives modified with thermally expandable particles (TEPs). These particles are embedded in the adhesive and expand upon the application of a strong heat source, fracturing the adhesive layer and disassembling the joint in a few seconds. Furthermore, repair is an expensive process and, in many cases, impossible because of limited access or the risk of further degradation of the structure. Thus, an adhesive with a built-in mechanism to repair cracks and restore the strength of damaged joints is of great interest for numerous applications to extend the service life and improve the safety of bonded structures.

All these aspects are the driving forces behind the growing development of what is known as the ‘smart’ adhesive bonding technology. This concept idealises the creation of active adhesive joints capable of bonding, reconnecting (to heal broken bonds), and/or decoupling in response to a stimulus (i.e. mechanical, thermal, electrical, magnetic, etc.).

We have seen that the sustainable growth of adhesive application is inextricably linked to environmental and health and safety concerns. Thus, it is essential to know in detail the characteristics of the materials and adhesives, the risks associated with its misuse, and the precautions that must be taken when handling these materials.

The industrial use of adhesives can be a daily task with prolonged exposure. For example, an operator of a company dedicated to glass laying in car manufacturing spends almost all of his working time handling adhesives, surface preparation elements, and application tools. Adhesives are not something inherently toxic, although most of us view them as hazardous chemicals. Still, an adhesive bonding process relies on many materials besides the adhesive, such as the chemicals used in surface preparation and release agents, both of which often have a greater amount of risk associated. These issues will be discussed in detail in all sections of this chapter.

Perhaps the most important information that the reader should retain from this chapter is the importance of reading the safety datasheets of the different materials and the equipment to be used in an adhesive bonding process. These documents provide a very accessible and succinct description of the potential dangers associated with the products and indicate the best way to handle it. Thus, they should always serve as the starting point for the establishment of any new bonding procedure.

7.1 Toxicity of Adhesives: Are Adhesives Really Toxic?

The science of toxicology studies the health effects of chemical compounds and mixtures of chemicals. The assessment of the health risk of a given substance poses can be performed by an assessment of possible undesirable properties of substances based on recorded data and the quantification of the amount of material involved and the determination of the nature and degree of any possible contact.

The risk assessment determines whether, and to what extent, there is a health risk to humans as a result of the relevant hazard potential of the substance and the nature and degree of exposure. In an extreme case, there is no health risk for humans if there is no contact with the undesired material.

The same principle goes for adhesive joints, which necessitates an understanding of the dangers associated with its use and exposure. Considering the toxicity of some adhesives and of the methods used to manufacture adhesive joints, some of the risks can be significantly reduced by employing automated processing and by establishing suitable protective measures.

7.2 General Precautions for Handling Adhesives

In this section, the general precautions to be adopted when handling adhesives are described. A set of key health and safety characteristics of the most common adhesive technologies are discussed as well.

We must start this section by stressing that, irrespective of the product being used, work should never start without the operator reading and understanding the relevant safety and technical datasheets. When you are faced with the need to operate with these chemical substances, you should carefully evaluate the health and safety notices for the different stages of the adhesive joint production process, from storage/handling and surface preparation to adhesive application and curing.

7.2.1 Pictograms

Informative pictograms are highly effective tools to clearly communicate the hazards associated with the products used in a bonding process, and their inclusion on the labels of chemical containers is mandatory. On the labels, as shown in Figure 7.1, the pictograms are accompanied by signal keywords and hazard statements, describing the nature of the hazards of a substance or mixture, cautionary statements, that describe the recommended measures to minimise or prevent adverse effects and data on the product and the supplier.

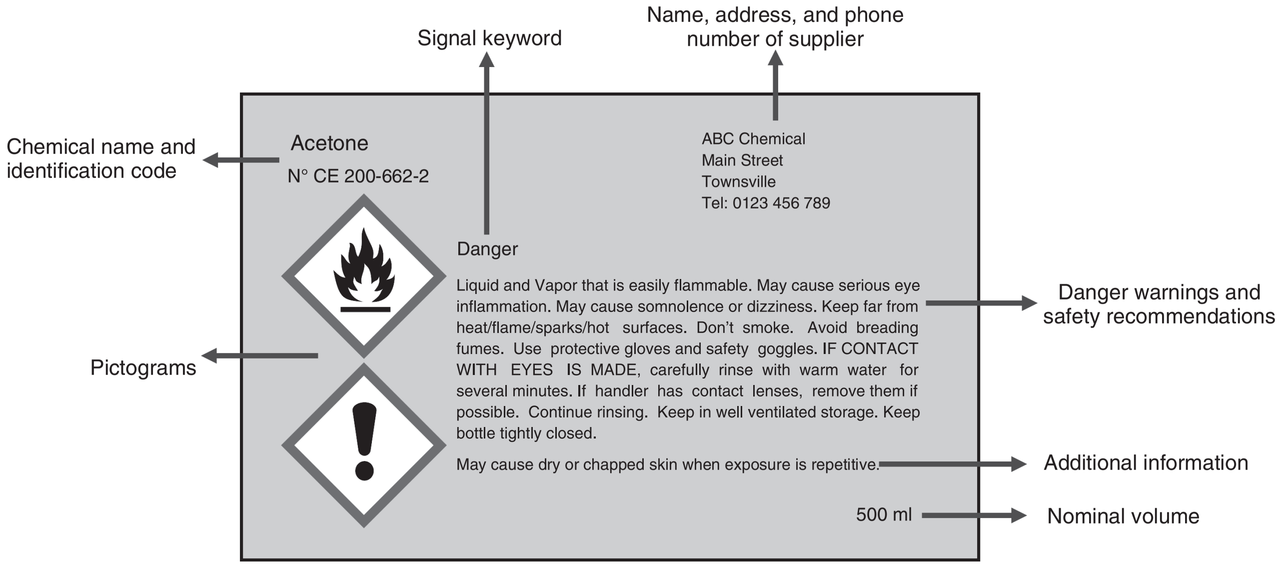
The pictograms are divided into three main classes, corresponding to health risks, environment risks, and risk associated with flammability and risk of explosion.

Regarding the health risks, it is important to be particularly aware of issues related to inflammation and noxiousness, corrosion, toxic and carcinogenic, or mutagenic materials (see Figure 7.2). Many products are known to cause skin or eye inflammation, sleepiness, dizziness, or poisoning. These effects may be diminished or even nullified if preventive measures are taken from basic hygiene measures such as washing hands and refraining from eating or smoking while handling this material up to the use of designated personal protective equipment (PPE). PPE is defined as any device or product, for individual use by the worker, intended to protect from risks that may threaten safety and health at work. It is the worker's responsibility to preserve the equipment and to report when it is damaged so that it can be replaced immediately.

When materials are known to be corrosive, this indicates that the substance may attack or destroy metals. If such substances are allowed to contact the human body, they have the potential to cause serious injuries such as skin or eye burns. The preventive measures are similar to the case presented above, but it is also imperative to conserve product in original packaging to avoid leaks.

When a product is labelled toxic, this indicates that when any contact with the skin, inhalation, or ingestion has the potential to cause nausea, vomits, headaches, loss of consciousness, amongst other effects, and may also alter one's organism and cause organ damage (liver, lungs, heart, nerves, etc.), which can easily have fatal consequences. The use of these products is only recommendable in highly ventilated locations, always using adequate PPE.

Carcinogenic or mutagenic products may cause cancer and/or mutation; affect one's fertility (foetus deformities); and may cause allergies, asthma, or respiratory issues when inhaled, all conditions that might be fatal. If ingested, these products are extremely harmful and may alter one's organism and cause organ damage (liver, lungs, heart, and nerves). These products should be handled only by operators equipped with adequate PPE and working under strict hygiene measures (washing hands and refraining from eating or smoking while handling this material).



Liquid and Vapor that is easily flammable. May cause serious eye inflammation. May cause somnolence or dizziness. Keep far from heat/flame/sparks/hot surfaces. Don't smoke. Avoid breading fumes. Use protective gloves and safety goggles. IF CONTACT WITH EYES IS MADE, carefully rinse with warm water for several minutes. If handler has contact lenses, remove them if possible. Continue rinsing. Keep in well ventilated storage. Keep bottle tightly closed.

May cause dry or chapped skin when exposure is repetitive.

Figure 7.1 Information on a chemical product label.

Figure 7.2 Pictograms that warn of health-related problems for the user: inflammation and noxiousness, corrosion, toxic, and carcinogenic or mutagenic.

Figure 7.3 Pictograms that warn of harmful materials for the environment.

When a product is labelled harmful for the environment, it indicates that it may harmfully influence the environment by causing, amongst others, ecological unbalances, degradation or destruction of the existing fauna, and/or flora (see Figure 7.3). These products are often toxic or noxious to aquatic species. Therefore, they must not be discarded in landfills, industrial effluents, or any industrial or civilian trash disposal systems. They must be disposed of in special treatment stations or in specific locations equipped to perform special and adequate treatments.

Some products have information that alerts to their explosion capability and flammability, categorising them as explosives, flammables, and oxidising agents, as presented in Figure 7.4. Explosive materials, self-reactive substances, and organic peroxides may detonate when in contact with electricity, heat, flames, sparks, friction, or mechanical shock. These materials must be moved away from heat sources, lamps, and fireplaces and must be shielded from solar radiation. The use of PPE is essential, especially with regards to facial and eye protection.

Diverse flammable products are used in adhesive bonding procedures and are encountered in the form solids, liquids, flammable gases, and aerosols. Within this range of flammable products, one should be extremely careful when handling

Figure 7.4 Pictograms that warn of explosion capabilities, flammability, and oxidising capabilities.

pyrophoric liquid and solids. These materials may emit flammable gases and self-combust when in contact with air and substances. Self-reactive substances and organic peroxides are included in the flammable material categories, as they may ignite when exposed to heat. It is recommended to keep these materials away from heat sources and hot surfaces, avoid smoking in their immediate vicinity, and ensure that storing facilities have adequate ventilation systems. Importantly, fire extinguishers of the type appropriate for dealing with these materials must be placed nearby.

Oxidising agents could be solids, liquids, or gas agents, which may cause or intensify fires and explosions. Therefore, it is recommended to not smoke near these materials, nor to handle these materials near heat sources. Storing facilities must have adequate ventilation systems and should not contain flammable materials. Fire extinguishers must be placed nearby. The use of PPE is again indispensable, especially with regards to facial and eye protection.

Gases under pressure are often be flammable and thus present a high risk of detonation or explosion when stored near a heat source, but even chemically neutral gases stored under large pressures pose similar hazards. Refrigerating gases can be highly dangerous to the environment and may also cause burns or cryogenic wounds on exposed skins. The appropriate preventive and protective measures are similar to those already exposed above for flammable materials.

7.2.2 Training for Handling Adhesives

A safe manufacturing procedure that employs adhesives should provide safety for all steps of the process and can even extend beyond this, for example, ensuring that there is no release of harmful materials such as solvents and plasticisers during service life.

Bonders, who will contact more closely with the adhesive bonding procedure, are those who most require special protections. PPE, a suitable workplace and the proper use procedures, should always be available, irrespectively of the industry and specific application. This is usually enforced by safety officers, whose responsibility is to monitor the work being carried out and to ensure that all these conditions are in place.

Training is mandatory for all the works involved in the joining process and bonders that work on a daily basis with adhesive technologies should undergo regular training related to work safety and environmental protection. An excellent example of these training programmes are the EWF (European Federation for Welding, Joining and Cutting) certified courses. These courses define profiles for bonders, specialists, and engineers with harmonised curricula for different countries of the European Community. A good educational background (preferentially provided by certified training institutions) can not only prevent mistakes in the preparation of the adhesive and substrate (such as choosing the optimal adhesive solution and defining the correct application procedure) but will also inform of the hazards that exist in the process and how they can be mitigated. These training courses inform about the PPE that should be applied for each stage of the production process.

7.2.3 Safety Eyewear

The human eye is a delicate, fragile structure, and thus, extreme care with the protection of visual health must be taken in our daily life. Adequate safety eyewear protects the eyes from impacts with objects and impedes the penetration and contact with dust and other contaminants. There are several types of tasks associated with adhesive bonding with the potential to cause severe eye injuries. Therefore, understanding the environmental risks and identifying the agents in each environment is fundamental to ensure eye protection.

The use of safety glasses is mandatory in operations where a risk has been identified, and it cannot be fully eliminated or reduced. The choice of adequate safety eyewear will depend mainly on the nature of the risk and the tasks to be performed.

Safety eyewear should present comfortable nasal support and must have soft and comfortable support arms. If they are used in dusty environments, they must have foam surrounding the frame that prevents particles from entering the eye area. An anti-fog finish should also be present in order to ensure clear vision throughout long periods of use.

7.2.4 Hand Protection – Gloves

Because of the manual nature of many jobs related to adhesive bonding, a bonder will use his hands extensively when working, which exposes them to injury. Among all work accidents involving the bonder's hands, we can observe two important types: the traumatic injuries and the contact injuries. Both are equally worrying and can be the result of serious accidents. Among the traumatic injuries, we count cuts, punctures, fractures, amputations, blunt force trauma, among others. Contact injuries involve burns, shocks, contact with chemicals, extreme temperatures, etc. To ensure adequate hand protection, it is important to identify in advance each of these risks through the Environmental Risk Prevention Program (ERPP). ERPP is a document elaborated according to the regulatory standard No. 09, which seeks to apply actions that neutralise or minimise agents of environmental risk that employees are exposed to in the occupational environment. Accordingly, risk control measures can be taken to protect the health and physical integrity of the bonder.

Most accidents involving the hands can be avoided if the worker uses the appropriate PPE. However, the selection of the optimal PPE is sometimes difficult. There are at least 10 different types of safety gloves, and it is essential to know how to differentiate between them, as each type will be suited to protect from a very specific set of risks.

Among these glove types are the anti-cut glove, natural latex glove, nitrilic latex glove, knit glove, polyvinyl chloride (PVC) glove, high-performance glove, and the temperature glove. The gloves most commonly used to handle chemical products are the nitrilic and natural latex gloves because they assure good flexibility and resistance against most chemical products. When surface preparation is carried using shotblasting, the use of PVC gloves is recommended because it provides excellent protection against abrasion. The use of thermal gloves is mandatory when work is carried out at extreme temperatures. These gloves protect against thermal burns caused by contact with very high or very low temperatures.

Protection creams are equally important and diverse, with different formulations being available to ensure both the comfort and protection. Protection creams are usually nicknamed ‘chemical gloves’ because they are used to create a barrier in the skin that protects directly against chemical agents.

7.2.5 Safety Shoes

Safety shoes are one of the most commonly used PPEs. During the work routine of a bonder, several large, heavy, and hazardous materials and objects are often moved over the feet, which can lead to feet injuries if these materials are dropped. These injuries often include cuts, punctures, and burns. There are numerous activities in which they are mandatory, as there are many risks to which they offer protection.

The different risks that the safety shoes will protect will depend on the type of PPE and also on the materials that make up the footwear. Protective shoes are generally composed of leather, midsole, and sole. The leather is the upper part of the PPE, being responsible for protecting the upper part of the worker’s foot. This specific part of the footwear can be made from leather, scraping, cowl, synthetic materials, or even rubber. The midsole has the purpose of absorbing the impacts caused by the weight of the user’s body, a very important role, because the bonder usually spends the whole day using the same PPE and carrying heavy equipment. Thus, the midsole is usually made of polyurethane (PU), a highly resistant, yet comfortable material. The sole, on the other hand, should offer resistance against abrasion, slippage, punctures, and protect from contact with toxic, chemical, and hot substances. To choose the ideal safety shoes for a given application, it is essential to be aware of the types of materials in which they are manufactured. This is because each material is better suited for a specific activity.

7.2.6 Lab Coat

The lab coat is a garment that serves to protect the user against some types of risk, such as splashes, contamination, and high temperature. The lab coat is often erroneously seen as a uniform and not as a PPE. However, it is worth noting that there are garments that might resemble lab coats but are in fact jackets that do not have a certificate of approval, or laboratory coats produced in unsuitable fabrics that only serve to protect the worker’s clothing from dirt or minor splashes.

7.2.7 Ventilation Systems

As we have seen, some substances used in adhesive bonding processes release harmful substances and volatiles that can remain in the air and be inhaled by the workers. Thus, air quality in a laboratory or industrial environment dedicated to bonding should always be controlled to guarantee the wellbeing of the workers. To ensure air quality where the volatile content (usually abbreviated as VOC) does not reach toxic levels, the workplace must be adequately ventilated and/or equipped with devices to ensure replenishment of air and its filtering.

At the same time, workplace labelling measures should be installed, and it should be forbidden to eat and drink in the work area (specific spaces should be created for workers to rest), workers should be trained, and appropriate PPE should be provided. Personal hygiene should also be encouraged, and exposed skin should be washed when entering and leaving the work area.

Even when the bonder is working with less harmful water-based materials, proper ventilation is paramount as is the use of personal respiratory filters whenever the task requires it. An optimisation of the adhesive quantities being used can be an effective measure to ensure unnecessary evaporation of solvents. Good practice advises to use only the minimum amount of adhesive necessary to ensure joint quality and performance.

Storage and handling practices of chemical products should be reviewed, i.e. the data in the datasheet should be carefully studied and materials that include solvents in their composition should not be left open.

7.3 Hazardous Characteristics of the Most Common Adhesives

This section provides a summary of the key hazards associated with a set of commonly used adhesive materials, allowing us to make an informed comparison of the risk associated with their use. However, please be aware that this is not an exhaustive list and cannot possibly cover all variations available in the market. When you carry out an adhesive bonding procedure, it is your responsibility to determine the hazard characteristics and the necessary safety precautions necessary for the adhesives being used by reading the technical and safety datasheets.

7.3.1 Structural Adhesives

7.3.1.1 Epoxies

Epoxy resins are the most widely used adhesives in structural applications. Considering a two-component epoxy adhesive (hardener and resin), the resin is usually the one with the most severe associated risks. The main epoxy hardeners include mercaptans, carboxylic acids, anhydrides, amines, and phenols. Nevertheless, amines are the most used and are applied for different purposes, depending on their structures. Amine hardeners are usually corrosive and toxic. Epoxy resins in liquid or paste form (uncured) are usually irritating to eyes and skin and toxic to aquatic organisms. The main hazards associated with epoxy adhesives are twofold: their exothermic reaction and the sensitisation of human skin to resin. The first of this is minimised by mixing the adhesive components in quantities and ratios recommended by the manufacturer in the technical sheet and avoiding direct contact with the mixture, using tools instead. Sensitisation often takes the form of an allergic reaction that develops after repeated contact with the skin. This reaction can occur several days after contact with the material and it usually appears in the form of dermatitis in the areas where contact has occurred.

7.3.1.2 Polyurethanes

Polyurethanes are formed by the reaction of a polyol with diisocyanates or polymer isocyanates in the presence of catalysts and additives. Diisocyanates cause irritation of the eyes, nose, throat, lungs, and skin. These materials can also cause allergic reactions via skin and lung sensitisation. However, once cured, polyurethanes are generally considered as safe materials.

Single-component formulations do not need, with no exceptions, special precautions because they are pre-linked and do not release free isocyanate monomers. In two-component adhesives, we must ensure the correct and adequate mixing ratio to avoid releasing products resulting from incomplete reactions. In many cases, additional precautionary measures such as the use of masks, respiratory filters, and filtered application chambers may be necessary. Two-component polyurethanes cure exothermically, and the temperature generated in this process can also pose important hazards.

7.3.1.3 Acrylic Adhesives

As already fully described in Chapter 4, acrylic-based adhesives are typically divided into three major groups: anaerobic adhesives, cyanoacrylates, and finally the modified acrylics. Acrylic resins used as adhesives are usually the result of mixing acrylic and methacrylic acid with other chemicals. Once the chemical formation process is finished, the resultant acrylic resin is a high molecular weight material with good stability and relatively safe. However, it is possible that some of these resins have residual amounts of ethyl acrylate, which is recognised as a carcinogen. Cyanoacrylates adhere very quickly to the skin and may cause lesions on their removal.

Modified acrylics, in addition to the inherent hazard related to their chemical components, feature a strong and pungent smell, which while not necessarily dangerous, that can be very unpleasant.

7.3.1.4 Phenolic Adhesives

Phenolic adhesives contain diverse chemical compounds such as phenol and formaldehyde. Inhalation of phenol and exposure to phenol are extremely irritating to the skin, eyes, and mucous membranes. Excessive exposure may lead to irregular breathing, weakness, tremors, loss of coordination, convulsions, and even respiratory arrest. Formaldehyde is also a harmful substance. When present in the air at levels above 0.1 ppm, some individuals may suffer from irritation in the eyes, nose, and throat. In this regard, the technical datasheet for this adhesive should be read carefully and the necessary measures should be implemented, given the risk presented.

7.3.1.5 Aromatic Adhesives

Different formulations of aromatic adhesives are available, the most common of which are the polyamides, bismaleimides, and polybenzimidazoles. High concentrations of the volatile solvents used in these adhesives can cause dizziness, nausea, fatigue, lack of coordination, and even coma. The probability of accidents increases under the influence of these compounds, and long-term exposure may eventually lead to brain damage. The application of this adhesive should take place in a well-ventilated environment, with the use of PPE being highly recommended.

7.3.2 Non-structural Adhesives

7.3.2.1 Synthetic Rubbers

Synthetic rubbers are relatively stable and safe compounds. In their uncured state, they can cause skin and eye irritation in the case of direct contact and should therefore be handled with gloves. Some types of silicone emit acetic acid during the curing process, which is corrosive in high concentrations.

7.3.2.2 Polyesters

The inhalation of polyester resin vapours is known to cause irritation to the respiratory system, causing nausea and breathing difficulties in the case of prolonged exposure. This effect is magnified if inhalation occurs in an enclosed space without ample ventilation. These materials can also cause irritation to the skin and eyes in the case of direct contact, and it is essential to wear PPE such as gloves and safety glasses.

7.3.2.3 Hot Melt Adhesives

Compared to most other adhesives, these are relatively safe and chemically stable products (both before and after curing). Their main risk is associated with the phase change during application, as fumes produced during melting may have volatile toxic compounds and good ventilation is necessary to prevent them from being inhaled. The main risk of working with these materials stems from the high temperatures needed to melt them (up to 200 °C). It must be ensured that no burns occur during the adhesive application process and the bonder should be equipped with protective gloves and clothing. In addition, the application equipment should provide a guard system that avoids direct contact with the heating elements.

7.3.2.4 Inorganic Adhesives

The main use of inorganic adhesives is to ensure resistance at very high temperatures and some older inorganic adhesive formulations included asbestos fibres to increase this resistance. These materials can still be found during repair of old equipment, so it is important to be careful in their handling. Nonetheless, inorganic adhesives are quite stable and pose no health risks.

7.4 Surface Preparation Precautions

The surface preparation of the materials to be bonded creates many of the most important health and safety associated with adhesive bonding. However, pretreatments of substrate materials, as presented in Chapter 3, have quite different specifications, which will inevitably lead to different safety measures. Each case must be analysed according to the specifications of the material and equipment used. It should be noted that close contact with suppliers can be an excellent practice because most of the time they provide highly specific training aimed at answering safety questions.

To better understand the potential risks associated with surface preparation, we will consider three main groups: risks and perilous situations related to chemical substances, materials to be bonded, and machinery. However, please note that there are risks that are transversal to all activities carried out in surface preparation, such as exposure to noise, ignorance, or non-compliance with ergonomic rules, risks associated with the impact of objects. In brief, general risks and perilous situations are commonly associated with an active industrial environment.

One of the most hazardous phases in surface preparation is the degreasing of the surfaces to be bonded. Various chemicals (depending on the method used and the material of the parts to be cleaned) are used in the degreasing processes. They could be mainly categorised as acidic solutions (sulphuric, nitric, etc.), solvents (trichloroethane, chloroform, carbon tetrachloride, trichloroethylene, etc.), and alkaline solutions (cyanides, borax, sodium silicates, etc.). You should carefully review the datasheet of each reagent and follow the indications suggested in Section 7.2.

Regarding the risks associated with chemical substances, we draw the reader's attention to the issues associated with handling of harmful chemicals (skin contact with substances), insufficient or wrongful ventilation of workstations, and projections of hazardous liquids because of large component immersion speed (manual or automatic) in treatment tanks.

The materials that compose the surfaces to be prepared also require special attention in their handling. Thus, it is also extremely important to be aware of the hazardous characteristics and safety precautions required by the materials to be joined. Polyester plates, for example, can emit styrene vapours that can be highly irritating. Another example is the plasticisers that can be released from some polymeric materials with ecological and functional complications. If solvent-based adhesives are used on polystyrene parts, there is also the possibility that the solvents will attack the polystyrene.

When metals are the subject of the work, electrostatic baths are often required for surface preparation or for corrosion protection. When adhesives are applied prior to this process, the adhesive must not contaminate the bath. This is a very common case in the automotive industry.

In this case, we highlight the potential risks associated with thermal exposure, vibration, and the risks associated with cutting, bruising, and crushing.

Handling heavy machinery can also pose risk for the operator in many circumstances, especially in mechanical preparations of the surface in preparations that require an active physical–chemical alteration of the surfaces. The specifications of each machine should be carefully analysed, and close contact with suppliers is recommended, as previously highlighted. In addition to the risks previously presented, these activities can also expose the workers to dangerous amounts of dust (silica and metal particles). This risk can be mitigated by following regulations on particle size and exposure times, which are crucial to ensure the wellbeing of users both in the short and the long term.

7.5 Adhesive Application Precautions

The equipment used in adhesive application can involve large forces and pressures and must be operated with special care. If used correctly and adequately maintained, application guns, in general, do not present any initial danger. The use of power-assisted quality tools is desirable and advisable. As an example, the use of low-quality, unpowered applicator guns to continuously apply viscous adhesives may excessively strain the operator and cause muscular problems in the long term. Thus, the weight and the ease of actuation of the equipment are important, and it can be improved with the use of an automatic support or levelling system. On an industrial level, an electric or pneumatic applicator is always desirable compared to a manually operated gun. In case of application using extrusion pumps, the proper maintenance of the machines is also essential. An obstruction in an adhesive hose working at 300 bar of pressure can cause a violent failure of the hose or other device that can cause significant and irreparable damage.

7.6 Environmental Protection

As you have certainly understood, to ensure the sustainability of an adhesive bonding process, its impact on the environment must be well understood, as only then it becomes possible to devise strategies to mitigate any negative effects. Although adhesives are not inherently dangerous, one must remember that these are industrial petrochemical products and the impact of their manufacture and disposal on the environment cannot be ignored. For a complete assessment of their impact, an analysis of the global environmental spectrum (water, soil, and air) must be made.

The analysis must be done downstream and upstream of the adhesive application. Companies that manufacture adhesives from raw materials should consider how the adhesive is manufactured and how the waste will be treated and handled. Storage is also an important issue, and risks with spills, VOCs, flammability, and toxicity should all be considered. In Figure 7.5, the full life cycle of an adhesive is shown, considering not only its application but also its impact on the environment.

After the adhesive has been applied, it must be ensured that any resultant waste is not a potential hazard. Most adhesives are not directly recyclable, so you should take care to forward the waste to the appropriate authorities. At present, this work of re-routing and treating waste is already well publicised, mainly because of the joint effort of the regulatory authorities and their awareness of local authorities, legal directives, and official regulations with respect to production, labelling, and transportation of adhesives. Information is made available in an open manner, both with regards to these legal directives and with the information supplied by the manufacturers (datasheets).

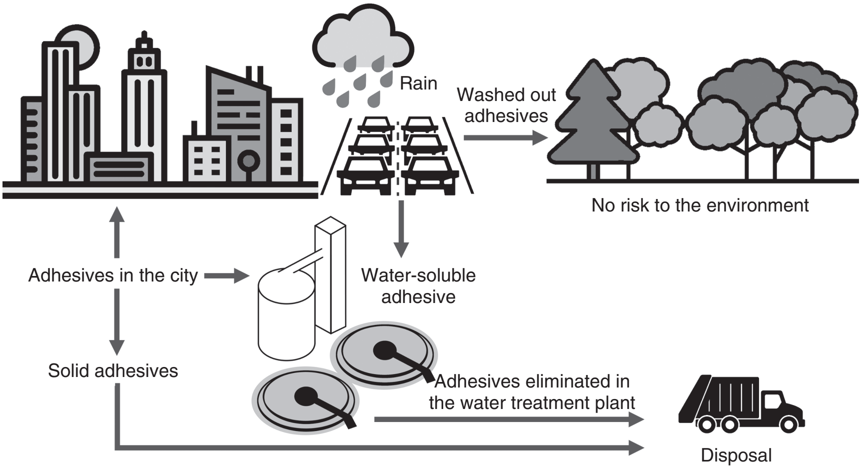


Figure 7.5 Life cycle of an adhesive considering its application and the impact on the environment.

7.6.1 Air

In the production and use of adhesives, air quality may be compromised by the emission of organic solvents. In the past decades, both the regulators and the producers of adhesives have made efforts towards the reduction of the use of these volatiles. Preference should be given to low-solvent adhesives or, if possible, change the adhesive formulation to one that is solvent free. This process is not always as easy or fast as desired and a considerable amount of research is still necessary to further complete this transition. In 2010, adhesive bonding was reported to be responsible for 3% of Europe's solvent emissions, but thanks to new research developments and stricter regulatory efforts, this figure is expected to be almost residual in the coming decades.

7.6.2 Water

When it comes to residual treatments, a clear separation must be made between industrial applications and small home use. In the case of small do it yourself (DIY) work, the amount of waste produced is minimal and you should follow the indications stated on the packaging/technical sheet. However, as you might imagine, the waste produced in an industrial environment should be treated very differently. Dispersed adhesives are the main risk for water contamination, as well as the solvents and chemical preparations used to prepare substrate surfaces. Organic polymers and solvents (such as oils) are not easily biodegradable, so treatment should be immediately carried out downstream of the manufacturing facility to minimise the risks of forming a contaminated sludge. These procedures are properly regulated, and residual adhesives and rinse water must be disposed of in accordance with the existing legislation.

7.6.3 Soil

The main risk of soil contamination lies in the way in which adhesive residues are disposed of. In a domestic application of adhesives, the waste will be mostly dumped in the household waste landfills, which, although not ideal, has a limited impact as the quantities are very small. In an industrial environment, waste should dispose of using specific procedures according to the manufacturers' instructions. Each type of material may have different disposal paths, which can include incineration, disposal in landfills, or integration in a recycling or reuse process.

8

Design of Bonded Joints

If you have been reading this book chapter by chapter, at this stage, you should already know what is an adhesive, how it works, how it hardens, and how we can prepare the surface of the adherends to ensure that there is a good level of adhesion between it and the adhesive. However, one of the most complex steps associated with the creation of an adhesive joint remains to be discussed. This is the design of the joint itself, the process of creating a joint that can withstand a specific load, or a set of loading conditions without failure.

However, in what consists the design of a bonded joint? Well, an adhesive joint is simply a geometrical construction. You have your adherends and your adhesive layer all joined together according to a specific geometry. The design of the joint includes all the geometrical parameters that define this joint. How are the adherends being joined together? How thick they are? How thick is the adhesive layer? What it is the overlap between the adherends that defined the bonded area? All these parameters have a major influence on the joint performance as we will see in this chapter. However, the design of the joint is not only limited to the selection of a geometry. We must also select the materials that will be a part of that joint. Typically, you will have a well-defined adherend material and must choose an adequate adhesive. Sometimes, you might have total freedom and will be able to select both the adherend and the adhesive material. By selecting different materials, with largely distinct mechanical properties, the joint will behave drastically different. In addition, as we will learn during this chapter, selecting the stronger materials will not necessarily lead to a strong joint, a counteractive observation that reveals that designing a well-performing joint is rarely a trivial activity.

In this chapter, we will address the subject of joint design by first learning what are the main loading modes that an adhesive joint might experience. We will see that adhesives perform better under shear loads and perform poorly under peel loads. In fact, you can easily compare the performance of an adhesive loaded in shear with that of a joint loaded in peel using a basic office supply: adhesive tape! To do this, first bond two small lengths of tape to the edge of your desk. Now pull one of them parallel to the table surface (a shear load) and the other perpendicular to the table surface (a peel load). Notice how the shear load will force you to make enough strength

Introduction to Adhesive Bonding, First Edition.
Eduardo André Sousa Marques, Ana Sofia Queirós Ferreira Barbosa, Ricardo Joao Camilo Carbas, Alireza Akhavan-Safar, and Lucas Filipe Martins da Silva.

to break the adhesive tape, while the peel load will cause the tape to unstick with almost no force.

Then, we will discuss the main joint configurations that are used in practice, understanding their relative advantages and disadvantages. We will then take a dive into the technical subject of the models used to predict joint strength. Classical joint strength prediction using continuous mechanics is composed of two separate steps. The first is the use of a numerical or analytical tool to determine how the joint is stressed. That is, what are the regions of the adhesive or the adherend that are being loaded more significantly. Then, it is necessary to establish a failure criterion, which will consider the stresses and the material properties to determine if a given stress level will indeed cause the joint to fail.

We will first discuss analytical models, relatively simple models that rely on specific but powerful equations to determine the stress levels and/or the failure loads. We will limit our discussion to analytical models suitable for single lap joints (SLJs) because of their widespread use. We will then discuss the more powerful numerical models and understand how highly detailed computer-designed models are being used to do much more than calculate the stress levels. We will see that by combining fracture mechanics and damage mechanics concepts, advanced numerical models are now able to accurately represent the behaviour of bonded structures, simulating damage initiation and damage propagation under complex loading conditions. Initially restricted to the realm of scientific research, these advanced numerical models now find use in many cutting-edge industrial sectors, such as the automotive and aerospace industry.

8.1 Main Loading Modes on Adhesive Joints

Adhesive joints can be used in a wide variety of structures, supporting diverse types of loads. However, it is important to first establish that the behaviour of the joint is highly dependent on the type of loading. In some cases, the adhesive joint will perform very well and provide an alternative to classical joining methods such as welding or fastening, while in others, it will be very weak and quickly lose strength. It is up to the designer to understand these particularities and adjust the geometry of the joint accordingly.

The four main loading modes that an adhesive joint can face are shown in Figure 8.1. These are shear, tension, peel, and cleavage. Tensile loads are known as ‘mode I’ loads and shear loads are known as ‘mode II’ or ‘mode III’ loads. Any type of load between these two is known as a mixed-mode loading.

Among these four loading modes, shear is by far the preferable for adhesive joints. In this loading condition, the adhesive layer is relatively well aligned with the loading direction, which indicates that all adhesive layers can positively contribute to sustain the load. When designing an adhesive joint, one should always try to ensure that this occurs, ensuring that the adherends carry the load as parallel to the adhesive layer as possible.

An alternative is the tension type of loading where the adhesive layer is spread apart by the forces acting on the two adherends. On a first look, this also seems to

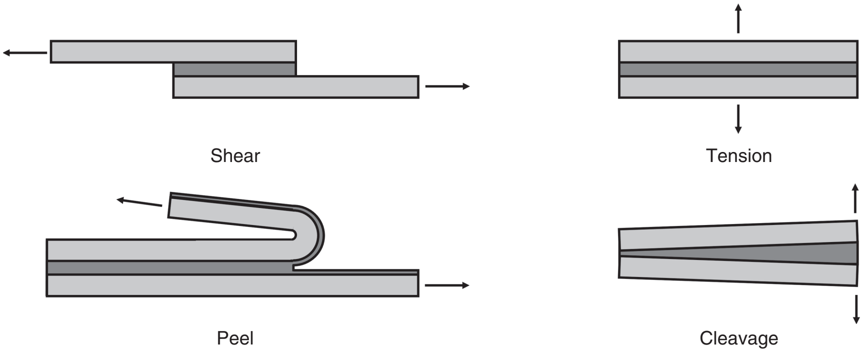


Figure 8.1 Schematic representation of the main types of loadings acting on adhesive joints.

be a quite good solution, but in fact, it almost always produces worst results than the shear loading. Why? This is because this a very unstable type of loading. If one side of the adhesive layer is less strong than the other, the joint will start to rotate and concentrate all the load on a single side, leading to a situation where we have a large adhesive layer that is not being fully used. In fact, this situation is equivalent to the cleavage condition, which is simply a tensile load that is concentrated in a single location of the adhesive layer. All the load acting on the joint is directed to a small area of the adhesive layer, the main cause for the fact that a joint loaded under cleavage performs much more poorly than a joint loaded in shear. More to that point, a joint loaded in tension will almost always fail in the adhesive because adherends are in general stronger than the adhesives and the loaded areas are practically the same. In contrast, in shear joints, we can use an overlap configuration to ensure that the adhesively bonded area is much larger than that of the adherends. This enables joints where a low-strength adhesive can outlast a stronger, metallic adherend.

Lastly, we can direct our attention to the absolute worst-case scenario, the peel-type loading. Most structural adhesives are rendered almost useless by this type of load, which concentrates the acting load on a thin area, only as wide as the adhesive layer itself. Concentrating a large load on this small region leads to an inevitable failure of the adhesive. However, please be aware that there are some adhesives that can operate somewhat satisfactorily under peel loads, most notably the polyurethanes and silicones. As we have seen before in Chapter 4, these adhesives are extremely elastic and flexible, and this characteristic allows them to spread the stresses through a larger area even in the face of concentrated peel loads.

Now that we are familiar with this concept, we can advance to the description of the joint geometries and understand how to play around with the loading modes to reach maximum performance.

8.2 Main Adhesive Joint Geometries

The number of geometries that can be used to create adhesive joints exist in the literature is vast, with many different alternatives being used in practice. Figure 8.2 shows schematically some of the most important.

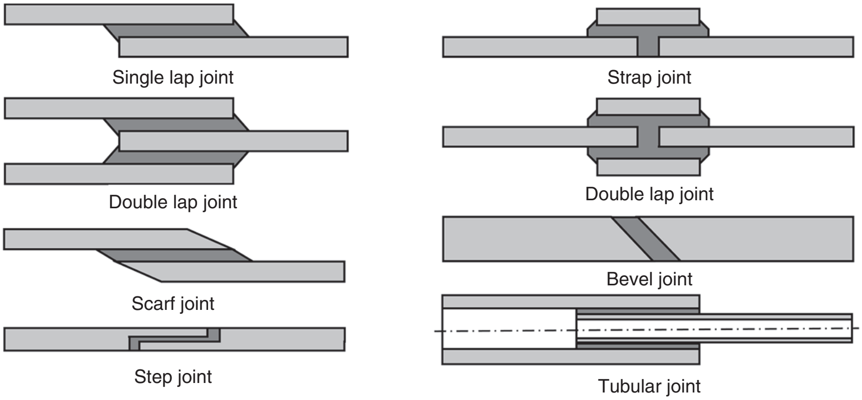


Figure 8.2 Typical bonded joint geometries.

Among these, the SLJ is perhaps the most important because of its simplicity and effectiveness. As we have learned, adhesive joints work better under shear, and the SLJ fully explores this fact by providing an adhesive layer that is relatively well aligned with the loading direction. Notice, however, that it is possible to improve the performance of the SLJ with more complex geometries. How? Well, the SLJ does possess an important drawback: the adherends are not perfectly aligned, which creates a load imbalance on the joint. This imbalance indicates that although the main loading mode is in shear, peel loads will still appear on the edges of the adhesive layer because of a bending momentum that twists the overlap portion of the join. The double lap joint (DLJ), for example, aligns the load quite effectively with the adhesive layers and operates in a more perfect shear state, but it is much more complex to manufacture. The same can be said for the step joint, for example. Notice that the adherends are perfectly aligned and that the adhesive layer is composed of a series of smaller adhesive layers operating in shear. Is it strong? Yes. However, is it practical to manufacture? Not really. This joint is a perfect example that trade-offs must always be considered for each specific application and that a perfect joint configuration rarely exists.

Before we advance further into the methodologies that allow to predict joint strength, let us briefly recall how an adhesive can fail, as understanding these failure modes is key for understanding the capabilities and limitations of some of the models. As stated in Chapter 2, in an adhesive joint, there are three possible main modes of failure, defined by the location of the failure itself. These are adhesive failure, where the joint fails at the interface between the adhesive and the adherend, cohesive failure in the adhesive, where only the adhesive layer fails, and lastly, failure in the adherend itself, while the adhesive and the interface remain intact.

The first we will discuss is failure on the adhesive–adherend interface, known as adhesive failure. This happens when there is a loss of adhesion between the adhesive and the adherend. The chemical and mechanical bond that should solidly connect the adhesive to the adherend is lost, and there is a clear separation between these two materials at the interface. Note that this is absolutely the worst-case scenario in an adhesive joint design, as the adhesive is essentially useless and the load that the joint will sustain is practically null. The theory of adhesion states that if there is good wetting of the adhesive on the surface, the work of adhesion is higher than the work of cohesion, ensuring that the failure will never occur at the interface. Since there is no model that can predict this type of failure, so our only course of action as adhesive joint designers is to entirely avoid this failure mode by using different, more compatible adherends and adhesive materials and use an effective surface treatment, promoting adequate surface wetting.

We can advance then to the second type of failure mode. This is the cohesive failure mode in the adhesive, where the adhesive itself becomes damaged and fails. In this case, we have good adhesion at the adhesive–adherend interface and have used the adhesive until its limit, making this failure mode much more acceptable than adhesive failure, although the joint is still the weak link in our hypothetical bonded structure. With this failure mode, it is possible to accurately determine the strength of the adhesive layer using a wide variety of models that rely on the mechanical properties of the adhesive materials. With adhesive failure this is not possible, as the properties of the interface are extremely hard to determine and can depend on diverse factors.

Lastly, we can take a look at the third type of failure mode, cohesive failure in the adherend. In truth, this is the most desirable of all failure modes. Why? Because when this failure occurs, we know that we have designed an adhesive joint that is in fact stronger than the material that we are joining. Our joint is not the weakest link in a bonded structure and this is in fact the ultimate aim that we strive for when designing an adhesive joint. An additional note is that failure in the adherend does not necessarily mean that the adherend will cleanly break apart. Often, the adherend will yield and become permanently deformed (in the case of metals) or will delaminate (in the case of composites), and this can lead the adhesive layer to fail. As we will see during this chapter, a number of models can predict if failure will occur in the adherend or in the adhesive and will allow us to design the joint in a way to ensure that the failure always occurs at the adherend and never at the adhesive layer.

8.3 Joint Strength Prediction Using Analytical Methods

Now that we understand how an adhesive layer can be loaded and the different joint geometries that are available to control the loading mode, we can start to discuss the methods that are available to effectively determine joint strength. We will mainly focus our analysis on the analytical methods that are available for the most commonly used joint geometry, the SLJ.

Practically all analytical methods rely on the determination of the stresses acting on the adhesive layer. Then, the peak stress or a combination of some different peak stresses is compared with the mechanical strength of the joint materials using some sort of failure criterion. If this strength is exceeded, the joint is expected to fail and we can determine if this will occur in the adhesive layer (cohesive failure of the adhesive) or the adherend (cohesive failure of the adherend). We will start by first comparing the stress calculation capabilities of the different analytical models for SLJs and then discuss the suitable failure criteria.

8.3.1 Determination of Stresses Acting on an Adhesive Joint

Let us start by defining what is a stress. Well, in the most basic definition, a stress is a force divided by an area, giving an idea how loaded a portion of adhesive is. Stresses come in many forms, depending on the load that creates them. A tensile stress, for example, is obtained by dividing a force that acts in tension by the area that resists this load. A shear stress follows the same concept but is calculated by considering a shearing force.

Now, the shear stress definition is in fact the basis for the simplest of all analytical models for SLJs. This model, shown in Figure 8.3 and known as generalised yielding of the adhesive, assumes that all the adhesive layer is being loaded (so the resistant area is the full bonded area) and that the shearing load is the load acting on the adherends (marked as P).

However, this model assumes that the adherend does not deform at all and that there is a uniform and constant shear stress distribution along the adhesive layer, which is not true for all adhesives. In practice, predicting joint strength assuming a uniform stress in the adhesive layer is only possible for elastic adhesives (very flexible and highly deformable) such as one-part polyurethanes or silicones.

In 1938, Volkersen pointed out that the elastic deformation is not uniform and is in fact highly important for joint strength determination, as it greatly impacts the stress distribution in the adhesive. Simply put, Volkersen found that if we apply a load to an SLJ and we assume that the adherends have some degree of elasticity (as all common engineering materials do), this elasticity will indicate that the adhesive layer will have to deform to accompany the adherends. The problem lies in the fact that the edges of the adherends will be under a relatively higher stress than their central sections, leading to what is called as ‘differential straining’. To put it simply, the adherends will force the adhesive to stretch unevenly, with the most drastic effect occurring at the ends of the overlap. The shear stress will be much

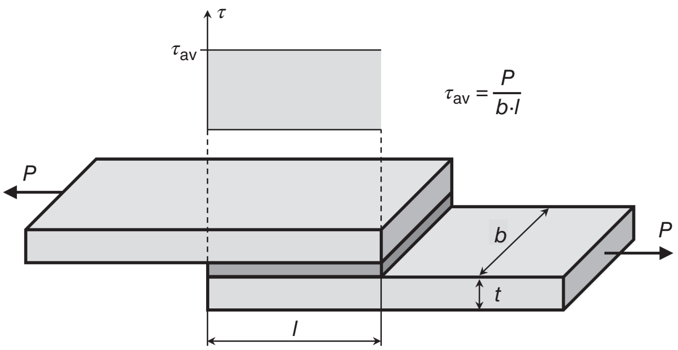


Figure 8.3 Calculation of generalised shear stress in a single lap joint.

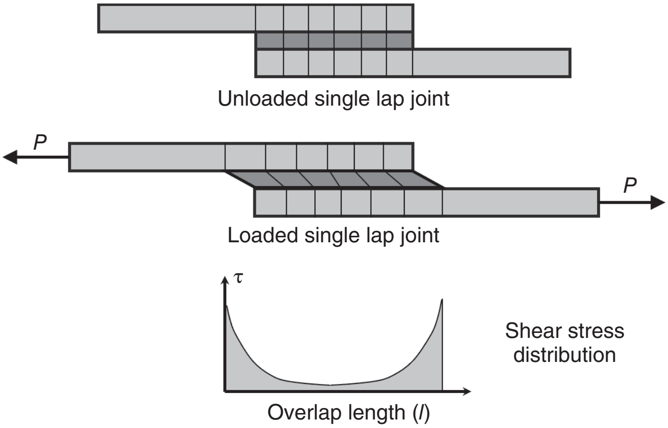


Figure 8.4 Shear stress in the adhesive layer as described by Volkersen.

higher at these locations that it would be expectable if we used the uniform shear stress definition. Figure 8.4 highlights this effect clearly and shows the resultant shear stress distribution, with peaks at the overlap edges. This stress distribution is obtained by establishing a balance of the loads acting on the joint and leads to differential equations that relate the elastic behaviour of the adhesive with the different displacements of the adherend.

The practical implications of this discovery are quite remarkable. When a stiff adhesive is used in an adhesive joint, it will respond with much higher stresses to this differential straining and its shear stress distribution will be more negatively affected. The conclusion is that an excessively stiff adhesive is not at all recommended for use in adhesive joints because they cannot accommodate the inevitable deformation of the adherends without generating large stresses. The more flexible the adherend, the worse a stiff adhesive will perform.

Just a few years later, in 1944, the work of Goland and Reissner improved on this initial analysis by adding the effect of the bending to the equation. This was a significant improvement because as we have seen before, the SLJ is naturally unbalanced, and this will create undesirable loads on the adhesive layer, the peel loads. Naturally, the formulation of Goland and Reissner shows that the thicker the adhesive layer, the bigger will be the effect of bending on the joint, as the thicker the adhesive, the more misaligned the adherends become, as shown in Figure 8.5.

These peel loads will also appear at the ends of the overlap, in the same exact place where Volkersen predicted peaks in the shear strength (Figure 8.6). It is now becoming evident that the adhesive present at these locations is quite strained, being sheared and peeled much more than what occurs at the middle of the overlap region.

As we have discussed before, both the peel and shear stress peaks can be reduced by changing the joint geometry. The DLJ we have discussed before is a very powerful alternative if we wish to completely reduce stress peaks. A schematic representation of the shear stresses acting on this type of joint, calculated taking into account the bending moments, is shown in Figure 8.7. Notice how this joint geometry can even exhibit some compression of the adhesive layer in some locations.

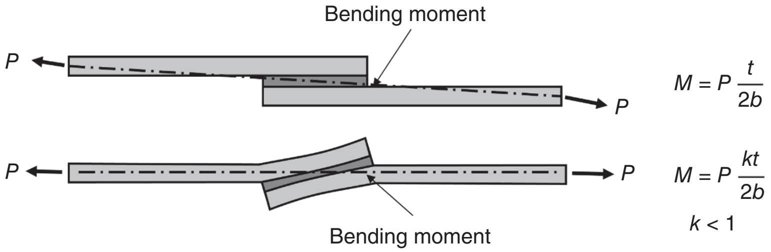


Figure 8.5 Bending moment on an SLJ as described by Goland and Reissner.

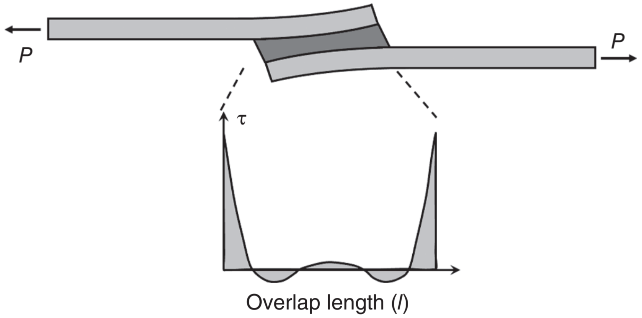


Figure 8.6 Peel stress in the adhesive layer of SLJs as described by Goland and Reissner.

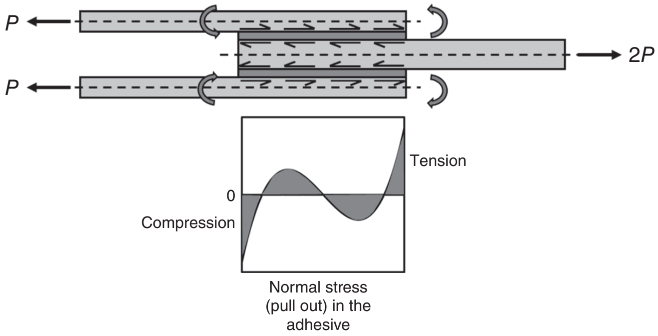


Figure 8.7 Peel stress in the adhesive layer of a DLJ as described by Goland and Reissner.

Until this point, we have discussed methodologies for predicting the joint strength that do not consider the fact that adhesive can deform plastically. Both the Volkersen and the Goland and Reissner models consider the adhesive to be a purely elastic material, which indicates that the stresses generated in the joint and directly proportional to how much the joint deforms. However, few adhesives behave in this way. In fact, most adhesives have the capability to deform plastically before they fail. Remember, while elastic deformation disappears once the material returns to an unloaded state, plastic deformation is permanent. If you stretch a material over its yield limit, you will start to cause this plastic deformation, and adhesives are no exception.

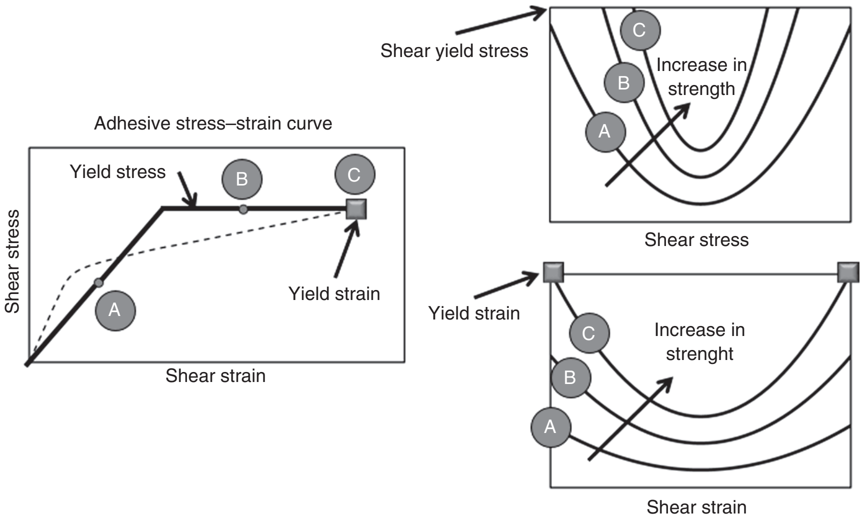


Figure 8.8 How plastic deformation leads to a stronger joint according to the work of Hart-Smith.

However, why is this plastic deformation important for determining the stress acting on the adhesive? This is simply because the loads are distributed differently along the adhesive layer if additional capability for plastic deformation exists. The work of Hart-Smith has led to a model able to determine stress distributions using the elastoplastic properties of the adhesive. This model was introduced in a 1973 technical report for NASA. Hart-Smith has shown that considering the plasticity of the adhesive shows a redistribution of stresses that is not captured by elastic analysis. Figure 8.8 shows the principle behind this model. It is evident that after reaching the yield stress, the adhesive stress–strain curve still allows for additional displacement.

The Hart-Smith model tells us that the even if the edges of the overlap yield (case B in Figure 8.8), a large portion of the adhesive layer is still able to provide additional strength. This can accurately represent the behaviour of an adhesive, especially suitable for ductile adhesives with large plastic deformations. However, its use is complicated by the fact that it is fundamental to possess accurate elastoplastic material properties of the adhesive, which requires a more complex and time-consuming testing procedure.

In Section 8.3.2, we will explore a set of procedures that are able to directly determine the strength of bonded joints by analysing the stresses acting on the joint and relating them with the inherent strength of the materials of the joint (both for adhesives and adherends).

8.3.2 Failure Criteria for Bonded Joints

At this stage, we have discussed a set of models that provide us with stress distributions along the adhesive layer or the adherend. However, you must be aware that these models do not allow us to determine joint strength by themselves; they merely indicate us which is the stress level for a given loading. To predict if a bonded joint will fail, we need to combine these models with a suitable failure criterion.

Note that failure criteria can be used to predict failure in the adhesive or the adherend but not in the interface (adhesive failure). This is because the mechanical properties of the interface are remarkably difficult to assess with precision, being highly dependent on several complex factors.

8.3.2.1 Failure in the Adhesive

In brittle adhesives, which allow for limited plastic deformation, failure often occurs because the failure shear stress of the adhesive is reached. In these cases, a purely elastic analysis such as Volkersen is well suited. For joints where the peel stress is the limiting factor, the Goland and Reissner based approach is suitable, as it also provides a peel stress distribution that can be used to identify when the adhesive has reached its maximum peel strength.

For ductile adhesives, as discussed in the introduction of the Hart-Smith model, the plastic yielding allows the adhesive to redistribute the stresses beyond what is predicted by a simple elastic analysis. In fact, even if the yield strength of the adhesive is reached, the joint can support additional load and fails only when its failure strain is reached.

If we perform a simple elastic analysis, we assume that the level of stress of generated in the adhesive layer is proportional to the load. If this stress reaches the yield stress, the elastic analysis will just consider that the adhesive has failed. However, in practice, what happens is that the adhesive does not fail after it reaches its yield stress. As we have seen, it becomes plastically deformed and still allows the joint to sustain additional load before its eventual failure. This limit condition is shown as case C in Figure 8.8. Figure 8.9 uses a load–displacement curve, similar to the ones that can be obtained by experimentally testing a specimen, to further illustrate how this consideration has an important impact on failure load prediction and in the accuracy of our results.

A special case of the Hart-Smith model is the generalised yielding of the adhesive. In this case, we are considering an adhesive that is so flexible that it is strained equally along the overlap length, spreading the stresses almost uniformly along the whole adhesive layer. This method is well suited for very ductile adhesives, with more than 20% of ductility in shear. The same model also works with elastic adhesives (highly deformable adhesive such as one-part polyurethanes or silicones). However, in this case, this is not because the adhesive is ductile but because the adhesive is so flexible that the stress distribution is uniform along the overlap.

We can use this method to design a joint in mere seconds. Let us run an example. Imagine an SLJ with an overlap length l (the length of the overlap between the two adherends) of 25 mm and a width of b equal to 25 mm. If we load it with 1000 N of

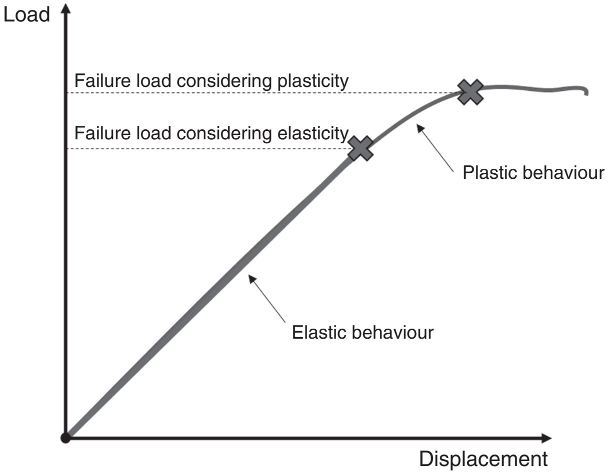


Figure 8.9 Differences in predicted failure load due to the use of an elastic analysis and an elastoplastic analysis.

force (around 98 kg in weight), the stresses acting on the adhesive layer are given by Eq. (8.1).

$$\tau = \frac{1000}{25 \times 25} = 1.7\,\text{N/mm}^2 \tag{8.1}$$

Therefore, 1.7 MPa (1.7 N/mm^2) of stress would be acting at whole locations of the adhesive layer. If we assume that a common polyurethane adhesive has a shear stress of around 8 MPa, we can safely say that this joint would withstand quite well this significant load (with a safety factor of almost 5!).

8.3.2.2 Failure in the Adherends

For metallic adherends, failure is usually initiated via plastic yielding. Thus, if we know that the stress level acting on an adherend will exceeded the yield strength of the metal being used, we can safely assume that the joint will fail. Note that this does not necessarily indicate that the metallic adherends rupture and the adhesive layer remains intact. In fact, the yielding of the metallic adherend will mainly occur near the edges of the overlap region, as shown in Figure 8.10 (where stress concentrations exist), and this yielding will excessively strain the adhesive. Thus, the failure of the adherend will in fact be translated into a failure of the adhesive layer. Still, this is a highly desirable failure mode, as the strength of the joint is solely limited by that of the adherend and not by the adhesive.

A simple, unified method for determining joint strength has been proposed by Adams in 2002, considering two conditions: the failure of the adhesive by generalised yielding and the failure of the adherend by plastic deformation, as shown in Figure 8.11. The generalised yielding of the adherend portion of the

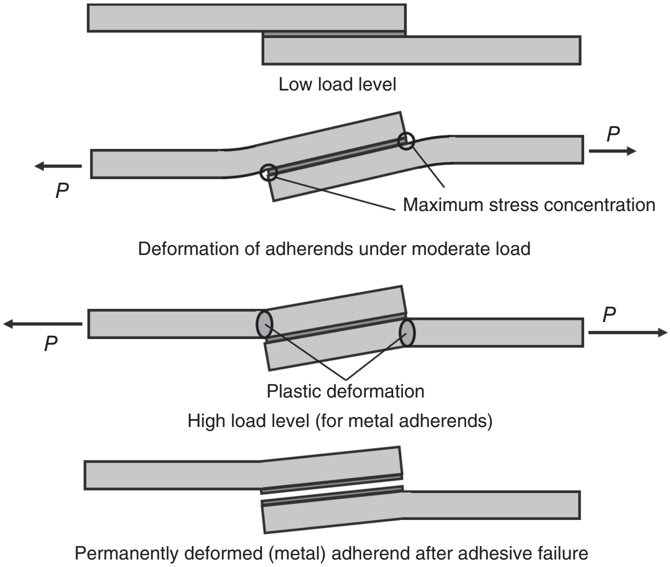


Figure 8.10 Localised plastic deformation of the adherends.

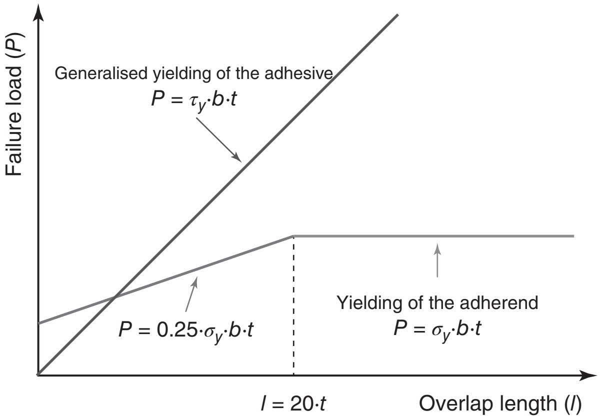


Figure 8.11 Adams method for failure load prediction as a function of overlap length.

model is the same as previously discussed, with the shear stress being assumed as uniformly distributed along the bonded area. However, the adherend yielding portion of the equation is a bit more complex, considering two different regions. In the first region, the failure of the adherend will be dependent on the overlap length, representing the localised yielding of the adherend. For larger overlap lengths, the load being generated is sufficient to yield and in some cases break the adherends, representing a tensile load that is higher than the tensile strength of the adherend material.

In more detail, the dark grey line in Figure 8.11 represents the failure of the adhesive, assuming a uniform shear stress in the adhesive layer. Thus, the predicted failure load is given by an equation that relates the length (b) and width (l) of the adhesive layer with the shear strength of the adhesive (τ_y).

On the other hand, the behaviour of the adherend is divided into two distinct regions that correspond to a special case of Eq. (8.2), proposed by Adams and based on the theoretical formulation of Goland and Reissner.

$$P = \frac{\sigma_y bt}{(1+3k)} \tag{8.2}$$

This equation states that the failure load is dependent on the yield strength of the adherend, the thickness of the adherend (t), the width of the adherend (b), and a k factor, which includes the effect of joint rotation in the relationship between the bending moment and the applied load. For reduced loads and small overlap lengths, it is possible to consider $k \approx 1$, which leads to Eq. (8.3).

$$P = \frac{\sigma_y bt}{4} \tag{8.3}$$

If we are considering overlap lengths that are more than 20 times larger than the adhesive thickness, k is assumed to be approximately zero. Thus, the load necessary to achieve yielding in the adherend is given by Eq. (8.4).

$$P = \sigma_y bt \tag{8.4}$$

For composite adherends, appropriate failure criteria usually rely on the analysis of the peel stress generated at the joint. When we first discussed peel loads, we mentioned that they are undesirable because of the way they concentrate the stress on a very small area, which can easily overwhelm and damage the adhesive. However, one additional negative aspect associated with peel loads is the fact that they are highly damaging when composite adherends are used. The explanation is quite simple, but we first need to understand how composites are made.

A composite material is, by definition, a material composed of two or more different materials combined and working together. Most high-strength composites used in engineering applications use a layered construction where layers of a very strong fibre reinforcement (which can be, for example, carbon or glass fibre) are stacked on top of each other, held together by a resin. This construction indicates that if the composite is loaded parallel to the reinforcement layers, it will display extraordinarily high strength. However, if the load is applied perpendicularly to these layers, the strong and stiff fibres of the reinforcement will not be able to support it. In this case, the resin matrix that holds the layers together, which is almost always a polymeric material, will be the weakest link in the chain and failure will occur by a process of delamination. Now let us imagine an SLJ with composite adherends. If we allow for excessive peel stresses to develop in this joint geometry, we can easily have a situation where, even before the adhesive fails, the peel loads will reach the composite adherends and cause its failure by delamination, as illustrated in Figure 8.12.

Therefore, the design of joints that include composite adherends will inevitably require an analysis of the peel stress levels (obtained, for example, with the Goland and Reissner model) and the knowledge of the interlaminar shear strength of the composite material.

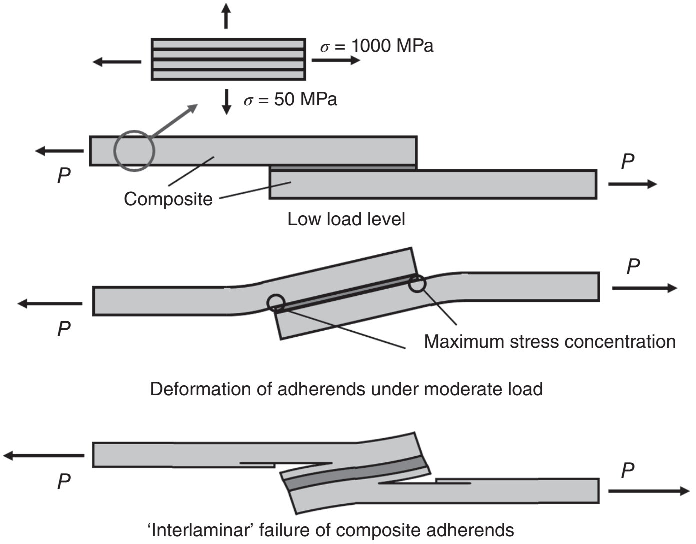


Figure 8.12 Strength of composite materials as a function of the loading direction (upper) and the process of delamination of a composite adherend induced by excessive peel loads at the overlap ends (lower images).

8.4 Joint Strength Prediction Using Numerical Methods

The use of finite element analysis (FEA) is a powerful modern design technique that has brought unheard flexibility to the design of structural elements and the design of adhesively bonded joint has also benefited from it. However, before we delve on its advantages for use with bonded joints, we should first explain what a finite element model is.

Simply put, the finite element method first divides a structure into a mesh (or a grid) of smaller, easier-to-study elements connected by nodes. A set of well-defined restrictions, known as boundary conditions, are applied to this network of elements, precisely defining the conditions that these elements are subjected to. The principle of minimum energy is used to determine the possible states of the nodes of this elastic body. From this, we can establish a system of equations that represent the full problem, combining the influence of each node and element and its boundary conditions. Variational calculus is then used to find approximate solutions (within a given margin of error) for this system of equations. Ultimately, the objective of a FEA is to determine the displacement of the nodes (D), having previous knowledge of the stiffness of the body (K) and the loads and reactions acting on it (R). Thus, we can establish the fundamental equation of FEA (Eq. (8.5)).

$$K \cdot D = R \tag{8.5}$$

For adhesive joints, a simple elastic analysis using FEA can serve as a very powerful alternative to most analytical models, allowing us to determine stress distributions for any complex geometry.

While the science behind them might seem complex at first, elastic finite element models are quite simple to create and run, necessitating only the geometrical configuration of the joint and basic data on the material stiffness. Their biggest advantage is the fact that they are not limited to a specific geometry, as is the case for the analytical models and that the results they return allows to quickly understand and visualise all the strains and stresses acting on the joint, including the very important shear and peel stresses. An important drawback is that parametric studies cannot be made as easily as is the case when using analytical models, as it is necessary to remesh and rerun the calculations each time a geometrical parameter is changed. This type of studies can be done automatically using appropriate software but is still a process that requires significant computation power.

Using FEA as described above, the solution becomes dependent on the size of the elements (or the size of the mesh). For example, while a coarse mesh with large elements will erroneously show a low stress in a region near the edges of the overlap length of an SLJ, a highly refined mesh (with very small elements near this critical area) will provide a much better representation of the local stress field, much closer to the actual stress acting on the adhesive layer (see Figure 8.13). However, extremely fine meshes are computationally heavy (take a long time to calculate), and thus, it is essential to select a mesh that can accurately represent the true stresses acting on the adhesive layer but light enough to be calculated quickly. This is usually done by testing meshes with gradually smaller element sizes and stop refining the mesh when results start to converge.

FEA also has a notorious difficulty in managing the stress singularities that occur at the edges of the joints (Figure 8.14). In fact, if we refine the mesh with extremely small elements, this will lead to infinite stresses being calculated. Obviously, if we wish to use a failure criterion based solely on stress level, this approach creates significant problems in correctly predicting joint performance, as different meshes will yield vastly different peaks stresses and, consequentially, failure loads.

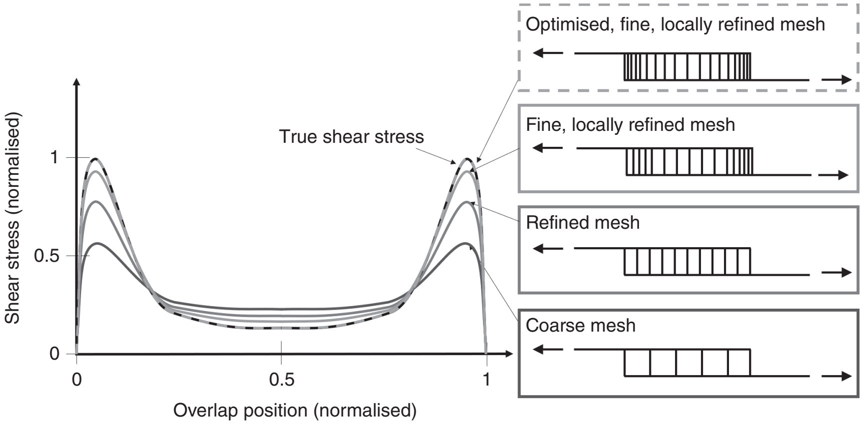


Figure 8.13 The influence of mesh size on the stress distribution distributions calculated with FEA (stresses taken in the middle of the adhesive layer).

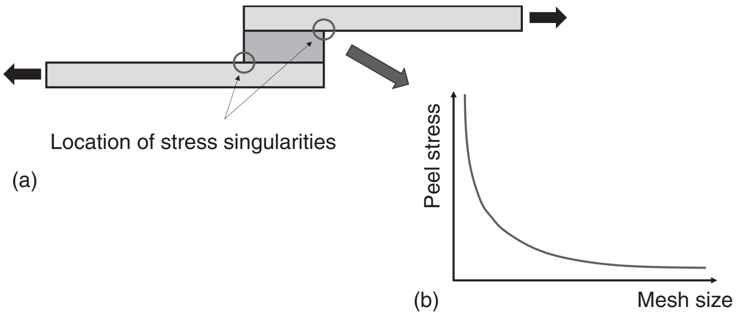


Figure 8.14 Location of stress singularities in SLJs (a) and the influence of the mesh size in determining the stresses acting on these singularities (b).

A solution to this issue relies in the use of damage mechanics to treat the singularity. This is achieved with the use of special elements known as cohesive elements. The cohesive zone models (CZMs) are advanced models suitable for reproducing the mechanical behaviour of adhesives, as they act as connections between the adherends. CZMs exhibit a behaviour that mimics that of a real adhesive, leading to a gradual separation of the adherends, as seen in the upper part of Figure 8.15.

When a CZM element is loaded, it will start to damage after a stress limit is reached, but the element will not fail instantaneously. Damage ahead of the crack tip will take place and progresses until a point where the fracture energy of the adhesive is reached, corresponding to failure of the adhesive (and debonding of the joint).

This behaviour can be directly measured experimentally with fracture mechanics specimens. In mode I, the double cantilever beam (DCB)specimen can be used. During this test, the load, displacement of the arms of the specimens, and their rotation enable to deduce the energy stored in the adhesive. The variation of that energy as a function of the displacement of the adhesive gives a plot of the stress vs. displacement, i.e. the cohesive law. The shape of the cohesive law is similar to that idealised in the central part of Figure 8.15. If the adhesive is brittle, then the damage is rather sudden and follows a triangular law. If the adhesive is ductile, it will show a plastic plateau, as in a stress–strain tensile curve, and a trapezoidal law is suitable to describe the real behaviour of the adhesive.

The initial portion of the cohesive law is defined by taking account of the yield stress and the material stiffness under a given mode (mode I or mode II). In addition, note that the area under the traction separation laws is representative of the critical fracture energy of the material. It is this second part of the traction separation law that explores the concept of damage mechanics to degrade the mechanical properties of the element. This damage comes in the form of stiffness degradation, as shown in the lower portion of Figure 8.15. Damage starts to occur as the stresses go over a certain limit, usually defined as the yield strength of the material in a given loading condition or mode and this damage corresponds to a softened traction separation law, with reduced mechanical properties. If we again load an element that has already become damaged, we will observe that the stiffness, degradation, and fracture energy are all lowered.

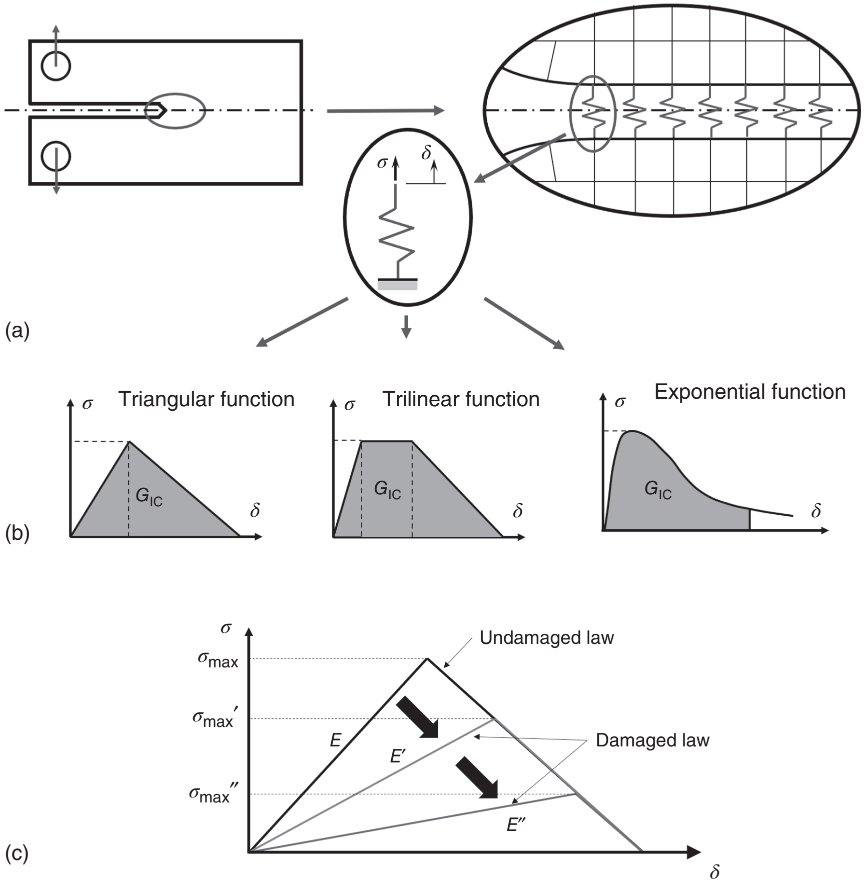


Figure 8.15 Principle of operation of cohesive models (a), different traction separation laws that can be used to model the adhesive behaviour (b), and an example of how damage is applied to a cohesive traction separation law (c).

The direct determination of the cohesive law is rather laborious and in general the approach followed is to use the strength of the adhesive obtained in strength tests (such as the tensile test for the stress at which damage starts to occur in the adhesive) and the fracture testing for the area under the cohesive law (such as DCB test to determine the fracture energy). Please see Chapter 4 for more details on these testing procedures. Another technique to deduce the cohesive law of the adhesive is to model the DCB test with a FEA and fit the model until the experimental and the numerical load–displacement curves fit. This technique is the called the inverse method.

8.5 Parameters That Affect Joint Performance

8.5.1 Effect of Adhesive Thickness

Adhesive thickness has always been one of the most studied geometrical parameters in the design of adhesive joints. Studies made on this parameter that have shown that

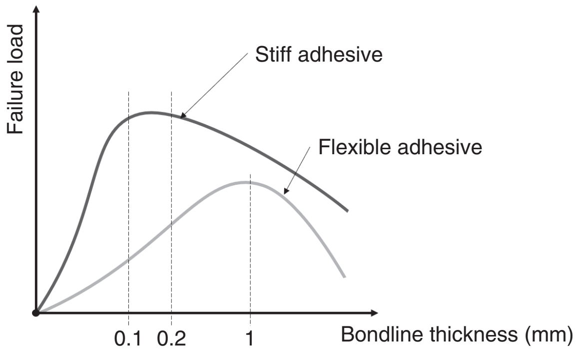


Figure 8.16 Representative curves showing the evolution of the failure load of an adhesive joint as a function of the bondline thickness for two different adhesive types.

using more adhesive is not necessarily the best option. Experimental testing demonstrated that there is an optimal adhesive thickness, which is around 0.1–0.2 mm for relatively stiff adhesives, such as epoxies (as shown in Figure 8.16). For more flexible adhesives with significant capacity to deform elastically (such as silicones), this value is a bit higher, rising to 1 mm.

The concept of an optimal adhesive thickness has always represented a point of contention because most analytical models show that increasing the adhesive thickness should result in an increase of the failure load of the joint, with the mechanics of the joint leading to a smoother stress field and consequently to a stronger joint. However, as stated above, practice shows that this is not entirely true. Several explanations have been proposed for this effect and the current consensus seems to be that larger adhesive thicknesses leads to greater misalignment of the loads acting on the adhesive layer, which is translated into large bending moments. These large bending moments are responsible for the generation of peel stresses which, as we have seen, are highly damaging to the strength of the adhesive layer. Although this explanation suggests that the ideal adhesive layer would have an almost zero thickness to minimise bending moments, in practice, this is not possible, as very thin adhesive layers can lead to the emergence of areas where there is simply no adhesive and the adherends touch each other, providing no load bearing capability. Experimental testing has suggested that an adhesive layer thickness below 0.05 mm is highly susceptible to the appearance of regions without adhesive, characterised by a large reduction of the joint strength.

8.5.2 Effect of Overlap Length

The effect of the overlap length in an adhesive joint has also been extensively studied and important experimental data are available to help in the design phase. It is important to first understand that if we increase the overlap length and maintain joint width constant, we are in fact increasing the bonded area directly in direct proportion to the overlap length. Therefore, the expectable would be that an increase of the overlap length should always result in an increase of the load carried by the joint. However, this is not always the case because, as the work of Volkersen first showed us, stresses are never truly constant along the overlap length. A more effective alternative to increase the bonded area and the joint strength is to change the width of the adhesive layer, as the stress field is uniform and unchanged along this direction. To better understand how the overlap length controls the joint performance and the factors that govern this behaviour, we analyse in detail a few specific examples in Sections 8.5.2.1–8.5.2.3.

8.5.2.1 Overlap Length and Adhesive Behaviour

We will first consider an adhesive joint using high-strength steel adherends and two different adhesives, a very ductile adhesive (with over 20% of shear strain) and a brittle adhesive. Because we wish to determine the influence of the adhesive, it is important to use high-strength steel adherends to ensure that our analysis is not influenced by yielding of the adherend.

If we plot the failure load of each joint configuration as a function of the overlap length (Figure 8.17), we will see that the very ductile adhesive will lead to a practically linear relationship between the failure load and the overlap length, while the same is not true for the brittle adhesive.

Let us first consider a stiff adhesive, bonding high-strength steel adherends. For very small overlap lengths, the joint strength will be mainly limited by the adhesive layer, which has a very small resistant area. As we increase the bonded area, we will see a linear increase in the joint strength and eventually reach a plateau. That is, increasing the overlap length any further will not be advantageous to joint performance. Why does this occur? To explain, let us recall the discussion of the shear stress distribution acting on an adhesive layer. As we have seen, the stress peaks at the ends of the overlap will be the main cause of failure of stiff adhesive layers, and even if we increase the overlap to extremely large values, these stress peaks will always be present, leading to a limited improvement in joint strength.

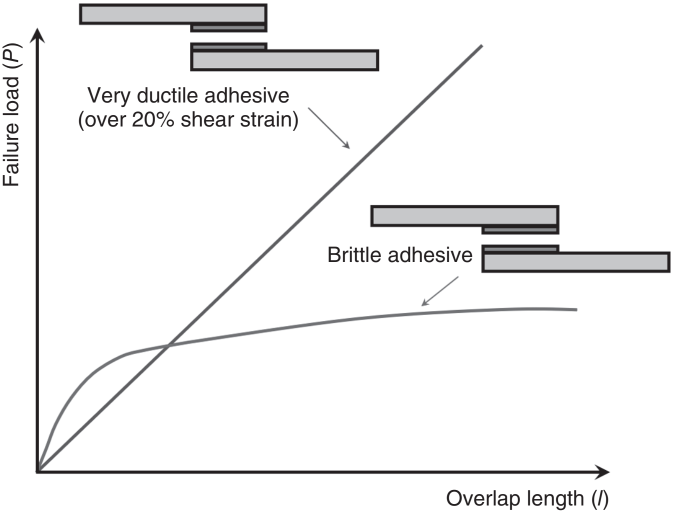


Figure 8.17 Failure load of an adhesive joint as a function of the overlap length for joints using high-strength steel adherends and two different adhesives (very ductile and brittle adhesive).

Simply put, the area in the middle of the overlap length is almost unloaded and adding more length to this region does nothing for joint strength.

In contrast, very ductile adhesives can yield and, as described by Hart-Smith, this will help to redistribute the stresses uniformly along the full overlap length. Thus, the formation of stress concentrations at the edges of the overlap is less likely, and the adhesive can use all the available bonded area. The result is a joint with failure load that is directly proportional to the overlap length. Note that although our example focuses on a very ductile adhesive, the same would be true for an adhesive that is extremely elastic and flexible, such as a polyurethane. In this case, the large flexibility of these adhesives is also conductive to the uniformisation of stresses.

An important note is that stiff adhesives can often overperform ductile adhesives for smaller overlap lengths as shown in Figure 8.17. Stiff adhesives are usually stronger than ductile adhesives and, for these smaller overlap lengths, the stress concentrations are quite close to the centre of the overlap, which roughly indicates that the full bonded area is being used.

8.5.2.2 Overlap Length and Adherend Strength

Now that we have understood the effect of the adhesive type, let us focus on the effect of the adherend material. For this purpose, we are going to consider three different adherent materials, bonded with the same ductile adhesive, as shown in Figure 8.18.

The first case we can discuss is that corresponding to the high strength steel and the ductile adhesive. As Figure 8.18 shows, this configuration has a proportional relationship between the failure load and the overlap length for the reasons we have explained above (uniform stress distribution that allows us to use all the bonded area).

Now let us consider a joint manufactured using the same ductile adhesive and adherends with low yield strength, such as a mild steel. In this case, we will initially

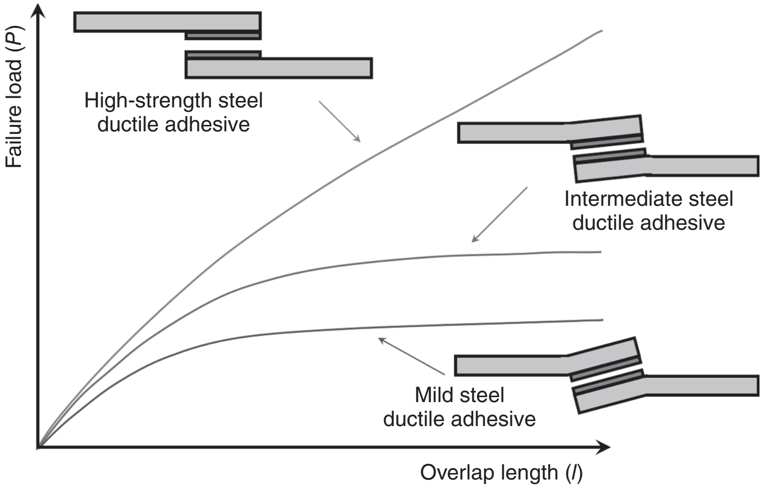


Figure 8.18 Failure load of an adhesive joint as a function of the overlap length for different adherend materials.

find a relatively linear increase in the joint strength as we increase the overlap length that will eventually transition into a plateau. Unlike what was shown in Figure 8.17, this plateau is not the product of failure of the adhesive but is instead caused by the yielding of the low-strength adherend. However, please be aware that the adherend does not necessarily fully yield or break. In fact, as the adherend starts to yield, large strains are imposed on the adhesive that force it to fail almost immediately after. Increasing the overlap length any further will not yield any improvement as the adherend strength is now the main limiting factor. This case is shown in the lower line in Figure 8.18

Finally, if we use adherends with intermediate strength (between high steel and mild steel), we will again find a plateau in joint strength, but for a higher failure load, as the intermediate steel adherend will require higher loads to yield. This behaviour is shown as the middle line in Figure 8.18.

These examples clearly show that the adherend strength plays a major role in determining how the joint strength evolves with the overlap length. High-strength adherends allow ductile adhesives to fully use the available overlap length, while low-strength adherends limit the joint performance as they will eventually yield and cause the adhesive layer to fail.

8.5.2.3 Overlap Length and Composite Adherends

A special case of overlap length dependence is often encountered when bonding composites. In this chapter, we have already discussed how peel stresses in the adhesive layer can be transferred to the composite adherends and cause delamination failure on adherend. However, this is also directly related to the overlap length. For smaller overlap lengths, the peel stress generated at the ends of the overlap is not enough to cause delamination of the composite adherends. However, as we increase the overlap length, the adhesive layer will be subjected to increasingly higher stresses and will eventually reach a peel stress level that can fail the composite adherend by delamination. In this case, even if we increase the overlap length, the strength of the joint is determined by the interlaminar strength composite adherend, again leading to a plateau in failure load (Figure 8.19). Of course, the nature of the adhesive also plays a key role in this phenomenon, as a very flexible adhesive will not generate severe peel stress peaks and will delay or even entirely avoid the onset of delamination. Generally speaking, flexible adhesives are preferable when bonding composites.

8.5.3 Effect of Temperature and Thermal Stresses

Temperature can have a significant effect on the performance of a bonded joint and this can occur in different ways. Perhaps the most important is the reduction in adhesive and adherend properties that usually occurs with rising service temperatures. Adhesives, as polymeric materials, are quite sensitive to temperature and might provide insufficient cohesive strength if forced to operate above their T_g. Thus, when designing a joint that will operate at relatively high or low temperatures, one must use mechanical properties that were determined at the actual service temperature

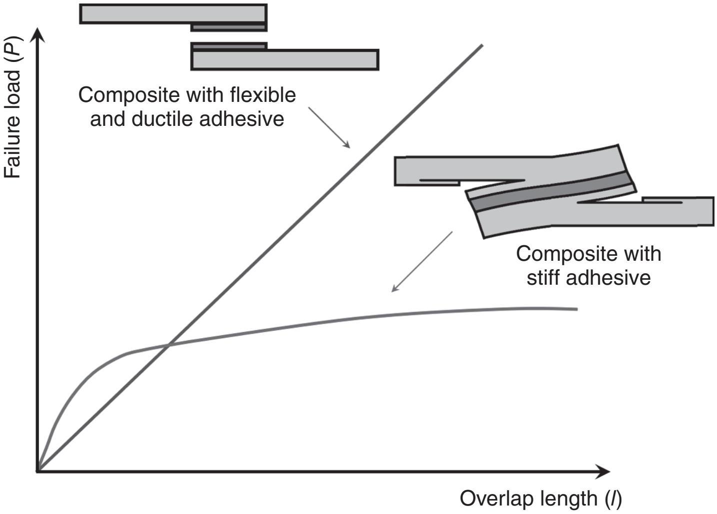


Figure 8.19 Failure load of a composite adhesive joint as a function of the overlap length, considering two different adhesives (flexible and stiff).

(see Chapter 4 for more details on the testing procedures for extreme temperatures and Chapter 9 for the effect of temperature on the properties of adhesives).

Another key effect of temperature on the performance of bonded joints is the thermal stresses caused by temperature variations. First, we must remember that adhesives and adherends have vastly different thermal expansion coefficients, often with difference of an order of magnitude (at least 10 times higher or lower). When they are exposed to high temperatures, they will tend to expand differently because of the dissimilar thermal expansion coefficients. However, as they are now bonded together, it is physically impossible for them to expand fully and freely. This creates residual stresses (strains) that are induced into the adhesives layer. Residual stresses are not usually significant when both the adherends are of the same material. In the case of joints with dissimilar adherends, where the material of one adherend is vastly

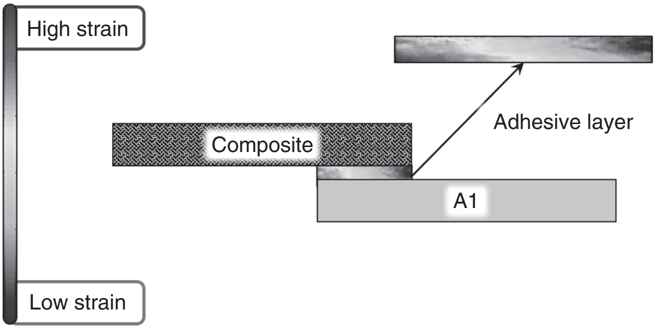


Figure 8.20 Thermally induced strains in the adhesive layer in joints with dissimilar adherends, when cooled from high temperatures.

different from the other, the joint is highly strained with thermal residual stresses, even before any mechanical load is applied to it. Figure 8.20 schematically shows these thermal stresses acting on a dissimilar joint.

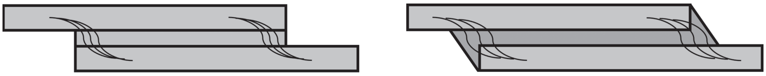
When designing a joint, one must be aware of the dangers created by these thermal stresses and should take appropriate measures to avoid their build-up. This can be, for example, the use of room temperature curing and the preference towards more flexible adhesives, which can easily accommodate differences in thermal expansion between adherends.

8.6 Methods to Improve Joint Strength

8.6.1 Adhesive Fillet

Throughout this chapter, we have repeatedly seen that the edges of the overlap are the most critical area of stress concentration and the key locations where failure can be expected to occur. Therefore, the question arises of what will happen if we change the geometry of this critical area of the joint to reduce the level of the stresses that are acting on it? Will we be able to improve joint strength? The answer for both these questions is yes. In fact, many of the geometrical optimisations available for improving the performance of bonded joint do so by providing some sort of method to reduce the stress concentration at the overlap. Among these, the use of an adhesive fillet is by far one of the simplest yet most effective methods. As shown in Figure 8.21, a fillet is a sloped portion of adhesive that gradually connects both adherends and allows stresses to be transferred over a large area. The result is a smoother, more uniform shear stress distribution, closer to the one that is obtained when a very flexible and ductile adhesive is used.

Adhesive fillets are quite simple to manufacture and, in some cases, no particular effort is necessary to create them as just the overflow of excess adhesive in the joint will create a rough fillet shape that will be able to transfer the loads quite well.



A – Load transfer concentrated at the edge

B – Load transfer over a larger area

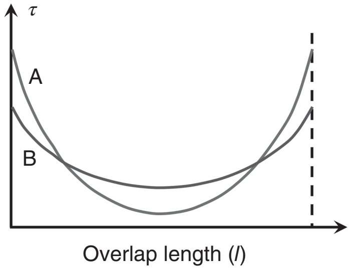


Figure 8.21 Load transfer in a fillet and resultant changes in the shear stress distribution.

8.6.2 Mixed Adhesive Joints

Mixed adhesive joints are the joints that combine two adhesives in the same overlap, as shown in Figure 8.22. The use of two distinct adhesives can be explored to reduce the stress concentrations at the ends of the overlap, typical for SLJs, and improve joint performance in diverse ways.

To work properly, the mixed adhesive joint concept requires the introduction of a more flexible adhesive at the ends of the overlap, while a stiff adhesive is used in the central section of the joint, less subjected to deformation during loading. The presence of the ductile adhesive at the ends of the overlap can successfully reduce the effect of the stress concentration, while the stiff adhesive in the central is able to support most of the load without failure. This combination leads to important gains in joint strength if the right combination of adhesives is selected. Simply stated, a well-designed mixed adhesive joint will exhibit performance that is greater than the sum of its parts, that is, that of each of the adhesives that compose it used alone.

However, please be aware that the usefulness of the mixed adhesive joint is not solely related to the improvement in joint strength. The use of mixed adhesive joints can also improve the joint behaviour at low or high temperatures, using a combination of high temperature-resistant and low temperature-resistant adhesives. This combination is especially well suited for use in mixed adhesive joints, as low-temperature adhesives (such as silicones) are inherently flexible and high-temperature adhesives (such as temperature-resistant epoxy formulations) are inherently stiff.

8.6.3 Functionally Graded Joints

Graded joints have been presented theoretically as the natural evolution of the mixed adhesive joint. They do not use the discrete, block-by-block approach of the mixed adhesive joint but instead adopt a smooth variation of the material properties. Figure 8.23 shows the working principle of a graded adhesive joint, exemplifying three different material properties found along the overlap length.

While theoretically advantageous over the mixed adhesive joint, the difficulty associated with the graded joint lies in its practical implementation. Although various techniques have been proposed for the development of this type of joint, only recently has the production of fully graded joints been experimentally demonstrated and published in the literature. Functionally graded joints were obtained experimentally by means of induction heating, leading to a graded cure of the adhesive along the joint. This study demonstrated that the functionally graded joint shows a good ductility and high strength when compared with joints cured isothermally.

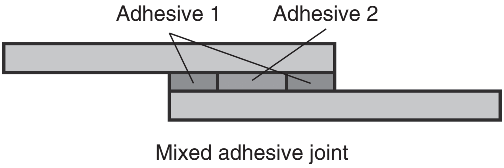


Figure 8.22 Mixed adhesive joint concept.

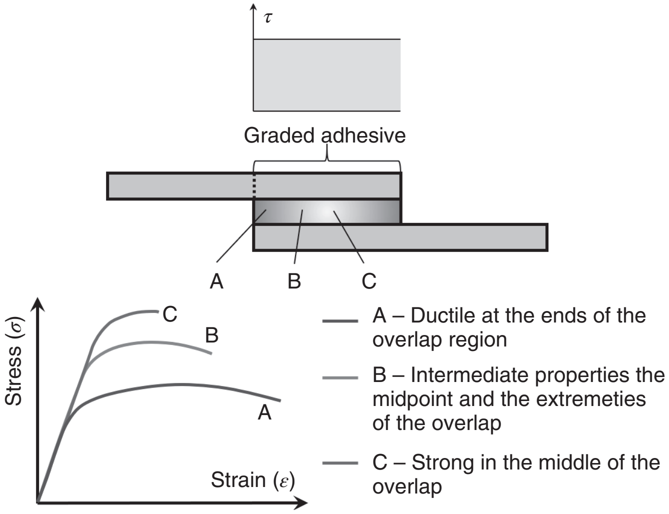


Figure 8.23 The graded adhesive joint concept.

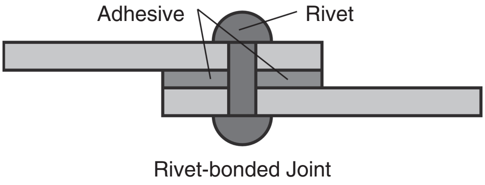
An alternative technique to achieve graded joints is the use of particles that are non-uniformly distributed along the overlap length. In practice, this is realised by adding magnetised particles to the adhesive, which are guided using a suitable magnetic field.

8.6.4 Hybrid Joints

The hybrid joint is another joint configuration that can be very useful to increase the performance of a bonded joint. Hybrid joints are joints that combine adhesives and other joining methods, such as welding, riveting, or fastening. An example of a rivet-bonded joint is shown in Figure 8.24.

Hybrid joints are commonly used to increase the joint strength but can also facilitate the fabrication process, providing an immediate method to hold the joint together while the adhesive cures. The automotive industry routinely combines spot-welding and adhesive bonding in the vehicles it manufactures, as the spot-weld will instantly ensure a solid connection between components while the adhesive is uncured. When the vehicle enters service, both the spot-weld and the adhesive layer contribute to the joint strength. Hybrid joints also improve safety by enabling more benign failure modes. For example, in aircraft structures, it is common to combine rivets and adhesive bonding. If one of these joining techniques fails, the other can still support the structure without catastrophic damage.

Figure 8.24 Example of a hybrid joint (rivet-bonded joint).



8.7 Case Studies

To conclude this section and consolidate your newly acquired knowledge on joint design, six different joint design examples are given. These are divided into four analytical case studies and two numerical studies with FEA.

- Case study 1 – Effect of adhesive type on the strength of adhesive joints;
- Case study 2 – Effect of overlap length and adherend type on the strength of adhesive joints;
- Case study 3 – Effect of adhesive thickness on the strength of adhesive joints;
- Case study 4 – Strength prediction of adhesive joints with composite adherends;
- Case study 5 – Strength prediction of an SLJ with cohesive zone modelling;
- Case study 6 – Effect of thermal stresses on adhesive joints.

8.7.1 Case Study 1 – Effect of Adhesive Type on the Strength of Adhesive Joints

Our first case study concerns the effect of adhesive type on the strength of an SLJ. To this end, we are going to consider two joints bonded with two vastly different adhesives. One of the adhesives is epoxy-based, stiff, and strong, while the other, polyurethane-based, is much weaker yet quite flexible. Properties for the two adhesives under study are shown in Table 8.1. High-strength steel adherends are used to ensure that the joint will not fail by plastic deformation of the adherend (Table 8.2), allowing us to concentrate solely on the performance of the adhesive. The joints are schematically shown in Figure 8.25.

The two joint configurations were tensile tested in a universal testing machine until failure occurred. Representative load–displacement curves, shown in

Table 8.1 Mechanical properties of the adhesives used for case study 1.

Mechanical properties	Polyurethane	Epoxy
Young's modulus, E (MPa)	2500	4590
Poisson's ratio, υ	0.38	0.35
Shear yield stress, τ_y (MPa)	20	34.1
Maximum shear strain, γ_f (%)	> 100	5.25

Table 8.2 Mechanical properties of the adherends used for case study 1.

Mechanical properties	High-strength steel
Young's modulus, E (MPa)	210 000
Poisson's ratio, υ	0.3
Yield stress, σ_y (MPa)	1 100

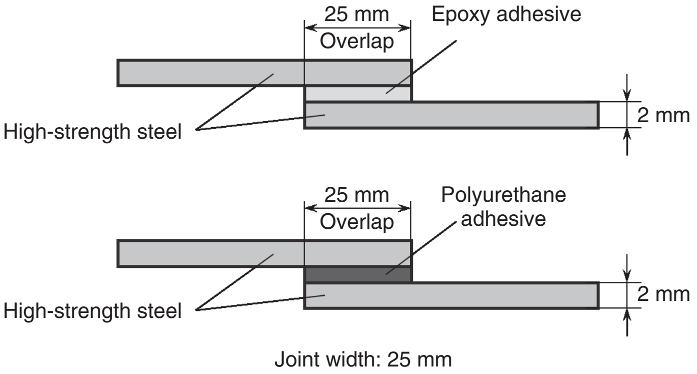


Figure 8.25 Joint configurations for case study 1.

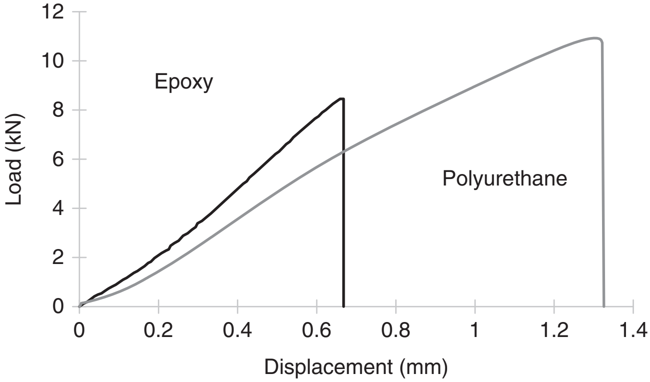


Figure 8.26 Representative load–displacement curves for the two joint configurations of case study 1.

Figure 8.26, clearly demonstrate that the strongest adhesive does not lead to the best performing joint, exhibiting a much lower failure load and displacement at failure than the ductile adhesive.

Surprisingly, the weakest of the two adhesives provides a considerably stronger joint. To shed light on the reasons behind this behaviour, we can use two analytical models to predict joint strength. These are the Volkersen model and the generalised yielding of the adhesive, which have been described in detail earlier in this chapter. The failure predictions for these two models were calculated with the help of the JointDesigner software (www.jointdesigner.pt), an analytical design software for adhesive joint design, created by the authors at the Faculty of Engineering of the University of Porto. The results are shown in Figure 8.27, compared against the experimentally determined failure loads for both adhesives.

The results indicate that the generalised yielding provides a reasonably good prediction of the failure load for the polyurethane adhesive, while the Volkersen criterion predicts the failure load by a considerable margin. This is due to the fact that the polyurethane adhesive is a very ductile and tough adhesive, which is able

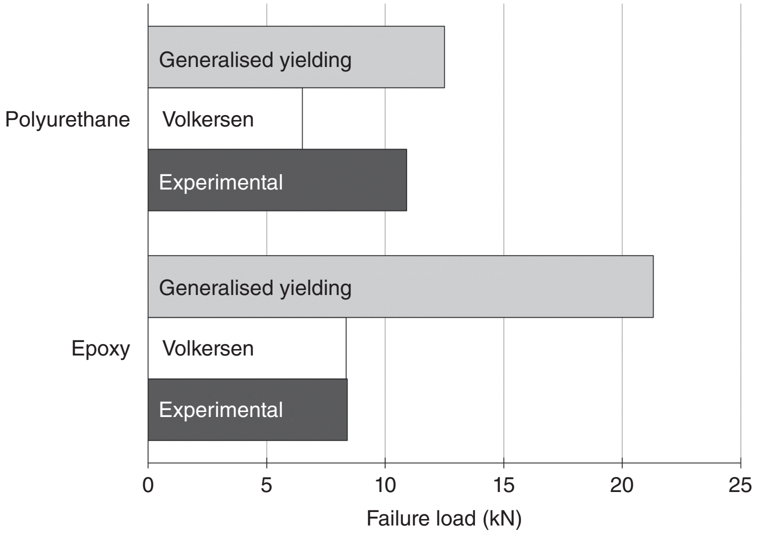


Figure 8.27 Comparison between experimental and analytically obtained failure loads for case study 1.

to redistribute the load uniformly along all of the bonded area. When we use the generalised yielding of the adhesive criterion, we are exactly assuming this.

In contrast, the epoxy adhesive is much stiffer and less ductile, which has the effect of concentrating stresses at the ends of the bonded area. In this case, the Volkersen criterion is extremely effective, as it is well suited to model the peaks in shear stress at the overlap ends. When applied to this adhesive, generalised yielding of the adhesive criterion overpredicts the failure load because it assumes that this very strong adhesive will use all of the overlap length to carry the load, which is obviously not true.

To summarise, this simple analysis provides us with clear evidence that the strength of a joint is not directly related to the strength of the adhesive used to bond it. In fact, what truly matters is how effectively the adhesive can use the available overlap length.

8.7.2 Case Study 2 – Effect of Overlap Length and Adherend Type on the Strength of Adhesive Joints

The second case study is a bit more complex than the first, as we are going to simultaneously study the effect of two factors on joint strength: the effect of the overlap length and the effect of adherend type.

We are now going to consider four joint configurations bonded with a crash-resistant epoxy adhesive typically used in the automotive industry. This adhesive offers relatively high strength, ductility, and toughness, which allows it to perform very well under impact conditions. The mechanical properties of the adhesive are given in Table 8.3. Two different overlap lengths (12.5 and 25 mm) and two adherend materials (mild steel and high strength steel) are considered. The studied

Table 8.3 Mechanical properties of the adhesive used for case study 2.

Mechanical properties	Crash-resistant epoxy
Young's modulus, E (MPa)	930
Poisson's ratio, υ	0.33
Shear yield stress, τ_y (MPa)	18.1
Maximum shear strain, γ_f (%)	56

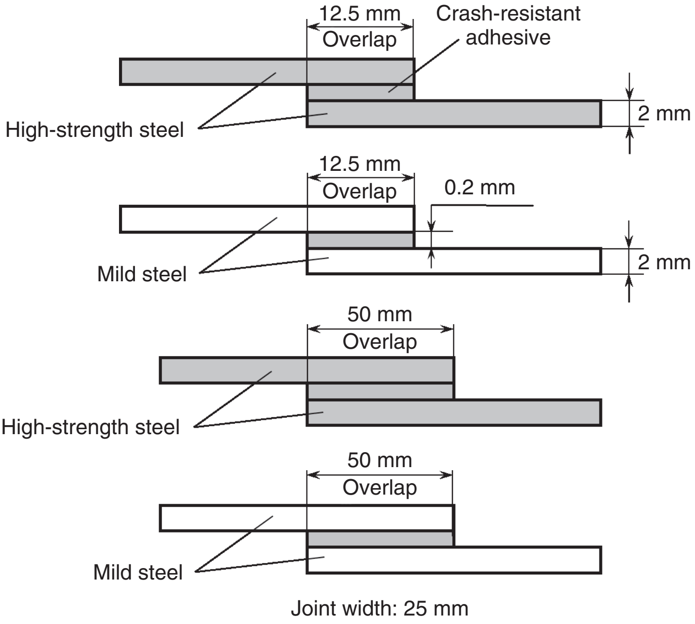


Figure 8.28 Joint configurations for case study 2.

joint configurations are schematically shown in Figure 8.28. The joints are bonded with a crash-resistant, epoxy-based adhesive.

The mechanical properties of the adherend materials are given in Tables 8.3 and 8.4. Varying these parameters allows us to understand how the joint failure mode can change from failure in the adhesive to failure in the adherend.

Again, the four joint configurations were tensile tested in a universal testing machine until failure occurred. The results, shown in Figure 8.29, are quite remarkable. Joints bonded with the 12.5 mm long overlap exhibit quite similar performance, independently of the type of the adherend material. This is because failure always occurs in the adhesive layer.

However, when the overlap length increases to 50 mm, the specimens will sustain larger failure loads and little displacement with high-strength steel adherends. The mild steel adherends have a more modest failure load but have an extremely

Table 8.4 Mechanical properties of the adherends used for case study 3.

Mechanical properties	High-strength steel	Mild steel
Young's modulus, E (MPa)	210 000	
Poisson's ratio, υ	0.3	
Yield stress, σ_y (MPa)	1100	185

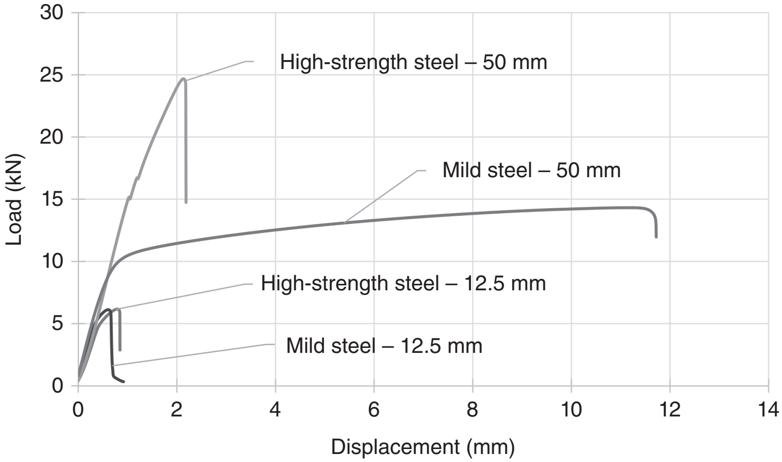


Figure 8.29 Representative load–displacement curves for the four joint configurations of case study.

large displacement at failure. This markedly different behaviour is the result of two different failure modes.

The mild steel joints with 50 mm of overlap fail because the large adhesive layer is now able to support loads that can yield the low-strength adherend (cause it to deform plastically). In contrast, joints with the long overlap and high-strength steel adherend fail in the adhesive layer as the adherend is extremely strong (no yielding occurs). In this case, the adhesive layer is taken to its ultimate limit and eventually fails.

We are going to use three different analytical models to reproduce the results obtained for this case. These are the Volkersen model, the generalised yielding of the adhesive and the yielding of the adherend. Results for these two models were calculated using the JointDesigner software and are shown in Figure 8.30, as well as experimental data points.

The first comment we can make is that the adhesive generalised yield criterion provides excellent results for the high-strength steel adherends. As we have seen before, a ductile adhesive with a very strong adherend allows the full use of the adhesive shear strength.

For mild steel adherends, the results obtained by the adhesive generalised yield criterion are still quite good for an overlap of 12.5 mm. This is because the failure

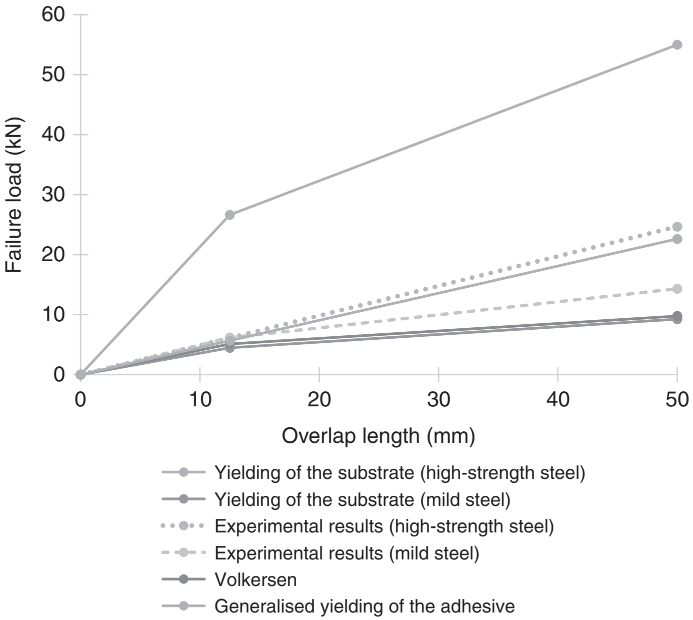


Figure 8.30 Comparison between the experimentally determined and the predicted failure loads using different analytical models for two overlap lengths (12.5 and 50 mm).

load attained is not sufficient to cause adherend yielding, so at this stage, the type of adherend does not matter very much. However, for 50 mm of overlap, this approach assumes that the adherend does not yield, when in fact there is a large amount of yielding.

The adherend yield criterion provides completely incorrect results for the high-strength steel adherends as the adhesive fails significantly earlier. For the mild steel adherends, the result given by the adherend yield criterion for the 12.5 mm adherend is not to be relied on, as there is very little plastic deformation with such a small overlap length.

For the mild steel and 50 mm overlap combination, there is plastic deformation of the adherends, and the value predicted by adherend yielding criterion is reasonable. However, this is an underestimation of the actual failure load as it represents the start of the long adherend yielding phase. Strain hardening sets in from this point and increases the actual joint strength.

Lastly, as we have seen before, the Volkersen model is not well suited for any of the combinations tested in this work as the adhesive is quite ductile.

8.7.3 Case Study 3 – Effect of Adhesive Thickness on the Strength of Adhesive Joints

The third case study is dedicated to one of the most important questions in adhesive design. Does the adhesive thickness influence joint strength? And if so, how can we predict its effect? To explore this subject, we are now going to consider three

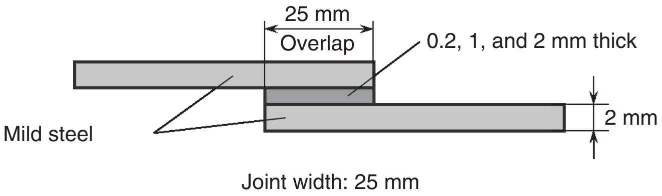


Figure 8.31 Joint configurations for case study 3.

joint configurations, bonded with a crash-resistant epoxy adhesive (the same used in case study 2), with mechanical properties given in Table 8.3 and with three different adhesive layer thicknesses under consideration (0.2, 1, and 2 mm). Mild steel adherends are used, with the mechanical properties already shown in Table 8.4. The three joint configurations under study are schematically shown in Figure 8.31.

The three joint configurations are tested in traction in a universal testing machine until failure occurred.

The results shown in Figure 8.32 clearly highlight the practical effect of varying the adhesive thickness. The best performing adhesive thickness is 0.2 mm, leading to maximum strength and displacement. As the adhesive layer thickness increases, the failure load is reduced as well as the maximum displacement. As we will see, this goes against the prediction of some models, which erroneously predict that increasing the adhesive layer thickness leads to stronger joints.

Additional information can be obtained by analysing the fracture surfaces of the specimens, as shown in Figures 8.33–8.35. These images show that there is a degree of plastic deformation in the mild steel adherends and that as the adhesive thickness increases, there is an indication of an increasingly larger amount of interfacial failure. Simply put, as the thickness increases, the failure locus will change from the middle of the adhesive layer to very close to the interface, approaching adhesive failure in some cases.

As the objective is to highlight the difficulties analytical models face in these cases, three different models are under consideration. These are the Volkersen model, the

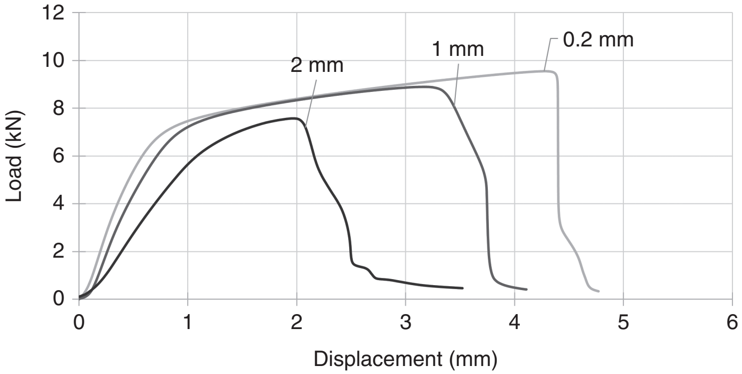
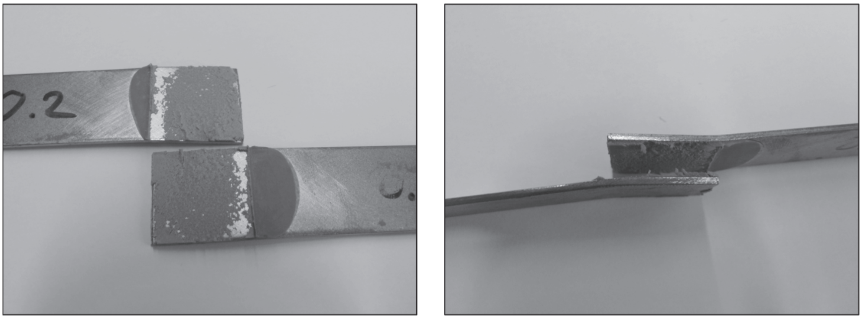


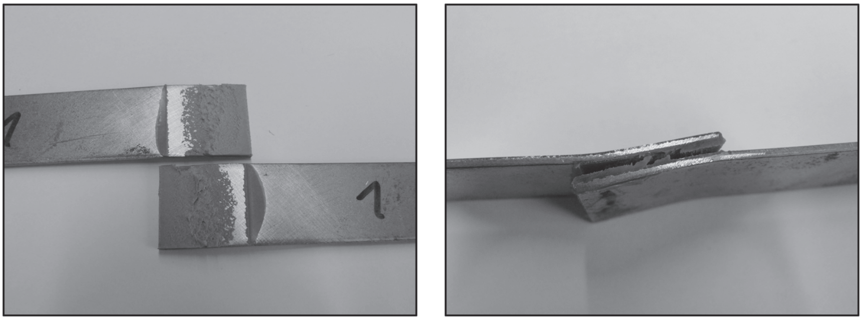
Figure 8.32 Representative load–displacement curves for the three different values of adhesive joint thickness analysed in case study 3.



(a)

(b)

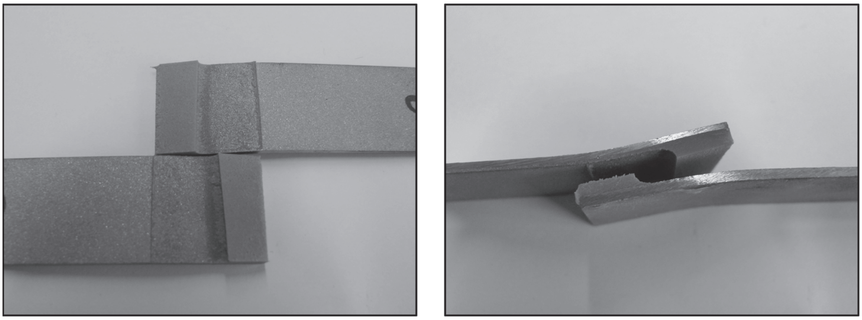
Figure 8.33 Joint fracture surfaces for 0.2 mm of adhesive layer thickness. (a) Top view. (b) Side view.



(a)

(b)

Figure 8.34 Joint fracture surfaces for 1 mm of adhesive layer thickness. (a) Top view. (b) Side view.



(a)

(b)

Figure 8.35 Joint fracture surfaces for 2 mm of adhesive layer thickness. (a) Top view. (b) Side view.

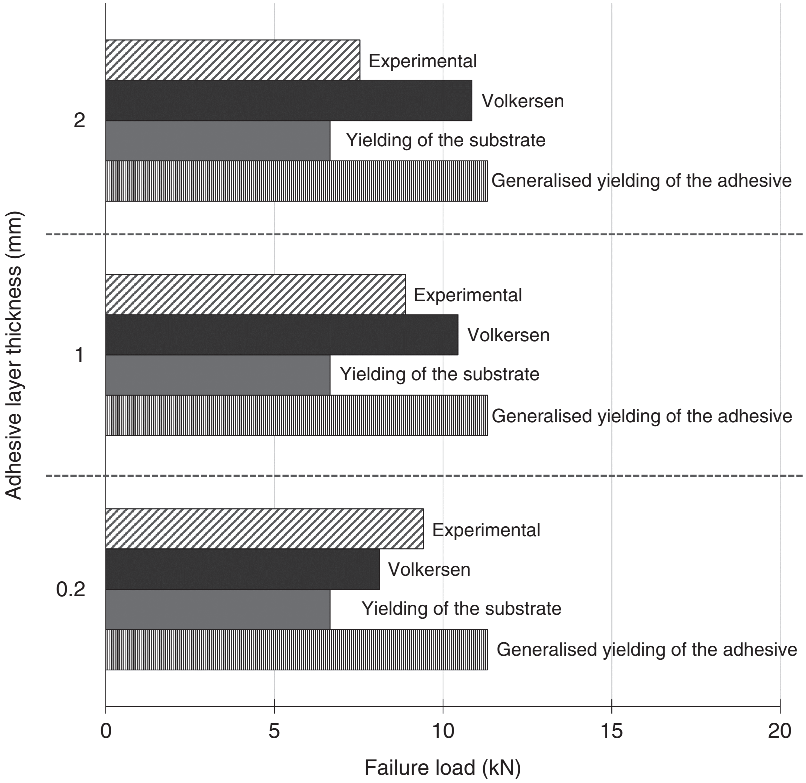


Figure 8.36 Comparison between experimental and numerical results for case study 3.

generalised yielding of the adhesive, and the yielding of the adherend. The predictions obtained with each of these models are shown in Figure 8.36, compared against the experimental data.

Yielding of the adherend is not very far from the actual results as we do have failure initiated by plastic deformation of the adherends. However, it predicts loads lower than experimental results because the value it provides corresponds to the start of the adherend yielding. In addition, the generalised yielding of the adherend criterion is also not sensitive to the adhesive thickness, therefore provides a constant result for all thicknesses.

This adhesive is extremely ductile, so there is an expectation that the adhesive generalised yield criterion will reach the correct results, but this only occurs for 0.2 mm of thickness, when the adhesive joint is at the peak of its performance. This is to be expected, as this criterion only uses the adhesive area and does not take the thickness into account.

The Volkersen criterion predicts a gradual increase in strength with an increase in adhesive thickness, but this is not verified experimentally.

In conclusion, it is not possible to analytically model the decrease in strength of an adhesive joint with increasing thickness. As we have discussed already in this chapter, this is due to various causes. Some authors propose that larger thicknesses lead to an increase in defects and voids, reducing the joint strength. The most likely explanation is related to the fact that the increased thickness leads to increased bending moments acting on the adhesive layer, creating large stress concentrations and premature failure near the interfaces, which seems to fit the fracture surfaces we have encountered in this case.

8.7.4 Case Study 4 – Strength Prediction of Adhesive Joints with Composite Adherends

As we have discussed before in this chapter, the process of designing bonded joints with composite adherends is mostly concerned with the determination of the peel loads that act on the composite layers, which allows us to determine if the joint will fail cohesively in the adhesive layer or will instead fail by delamination as the interlaminar strength of the composite is overwhelmed.

In this case study, we will analyse the mechanical performance of SLJs manufactured with composite adherends and understand how two different criteria (generalised yielding and Goland and Reissner) can be used to determine joint strength. As we will see, the use of the generalised yielding will only allow to determine the shear stresses acting on the adhesive layer, while the Goland and Reissner criterion goes further and allows to determine both the shear and the peel stresses acting on the adhesive layer, providing an insight into the peel stresses that are transferred to the composite adherend.

Two different joint configurations are studied. These are SLJs manufactured with composite adherends but bonded with two very different adhesives. One set of joints is bonded with a methacrylate adhesive, while the other uses the stiff epoxy already used in case study 1.

Figure 8.37 shows the geometry of the SLJ being tested and the materials used.

Table 8.5 provides the mechanical properties of the two adhesives used.

The composite adherends used in the joint manufacture are composed of a carbon fibre-reinforced plastic (CFRP) using an epoxy matrix. This material is supplied in

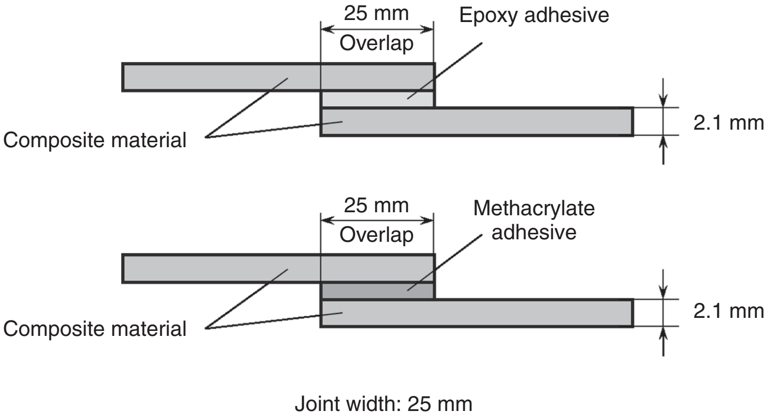


Figure 8.37 Geometry and materials of the specimens used in this case study.

Table 8.5 Mechanical properties of the adhesives used in case study 4.

Mechanical properties	Methacrylate	Epoxy
Young's modulus, E (MPa)	994	4590
Poisson's ratio, υ	0.38	0.35
Shear yield stress, τ_y (MPa)	15	34.1
Maximum shear strain, γ_f (%)	>100	5

a pre-impregnated form, where the carbon fibre reinforcement is already embedded with resin. The plates from which the adherends are cut are the result of stacking many plies of this material and curing under high pressure and temperature. To ensure that there is no interfacial failure (adhesive failure), the adherends were treated with plasma before bonding.

The properties of the CFRP material used as an adherend are provided in Table 8.6. Please note that for our work, the most important of these parameters is the strength in the transverse direction, with a cohesive strength of 55 MPa between the CFRP plies.

Please note that the properties are given in two different directions (11 and 22). In the study of composite materials, direction 11 is defined to correspond to the direction of the fibres and direction 22 corresponds to the direction perpendicular to the fibres. In practice, these are properties of the matrix as the fibres cannot contribute to this direction. You will find data for the directions, these being directions of shear, occurring between the directions 11 and 22.

The SLJ specimens were tested in a tensile testing machine until failure occurred. The failure loads and the failure mode for each of the specimen configurations are given in Figure 8.38. The specimens bonded with epoxy adhesive suffered delamination of the composite adherend, while those bonded with methacrylate failed on the adhesive layer.

It immediately becomes obvious that although the methacrylate is generally weaker than the epoxy adhesive (15 vs. 34.1 MPa of shear yield strength), it nonetheless allows for stronger joints, without failure of the composite adherend.

Table 8.6 Mechanical properties of the composite adherends used for case study 4.

Mechanical properties	CFRP
Tensile stiffness in the fibre direction, E_{11} (GPa)	130
Tensile stiffness in the transverse direction, E_{22} (GPa)	8.9
Shear stiffness, G (GPa)	4.7
Poisson's ratio, direction 12, υ_{12}	0.3
Poisson's ratio, direction 23, υ_{23}	0.02
Tensile strength in the transverse direction, σ_{22}, σ_{33} (MPa)	55

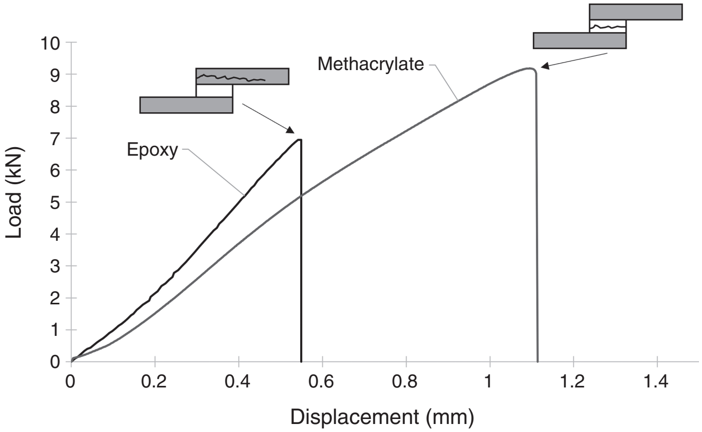


Figure 8.38 Experimentally obtained load–displacement curves for both specimens tested and the failure modes encountered.

Although quite strong, the epoxy adhesive is also very stiff and generates large peel stresses that will cause premature delamination of the composite adherend.

Since it accounts for the bending moments acting on the joint, the Goland and Reissner model can be used to provide an estimate of the peel stresses acting on an adhesive layer, which makes it especially well suited to analyse composite adherends. To better explain, let us analyse peel stress distributions for two joint configurations under consideration in this case study, determined using the Goland and Reissner criterion and the JointDesigner software. This is shown in Figure 8.39.

The peel stresses shown are those that are present at the experimentally determined failure load of each of the adhesives (9.1 kN for the methacrylate adhesive and

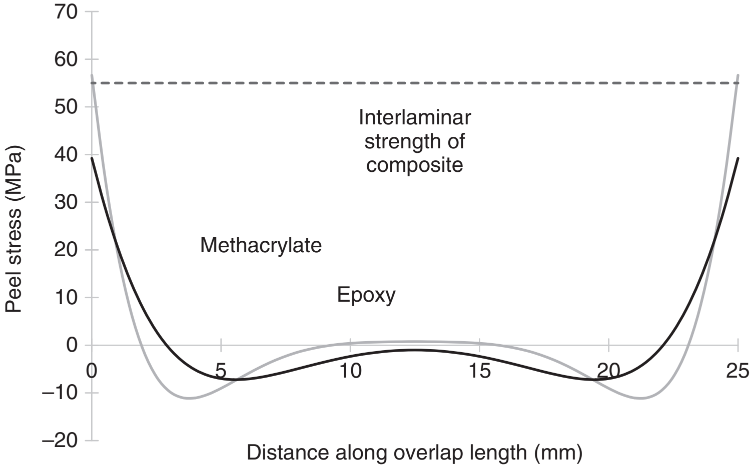


Figure 8.39 Peel stresses acting on the adhesive layer at failure, calculated with the Goland and Reissner model. Peel stresses generated by the epoxy adhesive exceed the interlaminar strength of the composite.

6.0 kN for the epoxy adhesive). These peel stresses are transferred into the upper plies of the composite adherend, and if they exceed the interlaminar strength of the composite (the dotted line superimposed over this graph), failure will inevitably occur by delamination of the composite. An analysis of the results shows that at 6.0 kN, the epoxy adhesive generates a peel stress of over 55 MPa, which corresponds to the interlaminar strength of the composite. Thus, failure in the adherend is expected to occur, and this is what was found to occur in practice.

To provide a more complete picture, a comparison between the predicted failure loads and the failure loads calculated using the three different criteria under study are shown in Figure 8.40.

The complete results clearly show that for the joints bonded with the ductile adhesive (methacrylate), failure is more precisely captured by the generalised yield criterion. For this joint configuration, an analysis of the peel loads calculated by the Goland and Reissner model estimates a failure load of almost 14 kN, which indicates that the composite will never fail as the adhesive fails much at a much lower failure load (9.1 kN).

Diverting our attention towards the case of the composite joints bonded with the stiff epoxy adhesive, the most accurate model is the Goland and Reissner model (when calculating peel stresses in the adhesive). The generalised yield criterion vastly overpredicts the failure load as it assumes that all bonded area is actively contributing to the load bearing capability of the joint, which is not possible for a stiff adhesive with its large stress concentrations at the edges of the overlap.

In summary, this case study shows that the design of bonded composite components should never overlook at least a simple analysis of the peel stresses acting on the adhesive layer because this quickly understand if there is a high likelihood of exceeding the interlaminar strength of the composite material. Although the use of

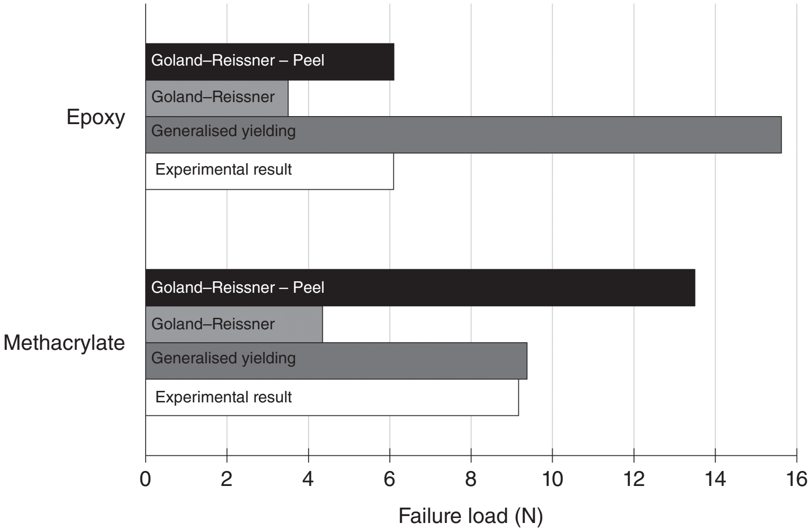


Figure 8.40 Predicted and numerical failure loads for the two adhesives under study.

a model such as the Goland and Reissner model is not always possible, as it is relatively limited to a simple SLJ geometry, a recommended approach is to use FEA packages to support joint design activities because these packages can quickly be used to extract peel stresses in practically any geometry and material combination. To that effect, the last of the case studies focuses on the use of a finite element-based analysis using cohesive elements and taking into account complex loading conditions that include not only external loads but also thermally induced stresses.

8.7.5 Case Study 5 – Strength Prediction of an SLJ with Cohesive Zone Modelling

As stated before in this chapter, CZMs are a special type of numerical model that can be used to predict the failure process of an adhesive. These models combine the strength of materials approach with a fracture mechanics approach. To use these models, commercial finite element packages, such as ABAQUS or Ansys, are often used. A geometrical model of the joint is constructed, material properties are attributed to the different elements, and the loads and other boundary conditions are applied.

In this case study, we are going to consider a model of an SLJ bonded with a stiff adhesive. We are going to consider an SLJ with 25 mm of overlap, as shown in Figure 8.41.

A two-dimensional model suffices to obtain good predictions of the mechanical performance of this type of SLJ as the main stress variations on SLJs occur in the direction of the overlap length and stresses are relatively uniform along the joint width.

After we defined the geometry, we then need to define the properties of all the materials under study. The adherends will use high-strength steel without any consideration for yielding. This indicates that only elastic properties (the stiffness and Poisson's coefficient) are necessary. However, the model for the adhesive requires the definition of two traction separation laws that will drive the cohesive element. For this epoxy adhesive, the appropriate laws are shown in Figure 8.42. The laws can be constructed in a few different ways, but the ones shown are constructed using the stiffness, the yield strength, and fracture toughness of the material, both for modes I and II.

The boundary conditions must then be applied to the mode. In this case, the boundary conditions are quite simple and represent a tensile test. As shown in

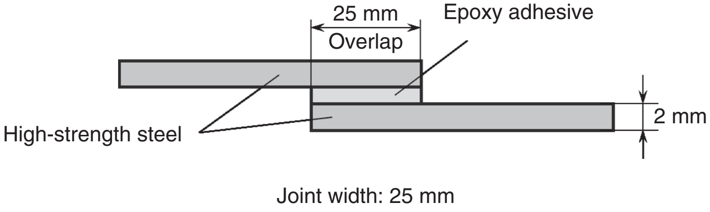


Figure 8.41 SLJ geometry considered for case study 5.

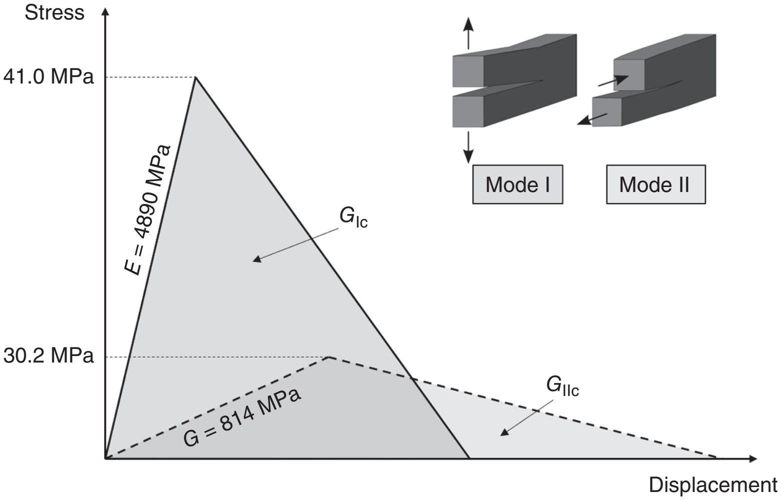


Figure 8.42 Mode I and II triangular traction separation laws used for cohesive zone modelling of an epoxy adhesive (not to scale).

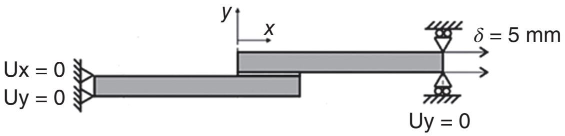


Figure 8.43 Boundary conditions used for the model construction.

Figure 8.43, one end of the joint is restrained in the x and y directions, while the opposite side is subjected to a displacement along the x direction, while movement on the y direction is restricted.

To use the model, it is also necessary to define a mesh. The mesh should be carefully constructed to ensure maximum element density near the areas where there are geometrical discontinuities, where stress concentrations will be maximum, as shown in Figure 8.44. However, it is important to stress that cohesive elements are quite insensitive to mesh size that other type of solid elements.

In this case, elastic elements are placed on the adherends and cohesive elements are placed in the adhesive layer. These cohesive elements use the material properties defined in the traction separation law and can model crack propagation.

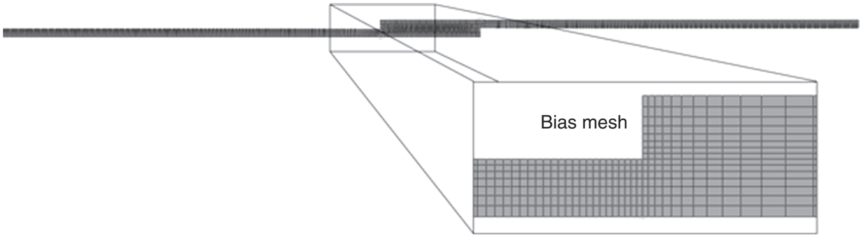


Figure 8.44 Biased mesh to minimise computational time and improve quality of the results.

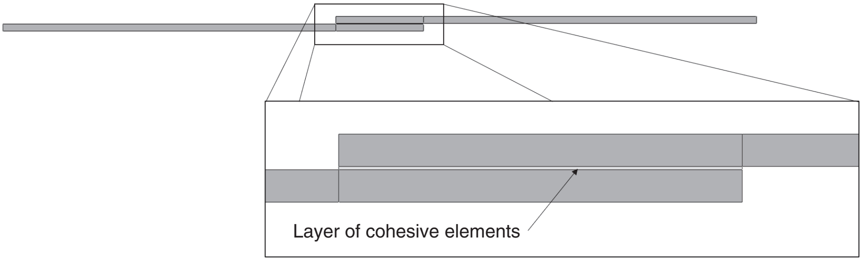


Figure 8.45 Location of cohesive elements in the numerical model of an SLJ.

In this specific model, built using the ABAQUS finite software package, cohesive elements are used to model the adhesive and elastic elements are used to model the adherends, as these do not deform plastically or become damaged. The location of the cohesive elements is given in Figure 8.45.

The predicted damage in the adhesive is visually shown in Figure 8.46. The stiffness degradation parameter is shown, where a dark grey element is undamaged and a light grey element is reaching failure (damage parameter = 1). The results show that the failure occurs first at the edges of the overlap, as we expected for an SLJ bonded with a stiff adhesive, and then progresses towards the central portion of the overlap.

To finish this analysis, we can compare the numerical and experimental load–displacement curves, as shown in Figure 8.47.

The results show that these models can accurately predict the failure load and general mechanical behaviour of an adhesive joint. The difference between the maximum load values is mainly because the finite element model is a perfect theoretical construction and does not consider the small defects and imperfections that exist on

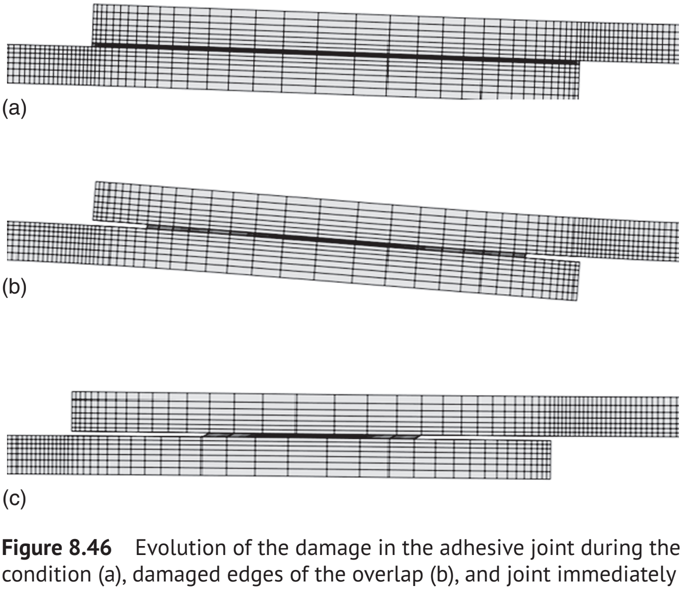


Figure 8.46 Evolution of the damage in the adhesive joint during the test. Undamaged condition (a), damaged edges of the overlap (b), and joint immediately before failure (c).

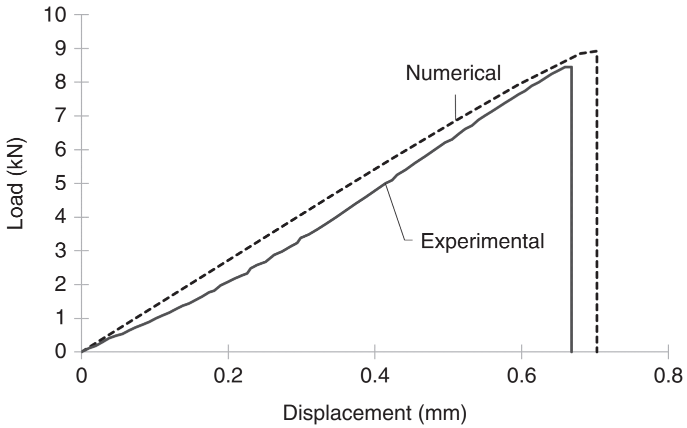


Figure 8.47 Comparison between numerical and experimental load–displacement curves.

an actual specimen. However, it must be noted that this model, which uses the triangular cohesive zone law, is better suited for stiff adhesives than for ductile adhesives. For ductile materials, it is advisable to explore the use of other types of cohesive laws that better capture the plastic deformation typical of the yielding phase, as is the case of the trapezoidal law.

8.7.6 Case Study 6 – Effect of Thermal Stresses on Adhesive Joints

FEA of adhesive joints can allow us to go further than simple static strength analysis, as we can explore more complex loadings acting on the joint. One of the most important of these loadings is the thermal stresses induced during joint curing. If excessive, these stresses can damage the adhesive layer even before it is loaded. However, in other cases, these stresses can be beneficial to the joint, if they act in a direction that is opposite to the stresses that the load introduces in the joint. The intensity of the thermal stresses is mainly a function of the dissimilarity between the coefficients of thermal expansion of the adherends. Adherends of similar coefficients of thermal expansion will expand or contract to the same degree, minimising the stresses acting on the joint. However, in joints where the adherends have markedly different coefficients of thermal expansion, the adhesive can be subjected to large thermal stresses as the adherends contract or expand differently.

In this example, we will introduce thermal stresses on a joint with a steel and a composite adherend bonded with a crash-resistant, epoxy-based adhesive that cures at the relatively high temperature of 150 °C. The properties of the adhesive are given in Table 8.7. The behaviour of the adhesive is also reproduced using a CZM to ensure that the damage induced by the thermal stresses and/or mechanical loads can be fully captured.

The materials used in this example have very different coefficients of thermal expansion. For steel, the coefficient of thermal expansion is of $1.2 \times 10^{-5}\ {}^\circ\mathrm{C}^{-1}$, while the composite has a coefficient of thermal expansion that can be assumed to be near zero in the fibre direction. Figure 8.48 shows the geometrical and material configuration considered for this case study.

Table 8.7 Mechanical properties of the adhesive used in case study 6.

Mechanical properties	Crash-resistant epoxy
Young's modulus, E (MPa)	2270
Poisson's ratio, υ	0.33
Shear yield stress, τ_y (MPa)	34.1
Maximum shear strain, γ_f (%)	>20
Coefficient of thermal expansion (°C^{-1})	2.6×10^{-8}

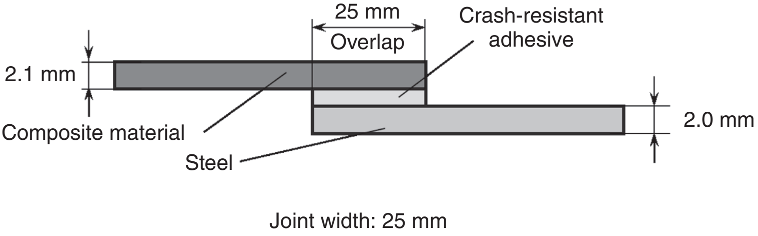


Figure 8.48 SLJ geometry and materials considered for case study 6.

In this example, thermal stresses are generated as the joint cools from the curing temperature (around 150 °C) to the ambient temperature (around 20 °C). This adhesive hardens at a relatively high temperature, which creates significant thermal stresses on the adhesive as the adherends must contract more. This effect can be introduced in the model by creating a new analysis step prior the introduction of any static loading, where all the materials that comprise the joint are subjected to a temperature variation of −130 °C. The two steps and the respective boundary conditions are schematically shown in Figure 8.49.

The shape of the deformed adhesive layer (in exaggerated scale) is shown in Figure 8.50. The contraction of the upper part of the adhesive layer (bonded to the steel adherend) is evident.

The resulting shear stress acting on the adhesive layer in shown in Figure 8.51, calculated using FEA with the ABAQUS software.

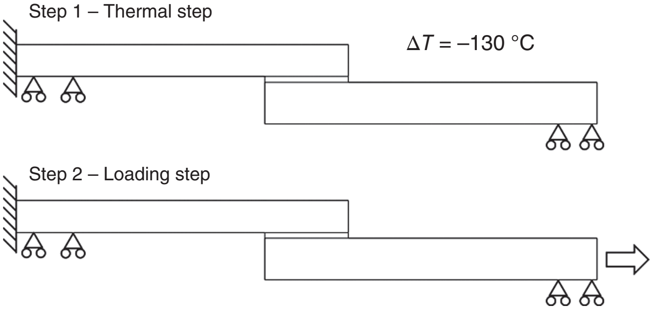


Figure 8.49 Thermal and mechanical boundary conditions applied to the joint in a two-step approach.

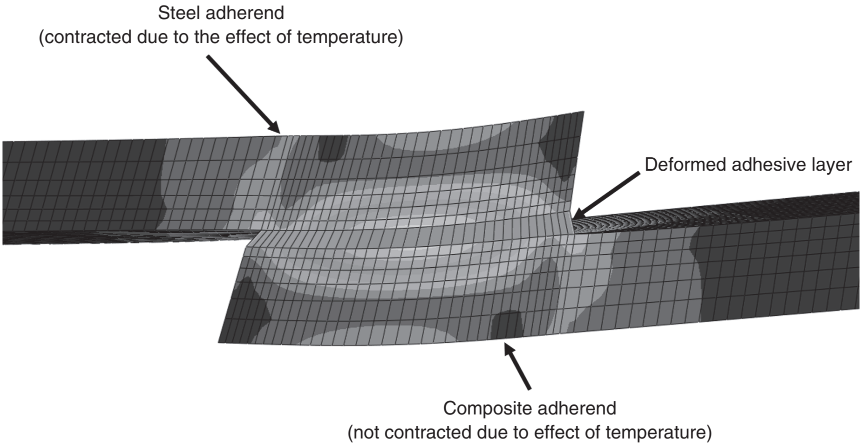


Figure 8.50 Deformed shape of the adherends and the adhesive layer due to effect of the thermal stresses.

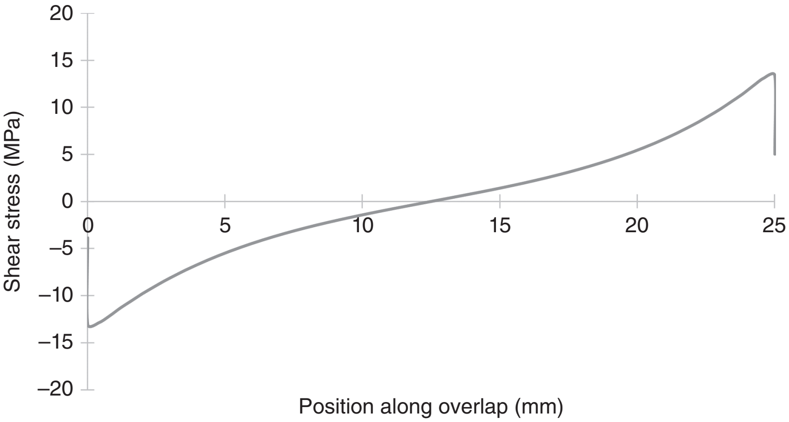


Figure 8.51 Distribution of the thermally induced shear stresses acting on the adhesive layer.

This result shows that simply cooling a bonded joint from the cure temperature of the adhesive to ambient temperature can induce up to 15 MPa of shear stress in the adhesive layer. However, in this case, this does cause permanent damage to the adhesive nor to the specimen, as both are sufficiently strong to withstand this level of loading. Also of note is the fact that as the adherends contract during cooling, the adhesive is drawn towards the centre of the joint by the adherends. The further away from the centre of the joint, the larger the shear stresses. As we know, this corresponds to the critical points of stress concentration, which can exacerbate the effect of the thermal stresses.

As the joint is mechanically loaded (Step 2 in Figure 8.49), the thermally induced shear stresses will gradually overwhelm the shear stressed induced by this loading. Figure 8.52 shows the gradual evolution of the shear stresses as the joint is being

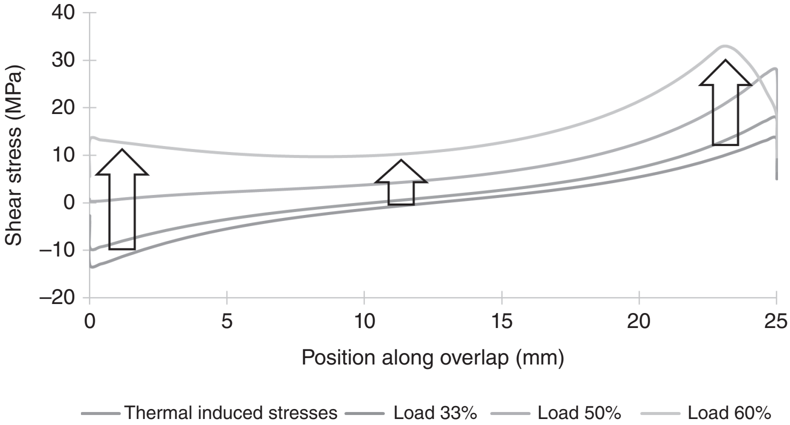


Figure 8.52 Gradual evolution of the shear stresses acting on the adhesive layer, highlighting the combined contribution from thermally and mechanically induced stresses.

loaded. Here, it becomes clear how the negative thermally induced shear stresses present on the left side of the joint can help reduce the loads felt there. However, on the other side of the joint, the opposite effect is true. The peak shear stresses acting on that side of the joint are increased as they correspond to the sum of the installed thermal stresses and those induced by the mechanical loading.

If we observe the evolution of the cohesive damage parameter (the stiffness degradation), shown in Figure 8.53, we will see that the damage (dark grey) initiates on the side of the joint where the thermally induced stresses are superimposed to those resulting from the mechanical load. It is also evident that the opposite side of the joint remains completely undamaged.

To conclude, we can compare the numerical load–displacement curve obtained with this model, including the effect of the thermal stresses, as shown in Figure 8.54.

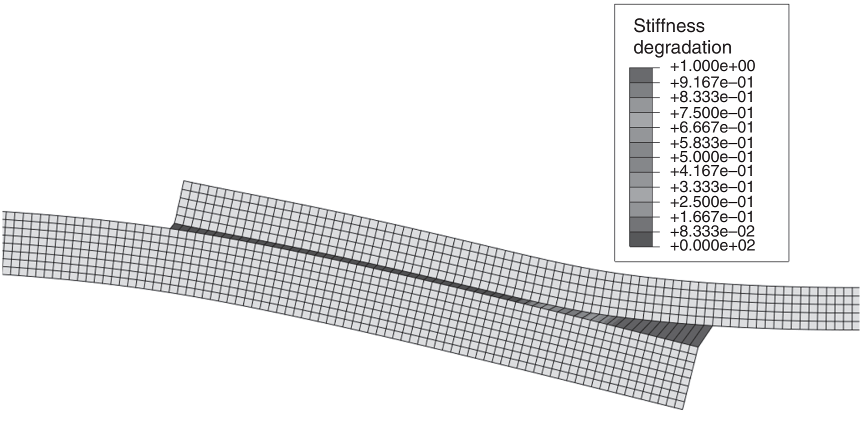


Figure 8.53 Damage evolution (stiffness degradation of the cohesive element) in the adhesive layer, showing damage initiation on the edge of the overlap where there is a combination of mechanically and thermally induced stresses.

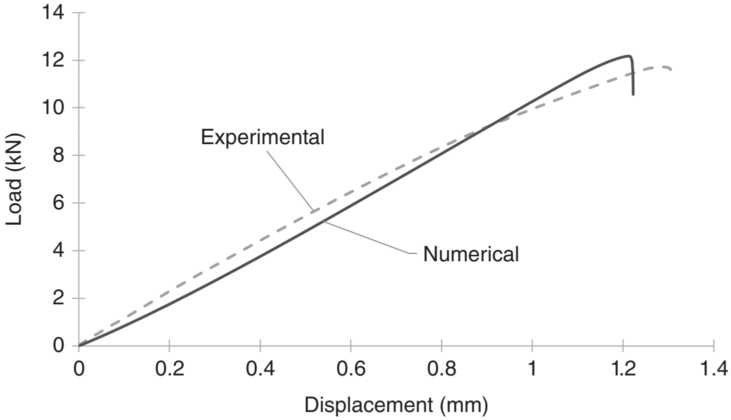


Figure 8.54 Experimental and numerical load–displacement curves obtained for the composite–steel joints subjected to thermal stresses.

The numerical model can satisfactorily capture the performance of this joint, cured at very high temperature and using adherends with highly distinct coefficients of thermal expansion.

To summarise, this case study shows that the influence of the thermal stresses on bonded joint should not be discounted as it has the potential to cause damage in two different moments in the joint life. The first is immediately after curing, where the thermal stresses caused by the contraction of the adherend materials have the potential to reach levels that can immediately fracture the joint. The second of these moments is during service, where the joint is being mechanically loaded. In this case, locked in thermal stresses can add to the stresses generated by the service loads and add to them, leading to premature joint failure. It is the task of the joint designer to anticipate the presence of these stresses and take measures to include them in the relevant joint design calculations.

9

Durability of Adhesively Bonded Joints

At this stage of this book, you should already be comfortable with the basic principles and concepts behind the design of an adhesive joint. You should even understand how the stresses are generated in a joint and how the different material responses control the joint strength. However, note that these design methodologies are mainly oriented towards the static strength of the joint, immediately after manufacture and hardening. What happens if you take your newly manufactured joint, and instead of testing it, you expose it to harsh environmental conditions, such as high moisture levels and temperatures, for long periods of time? And what if we load this joint under long-lasting cyclic loads? Can we even predict joint performance under these conditions? The truth is that these complex loading and environmental conditions can lead to an important degradation of the mechanical properties of the adhesives, and this will have a significant impact in the joint strength, which can ultimately lead to premature joint failure. It is thus very important to consider the degradation process to guarantee that the joint will not fail in service. As a result, designers should be able to know for how long the adhesive joint can withstand the service environmental and loading conditions without failure. To answer this question, a durability analysis should be conducted on the joints. Durability analysis determines the life of adhesive joints considering the service conditions.

Different test procedures exist for durability analysis of adhesive materials. As it was mentioned earlier, the properties of the adhesives change during service when they are subjected to cyclic loading (fatigue) or steady long-term loads (creep). The environment can also affect the mechanical response of the joints, with humidity and extreme temperatures being the two most important parameters that govern the behaviour of the adhesives.

To analyse the durability of joints under service conditions, standard test procedures are usually conducted at laboratory level. Fatigue and creep are categorised as loading conditions and the humidity and temperature are classified as environmental parameters. The durability of joints can be separately analysed in terms of the parameters of each group to simplify the process, but in practice, most joints will experience a combination of demanding loading and ambient conditions.

In this chapter, you will learn about the different testing approaches that are suitable for durability analysis of adhesive joints. First, we will look at durability from

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Eduardo André Sousa Marques, Ana Sofia Queirós Ferreira Barbosa, Ricardo Joao Camilo Carbas, Alireza Akhavan-Safar, and Lucas Filipe Martins da Silva.

the perspective of the environmental conditions, where the effects of humidity and temperature are studied. In the second part, we will discuss the effects of loading conditions, including fatigue and creep, on the durability of adhesively bonded structures.

9.1 Environmental Effects

9.1.1 Hygrothermal Ageing

Adhesives are permeable materials, and water will ingress into them if an adhesive joint is kept in a wet environment for a long period of time. It is known that the level of water that is present in the adhesive layer increases proportionally with time. Water molecules within the adhesive layer will bind with the polymer chains of the adhesive or, in another phenomenon, occupy the free spaces of the adhesive (see Figure 9.1). However, after a specific time, the joint will reach the saturation condition where the water will no longer penetrate into the adhesive layer.

It is very important for us to understand this phenomenon because the presence of water in the adhesive will have an important effect on its properties. Because of the water diffusion, the adhesive will experience swelling and plasticisation. Swelling is the increase in volume of the adhesive layer and plasticisation is a phenomenon in which the adhesive becomes more flexible. Both phenomena are undesirable because they cause degradation of the adhesive joint performance. To analyse the durability of the joint in wet environments, the rate of water diffusion into the adhesive layer should first be calculated. This step is normally carried out with a set of experimental and numerical procedures. Typically, the experimental part is done using plates of adhesive immersed in water and weighed regularly. By registering the weight increase as a function of time, we can understand the

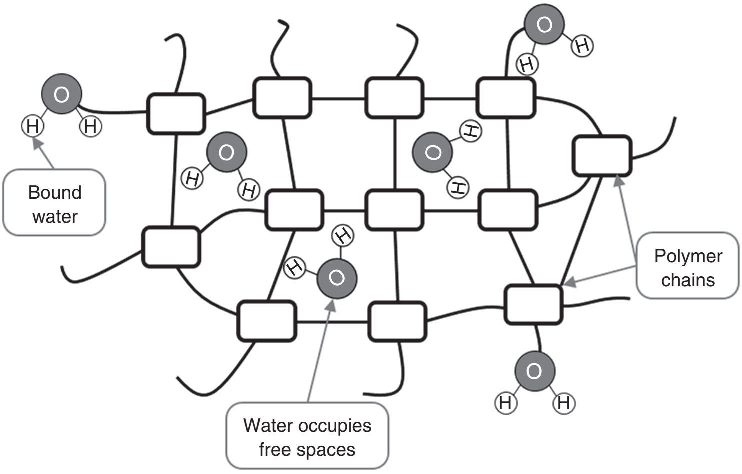


Figure 9.1 Schematic representation of the two different water absorption processes.

water absorption process. The specimens used for this procedure are usually based on ISO/DIS 294-3 standard, corresponding to a 60 mm by a 60 mm plate with a thickness of 1 mm.

Before the ageing process begins, a pre-drying step is usually performed. In the pre-drying process, the sample is exposed to a dried environment for a few days. In subsequent numerical analysis, it can then be assumed that no water exists in the adhesive plate in its initial condition. However, the pre-drying step should be carried out at a temperature below the glass transition temperature (T_g) of the adhesive. After pre-drying, the water diffusion process starts by exposing the sample to a wet/humid environment. Ageing is usually a long-term process, and to accelerate it, the samples are usually maintained in a wet environment but at an elevated temperature using an environmental chamber. Figure 9.2 shows a schematic of the process, showing an adhesive plate immersed in water where the water is maintained at high temperature.

At specific time intervals, the weight of the plate should be measured to calculate the amount of water uptake. To do this, you should check the current weight of the plate when it has experienced ageing for a specific time (we can call it w_t). Then, subtract its initial weight (let us call it w_0). By dividing the result by the initial weight, the fractional mass uptake is obtained, which we can call M_t. This process should be repeated at different times (days) until the changes in M_t are almost negligible with time. In these conditions, we say that the plate is saturated.

By plotting the M_t as a function of time, the rate of water uptake into the adhesive is obtained, which is schematically shown in Figure 9.3. Different environments (e.g. distilled water, salt water, acid, etc.) will show different rates of ingress for the same adhesive.

As shown in Figure 9.3, the typical rate of water uptake is higher during the initial stages of the ageing process. During this initial stage, it is crucial to measure the mass of the plate for short-time intervals. These initial data points are used for measuring a set of key parameters necessary for establishing a law that describes the water uptake process, called Fick's law in honour of its creator, Adolf Fick. Fick's

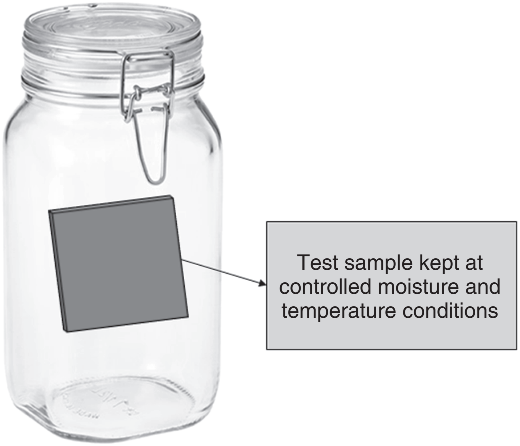


Figure 9.2 Test sample immersed in water maintained at high temperature during the ageing.

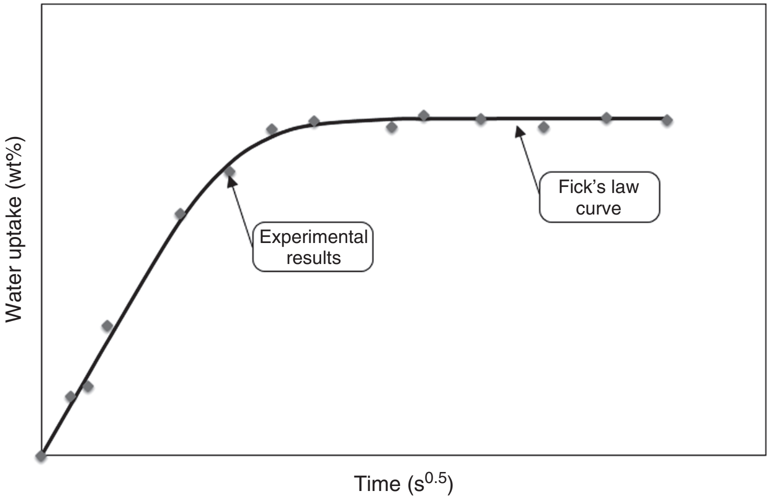


Figure 9.3 Fick's law curve and the experimental data point for an adhesive immersed in water.

law is a relation (see Eq. (9.1)) that describes the water absorption and desorption behaviour of adhesives exposed to a wet environment.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{9.1}$$

where c is the concentration of water, t is time, and D is the diffusion coefficient. In Eq. (9.1), $\frac{\partial c}{\partial t}$ is the rate of change in water concentration in adhesive (as a function of time), which is proportional to $\frac{\partial^2 c}{\partial x^2}$, which is the second derivative of the water concentration as a function of distance. According to Fick's law (Eq. (9.1)), when an adhesive is in a humid environment, the water concentration (c) within the adhesive layer increases with time. According to this equation, the change in water concentration $\left(\frac{\partial c}{\partial t}\right)$ is proportional to the change in the gradient of the water concentration along the x direction $\left(\frac{\partial^2 c}{\partial x^2}\right)$.

Fick's law is a partial differential equation proposed for one-dimensional problems. Simply put, this indicates that the water diffusion is supposed to take place within the sample along a single direction (e.g. only along the thickness of the specimen). That is the reason why a thin plate with a thickness of 1 mm should be used for the experimental procedure.

Using the experimental data and knowing the amount of water uptake at saturation condition, the diffusion coefficient (D) can then be obtained. D corresponds to the initial slope of the water uptake curve and is calculated using Eq. (9.2). In Eq. (9.2), the value of the water uptake at two different times (t_1 and t_2) is considered for obtaining the D value. M_t is already defined as the amount of water uptake at time t and M_∞ is the fractional mass uptake when the sample is saturated.

$$D = \frac{\pi}{16}\left(\frac{d\,(M_2 - M_1)}{M_\infty(\sqrt{t_2} - \sqrt{t_1})}\right)^2 \tag{9.2}$$

To calculate this, two points from the initial part of the ageing process (the linear part in Figure 9.3) should be selected and, by taking into account Fick's law relations, the rate of water uptake for the adhesive can be obtained. For more information about Fick's law relations, you can review the suggested documents listed at the end of this book.

By knowing the *D* value, one can numerically analyse the level of water uptake for the real joints at different service times. Then, as the properties of the adhesive are a function of the water present in it, it becomes possible to numerically estimate the performance of aged bonded structures.

The desorption process is also an important step in ageing analysis of the joints, with similarities to the water absorption process. As you might recall from the beginning of this chapter, water is absorbed into the adhesives in two different ways. One is the water that occupies free spaces in the material and the other is the bound water (see Figure 9.1). Accordingly, adhesive experiences two different ageing phenomena. The first one is called physical ageing that corresponds to the water molecules that occupy the free spaces. Because of the desorption process, the water that has occupied the free spaces will evaporate. Consequently, adhesive properties that have been degraded because of the physical ageing will be almost fully recovered after drying. However, the second ageing phenomenon is the chemical (hydrolysis) ageing that corresponds to the bound water. Water molecules absorbed as bound water usually remain in the material even after drying. Therefore, the degradation of the properties associated with the chemical ageing will not be recovered after drying.

The desorption process can also be modelled using Fick's law, allowing the extraction of a value of *D*. However, note that the desorption process is much faster than the absorption procedure and, to precisely measure the *D* value for the desorption stage, the time intervals between the measurements should be much shorter (e.g. every two hours for the first day). For the desorption process, the sample should be maintained in a dry environment. A suitable dry environment for these tests is similar to that used in the pre-drying procedures.

The specific case of ageing in saltwater is quite interesting and deserves special attention. In this case, because of the presence of chloride and sodium elements, the rate of the diffusion coefficient is much lower than that encountered for pure or distilled water. Chloride and sodium are too big to easily enter the adhesive and will stick to the outer surface of the sample and block the path of water molecules to diffuse within the adhesive. Consequently, the fractional mass of water at saturation is noticeably lower for salt water.

As shown in Figure 9.4, after desorption, a big drop in the fractional mass of water is observed for the adhesive aged in distilled water. However, for the adhesive aged in salt water, a small reduction is found during the drying process. This difference in desorption process can be explained by the presence of chloride and the sodium elements at outer surfaces of the specimen. These elements are located on the outer surface of the adhesive and block the water within the sample and consequently do not allow the water molecules to easily evaporate.

These tests can also be done for different liquids that can be absorbed by the adhesive material. For example, Figure 9.4 shows the uptake of three different types of fluids by an adhesive.

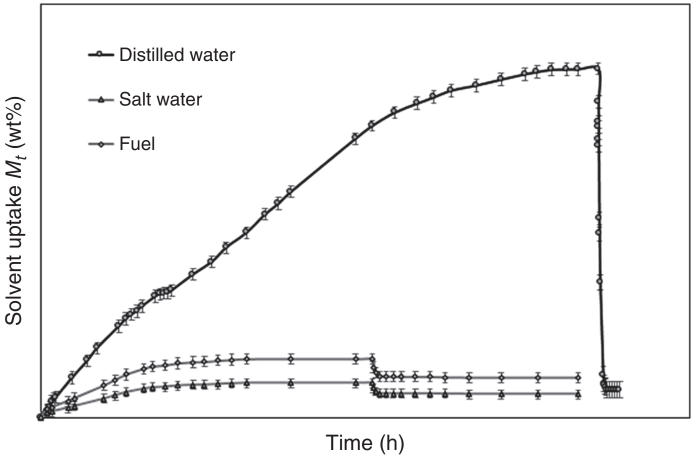


Figure 9.4 Water absorption and desorption (drying) of an adhesive immersed in distilled water, salt water, and fuel.

As mentioned above, the chemical structure of the adhesive can also change because of ageing. To analyse the changes in the structure of the joint because of the ageing process, a powerful technique called Fourier transform infrared spectroscopy (FTIR) can be employed. This technique is explained in Chapter 6.

Until now, we have discussed the ageing process as a single cycle of water absorption and desorption. However, it is evident that in real-world applications, joints are most likely to experience many ageing cycles. This indicates that the adhesive will absorb and desorb the water several times during service. Accordingly, it is important to analyse the ageing behaviour of the adhesive materials when they are subjected to repeated absorption–desorption processes. According to these studies, the adhesive will show different coefficients of diffusion for different cycles, with the rate of water uptake increasing as the number of ageing cycles increases. This indicates that for real applications where the service environment is cyclic, performing a cyclic ageing test is highly recommended to precisely evaluate the long-term durability of the joints.

Bound water causes dimensional expansion of the adhesive called swelling. To analyse the effect of water diffusion on the swelling, the dimensional expansion of the specimen should also be measured during the ageing process. Swelling can be easily measured using a precise measuring instrument such as a micrometre or a laser sensor. Similarly, to the water absorption process, the rate of swelling is higher at the initial stage of the ageing process, but it eventually reaches a steady state after a specific time has passed.

Paralleling the plasticisation process, swelling can also change the durability of the adhesively bonded structures by inducing stresses in the adhesive layer. This is because when the adhesive layer swells but is restricted between the substrates, it is not allowed to expand. This restricted swelling induces important stresses within the adhesive layer, even when no external load is applied to the joint, reducing the

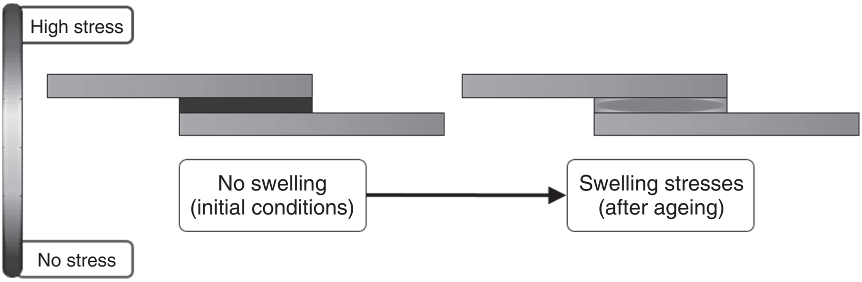


Figure 9.5 Schematic representation of the effect of swelling stresses on the stress level in adhesive joints.

service life. Figure 9.5 schematically shows the effect of swelling stresses on the stress level in adhesive joints.

Durability of the aged adhesives and adhesive joints can be analysed using the same mechanical tests already explained in Chapter 4. The durability tests include the strength tests and the fracture mechanics experiments. Dogbone specimens are used to evaluate the tensile durability of the aged adhesives. Likewise, thick adherend shear test (TAST) or Arcan testing can be conducted to analyse the shear properties of the aged adhesives. Fracture mechanics tests using double cantilever beam (DCB) and end notch flexure (ENF) specimens also allow us to analyse the effect of ageing on fracture energy of the adhesives. These testing procedures follow the practices already discussed in Chapter 4, with the only difference being the ageing process that the specimens must undergo before testing. Using these methodologies, many authors have investigated the effect of ageing on durability of adhesives. The consensus is that ageing can significantly decrease the stiffness and the tensile strength of adhesives. The effect of ageing on tensile strength of an adhesive is shown in Figure 9.6. Ageing decreases the strength of the joints, but its ductility increases unless the adhesive experiences a significant degradation,

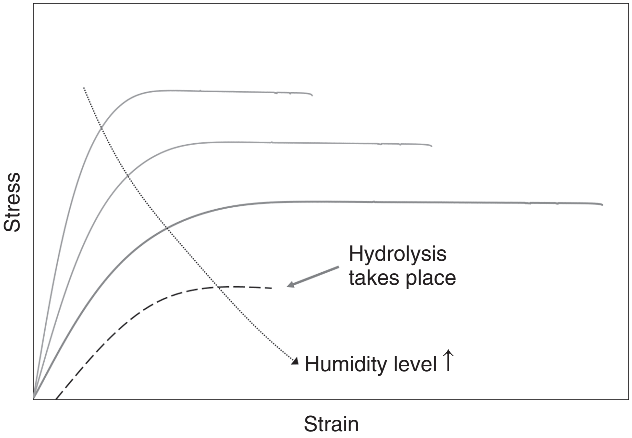


Figure 9.6 Effect of hygrothermal ageing on the tensile strength of adhesives.

as shown by the dashed curve in Figure 9.6. As mentioned before, degradation of the properties because of the physical ageing is recoverable by drying the sample. However, degradation because of the chemical (hydrolysis) ageing is not recoverable.

The effect of ageing in fracture energy is a more nuanced subject, as this parameter is a function of both the strength and the elongation of the material. As stated before, ageing decreases the strength of the joints but its ductility increases unless in the case of significant degradation where the adhesive properties are not recoverable even after drying. Therefore, depending on the level of strength and elongation exhibited by the aged sample, the fracture energy may decrease or it can even increase.

Until now, we have thought of an aged adhesive a solid block of material that reacts to the water independently. However, when an adhesive is in a joint, the water diffusion is faster through the interface between the adhesive and the adherend, as it provides a path for the moisture to travel more freely. The interface of the adhesive and adherend experiences higher degree of degradation and the failure mode may change from cohesive failure (failure through the adhesive layer) to the adhesive failure (failure through the interface) that, as we have repeatedly seen throughout this book, drastically reduces the strength of the joint.

Although most of the studies have dealt with the ageing process of adhesive materials using unloaded joints, it has been found that the rate of water diffusion in stressed samples is significantly higher than the unstressed joints. In practice, joints experience a combination of stress and wet environment conditions. Accordingly, it is necessary to analyse the durability of stressed joints subjected to wet environments. Dogbone or standard joint configurations aged in wet environments for a specific duration of time can be tested for durability assessment of the stressed adhesives subjected to wet environments.

9.1.2 Temperature

At this stage, you are certainly aware that not only moisture is damaging for the durability of adhesives, as temperature also plays a significant role. However, please note that the durability of adhesives at high temperatures is strongly dependent on the adhesive type. As it was already discussed in Chapter 4, thermoset and thermoplastic are the two main groups of adhesives with different susceptibilities to temperature. Although thermoplastic adhesives are usually suitable for room temperature services, their stiffness and strength severely decrease at elevated temperatures. In these conditions, thermoset adhesives are the only suitable option.

Exposure to high temperature affects the properties of the adhesives by increasing the mobility of the polymer chains. In addition, the volume of the adhesives and the adherends expands with temperature, inducing residual stresses and strains at elevated temperatures. This has a major influence on the strength of the joints, especially for joints with dissimilar adherends as we have seen in Chapter 8.

In some cases, a short exposure to high temperature can increase the strength of the joint because of the post-hardening phenomenon, but in most applications, the durability of the joints is significantly decreased by increasing its service temperature. At high temperature, the stiffness and the strength of the adhesive decreases and the elongation of the specimen at failure usually increases (see Figure 9.7). Accordingly, fracture energy (a function of both the elongation and the strength) can

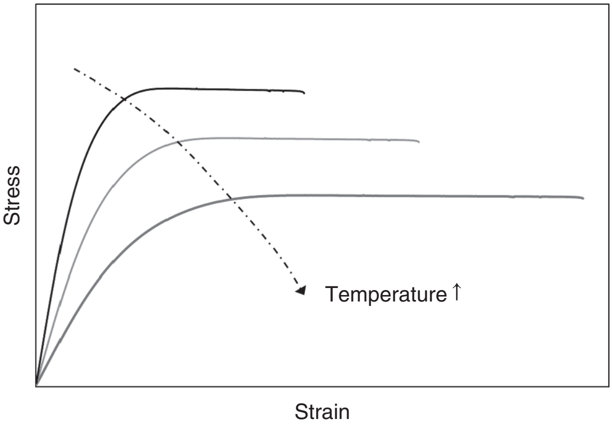


Figure 9.7 Effect of temperature on the stress–strain response of adhesives.

remain almost constant for some adhesives when the temperature rises. However, in these adhesives, any further increase in temperature (specifically for the temperatures higher than the T_g of the adhesive) will lead to severe degradation of its chemical structure and inevitably cause a drastic reduction in the fracture energy.

The effect of service temperature on the performance and durability of adhesives can be assessed with suitable strength and fracture mechanics tests. The geometry and dimensions of the test specimens as well as the testing procedures have been already discussed in Chapter 4.

By knowing the properties of the adhesive as a function of the different environmental conditions (mainly the humidity and temperature) and by defining the properties of the adhesive as a function of the ambient conditions, one will be able to estimate the durability of the bonded structures using numerical tools. To achieve this, the properties of the material (such as the stiffness, strength, and toughness) should be defined as a function of temperature and the ageing level in a suitable material model. The simulation results help the joint designers to get an estimation of the service life of the adhesive joint.

However, it should be noted that besides the temperature (and moisture), there are many other parameters that can change the performance and durability of an adhesive and adhesive joint. Surface preparation techniques, the joint geometry, and substrate materials are part of these parameters. Thus, the results obtained with these standard procedures cannot cover all conditions and one must exert care when designing a test procedure intended to determine the effect of given environmental conditions.

9.2 Loading Conditions

9.2.1 Fatigue

In most industrial applications, adhesive joints experience cyclic loading where the applied loads are not constant with time. The damage mechanism associated with this loading type is called fatigue and different types of fatigue loadings exist.

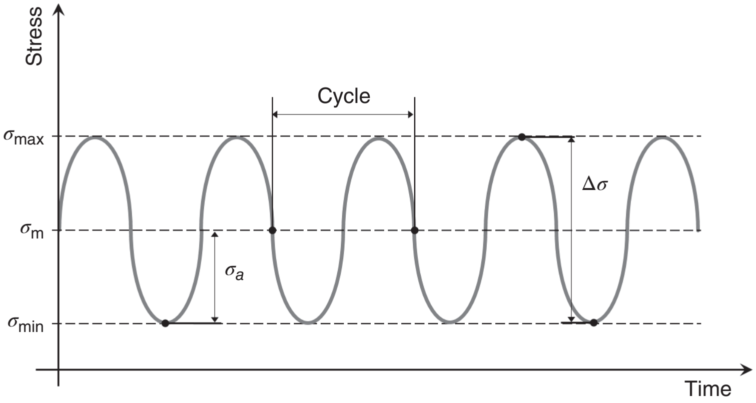


Figure 9.8 A typical sinusoidal fatigue loading.

Figure 9.8 shows a typical sinusoidal fatigue loading that is the most commonly used for fatigue analysis of adhesive joints. The distance between the two peaks, shown in Figure 9.8, is called a load cycle. To define a loading cycle, several parameters shown in Figure 9.8 should be determined. Maximum and minimum loads at each cycle are the most important parameters. By knowing the maximum and minimum loads, the average load (σ_m), loading range ($\Delta\sigma$), and the loading amplitude (σ_a) can be defined using Eqs. (9.3)–(9.6). The ratio of the minimum load to the maximum load is also an important parameter called R ratio. The loading frequency is also a critical parameter defined as the number of cycles per second.

$$\Delta\sigma = \sigma_{\max} - \sigma_{\min} \tag{9.3}$$

$$\sigma_a = \frac{\sigma_{\max} - \sigma_{\min}}{2} \tag{9.4}$$

$$\sigma_m = \frac{\sigma_{\max} + \sigma_{\min}}{2} \tag{9.5}$$

$$R = \frac{\sigma_{\min}}{\sigma_{\max}} \tag{9.6}$$

Although most of the fatigue analyses are carried out using sinusoidal fatigue loading with a constant amplitude, in real-world applications, the loading amplitude is not constant cycle by cycle. This type of loading is called a variable amplitude fatigue loading. A typical variable amplitude fatigue loading is shown in Figure 9.9.

When an adhesive joint is subjected to a cyclic loading, the mechanical properties of the adhesive degrade cycle by cycle, which finally leads to joint failure. This phenomenon is called fatigue failure. In fatigue failure, a joint usually fails at a load level much lower than its own static strength. The total fatigue life of the joint is a function of the loading conditions described above and is also a function of the adhesive properties. With the same R ratio, for higher load levels, the life is shorter and by decreasing the load level, the fatigue life increases.

When a joint is subjected to fatigue loading, damage initiates within the specimen after a specific number of load cycles has passed. Then, by continuing the cyclic

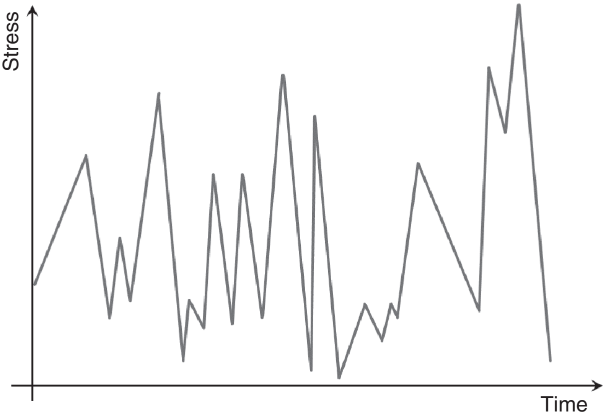


Figure 9.9 Schematic of a variable amplitude fatigue loading.

loading, damage will propagate within the adhesive layer until the final failure of the joint. Accordingly, the total fatigue life of a joint is categorised into two stages: first the fatigue damage initiation and the second the fatigue damage propagation. Depending on the stress condition and the material properties, in some cases, the damage initiation life governs the total fatigue life of a joint. In this condition, the damage propagation is very fast. For this type of joint, the fatigue initiation life is usually considered at the total fatigue life of the joint. On the other hand, there are some loading and material conditions in which the total life is mainly spent in the second fatigue stage, which corresponds to the fatigue crack propagation.

In this section, we will discuss the issue of the fatigue durability of the joints subjected to fatigue loading under two different approaches. These are the total fatigue life evaluation and the fatigue crack growth analysis (see Eq. (9.7)).

$$\text{Total fatigue life } (N_T) = \text{Crack initiation life } (N_i) + \text{Crack propagation life } (N_p) \tag{9.7}$$

We will start our analysis by looking at the total fatigue life approach.

9.2.1.1 Total Fatigue Life (S–N) Approach

When the crack propagation life is very short compared to the total fatigue life (for example, for brittle adhesives), the fatigue initiation is usually considered as the total fatigue life of the joints. In a total fatigue life analysis, the specimen is subjected to cyclic loads, and the testing will continue until failure of the sample occurs. The test procedure is repeated many times under different load levels, allowing us to understand the effect of the load (or stress) level on the life. To analyse the relationship between the applied load and the corresponding fatigue life, the fatigue life should be plotted against the applied load (stress) in a logarithmic scale diagram. This curve is called the S–N (stress–life) curve that is typically shown in Figure 9.10. The S–N diagram gives helpful information to design joints that are susceptible to fatigue damage.

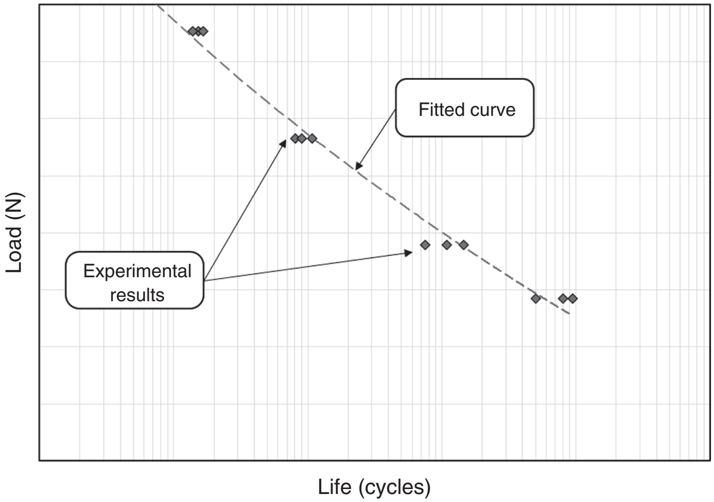


Figure 9.10 A typical S–N curve.

To analyse the durability to fatigue of joints in terms of the total fatigue life, the S–N curve should be first experimentally obtained. To achieve this, two different strategies can be followed. The first strategy is the direct method where a practical, real joint is tested under different load levels. This strategy is recommended for joints to be used in critical applications. No extra post-processing or numerical analysis is usually needed in this strategy. The results are highly reliable as the real joint is tested in real loading conditions. However, this strategy is costly and the obtained experimental results are limited to the tested configuration and the considered loading conditions. Additionally, real joints are often complex in terms of geometry and, in some cases, are often too large to be tested using commercial testing equipment. Furthermore, in some applications, the real loads are biaxial or multiaxial, which is also difficult to test. Because of these limitations, a second strategy is usually preferred by designers. In the second strategy, known as the indirect method, simple joint geometries (instead of the real joint) are fatigue tested at different load levels and under different mode mixities. The Arcan joint is one of these simple geometries that has been considered by designers.

Arcan joints are used to analyse the durability of the adhesives in terms of fatigue loadings. The use of Arcan specimens enables us to simply vary the loading angle by rotating the Arcan device and thus simulate the real loading conditions. Using the test results at different loading angles, it will be possible to simulate the life of a real joint.

By rotating the Arcan device (previously described in Chapter 4), the mode mixity can be simply changed from pure mode I to pure mode II. For each mode mixity, Arcan joints should be tested at different load levels to construct the S–N curves. Arcan results can give useful information about the effect of stress level on the total fatigue life of adhesives for specific mode mixities. However, in practical applications, the adhesive layer usually experiences a complex mode mixity and the load is usually multiaxial. Therefore, the obtained Arcan S–N results cannot be directly used for durability analysis of the real joints.

To be able to use the Arcan fatigue data for the life assessment of real joints, a master curve should be first constructed using the Arcan S–N data. The master curve is a single S–N curve in which the fatigue life is plotted against an equivalent stress. Using this equivalent stress, it will be possible to merge the S–N curves obtained for different mode mixities into just one. The next step is to use this master S–N curve for fatigue life prediction of the real joint. In this step, the only thing that one needs to be done is to measure the value of the equivalent stress within the adhesive laser in the real joint and determine the corresponding fatigue life using the already obtained master S–N graph. To achieve this, the real joint should be numerically analysed using finite element method (FEM). This procedure is schematically shown in Figure 9.11.

Several relations have been proposed by researchers to construct the master S–N curves, but the indirect method still suffers from a lack of a universal post-processing approach. This is perhaps the main disadvantage of the indirect method compared to the direct strategy. Figure 9.12 compares the direct and indirect methods. Note that as the indirect method gives more general data about the durability of the adhesives subjected to cyclic loading, its results can be used for joints with vastly different geometries and loading conditions.

Although the Arcan joint itself has a simple geometry, an Arcan testing assembly consists of the Arcan device, connectors, and pins, which can make this procedure more complex to analyse. Accordingly, because of the ease of manufacturing and testing procedure, some researchers instead choose to assess the fatigue durability of the adhesives using single lap joints (SLJs). Such approach is inherently limited, as the results of SLJ testing cannot be directly employed for fatigue durability analysis of real joints as SLJs do not experience a specific mode mixity. SLJs show a complex mode mixity along the overlap, which is influenced by the geometry of the tested joint. On the other hand, the SLJs tested in laboratory conditions are inevitably different in terms of size, geometry, and even materials from the real joint that is the ultimate target of the fatigue analysis process.

In fatigue tests, the mechanical properties of the adhesive materials are degraded cycle by cycle. However, the degradation process can be accelerated if the adhesive experiences an aggressive environment at the same time. For example, the durability of an adhesive that experiences both mechanical cyclic loads and hydrothermal ageing will be lower than that of a joint that only experiences cyclic loads. In this condition, with the same load level, the total fatigue life decreases by increasing the ageing level. Temperature also has similar effects on the fatigue life of the joints. The higher the temperature, the lower is the total fatigue life for the same applied fatigue load (Figure 9.13).

9.2.1.2 Fatigue Crack Growth Approach

Fatigue crack propagation deals with the second stage of fatigue life where the crack is already initiated and it is now going to propagate because of the applied cyclic loads. Although in most applications, the initiation life is considered as the

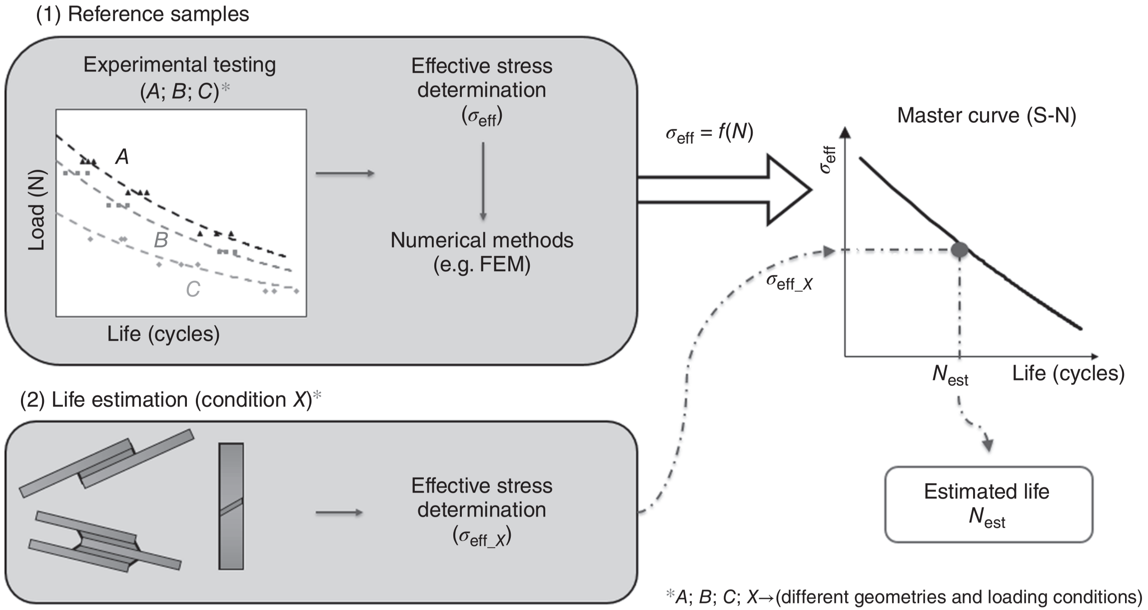


Figure 9.11 Schematic view of the S–N procedure for fatigue life estimation of bonded joints.

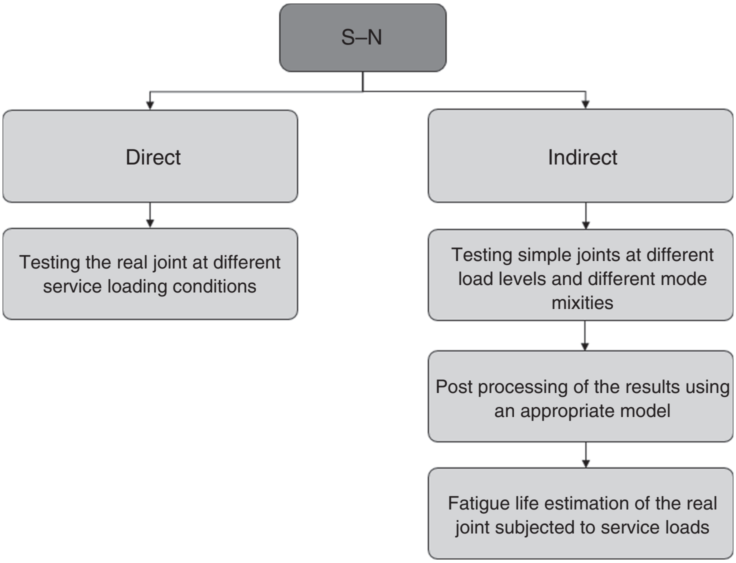


Figure 9.12 Different strategies for S–N analysis of adhesive joints.

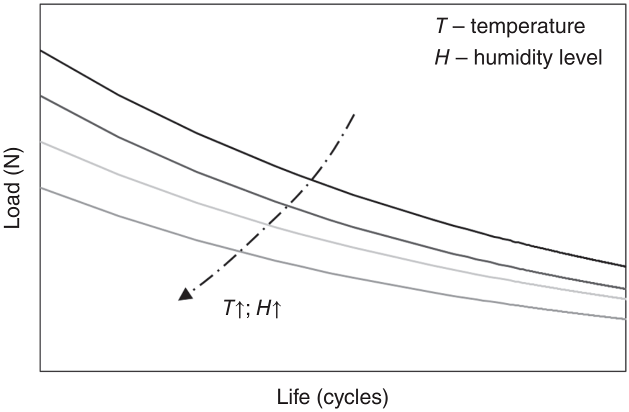


Figure 9.13 Effect of temperature and ageing on the S–N curve of adhesives.

total fatigue life of the joints for large bonded areas, and in advanced applications, the fatigue crack propagation life is often considered separately in fatigue durability analysis of adhesive joints. Fatigue crack propagation tests are the same as the fracture mechanics tests already explained in Chapter 4. However, instead of a quasi-static load, cyclic loads are applied to the joints. DCB, ENF, and mixed mode bending (MMB) tests are considered for fatigue crack growth analysis in mode I, mode II, and mixed mode, respectively. During these tests, the load and corresponding displacement for each cycle should be recorded. Using this information and by employing an appropriate data reduction method, the fracture energy for each cycle is obtained.

To analyse the fatigue crack growth, the rate of crack propagation (da) is measured at a specific range of load cycles (dN). The ratio of da/dN is called fatigue crack growth rate. On the other hand, the fracture energy of the adhesive also changes cycle by cycle. For each load cycle, G_{min} is the minimum fracture energy at each cycle and which corresponds to the minimum applied load and G_{max} is the maximum fracture energy at each cycle and which corresponds to the maximum load. The difference between G_{max} and G_{min} is called $\Delta G = G_{\mathrm{max}} - G_{\mathrm{min}}$. By plotting the da/dN as a function of ΔG in a log–log diagram, a curve is obtained, which is called Paris law curve. Figure 9.14 shows a typical Paris law curve.

The Paris law curve has three different sections, known as stages. The first stage shown in Figure 9.14 corresponds to the fatigue initiation part. In this region, the fatigue crack propagation is not significant. This region corresponds to the fatigue initiation life. If the strain energy release rate (G) is less than a specific value (called the threshold energy, G_{th}), then the crack propagation will be negligible. However, fatigue is an accumulative damage mechanism, and this indicates that the damage increases cycle by cycle. By increasing the damage, the displacement usually increases at the same load level and consequently the strain energy at each cycle increases. As soon as the energy reaches the G_{th}, the crack starts to propagate. This step shapes the second stage of fatigue life where the crack grows in a stable manner. When the crack length reaches a critical value, an unstable and fast crack propagation occurs, which forms the third part of the Paris law curve. The Paris law curve is the most famous approach for durability analysis of adhesives in terms of fatigue crack growth. The slope of the Paris law curve, m, in the second stage of fatigue crack growth, is the most important parameter in fatigue crack propagation life analysis of adhesives.

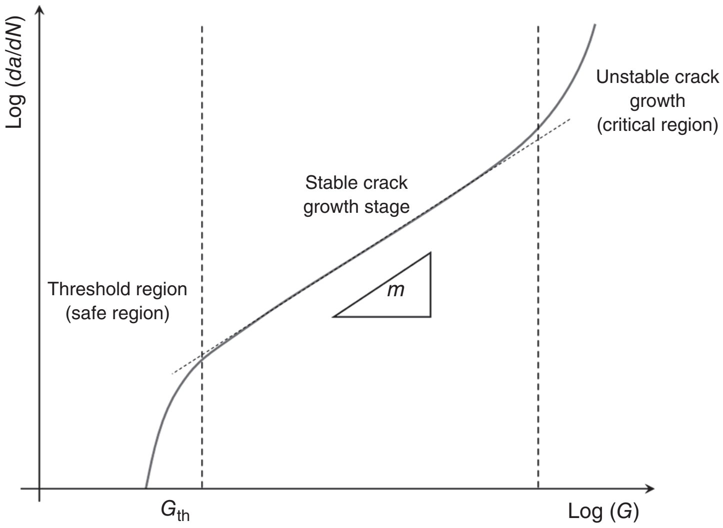


Figure 9.14 Paris law curve.

A relation (see Eq. (9.8)) can be defined for the linear part of the Paris law curve. The Paris law relates the rate of crack growth (da/dN) to the strain energy release rate (G) using fitting parameters (C and m)

$$\frac{da}{dN} = C\,(G)^m \tag{9.8}$$

However, it should be noted that the Paris law relation has several different forms. For more information about the various forms of the Paris law, read the suggested documents listed at the end of this book.

Similar to the S–N curve, the Paris law curve is also influenced by loading and environmental conditions. It indicates that the slope of the Paris law curve (m) changes by changing the mode mixity, ambient temperature, or humidity. Figure 9.15 shows the effects of mode mixity, temperature, and humidity on the Paris law curve on and adhesive.

As it was mentioned above, using the Paris law relation, it is possible to estimate the fatigue crack propagation life of adhesive joints. The fatigue crack propagation life is the number of cycles required to increase the crack size from an initial value (a_0) to a critical size (a_c). By knowing the values of a_0 *and* a_c and by considering the slope of the Paris law curve, one can estimate the fatigue life of the joint. This approach is mainly used when the crack propagation is dominating the total fatigue life of the bonded structure.

9.2.2 Creep

Creep is a time-dependent phenomenon defined as the deformation of materials subjected to a constant load for a long time. Although the applied load is constant and

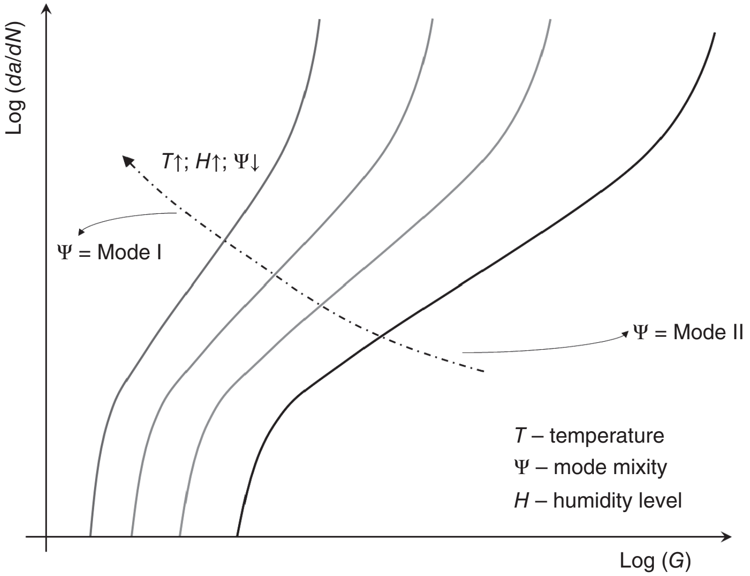


Figure 9.15 Effects of mode mixity, temperature, and humidity on the Paris law curve.

less than the static strength of the joint, the creep deformation may still cause joint failure after a specific period has elapsed. Accordingly, it is crucial to analyse the durability of the joints in terms of the creep damage.

Still, creep testing is often neglected when characterising adhesives. This is because creep tests are long-term experiments and the equipment necessary to conduct them is usually expensive. Nonetheless, some simple apparatuses have been created to conduct the creep tests of adhesive joints. Figure 9.16 shows an example of a creep testing apparatus. In this simplified creep test machine, the load is applied by a weight shown in Figure 9.16, and the displacement is measured by a dial indicator. Another practical and simple creep testing equipment configuration is the spring-based creep tester. In this equipment, the load is applied by a spring to the specimen and the displacement is usually measured using a dial indicator. Figure 9.17 shows a spring creep tester. Because of the simple construction and small dimensions, large numbers of spring-based machines can be used in parallel,

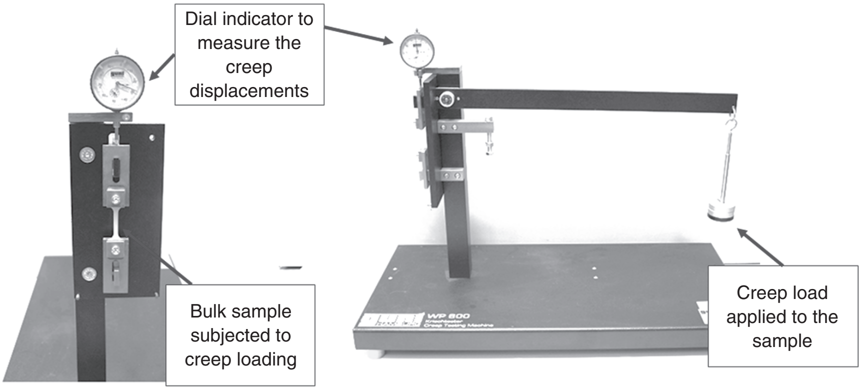


Figure 9.16 Apparatus for creep testing of bonded joints.

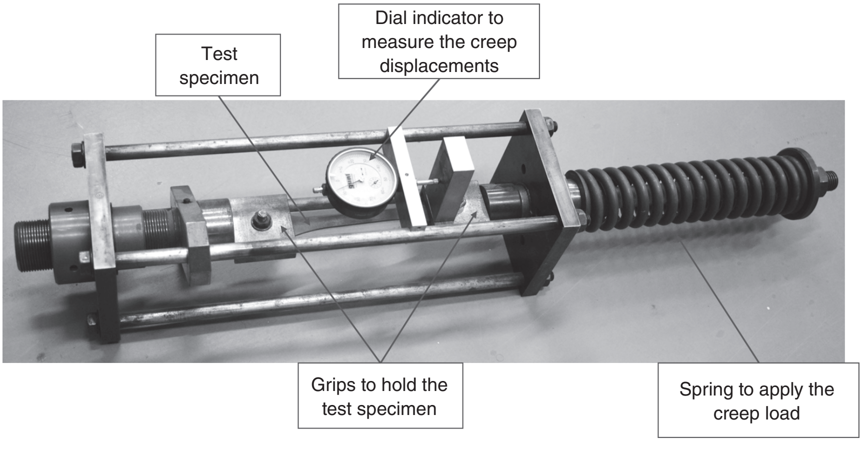


Figure 9.17 Spring-based creep tester.

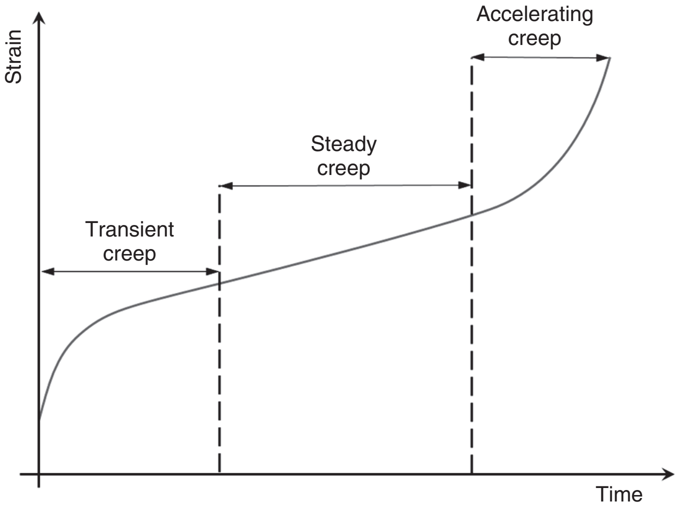


Figure 9.18 A typical creep curve.

under different load and temperature conditions, to accelerate the process of creep data determination.

Creep deformation has three different steps as it is shown in Figure 9.18. In the first region, the creep rate is not constant, and it changes with time. However, the creep rate decreases by increasing the creep time. The rate of creep deformation finally reaches a stable value at the end of the first stage where the second stage starts. In this region, the creep rate is constant and does not change with time. However, as soon as the creep damage initiates and propagates through the adhesive layer, the creep strain starts to increase with time. This phenomenon forms the third stage of the creep curve. In this step, the creep strain rate increases with time and in an unstable manner. This behaviour will continue until the joint eventually fails.

The stress level and the service temperature are the two most important parameters that influence the creep deformation. Increasing the load level and working temperature decreases the durability of the adhesives in terms of the creep life. In Figure 9.19, the effect of temperature on the creep response of the materials is schematically shown. By increasing the temperature, the time necessary to reach creep failure time decreases. However, the elongation corresponding to the creep failure increases with temperature. The same response is expected when the creep loads are applied to aged samples. Ageing usually increases the maximum elongation at failure but decreases the strength of the joint.

Creep ageing can significantly alter the life span of adhesively bonded joints. According to the experimental results for a safe design, the applied creep stress should be much lower than the static strength of the joint. Even for cyclic loading conditions, the mean stress acts as a creep stress and causes creep ageing of the adhesive inside the bonded structures. Thus, to account for this and create a safe joint design, the creep life of a joint should be considered even for the cyclic loading conditions.

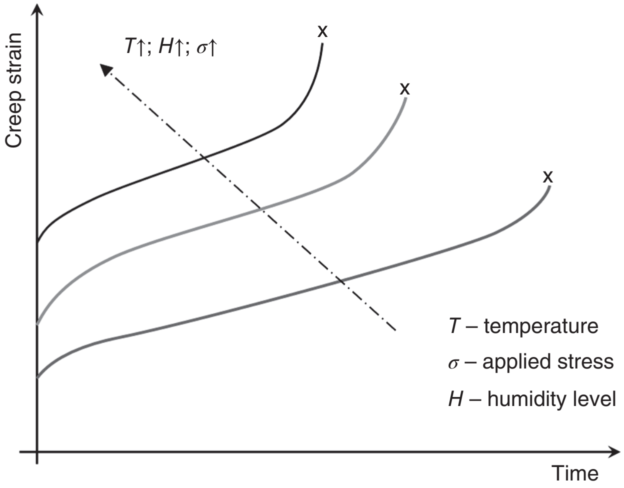


Figure 9.19 Effect of ambient temperature on the creep deformation of adhesives, a schematic view.

Although, as stated, creep testing procedures are quite long, the creep testing procedures can be accelerated by conducting at higher temperatures, using simple geometries (for example, using dogbone shape bulk samples). The resultant data will allow us to plot the creep life as a function of the applied creep load and this creep life span diagram will help the designers to have an idea about the creep response of the real structure (Figure 9.20).

As was mentioned before, creep tests are long-term tests, and in real applications, not only the load level may change in service but also variations of the ambient temperature may also occur. Accordingly, an analysis of the creep response of adhesive joints using numerical approaches is preferred by designers. To perform a creep analysis using numerical methods, it is necessary to first define the constitutive relations of the material subjected to creep. These constitutive relations (laws) are equations that relate the applied force on the material and the corresponding displacement. By

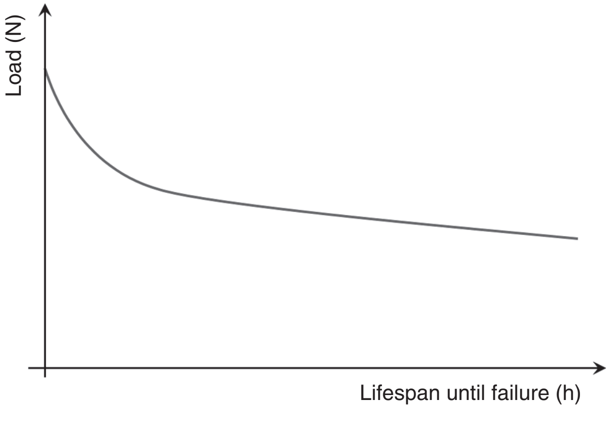
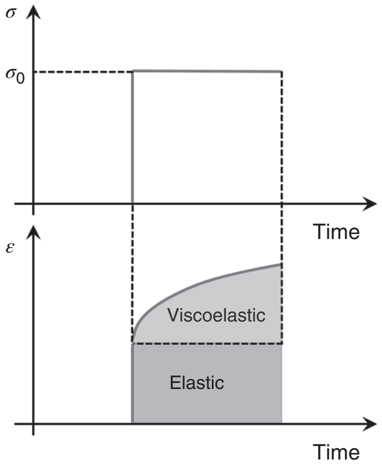


Figure 9.20 Creep life span as a function of applied creep load.

Figure 9.21 Typical viscoelastic response of an adhesive material.

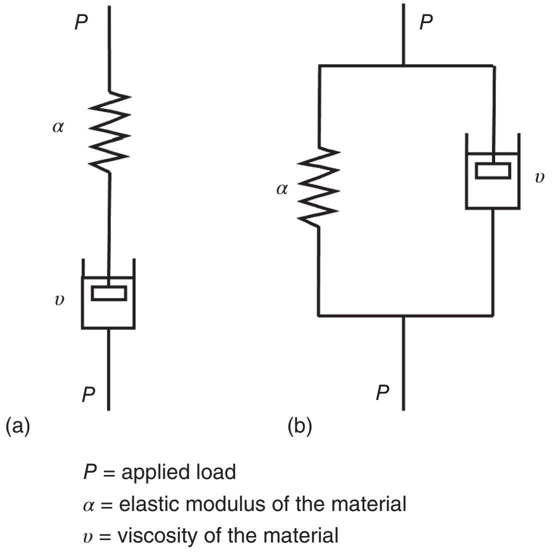


knowing these relations, it is possible to simulate the creep behaviour of adhesive joints using numerical approaches such as FEM.

Different constitutive equations have been developed by researchers to simulate the creep behaviour of adhesives. The proposed models should take into account the effect of viscoelasticity of the material. Based on the viscoelasticity effect, for a constant applied load (stress), the deformation (strain) changes with time. Figure 9.21 schematically shows the viscoelastic response of a material.

To provide a physical understanding of the creep phenomenon, creep models have been proposed based on different combinations of springs and dashpots to model the viscoelastic material behaviour. Maxwell and Kelvin are the most famous and simplest methods to simulate creep of materials. In Maxwell approach (Figure 9.22a), the dashpot and spring are arranged in a series configuration, while for the Kelvin model (Figure 9.22b), they are parallel.

Figure 9.22 Typical creep models suitable for adhesive materials, Maxwell model (a), and Kelvin model (b).



P = applied load
α = elastic modulus of the material
υ = viscosity of the material

10

Case Studies

As we near the conclusion of this book, you have now certainly become more aware not only of the main capabilities and advantages of adhesive bonding but also of the difficulties that arise with its implementation. We have repeatedly seen how adhesive bonding can lead to strong and durable structures, but it was also stressed that aspects such as surface treatment, durability, and quality control remain as important challenges. To consolidate this knowledge, this final chapter will allow you to have a more comprehensive insight into how adhesive bonding technology can be implemented in industrial applications. This is done by describing a set of research studies on the subject of adhesive of bonding, where joint design and the manufacture processes are all optimised. The case studies shown are related to a varied set of different industries, including the automotive, railway, aerospace, and packaging sectors.

One main aspect that is transversal to all these works is the study of adhesion, often a critical issue when adhesive bonding is implemented in a practical application. In the end of each study, a corresponding scientific journal reference is provided, allowing those interested to obtain further details on each study.

10.1 Vehicle Construction

The automotive industry is facing many challenges, the most important of the development of vehicles that meet stricter regulations for pollutant gas emission and fuel consumption. To achieve these goals, vehicle manufacturers are progressively introducing lighter structures, such as aluminium alloys and composites, avoiding the traditional welded steel structures. To join these light materials efficiently, adhesive bonding is a key technique. Adhesive joints already fulfil all the requirements imposed by the automotive industry, especially those related to impact, ensuring passengers' safety. Nonetheless, because of the relative novelty of this technology, there is still margin for improvement, opening the door to even lighter and more efficient structures. The adhesive joints used in automotive industries must behave well under extreme conditions, especially under impact, in order to ensure the safety

Introduction to Adhesive Bonding, First Edition.
Eduardo André Sousa Marques, Ana Sofia Queirós Ferreira Barbosa, Ricardo Joao Camilo Carbas, Alireza Akhavan-Safar, and Lucas Filipe Martins da Silva.

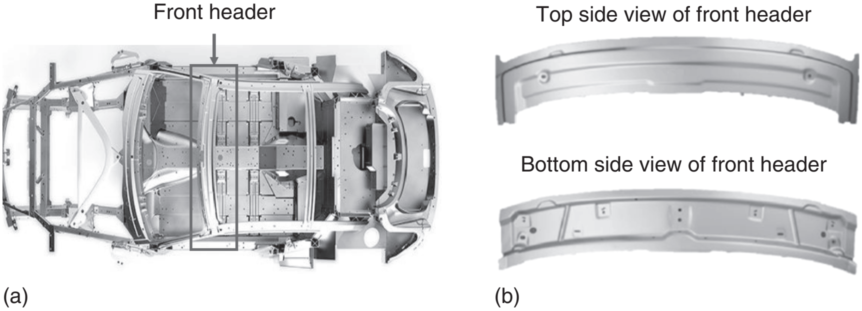


Figure 10.1 Car body component studied, location of test specimen used in the real car body (a) and parts used to perform the test specimen (b).

of passengers. The combination of safety standards and weight savings is not easy and therefore poses the biggest challenge for engineers when designing automotive components. Studies of real-scale adhesively bonded automotive structures, using numerical approaches with experimental data validation, must be carried out to evaluate its behaviour and validate the application of adhesives in this field.

An important car component is the roof frame header that supports the roof and the windshield of the car and is composed of an upper and a lower adherend (Figure 10.1). This structural component should guarantee the passengers safety in the case of accident during a vehicle rollover. Under impact, this component should deform plastically and not fail completely. This will allow it to absorb as much as possible the impact energy, while keeping the integrity of the structure and passenger's safety.

Epoxy adhesives are widely used to bond car bodies, although they are usually employed in a reinforced form, known as 'crash-resistant adhesives'. These are adhesives with high strength and toughness, but their behaviour is strain rate dependent, which indicates that they will respond differently under impact. For these adhesives, an increase of strain rate leads to an increase in the fracture toughness and higher strength. When selecting an adhesive for use under impact conditions, it is also important to ensure large strain to failure in order to enhance the energy absorption and increase the damage tolerance.

When bonding vehicle bodies, the adhesive application process can be automatised and easily implemented in a production line. The adhesive thickness can be controlled with the use of suitable spacers or by the use of small glass spheres uniformly dispersed into the adhesive. Adhesive thickness control is a crucial step in the manufacturing process in order to ensure highest joint performance.

In applications for the automotive industry, it is crucial to evaluate the performance of all bonded structures under impact conditions. The correct selection of adhesive can conduct to a failure in the metallic adherend, with maximum energy absorption. Figure 10.2 compares the mechanical response of a real bonded joint using two different structural adhesives. The joints bonded with structural polyurethane (PU) show a higher energy absorption capability because of the fact that polyurethane, although weaker, is more flexible and tougher than epoxy.

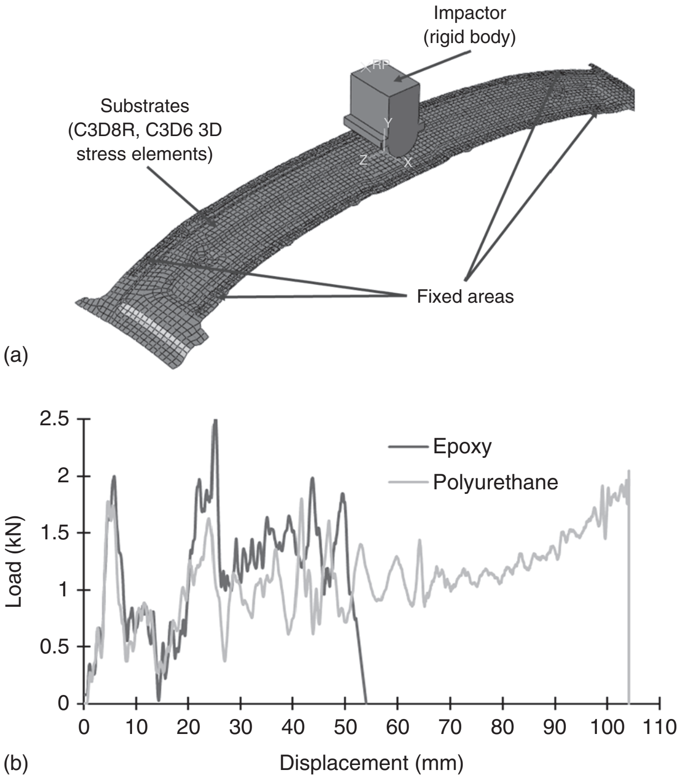


Figure 10.2 Simulation of real component (a) and load–displacement curves as a function of different adhesives (b).

An adhesive joint with higher absorption energy results in a lower transmitted load to the adherends, reducing the probability of complete failure of the metallic structure.

Detailed information of this case study can be seen in the recommend bibliography, in the paper entitled 'Experimental and numerical study of the dynamic response of an adhesively bonded automotive structure'.

10.2 Seat Fixation in Passenger Trains

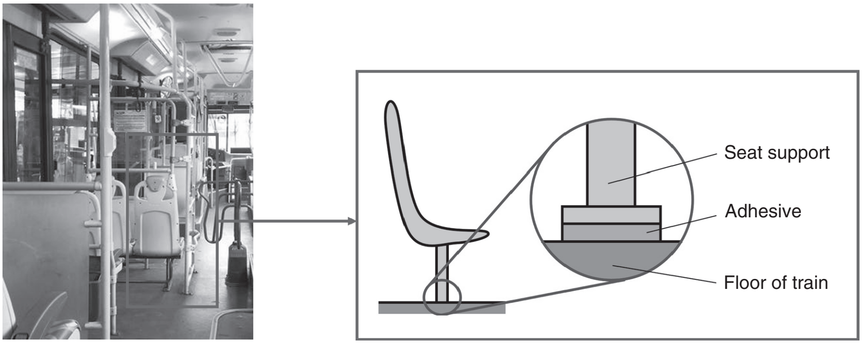
In train construction, the rails used to connect the seats to the passenger carriage floor are usually attached with bolts or rivets to the floor. This fastening method introduces stress concentrations, conducting to a severe fatigue resistance reduction. The use of adhesive bonding is an alternative to mechanical fastening, allowing reducing the cost of structures. It can be more easily automatised and offers the potential to last much longer as adhesive joints are less susceptible to fatigue damage. Nonetheless, special care must be taken in the design phase as the adhesives used in this application must operate in various environmental conditions and must maintain the structural integrity of the joint at high-moisture environments and at high and low temperatures. Moisture may attack the interface between the adhesive and the adherend, being responsible for adhesive failure of the joint. Extreme temperatures also affect the mechanical properties of the adhesive.

The design of adhesive joints for short-term strength can now be accomplished relatively easily, making use of advanced tools that allow the engineer to reliably predict the mechanical behaviour of the joint in the short term. However, in the long term, there is a chance the adhesive joint will degrade, and its properties will deteriorate. This is arguably the most important disadvantage or limitation of adhesive bonding today. The work shown here is dedicated to understanding how moisture degrades the joint strength and how stronger joints can be designed by taking these effects into account.

In this work, the rails used were made in high-strength aluminium alloy (Figure 10.3) and were anodised. The anodisation process was carried out in order to avoid the onset of galvanic corrosion. Additionally, a primer was applied before adhesive application to ensure good adhesion between the adhesive and the anodised surfaces. Epoxy-based adhesives were selected for this application, as they offer good adhesion properties and environmental resistance. While the adhesive selected must be strong enough to resist the mechanical loads that the joints will be subjected to, it must also provide stable properties within the range of service temperatures of the structure.

In order to evaluate the bonded joint strength under the environmental conditions that the seat rail faces when assembled inside the floor of the train, the joints were mechanically tested under a wide range of temperatures (from −40 to 80 °C) before and after ageing in order to simulate real-life conditions. The joints were tested under tensile and cleavage loads, simulating the conditions encountered during service, including the worst-case scenario for adhesive behaviour (peel load).

The mechanical response of bonded joints shows higher strength at low temperature and low strength at high temperature and this decrease is due to the closeness to the T_g. The moisture also changes the failure mechanism from the middle of the adhesive to the interface between the adhesive and the adherend. The numerical



(a)

(b)

Figure 10.3 Seat fixation in train (a) and bonded component used (b).

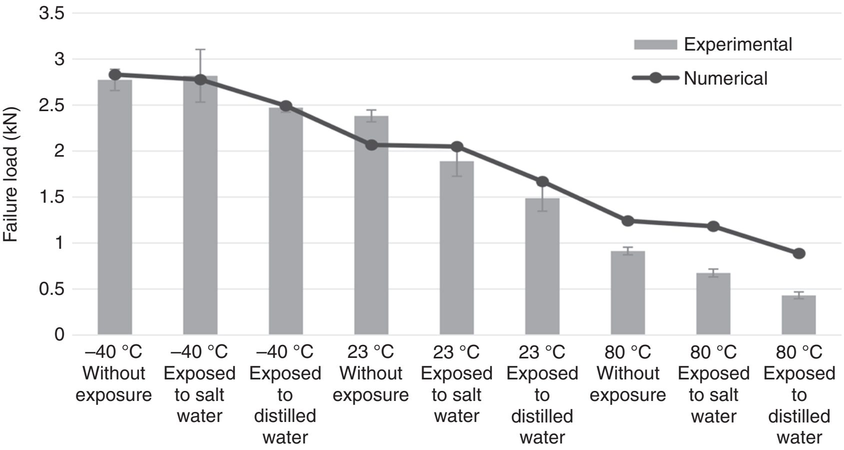


Figure 10.4 Failure load response of seat fixation as a function of temperature and ageing.

response of joints showed a good agreement with the experimental response of the joints. In a parallel numerical modelling procedure, cohesive elements that consider moisture- and temperature-induced degradation of adhesive were developed and used (Figure 10.4).

Detailed information of this case study can be seen in the recommend bibliography, in the paper entitled ‘A new cohesive element to model environmental degradation of adhesive joints in the rail industry’.

10.3 Aeronautical Applications

The aerospace industry was a pioneer in the use of adhesive in high-performance structures. In this sector, structural weight is the most important design factor, requiring the use of technological advanced materials such as composites and high-strength aluminium alloys. These materials are very hard to join using conventional fastening or welding methods but can be easily joined with structural adhesives. In space application, vehicle structures are loaded under very extreme conditions, as is the case, for example, of heat shields on the external skin of the aerospace vehicles. The main purpose of these components is to insulate the internal structure of the vehicle from the heat generated during the re-entry into the atmosphere (Figure 10.5a). The type of adhesive that can be used for this application (to join heat shields to the structure of the vehicle) is a room temperature vulcanising (RTV) silicone, an adhesive that although has low cohesive strength exhibits extremely high temperature tolerance. The flexibility of the RTV adhesives is also fundamental as the ceramic heat shields have coefficients of thermal expansion that differ greatly from that of the metallic structure to which they are bonded. As the joint is subjected to extreme temperatures, the adhesive must be able to accommodate these vastly different material behaviours without any failure (Figure 10.5b).

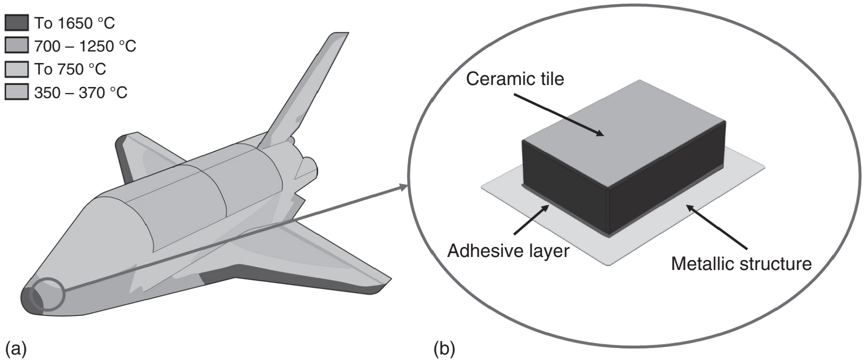


Figure 10.5 The temperature reached by an aerospace vehicle in the re-entry into the atmosphere (a) and the geometry of the specimens used (b).

The joints were tested at different temperatures in the adhesive layer, ranging from low (−65 °C) values that simulate space conditions to high values encountered during re-entry (100 °C). The adhesive joint was found to perform well under these conditions and the testing providing important information on the strength of the joints as a function of temperature.

The joints bonded only with a single adhesive, silicone adhesive or epoxy adhesive, are shown to be very sensitive at the temperature tested. When the mixed adhesive is used, it can be seen that the failure load remains almost constant independently of the temperature level subjected (Figure 10.6). The mixed adhesive joints, when subjected at extreme temperatures (−65 and 100 °C), show a good displacement at failure, similar to or higher that the flexible joint (bonded with silicone adhesive).

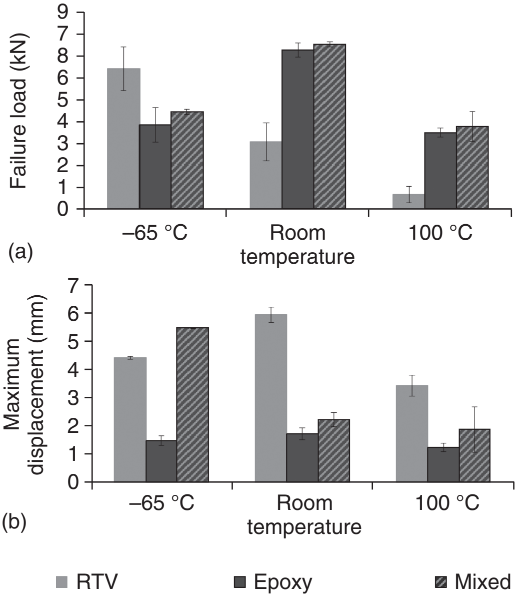


Figure 10.6 The failure load (a) and displacement at failure (b) of ceramic joints bonded with different techniques.

Detailed information of this case study can be seen in the recommended bibliography, in the paper entitled 'Testing and simulation of mixed adhesive joints for aerospace applications'.

10.4 Flexible Cooling Circuits

The constant need for technological systems capable of processing large amounts of data pushes the boundaries of what is needed in terms of computational requirements, promoting the development of both the systems required to store all the information and chips designed to process it. Moore's law is the observation and projection of a historical trend that the number of transistors in an integrated circuit doubles about every two years. In fact, Moore's law pushing the boundaries of engineering not only in terms of the development made to computers chips itself but also the need for machines to produce this kind of structures. More specifically, the need for cooling systems able to maintain the temperature of these systems within an acceptable range and at the same time fit within compact spaces as is the case for many applications of these systems is an engineering challenge.

Consequently, tubular systems are needed as the most efficient cooling mechanisms rely on fluids such as water or ethylene glycol to increase the efficiency of these systems when compared to air-cooled systems using extended surfaces (fins) and forced convection (generally using fans), as the thermal conductivity of these fluids is considerably higher than the previously mentioned mechanism using an airflow. Therefore, compact cooling systems can be designed by using liquids rather than large areas relying on fins and convection mechanisms.

RTV silicone adhesives were selected to join the tubes that will carry the coolant fluids (Figure 10.7). These are adhesives that exhibit optimal sealing capabilities and resistance to ageing under the most diverse conditions. These are also thixotropic silicone adhesives, which facilitate greatly the manufacture procedure.

Metallic tubes are typically used to carry the coolant fluids, but because of the vibration patent in some of these systems, it is often necessary to use additional components that permit relative movements within the structure, avoiding damage in the cooling system. For that to be possible, it is necessary to use flexible tubes that can accommodate vibrations of the metallic tubes that occur during regular operation of the cooling circuit.

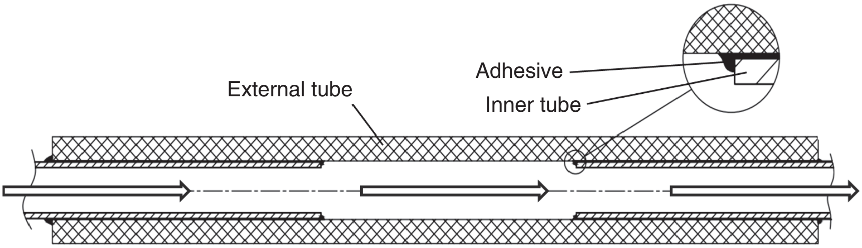


Figure 10.7 Tubular bonded joint.

The main problem associated with the use of polymeric tubes is their low surface energy that conducts to a poor adhesion. In order to be possible to ensure a good adhesion between the polymeric tubes and the adhesive, the selection of a suitable surface treatment is crucial. For polymeric materials, plasma treatment is widely used to induce modifications in the polymeric materials surface, allowing us to improve the adhesion between the polymeric adherend and the adhesive. Plasma treatment allows increases up to 100% of the surface energy of the polymers.

The correct tube alignment is also essential to ensure that the bonded tubular joints perform as intended. A bonding fixture is thus necessary to precisely control the overlap length, alignment, and adhesive thickness and to maintain the concentricity between the different tubes that make up the joint.

In order to evaluate the strength and the adhesion of the tubular joints, torsion and tensile tents should be performed in laboratorial settings. When tested under this configuration, the joints with suitable surface treatments were found to be capable of attaining high joint strength and always exhibited cohesive failure in the adhesive. In addition, permeation tests were performed to evaluate the tightness to gases and liquids. It was found that the optimal treatment selection allowed us to ensure excellent joint strength and low permeation rates, representing a joint that is highly suitable for its intended application.

A numerical analysis is a very powerful tool to evaluate and optimise the mechanical response of the bonded joints, but it is essential to validate its numerical response with experimental tests (Figure 10.8). One of the key findings of the study was that the maximum allowed rotation of a metal–polymer tubular bonded joint is mainly a function of the polymer tube-free length between the bonded areas and the polymer tube material.

Detailed information of this case study can be seen in the recommend bibliography, in the paper entitled ‘Numerical study of flexible tubular metal-polymer

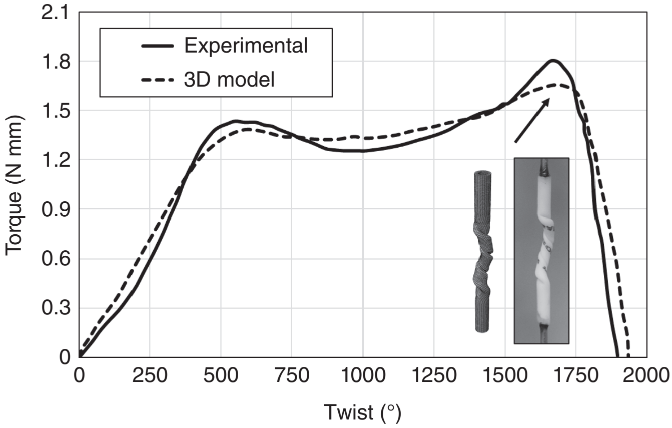


Figure 10.8 Experimental and numerical torque–twist curve of polymeric bonded tubes.

adhesive joints' and 'Flexible tubular metal-polymer adhesive joints under torsion loading'.

10.5 Glass to Metal Bonding in Appliances

Modern domestic appliances (e.g. hot water heaters) are progressively increasing the complexity of the technologies they use and constantly adopting novel designs. Such changes lead to the use of new materials, such as adhesives, which often poses challenges in the manufacturing process and might raise durability concerns. In the particular case of new generation of hot water heaters, the front panelling design changed from metal sheeting to a glass panel with touch screen functions that allow one to control a set of operating parameters of equipment. Traditional joining methods (such as visible fasteners or brackets) do not allow for an efficient and light connection between the glass and the structure of the water heater, which has led to the use of adhesive bonding in this application.

This type of equipment often operates on moist environments, and the durability of the adhesively bonded joints that are used in its construction is a major research topic. However, the complex nature of the time-dependent (viscoelastic) behaviour of adhesives leads to significant difficulties in making long-term behaviour predictions. During service, the final product is submitted to creep loads for a large period of time and the manufacturers must accurately determine the work life of the product. The determination of creep behaviour of the adhesive joints until failure is only possible through a large number of experimental tests, requiring significant amount of time and resources to provide results that are representative of the final product. In the literature, there are some approaches that provide accelerated tests in order to predict the work life of bonded structures, involving the use of *master curves* (it is based on time–temperature superposition principle and consists in combination of data from shorter tests performed at elevated temperatures to construct a single curve). Such approach is essential for industrial users, as it allows us to quickly design and experimentally validate new products.

In this type of applications, the adhesive must bond dissimilar materials (with different coefficients of thermal expansion), damp vibrations, and resist the high level of humidity. Silicone adhesives, although limited in mechanical strength, provide the necessary flexibility to handle these conditions. Experimentally, the research procedure starts with a study of the adhesion and the strength in a representative joint specimen (Figure 10.9), manufactured using the same materials employed in the full-scale equipment (aluminium and tempered glass).

After all steps of the manufacturing process were validated, the joints were subjected to creep loads under different conditions, allowing us to construct a final master curve. The final goal of this curve was to predict the service life using solely accelerated tests. Creep tests at various temperatures were performed to assess long-term durability using the time temperature superposition concept and it was

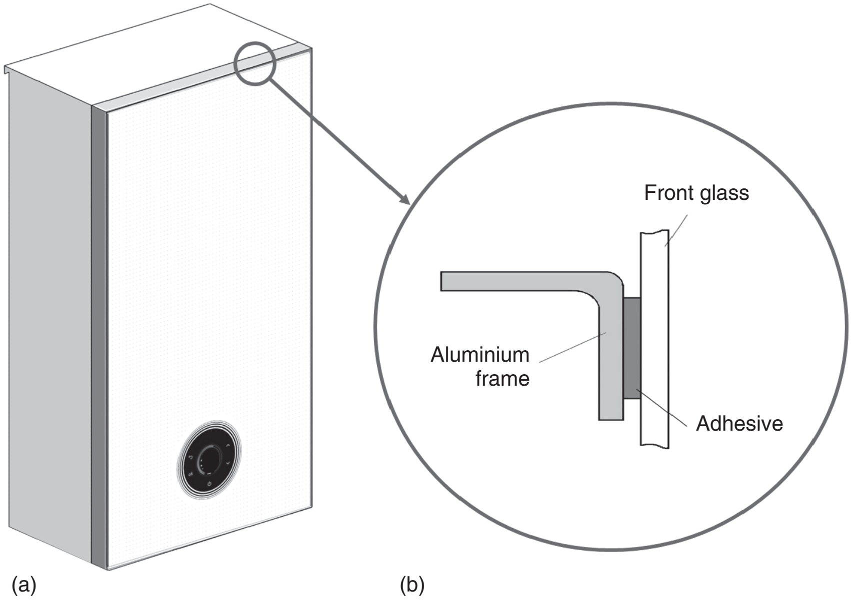


Figure 10.9 Schematic representation of a commercial heater with a bonded front (a) and a bonded detailed part used in the heater (b).

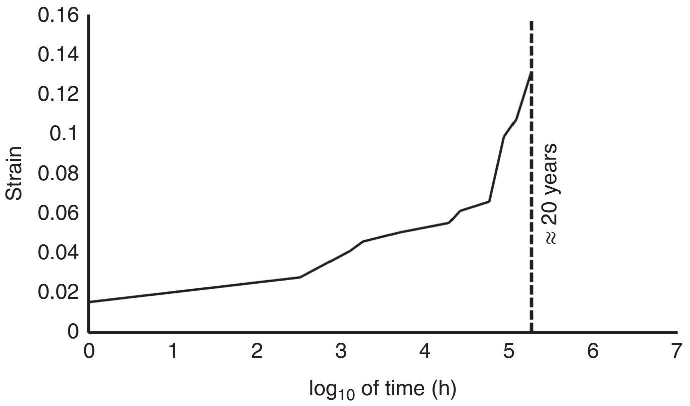


Figure 10.10 Adhesive joint tested statically and under creep conditions.

found that the creep rate increased with higher temperatures. These data allowed us to construct the master curve, which was used to extrapolate the creep period to a larger time scale. In the tested joint, a minimum expected durability of 20 years was obtained (Figure 10.10).

Detailed information of this case study can be found in the recommend bibliography, in the paper entitled 'Use of master curves based on time–temperature superposition to predict creep failure of aluminium-glass adhesive joints'.

10.6 Roof Coverings

Asphalt is a versatile material that finds use in many different applications, such as on roads and motorways, in the foundations of building constructions, and in roofs. When used in the roof covering, asphalt can be used in individual shingles or in roof sheeting materials, helping to create a durable and watertight barrier.

Typically, roof sheets are made of multiple layers with several different functions. An outer layer (the layer that will be exposed directly to weather conditions) of a bituminous material reinforced with mineral granules (such as silica, slate, etc.) is usually followed by a bituminous layer for waterproofing. In some roof sheets, there may be a layer for thermal insulation purposes (such as rock wool, cork, etc.). The exact materials used in these constructions can vary depending on the weather conditions that the roof will be exposed to. However, the main material that composes these roof sheets is the asphalt itself.

When applying these coatings to a roof, it is essential to ensure that sufficient heating is applied to the sheeting, so that all the bituminous layers to be joined are melted properly and that a good level of adhesion exists between them. Gas torches are usually employed for this process. No additional joint joining elements is incorporated (neither adhesive nor mechanical fixation) besides the materials that are already presented in the roof sheet construction. The application of this type of product is typically performed in situ, which requires a simple, fast, and very efficient technique, to ensure good adhesion and reduce permeability of the roof. Figure 10.11a shows an image of asphaltic sheets used in a roof.

A good adhesion between roof sheets should be assured. Damage can be avoided using a careful and well-controlled process of application. The most common damage that can occur in a roof sheet is the debonding caused by high wind intensity due to storms. The wind forces generated during a storm can subject the roof to severe mechanical loadings. If peel loads are generated, this can promote a debonding of the layers of the roof coating. Figure 10.11b shows an example of damage that occurred because of a wind-induced peel load. Such damage is not acceptable and can be avoided by ensuring a good adhesion between the roof sheets. In this type of


(a)

(b)

Figure 10.11 Roof covering of industrial builds (a) and the damage caused by to poor adhesion (b).

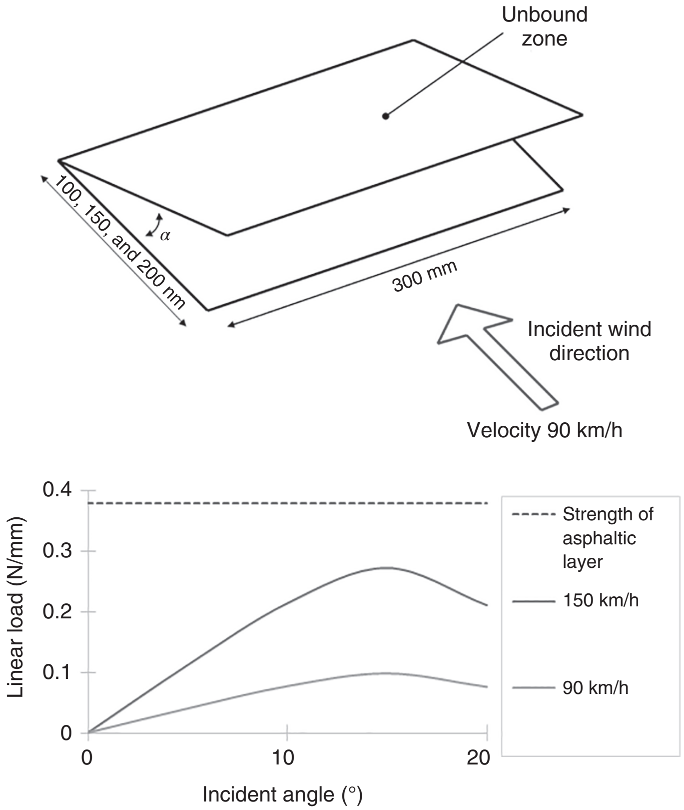


Figure 10.12 Effect of wind as a function of size defect.

application, an important issue is the determination of the minimum size of joint defect in the upper asphaltic layer which, because of wind loads, can lead to the failure of the base insulation layer (the layer immediately below the asphaltic layer). This can be estimated using an analysis that considers the minimum limit for wind speed (90 km/h) and three different depths of glue defects (100, 150, and 200 mm) as can be seen in Figure 10.12. The glue defects in the upper asphaltic layer were found to create open areas, fully exposed to the wind. Simple calculations indicate that, in extreme wind situations, defects with a depth greater than 100 mm can generate pull-out forces capable of destroying the thermal insulation layer and consequently damaging the entire roof. Without any defect, this type of roof covering (asphaltic layer) ensures the integrity for wind velocity higher than 90 km/h.

10.7 Shoe Manufacture

The footwear industry uses adhesives to join a large variety of materials during the shoe manufacturing process. In the manufacture process, the adhesive selection is an important item, as it must be compatible with a wide range of natural and

Figure 10.13 Example of an adhesive connection between the sole and the leather upper in a shoe.

synthetic materials. The adhesive formulation must balance parameters such as the viscosity, wettability, working time, and compatibility with the shoe materials. Also important is the surface treatment selection, which must ensure good adhesion strength and the durability of the shoe. The surface treatments that are typically applied in the footwear industry are extensive and use physical and chemical transformation as well as primers and solvents.

All shoe manufacturing processes are carefully designed as a function of the raw materials that will be used to manufacture the shoes and demands imposed on the shoe during service. Adhesive bonding is no exception and needs to ensure the performance required as a function of type of shoes (for work, for children, etc.). The tests that are most effective to evaluate the performance of the shoes are the peel and creep tests. The sole is bonded with the leather and this joint must exhibit very high peel strength and creep resistance to resist the loads associated with wearing a shoe (Figure 10.13).

In order to reduce the number of experimental tests necessary to formulate an adhesive for the shoe industry, a novel algorithm was developed. This algorithm allows the process of adhesive formulation to be quickly optimised and must be trained with an initial set of experimental data. Ultimately, this technique allows us to determine the necessary chemical formulation to achieve a desired final strength, considering the type of raw materials that are typically used in shoe construction (Figure 10.14).

The algorithm was shown to be a robust tool to optimise the creep rate properties of the footwear adhesive joint using the raw material constituents as design variables. The optimal results for a lower creep rate are reached when a large quantity of PUs and additives are used. The algorithm also showed that the creep rate of the adhesive joint is very sensitive to some constituents used. This algorithm allowed us to determine the exact content of different constituents (PUs, resins, and additives) that must be mixed to obtain the optimum adhesive composition for different shoes with distinct uses.

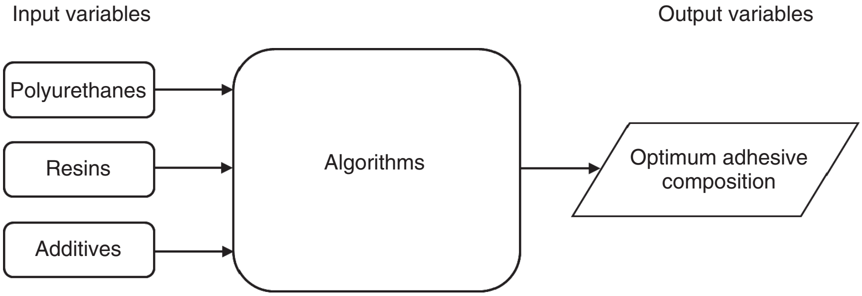


Figure 10.14 Algorithm developed to determine the optimum adhesive composition for a given shoe bonding application.

Detailed information of this case study can be seen in the recommend bibliography, in the patent request entitled 'Effect of the surface treatment in polyurethane and natural leather for the footwear industry'.

10.8 Food Packaging

The packaging industry uses polymeric materials extensively to package food and beverage products. An example of these packages are the disposable coffee capsules for use in domestic coffee machines. Figure 10.15 shows an example of such capsule. There are different types of capsule constructions using different materials and geometries. The capsules studied in this work are constructed in two parts, a main body that will contain the coffee and any filters and a sealing film. All of these parts are manufactured from polymeric materials.

During the manufacturing process, the coffee producers fill the capsule with coffee and then immediately seal the capsule with the polymeric film with heat. The application of heat causes local melting of the capsule body and the film, creating a ring around the capsule edge where there is adhesion between these two materials.

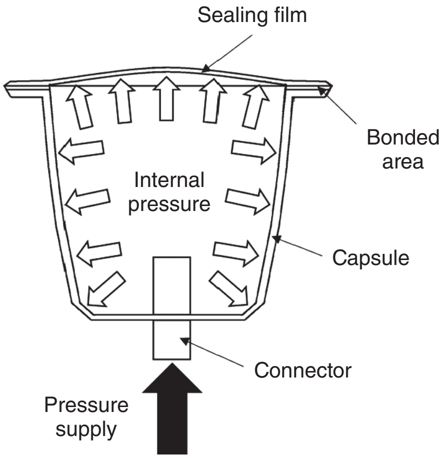


Figure 10.15 Schematic representation of the capsules and testing principle.

However, this a relatively low-strength joint and any defect can result in deficient sealing. Because of this low strength, it is crucial to ensure that poor adhesion is always avoided. When polymeric adherends are used, it is mandatory to carefully select the surface treatment to improve the surface energy and consequently enhance adhesion levels. This improvement of surface energy can be achieved with the use of physical chemical processes (corona, flame, or plasma treatment).

To easily control the sealing quality, an apparatus to test the adhesion of a sealing film to capsules was developed. This apparatus enables capsule manufacturers to quickly test the adhesion strength and identify any problem in an early stage of capsules. The working principle of the apparatus consists in the gradual introduction of pressure inside the capsule while a manometer registers the force/pressure necessary for causing failure.

This invention is very useful for many encapsulated food and beverage manufacturers, such as soups, yoghourts, etc. It allows the evaluation of the adhesion of the sealing film to the capsules immediately after manufacturing. This apparatus can also be used directly in production lines enabling adjustments of the manufacturing parameters in situ, providing save time and money the industries that use this type of equipment.

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Index

Introduction to Adhesive Bonding, First Edition.
Eduardo André Sousa Marques, Ana Sofia Queirós Ferreira Barbosa, Ricardo Joao Camilo Carbas, Alireza Akhavan-Safar, and Lucas Filipe Martins da Silva.