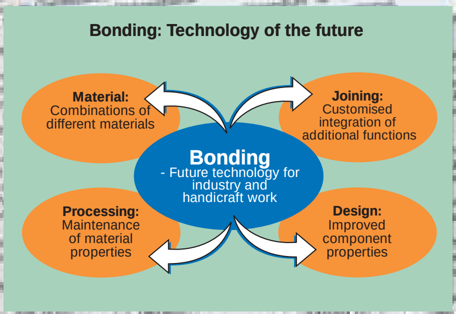
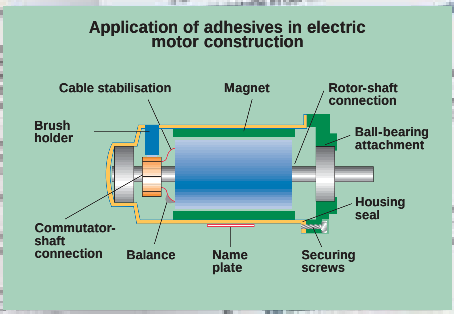
Educational Materials

Bonding / Adhesives

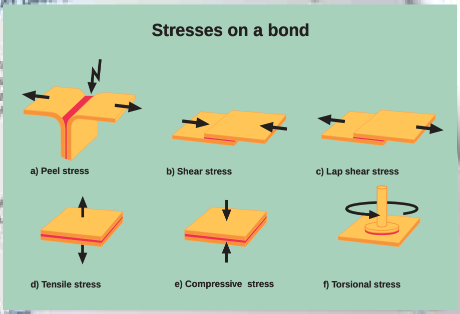
Textbook



Bonding: Technology of the future



Application of adhesives in electric motor construction



Stresses on a bond

Thank you...

The Association of European Adhesives Manufacturers (FEICA) would like to thank the following companies for their support in realising these “Educational Materials”.

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Foreword

Bonding has become an indispensable technique for joining two or more substrates with each other, not only in industry but also in everyday life. Bonding allows the production of laminated materials, facilitates mobility and communications, positively influences the handling of foods, supports health and hygiene and improves the quality of our lives. Moreover, many innovative products could not be manufactured without the use of bonding techniques. This "Educational Materials" series textbook entitled "Bonding/Adhesives" offers numerous examples.

More than 2,300,000 tonnes of adhesives are produced and used in Europe each year and this volume is on the increase. Adhesive manufacturers offer more than 250,000 different products for the most diverse applications – and these products are customised for virtually every purpose. This is important, because each adhesive must satisfy different requirements. Depending on the application, an adhesive may have to withstand extremely low temperatures or heat of several hundred degrees, it may have to be highly elastic or extremely stable. This "Educational Materials" textbook "Bonding/Adhesives" is being supplied free of charge to schools and training establishments in Europe. This material is also available on CD-ROM and on the Internet at **www.feica.com**.

The aim of the European Adhesive Industry in publishing these "Educational Materials" is to provide information on adhesives and bonding technology. We wish to show how the discovery of chemical processes and industrial development and production have led to everyday products. Chance and nature often play a part in making a discovery but, in the commercial world, only those products which meet our current and ever more demanding requirements are able to survive in the marketplace.

This "Educational Materials" textbook is a translation from the German information series "Kleben/Klebstoffe", written and published by Fonds der Chemischen Industrie, Frankfurt, in co-operation with the German Adhesives Association (Industrieverband Klebstoffe), Düsseldorf. Representatives of the chemical and adhesive industry have collaborated in committees with chemistry teachers and lecturers from technical colleges and universities. Building on with the reader's everyday experience of bonding and adhesives, we hope that this material will generate an interest in high-performance bonding in industry and in the chemical and physical processes involved.

Düsseldorf, August 2004

The Editor

FEICA in brief

FEICA, the Association of European Adhesives Manufacturers, was founded in 1972.

In an atmosphere of growing international co-operation, the European adhesives industries needed an organisation to promote their common interests at European level. In this function FEICA represents the national adhesives manufacturers' associations of 15 European countries.

More than 480 manufacturers of adhesives, sealants, tapes and raw materials support FEICA through their membership of their national associations – and can expect the services of FEICA in affairs with a European dimension.

Thus FEICA's service profile comprises legal and technical aspects as well as the promotion of the positive image of the adhesives industry and the value-adding character of its unique products throughout Europe.

FEICA Member Associations

Vereinigung der österreichischen Klebstoffindustrie

DETIC Comité Professionnel BELCAM

Fachverband Klebstoffindustrie Schweiz

Industrieverband Klebstoffe e.V.

Brancheforeningen for Lim og Fugemasser

Asociación Española de Fabricantes de Colas y Adhesivos (ASEFCA)

Syndicat Français des Colles et Adhésifs (S.F.C.A.)

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British Adhesives & Sealants Association (BASA)

Associazione Nazionale Vernici Inchiostri Sigillanti e Adesivi (AVISA)

Maling og Lakkindustriens Forbund

Vereniging Nederlandse Lijmindustrie (VNL)

Associação da Indústria e Comércio de Colas e Similares

Sveriges Limleverantörers Förening

Združenje kemijske in gumarske industrije (APA)

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1 People – Nature – Bonding Technology

1.1 Materials and bonding technology

The world around us and hence our lifestyle and the way we work are changing at breakneck pace. Who would have thought 15 years ago that computers and mobile phones would now be a part of everyday life? Who could have imagined a 3-litre car engine? And who could have dreamed of detachable adhesive strips which do not tear away the wallpaper when a poster is removed? The constantly increasing requirements being put on new consumer products is the driving force for technological progress: Nowadays, each new product that is developed must – as in the past – not only be better and more favourably priced than its predecessor but must also meet the requirement of sustainability. The consideration of environmental aspects means that the development of new products is becoming ever more demanding and that manufacturers must take into consideration more complex requirements for their new products. The increasing requirements put on products has since time immemorial been the key driving force for the development of advanced and new materials.

In addition to the classic metals, these materials include special alloys, plastics and also ceramics and glass. So-called composite materials, produced by combining different materials, have played a major role in this development.

Reinforced concrete is a well known composite material that has been around a long time. Newer composite materials are glass-fibre reinforced plastics and carbon fibre reinforced plastics which are used, for example, for constructing speed boats and yachts and increasingly also for car, rail vehicle and aircraft manufacture.

Another good example of the development and use of new materials is the wheel and tyres *(Figure 1)*. Spoked wheels made of wood met the requirements of the ancient Egyptians. Today, the manufacture of tyres for modern means of transport can no longer be achieved using even natural rubber. The high speeds we now expect of a car can only be achieved using composites of different materials – and a car tyre is nothing more than that.

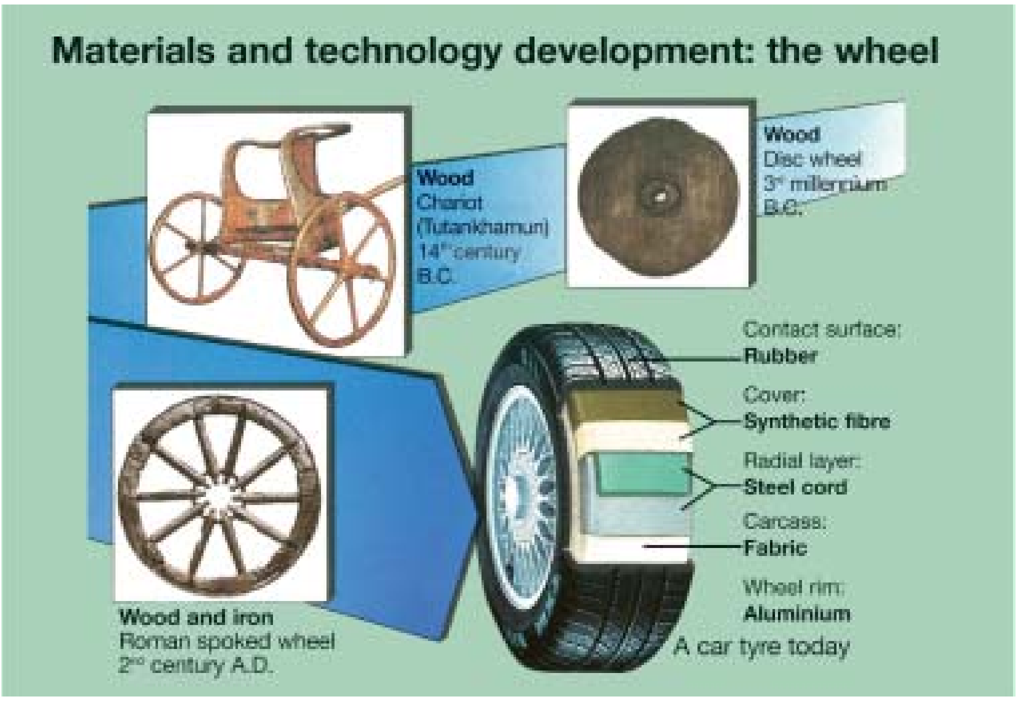


Figure 1

Joining techniques

The development of new materials with diverse applications puts additional challenges on processing technology. This is particularly so when different materials have to be joined to make components which retain their individual beneficial properties in the composite product. This raises the question: Which joining technique *(Figure 2)* is able to join these different materials in such a way that their specific properties are retained? Traditional joining techniques have well-known disadvantages. With thermal techniques such as welding, the specific properties of the material alter within the heat-affected zone. Mechanical techniques such as riveting or the use of screws in their turn only allow force transfer at points; In addition, it is necessary to drill holes in the workpieces that are being joined, and this "damages" and hence weakens the materials. In contrast, it is anticipated that bonding technology will assume an ever more important role in industry and the handicraft sector in the future. There are four key reasons for this *(Figure 3)*:

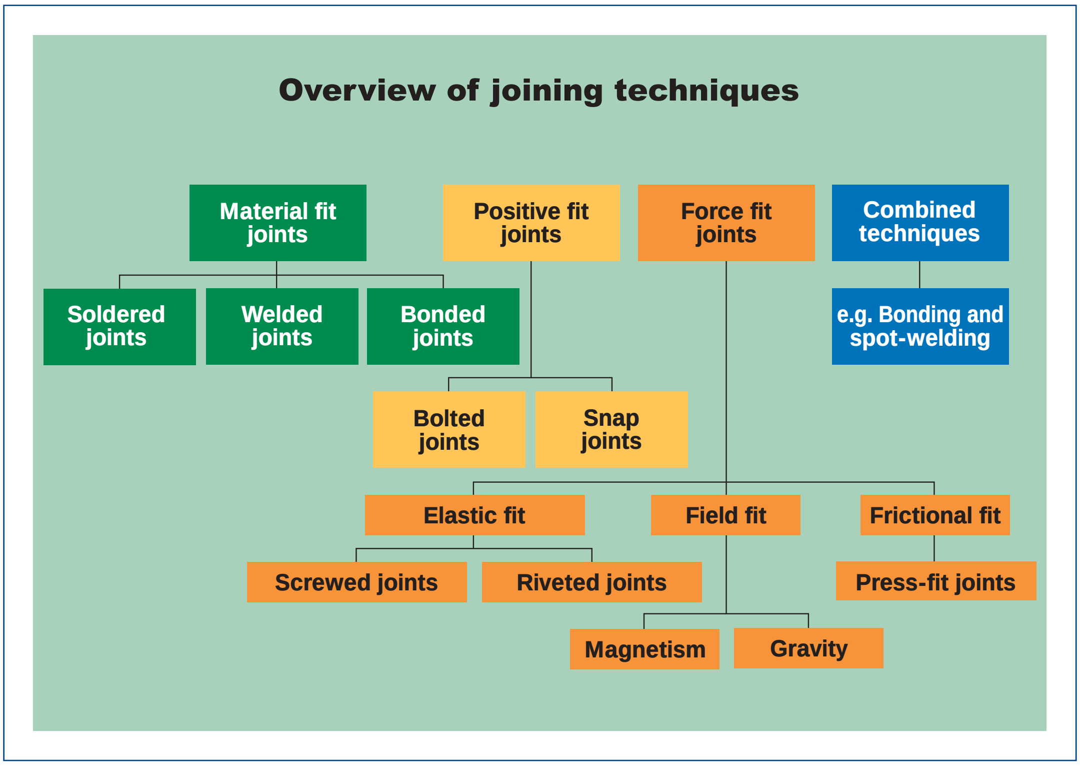
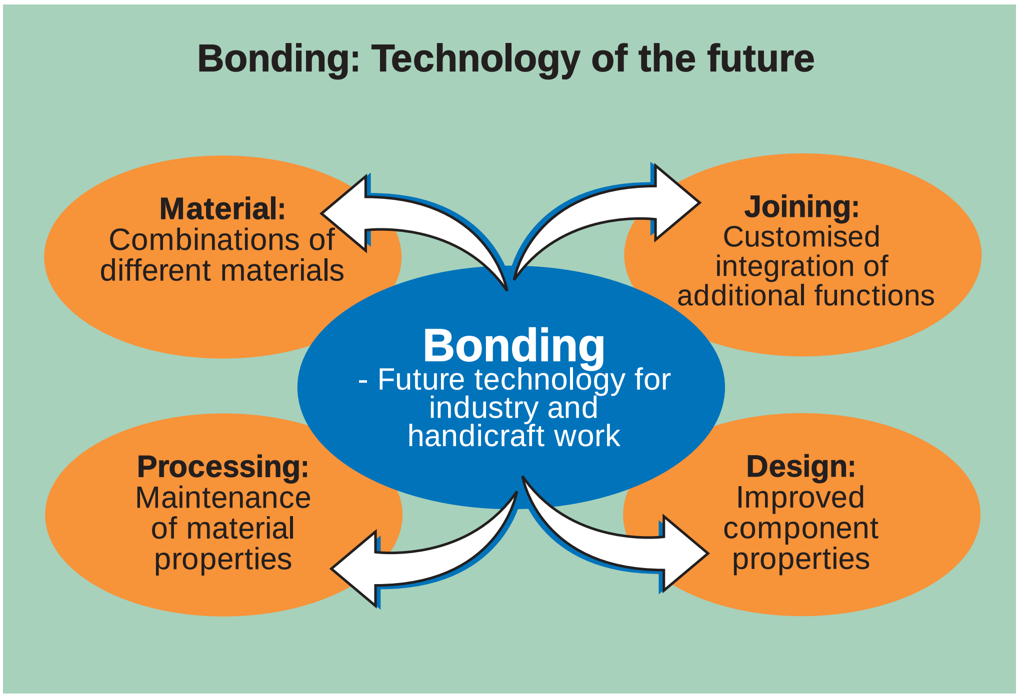


Figure 2

1. With specialist application, bonding technology can be used to bond virtually any desired combination of materials with each other, creating long-lasting bonds.
2. The use of bonding technology in production processes in general allows the material properties of the substrates to be retained: Compared to welding and soldering/brazing, the bonding process requires relatively little heat input. No damage occurs, unlike when rivets or screws are used.
3. In product manufacture, the two aforementioned considerations enable the specific material properties of substrates to be optimally utilised in components. This allows new construction methods to be employed.
4. It is also possible to use bonding technology to introduce customised additional properties into the component via the actual joining.

In addition, the use of bonding technology in industrial production can lead to time savings, can accelerate the production process and hence give rise to specific economic benefits. In shipbuilding, for example, the inside decks can nowadays be bonded into the primary structure, so eliminating time-consuming straightening work that would be required if the inside decks were attached by welding. Bonding technology also has the following further advantages:

- Transfer of high lap shear stresses due to the large bonding areas. For example: hot curing epoxy resin adhesives – ca. 40 MPa on aluminium; 1-C polyurethane adhesives, crosslinking initiated by moisture – ca. 5 MPa *(values according to DIN EN 1465, see page 49)*.
- Removal of unevenness on material surfaces; greater tolerances possible using gap-filling adhesives.
- Prevention of contact corrosion for metal bonds, in contrast to when rivets or screws are used (the adhesive functions as an insulator).



Bonding: Technology of the future

Material: Combinations of different materials

Joining: Customised integration of additional functions

Bonding - Future technology for industry and handicraft work

Processing: Maintenance of material properties

Design: Improved component properties

Figure 3

Examples of bonding in everyday life and industry

The adhesive we use in everyday life to undertake small repair jobs has long been widely employed by industry. This adhesive does however generally remain hidden between two or more substrates, out of sight to consumers.

Example: Food industry

The modern way of food retailing and self-service with its ready-to-eat meals, frozen products and instant foods would be unimaginable without adhesives for manufacturing impermeable packaging materials, such as laminated films, or for hermetically sealing packaging. Bottle labelling *(Figure 4)* is used here to exemplify the extent to which seemingly simple "everyday" applications of bonding are in reality "high-tech" solutions: Gluing paper together is child's play, using either a stick of adhesive or a liquid paper adhesive. The strength is determined by the tear strength of the paper surface and is therefore limited. There is however something special about bonding labels to bottles: The high operating speeds of the automatic filling machines mean that the adhesive must have high initial tack and the label must be cleanly taken from a magazine. After being rolled onto the usually damp bottle, the label must neither slip nor ripple. And if the bottle ever has to stand in rain or if water condenses on the label, then the labels must

Labelling bottles

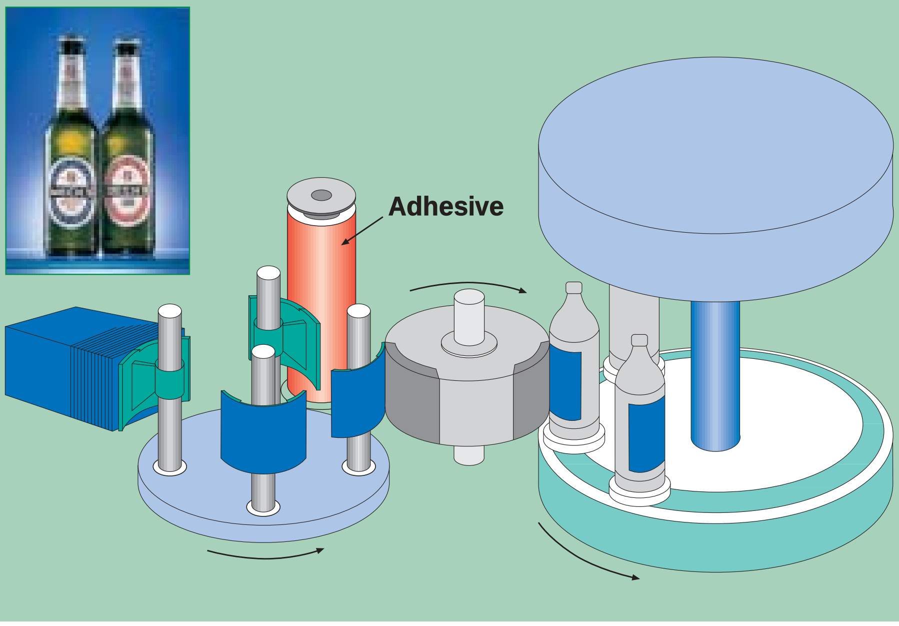


Figure 4

remain attached. However, when the empty bottle is returned for reuse at a later date, the label must be able to be easily detached during the rinsing stage before being refilled. A special casein adhesive is able to meet all these requirements: It bonds rapidly, is resistant to water and is soluble in the alkaline washing liquid.

Example: Medical technology
Adhesives are used extensively in the medical world, from simple plasters to advanced medical applications. Adhesives are used in the production of paper tissues and nappies, allow tablets to be protected from the effects of moisture and allow wounds to be dressed.

Example: The home
Remember getting annoyed with the towel holder that was fastened by suction, and how often it seemed to fall with the towel to the floor? Plastic hooks with an adhesive foam strip have also proved unsatisfactory up until now for this application. The answer is a contact adhesive *(see section 2.2.1)*: The bonding surface of the hook is coated with this adhesive, this surface is pressed for a short time against the wall tiles and then removed again. This procedure transfers adhesive to the wall tiles. The adhesive film is then left for about 15 minutes in the air, until the adhesive feels dry to touch. The two adhesive films are then brought together by pressing the hook firmly against the wall tiles. A short time later the bond is strong enough for the hook to be used. Normally adhesives that bond via evaporation of a volatile solvent are not particularly suitable for bonding two non-absorbent materials. This is because it can take a very long time for the solvent to escape from the bonded joint. This problem is circumvented here by using contact adhesives whereby the solvent in the two adhesive films is first allowed to evaporate before the films are firmly joined together.

The apparently simple task of using an adhesive to mend a broken handle on a coffee cup gives a first insight into the complexity of the requirements that are put on bonding technology: If a universal adhesive, which gives satisfactory results for many everyday repairs in the home, is used for the coffee cup then the result is disappointing. After being washed a few times in a dishwasher this bond will detach. This is because the universal adhesive is not suitable for the particular conditions encountered in dishwashers (alkaline, detergent-containing dishwasher liquids and temperatures of up to 70°C). A 2-component (2-C) epoxy resin adhesive *(see section 2.2.2)* is recommended for such applications: Mix the resin and hardener components of the epoxy resin adhesive, apply a thin film to the fractured surfaces, press the handle against the cup and use adhesive tape to keep the handle in position until the curing process is complete. A tip for difficult jobs: If there are several broken pieces, wait until the adhesive is viscous before joining the pieces. This enables the pieces to be fixed together more easily.

Example: Handicrafts
They next time you see a cobbler at work in a quick-repair shop, watch how he glues on a new rubber heel. He removes the old heel from the shoe using a pair of pliers, roughens the joining area and so removes any residues of old adhesive. He then applies a medium viscosity adhesive around the edge of the new heel, over a width of about half a centimetre. He then presses the heel against the shoe and presses it for a short time in a press. The bond is now intact and the edge can be cleaned up. The reactive adhesive that allows him to work so fast is a cyanoacrylate, also commonly called a superglue *(see section 2.2.2)*. When present as a thin film, this adhesive cures very rapidly in contact with moisture or traces of alkaline substances. For the cobbler’s work, it is not necessary to apply the adhesive to the entire joining area. This would in any case be problematic when it was time for the shoes to be repaired again, because the extremely strong bond would not be able to be mechanically detached without damaging the shoes. In contrast, leather and rubber shoe soles are normally bonded on using a contact adhesive *(see section 2.2.1)* based on polychlorobutadiene. Unlike cyanoacrylates this forms a flexible-elastic film. Both joining areas are coated with the contact adhesive. After leaving in air for about 15 minutes, the sole is pressed against the shoe. Once again here, the high initial strength of the bond immediately after joining is beneficial.

The above examples have described bonding effects based on adhesion and cohesion mechanisms *(see section 2.1)*. In the next example, another feature is considered, namely the ability of the adhesive to dissolve the surface of the substrate.

Example: Model-making
The popular adhesive used in model-making for polystyrene components, e.g. for making model houses for train sets, is essentially a solution of polystyrene in an organic solvent. After application of the adhesive, the surface of the material being bonded starts to dissolve and swells. When the other component is pressed against this surface, the same effect occurs. In practice the interface between the two components disappears as a result of amalgamation or diffusion. After the solvent has evaporated, the components bond to one another strongly. This is called “diffusion bonding”, and also sometimes cold welding. (Indeed, the same principle is used for bonding utility pipes made of plastic/PVC).

Example: Industrial production

The aircraft manufacturing industry provided the key technology impulse for modern bonding technology. The basic need for weight saving was the driving force for new design and construction methods. In modern Airbus aircraft, for example, about 30% of all components are joined using bonding technology.

In the car manufacturing industry, classic joining techniques are nowadays used in combination with bonding. In some areas bonding has completely replaced the classic techniques. The increased demand put on engine seals has resulted in bonding technology being used extensively in modern engines, for example for cylinder head seals, in various components for cooling water provision and for the oil sump. Adhesives are also increasingly being used as structural materials. Modern cars contain up to 150 metres of bonded joints in the body construction. In addition, bonded front and back windscreens increase the rigidity of the bodies and result in weight reduction. A customised thick-film bonding system dampens vibrations and also improves the heat insulation without using additional materials as is required in conventional designs. Optimised designs with improved driving performance, reduced weight and lower susceptibility to corrosion result in low C_W values *(see Glossary)* and significant energy savings.

Bonding technology plays a special role for lightweight constructions with integrated functions: This means of construction attempts to create products having additional functions, without adding extra components. For example, suitably designed bonded joints between two metals, panes of glass or wooden slats can act as a hinge.

In the area of electronics, the classic joining technique of soldering is being increasingly replaced by bonding, in order for example to connect highly integrated components with each other in a stress-free way and without the need to use excessive heat.

Limitations of bonding technology

Just like other advanced technologies, the application of adhesives in a production environment necessitates that special processing procedures are adopted. In general, detailed examination of the quality of a bond by non-destructive testing is not possible. Bonding – like welding and brazing/soldering – is hence considered to be a so-called special process. When using bonding in a production environment, appropriately high production quality is therefore required, because the product quality is not tested. Degradation mechanisms have to be taken into account when considering the long-term stability of bonded joints. Degradation can reduce the strength of bonds but is generally known to be manageable. One limitation imposed by nature on the use of bonding technology must however not be forgotten: A clear disadvantage of bonding technology compared to other joining techniques is that the resulting bonds only have limited stability to heat due to the fact that adhesives are organic compounds.

1.2 Bonding – an ancient art but a new science

In the Neolithic period, namely ca. 8000 BC *(see Table 1)*, the people used a resin from birch trees to attach the heads of spears and axes *(Figure 5)*. When the glacier man “Ötzi” was discovered, tools and pieces of clothing were found, including an axe made from yew wood whose blade was attached with birch pitch (adhesive) and strips of leather. About 5000 BC, animal blood, protein, various plant resins and asphalt were used as adhesives in Babylon to build houses and temples. In ancient Egypt (about 3500 years ago) bonding was even a profession: the occupation of adhesive-maker was born (Kellopsos) *(Figure 5)*. The art of boiling glue which the ancient Egyptians had developed was later taken up by the Greeks and Romans. An indication that the art of bonding was already at an advanced stage of development at the time of the Romans is the oak box from the Roman era that was found in Breslau in about 1886: Five metal coins were bonded onto the top of this oak box. The adhesive that was used is thought to be based on a protein-chalk mixture and must have possessed an extremely high adhesive strength because four of the five coins are still bonded to the wooden surface after almost two thousand years. In the mid 14th century the Aztecs used the adhesive properties of blood for construction work. It is the albumin in blood which gives it these bonding properties. The Aztecs mixed this animal blood into cement. The structures built by the Aztecs are even today still in excellent condition and are evidence of the quality of the bonding agents *(Figure 5)*.

Natural rubber was first used as a raw material for adhesives in about 1830. The discovery of rubber vulcanisation in 1841 by Goodyear marked the birth of the history of synthetic plastics and hence synthetic adhesives. This was the first time in the history of mankind that a natural chemical was altered to make a semi-synthetic material (plastic) having new mechanical and technological properties. In 1864, W. Parks succeeded in making semi-synthetic celluloid. The first “real” synthetic plastics to emerge from chemists’ laboratories which had no parallels in nature were the phenolic resins. They were first used in 1902 and are closely associated with the name Baekeland. Indeed, Baekeland sold the first commercial phenolic resin in 1905 under the name Bakelite. This represented a key step in the chronological development of plastics, namely from natural materials, then on to chemically modified materials and finally to wholly synthetic plastics. Over the next decades the development of synthetic plastics and adhesives experienced a rapid boom. Synthetic rubbers such as polychloroprene, Buna

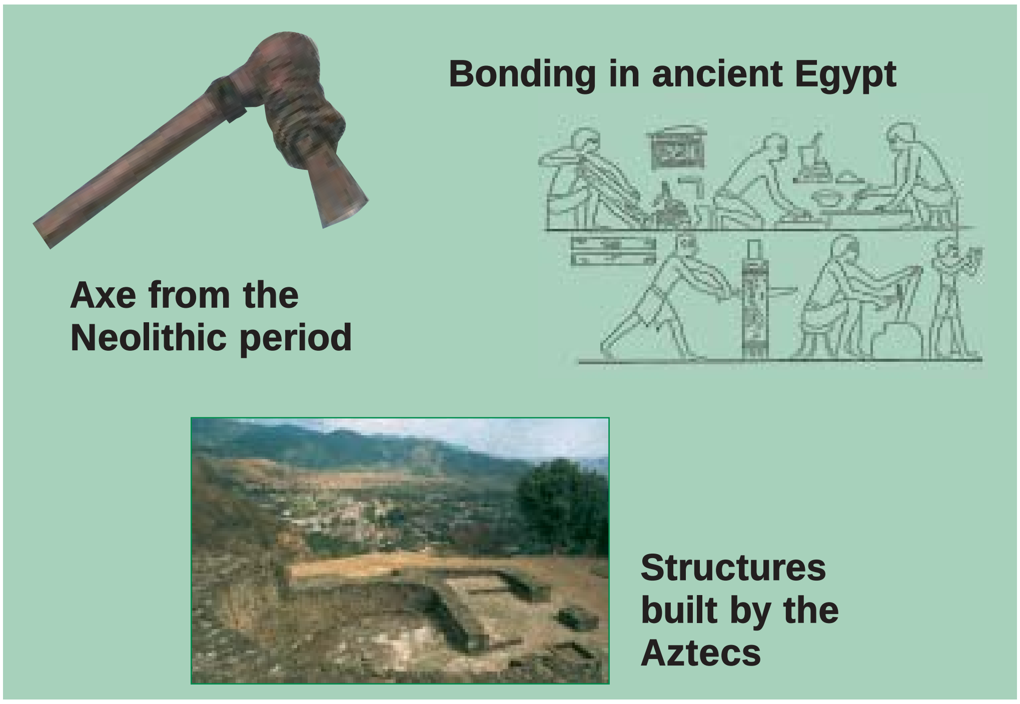


Figure 5

(polybutadiene) and silicone rubber were synthesised. Then followed epoxy resins and the polyurethanes and after the Second World War the methacrylate and the cyanoacrylate adhesives (superglues).

1.3 Bonding – nature shows us how!

The history of mankind provides so many examples of bonding applications throughout the different periods of time that it is tempting to consider bonding to be an invention of man. However, in truth it is nature that has shown us the way. The following examples of bonding from the plant and animal kingdoms demonstrate how man has learned from nature, so enabling us to develop the technology of bonding.

Example: Paper wasps
Thinking of bonding and the world of insects, let's consider for a moment the paper wasp that is native to Central Europe: It has pincers that enable it to break down wood mechanically, coarsely breaking down the long fibres of cellulose by means of a scraping motion. It then eats these fragments and mixes aqueous digestive juices with them. This further shortens the length of the cellulose fibres by chemical means. The adhesive for nest-building is now ready for use. On drying, the water evaporates from the mass, the cellulose fibres form a mat and the adhesive hardens. Paper wasps can build extremely strong nests using this technique. This technology has long been used by people for decorating their homes: The tackiness of wallpaper paste is based on the same principle.

Example: Rubber tree
Water, a solvent and dispersing agent, can be problematical for the long-term stability of bonds. Nature also provides a solution here, this time from the plant kingdom: Rubber milk from rubber tree foliage is a dispersion of polymers (natural latex) in water. Using a dispersion is hence a way of employing the environmentally friendly solvent water and at the same time creating bonds having good long-term stability. This trick of nature has long been used by the wood processing industry.

Example: Honey bees
In contrast to paper wasps which use an adhesive based on the solvent water, the adhesive used by honey bees for nest building contains no solvent - namely wax, which is a liquid at a bee's body temperature. Only on cooling does the adhesive solidify into its strong form. Bees' wax hence meets the ideal requirements of modern adhesives (hotmelts): solvent-free but can be applied as a liquid.

Table 1

History of bonding

3 billion years ago	Bonding-type processes in primordial cells: They produce a tacky outer membrane which allows them to stick to adjacent cells and form clumps and colonies. Mussels form high-strength bonds to a wide variety of surfaces; Sundew and spiders produce tacky secretions; Bees produce plates of wax; Birds make the first “bonded” composite materials for nest building.
80000 years ago	From this time onwards, people used bonding: Cavemen near the Dead Sea made collages. In excavations bonding materials have been identified as decoration on skulls, as sealant for containers and as adhesive.
35000 years ago	Animal blood and protein used as a binder for the base surface for cave paintings; Hut structures made of wood, brushwood and reeds that are strengthened with adhesive.
8000 B.C.	Weapons in advanced hunting cultures: Resins from trees provide enhanced bonding for joining flint and bone heads with wooden handles/shafts; “Adhesive pastes” produced by boiling down plant components; “Glues” produced by boiling down animal components.
5000 B.C.	In Mesopotamia and Egypt: Use of asphalt (naturally occurring) as an adhesive (mosaics), and in combination with resins used as a sealant for boats.
2000 B.C.	Near East: Gelatine glue for furniture manufacture.
1000 B.C.	China: Skin adhesives for lacquering work: Sap from the lacquer tree evaporates and can bond up to 30 different layers
1500 A.D.	The Spaniards brought rubber to Europe from Central America where it had already long been used by Aztecs and Mayas; Casein, which was even known to the Romans, was the first “plastic” to be used for coating paper and bookbinding.
1700	Large-scale glue boiling.
1841	Rubber vulcanisation was discovered (Goodyear).
1905	Baekeland brings the first phenolic resin onto the market under the name “Bakelite”.
1921	Principles of macromolecular chemistry resolved by Max Staudinger.
1922	BASF awarded a patent to manufacture urea-formaldehyde resins that were soluble in organic solvents.
1928	First production of polyvinyl chloride (PVC) in the USA; Production of polymethyl methacrylate (PMMA) as “Plexiglas” by Röhm & Haas.
1930	First industrial manufacture of polyvinyl acetate (PVAC), polystyrene (PS) and polyacrylonitrile (PAN).
1931	First stable plastic dispersion based on acrylic acid esters (BASF, Röhm & Haas) and vinyl acetate (Wacker, Hoechst); Start of production of polychloroprene.
1936	P. Castan (de Tre Frères, Switzerland) uses polyaddition to make plastics and invents epoxy resins that were patented by him in 1939. C. Ellis (Ellis-Foster Comp. USA) discovers the rapid curing of unsaturated esters and styrene by peroxides
1937	The polyaddition of diisocyanates and polyols to form polyurethanes (PUR) is based on the research work of O. Bayer in Leverkusen.
1940	IG Farben is awarded a patent for methacrylate adhesives (today “Agomet” of Degussa, Hanau).
1941	Large-scale production of saturated and unsaturated polyester resins.
1943	Manufacture of heat-resistant silicone rubbers; In the USA, the first use of phenolic resin – polyvinyl acetates in formulations for metal-wood bonds in aircraft manufacture.
1946	Industrial manufacture of epoxy resins.
1953	V. Krieble (USA) introduces anaerobically curing adhesives based on dimethacrylate under the name “Loctite”.
1958	The first cyanoacrylate adhesives are introduced: “Eastman 910” in the USA and in 1960 “Sicomet” in Germany.
1967	First heat-resistant polyimide adhesives (up to 300°C) introduced in the USA.
1968	Start of development work on moisture curing polyurethane adhesives “Sikaflex” and “Betaseal” for sealing/bonding the front and rear windscreens on cars.
1970	Rapid further development of polyurethane chemistry with a wide range of 1-C and 2-C adhesive formulations; First UV-curing acrylate formulations; development of MS-polymers in Japan, application in earthquake-proof buildings.
1980	Reactive hotmelts.
1984	Development of anisotropic, conducting adhesives. The conductivity arises from direct contact of the substrates via individual filler particles (e.g. gold-coated polystyrene spheres / diameter 5 mm) in the adhesive matrix which do not touch and which are electrically conducting.
1988	Development of high-strength adhesives for bonding oiled steel sheets under industrial production conditions (e.g. the car manufacturing industry). This involved special hot curing 1-C epoxy resin adhesives.
From 1990	Development of various adhesives involving a combination of curing mechanisms, e.g. cyanoacrylates which are initially cured by UV-light and then fully cured via the effect of moisture.
1993	Development of aerobically curing adhesives whose curing is triggered by oxygen. Hydroperoxide formers (e.g. hydrazone) are added to these adhesives. Under oxidising conditions peroxides are produced and start the polymerisation.
1995	Development of silane-crosslinking polyurethane prepolymers (S-PUR) that complement the range of 1-C moisture curing rubber-elastic adhesives. They have an improved balance between reactivity and storage stability, there is no bubble formation and no longer function via an isocyanate-based reaction mechanism.
2000	Development of detachable adhesive systems for repair and recycling based on a change in temperature, stress, voltage and/or pH.

Example: Barnacles

Barnacles *(Figure 6)* are crustaceans that live in coastal waters. The free-swimming larvae can bond to virtually all hard marine materials. The bonding is achieved by means of a secretion from the so-called “cement glands”. This secretion is a 2-component reactive adhesive possessing high resistance to water and prodigious long-term stability. The bonding is not at all dependent on the composition of the base surface. Even whilst the barnacle is growing and when its outer skin peels the barnacle remains firmly bonded to the base surface. This is because there is constantly new secretion of adhesive to ensure the bond remains intact.

Example: Termites

About 150 million years ago the soldiers of primitive termites possessed sabre-like jaws to repulse enemies. Some 30 million years later a nozzle-like structure developed above the pincers. The highest developed form was reached 70 million years later: The jaw pincers had disappeared and only the nozzle remained, from which adhesive is sprayed to incapacitate attackers. The production of modern cars would be unimaginable without being able to apply adhesive in this way.

Barnacles

Figure 6

2 What is bonding?

Bonding is the joining of two substrates using an adhesive. According to DIN EN 923 an adhesive is defined as:

- a non-metal
- a binder that acts via adhesion and cohesion.

Adhesion and cohesion

Adhesion is the adhering of similar or different types of materials to each other. Cohesion is the inner strength of a material, such as the adhesive in this case.

The adhesive interactions between an adhesive and a substrate not only concern the actual area of contact (adhesion zone) of the adhesive and substrate but also concern the state of the adhesive in the vicinity of the surface of the substrate (transition zone) *(Figure 7)*.

- In the cohesion zone, the adhesive is present in its normal state.

- In the adhesion zone, the adhesive has a modified structure and composition due to its adhesion to the surfaces of the substrates. This structure and composition is different from the state in the cohesion zone. As a result, the macroscopic properties of the adhesive in the adhesion zone are also altered.

- The structure, composition and macroscopic properties of the adhesive continuously change in the transition zone between the adhesion zone and the cohesion zone. There may for example be separation of the components of the adhesive due to diffusion of the small components of the adhesive into surface pores. The optimum composition of the adhesive is hence adversely affected.

2.1 Bonding mechanisms between the adhesive and substrate, and in the adhesive

- Adhesion zone] Boundary layer
- Transition zone
- Cohesion zone

The adhesion zone

As mentioned above, the adhesive has a modified molecular structure in the adhesion zone due to bonding to the substrate surface. The phenomenon of adhesion is caused by molecular interactions between the substrate surface and the adhesive. A distinction can be made here between weak intermolecular interactions and strong chemical bonds *(Table 2)*. Chemical bonds, however, only form for very few substrate/adhesive combinations, e.g. between silicone and glass, polyurethane and glass, and epoxy resin and aluminium. For some of these

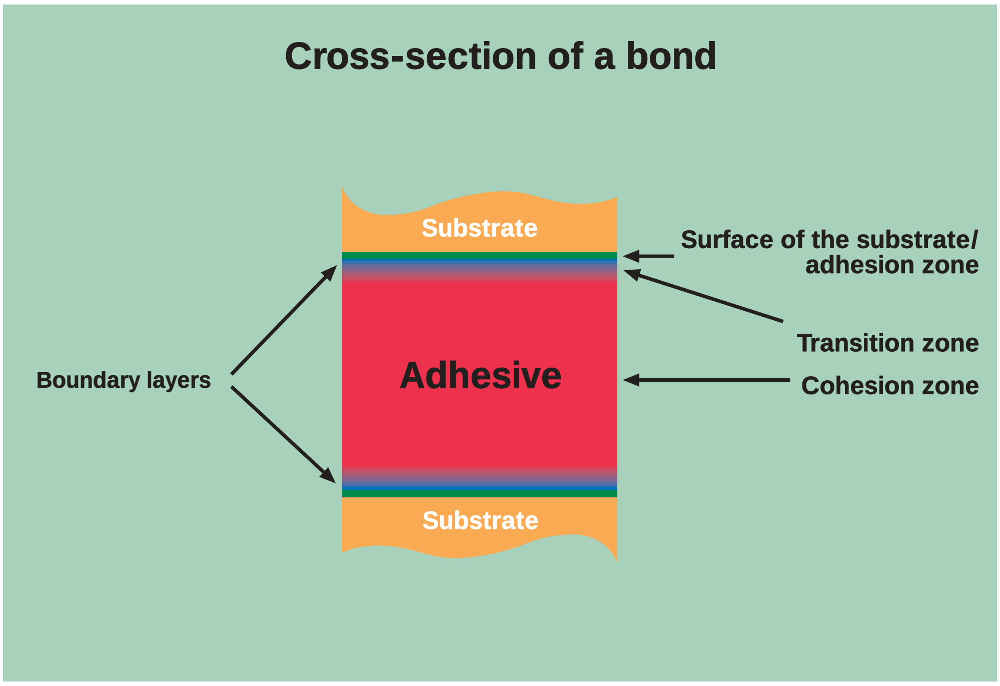


Figure 7

Adhesive forces

Type	Bond length in nm	Bond energy in kJ/mol
Chemical bonds		
• Covalent	0.1–0.2	150–950
• Metallic	0.3–0.5	100–400
• Ionic	0.2–0.3	400–800
Intermolecular interactions		
• Van der Waal forces	0.4–0.5	2–15
• Hydrogen bonds	0.2	20–30

Table 2

bonded joints it has been demonstrated that chemical bonds account for up to 50% of all the interactions. The long-term stability of these bonds depends directly on their resistance to moisture. In addition to the intermolecular and chemical adhesion forces, the bonding mechanism occasionally referred to as "micro-mechanical adhesion" can play a role, depending on the morphology of the substrate surface. This term is so-called because of the belief that an adhesive can effectively "mechanically cling" to a roughened substrate surface. "Micro-mechanical adhesion" is in general only considered to be of secondary importance. However if there are regular undercuts in the substrate – maybe even introduced by design – which the adhesive flows around, then this can increase the strength of the bonded joint.

The transition zone

The transition zone in which chemical, mechanical and optical properties of the adhesive are altered varies in thickness, from a few nanometres up to the millimetre range. The thickness depends on the nature of the substrate surface, the adhesive and the curing conditions. Where there are thick transition zones or thin bonded joints, the behaviour of the entire bonded joint may be determined by the properties of the transition zone because in this case there is no cohesion zone.

The cohesion zone

In the cohesion zone, the adhesive possesses its nominal properties, as indicated on the data sheets. These properties are determined by the following molecular forces *(Figure 8)*:

1. The chemical bonds within the adhesive polymers;
2. The chemical bonds resulting from crosslinking of the polymer;
3. The intermolecular interactions between the molecules in the adhesive;
4. The mechanical adhesion between various molecules in the adhesive.

The four cohesive forces mentioned above affect the properties of the non-cured adhesive and determine for example the viscosity of the adhesive. The curing of the adhesive chiefly involves solidification of the adhesive via bonds between the molecules in the adhesive. This involves new bonds being formed (e.g. crosslinking of short chained molecules to form long chained molecules) and existing bonds being strengthened.

Both adhesion (including the transition zone) and cohesion play their part in maximising the strength of a bond. Just as with a chain, the weakest link in a bonded joint determines what loads the joint can be subjected to.

- The cohesive properties of an adhesive are already determined by the manufacturer. It is up to users to try and attain these by curing under optimum conditions.
- Furthermore, the adhesive strength must be sufficiently high. This is the case when the natural strength of the adhesive, and not the adhesion, is the limiting factor in strength tests.

The adhesive-specific maximum load a bond can take is thus determined during a strength test *(see glossary)* when the fracture is in the adhesive (cohesive fracture) and not in the adhesion zone between the substrate and adhesive.

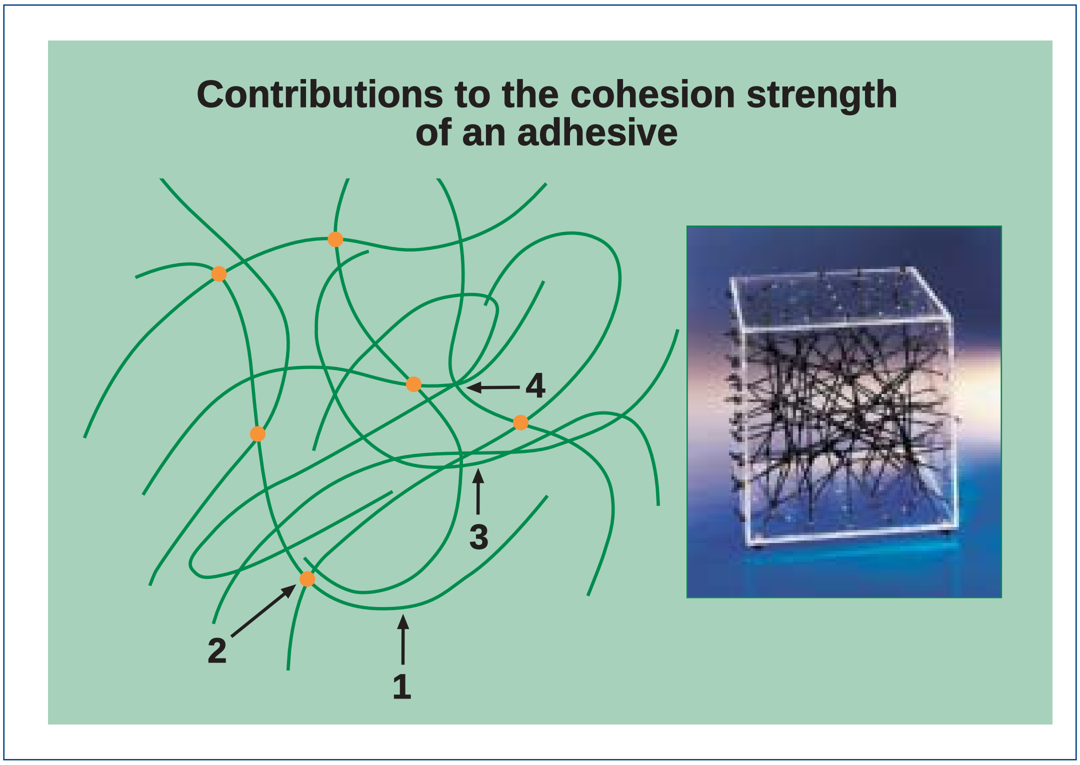


Figure 8

2.1.1 Wetting: a prerequisite for bonding

A prerequisite for forming the adhesive boundary layer is good wetting of the substrate surface by the liquid adhesive. The degree of wetting, which amongst other things is determined by the surface tension of the adhesive and substrate, is hence a criterion for the quality of the adhesion. The approaching of atoms is however only a prerequisite for the formation of adhesive forces. The determining factor for the actual adhesion is the accessibility of and number of physically or chemically active structures on the substrate surface and in the adhesive.

> The wetting of the substrate surface by the liquid adhesive is necessary for adhesion, but this alone is not sufficient. Good wetting alone does not necessarily guarantee the desired good long-term adhesion of the adhesive to the surface.

Consider, for example, high-grade steel: Although this has a high surface tension it can be easily wetted. However, due to its passive character (poor bonding properties) there is only relatively poor adhesion of adhesive to the surface.

If the substrate surface is incompatible with an adhesive – for example because the liquid adhesive does not adequately wet the surface or because the adhesive bonds are too weak – then the surface can be coated with a suitable adhesion promoter. These adhesion promoters function via different bifunctional chemical groups. Some of the groups are adapted to the chemistry of the substrate surface, whilst others are adapted to the adhesive. The most common adhesion promoters bond chemically to both substrates. Surface treatment methods (see Glossary) give other options for enhancing the wetting of the substrate surface.

Adhesion makes an important contribution to the strength of a bonded joint. Users can significantly affect the adhesion by:

- ensuring the surfaces of the substrates are clean and, if necessary, pretreating the substrate surfaces,
- selecting an adhesive, and if necessary an adhesion promoter / primer, that is suitable for the chemistry of the substrate surfaces.

However, an immediate conclusion cannot be drawn relating the (microscopic level) adhesion to the macroscopic joint strength (and vice-versa). The macroscopic cohesive properties of an adhesive (e.g. cohesion strength, elastic behaviour) are largely determined by the choice of the base adhesive and the adhesive formulation, and can be little influenced by users.

2.1.2 Wetting properties and rheology

Rheology falls under the broader subject of mechanics. It concerns how a body (solid, liquid or gas) is deformed on being exposed to external forces. Ideal fluids such as liquids or gases undergo irreversible deformation – they flow. Solids can also be irreversibly deformed if they are subjected to sufficiently large forces – and in that case they also flow.

In addition to the force, the time factor must also be taken into account here. The following example will demonstrate this relationship: The glass in the famous windows of Chartres Cathedral in France has “flowed” since these windows were made more than 600 years ago. In the Middle Ages, the glass panes that were fitted were equally thick at the top and bottom edges. However, over the course of time the silicates have flowed downwards under gravity to such an extent that the thickness of the individual panes of glass at the top has become wafer thin. At the bottom, the thickness of the glass has almost doubled. Solid glass can therefore be considered a fluid – but one must wait a long time to see it flow!

The ability of an adhesive to wet a substrate surface is also determined by its rheological properties. Here, the viscosity and thixotropy aspects are important *(see pages 84 and 85)* and these can be brought together under the term “rheological properties”. A key prerequisite for processing and applying an adhesive is knowledge of these specific properties (see Table 3 for typical viscosity values). Of critical importance for the viscosity of an adhesive *(Table 3)* is the molecular structure, especially the length of the main chains and the presence of any side chains, and the presence of polar groups. The latter are largely responsible for the forces that affect the mobility of the side-groups and chain segments.

Typical viscosity values

h in mPa s at 20°C

Petrol	0.65	Coffee cream	~ 10
Water	1.0	Honey	~ 10^4
Mercury	1.5	Polymer melts	~ 10^3–10^6
Grape juice	2–5	Bitumen	~ 10^8
Blood (at 37°C)	4–25	Glass	~ 10^{23}

Table 3

High viscosities are advantageous in order for example to avoid too much running of the adhesive at the edges of the bonded joints. Different viscosities are required depending on the intended method of application: for example, low viscosities are required for spraying and a paste-like material for application by screen printing. The viscosity can be increased to the desired application viscosity by adding thickening agents, e.g. silica gels. If the viscosity of solvent-based adhesives is too high, then more solvent can be added. The viscosity of solvent-free adhesives can be changed very little by the user; however the viscosity can be altered in adhesive systems that already contain reactive thinner in their formulation.

The viscosity of an adhesive is given as a value for the dynamic viscosity in Pa s; this is given in mPa s for adhesives of low viscosity. It is defined as the force in newtons that is necessary to move one boundary surface parallel to the opposite surface in a fluid layer of 1 m^2 surface area and 1 m height at a speed of 1 ms^{-1}. This is measured with viscometers or rheometers *(see Glossary)* that are constructed according to the nature of the flow processes being investigated.

Thixotropy is the property of a fluid material to temporarily transform into a state of lower viscosity as a result of the action of mechanical forces (e.g. stirring, shaking, kneading). Thixotropic adhesives are formulated in a customised way whereby thixotropic agents, e.g. silicic acid compounds, are added to formulations. This confers the following benefits on the adhesive:

- no running on vertical bonding areas;
- no or very little absorption of the adhesive by porous substrate materials;
- improved application and coverage of the adhesive;
- higher adhesive film thicknesses can be achieved.

2.1.3 Techniques for improving the bonding properties of substrates: surface treatment

From the foregoing discussion of fundamental bonding mechanisms, it is clear that certain requirements have to be met by the structure of the substrate if a high-quality, strong bond is to be achieved:

1. The substrate surface must have good wetting properties, namely the chosen adhesive should not form beads on the substrate surface but must rather distribute itself (spread) across the surface.
2. The substrate surface must have good bonding properties, namely there must be intermolecular and chemical interactions with the adhesive molecules.

3. The surface layer of the substrate must be securely attached to the substrate. Imagine for example highly rusted steel supports that have to be bonded together. If the surface rust layer is not removed, then rust is merely bonded to rust. On subjecting the substrates to loads, the rust breaks away together with the adhesive. In contrast to rust, the oxide layer on aluminium is very strongly attached to the base material and is a good base surface for adhesion.

4. After the bonding process, the surface must not change in an uncontrolled way. Ground steel, for example, rusts – even under the adhesive film – if the bond is in a moist environment. In order to create a bond having good long-term stability, solely grinding the steel surface is inadequate – and in addition suitable measures must be taken to prevent rusting under the adhesive film when using this steel component in a moist environment.

These facts emphasise the need for subjecting the substrate to a surface treatment, to create a surface that meets the abovementioned criteria. In general this means treating the materials such that:

1. In a production environment, conditions for bonding are created that guarantee reproducible bond quality;

2. Wetting and adhesion are improved;

3. The long-term stability of the bonded joints is improved.

In general, a distinction is made between 3 broad types of “surface treatment” *(Figure 9)*: Surface preparation, surface pretreatment and surface post-treatment.

Surface preparation covers cleaning (degreasing) and preparation (e.g. deburring) of the substrate surface.

Surface treatment encompasses all mechanical processes (e.g. grinding, jet-cleaning), chemical processes (Metals: e.g. etching *(see Glossary)*; Plastics: e.g. gas-phase fluorination) and physical processes (Plastics: low pressure plasma) that alter the structure and/or chemical composition of the surface, relative to the starting base material. As an example, the surface pretreatment of polyethylene is mentioned here. Without such pretreatment polyethylene is difficult to bond. The technique used for this pretreatment is the so-called corona method. In order for example to improve the adhesion properties for the manufacture of laminated films, electrical discharges in the presence of atmospheric oxygen at voltages of up to 60,000 volts are allowed to act on the materials.

Surface post-treatment covers all techniques that serve to preserve the treated surface, e.g. application of a primer.

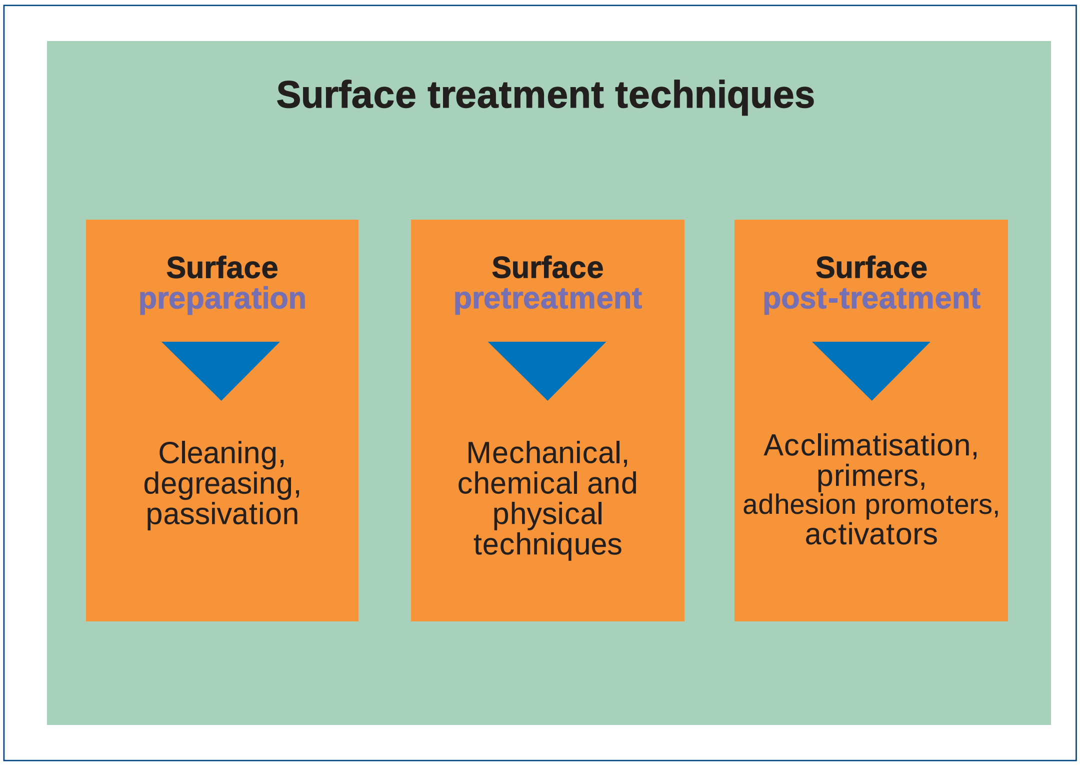


Figure 9

2.2 What are adhesives?

The iterations in section 1.3 have made it clear that a large number of different types of adhesives are used in “bio” and technical areas. Known types of adhesives can be classified either on the basis of their chemical make-up *(Figure 10)* or according to their curing mechanism *(Figure 11)*.

The usual classification of plastics into thermosets, thermoplastics and elastomers is of little help for adhesives. There are for example different polyurethane adhesives that cure as thermosets, thermoplastics and elastomers. So that each adhesive group has a defined position in the overall classification, there is a need for a further classification criterion based on the method and way an adhesive cures, namely whether the bonding involves a physical or chemical mechanism.

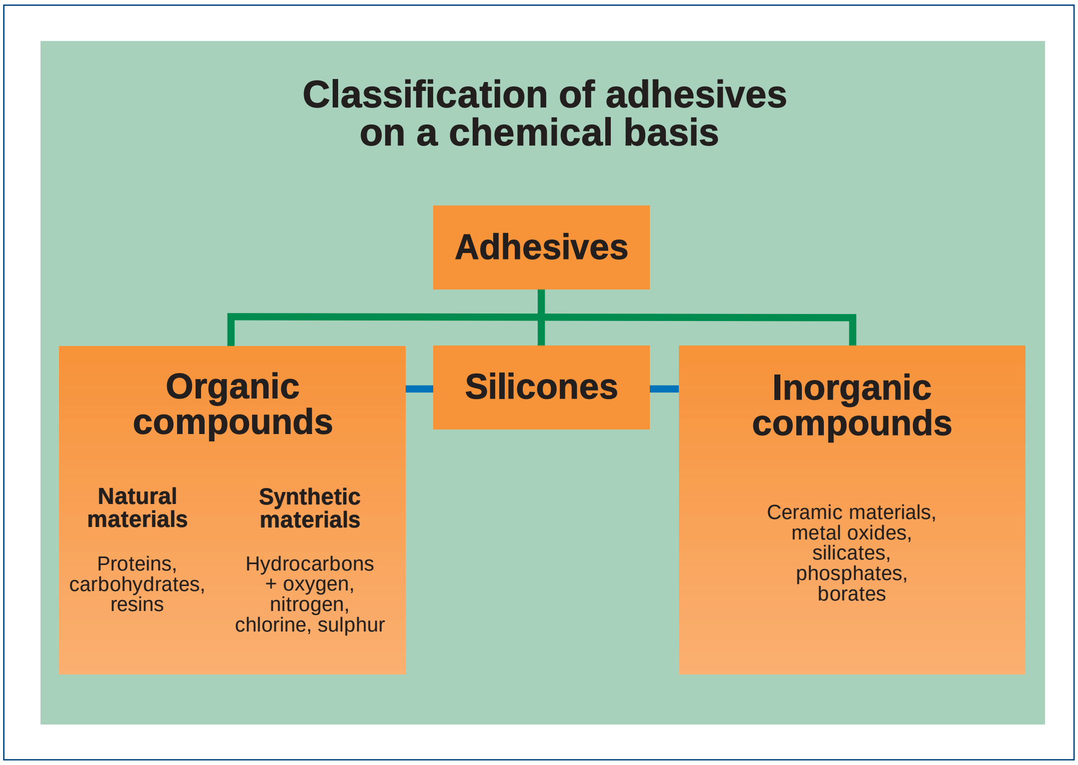


Figure 10

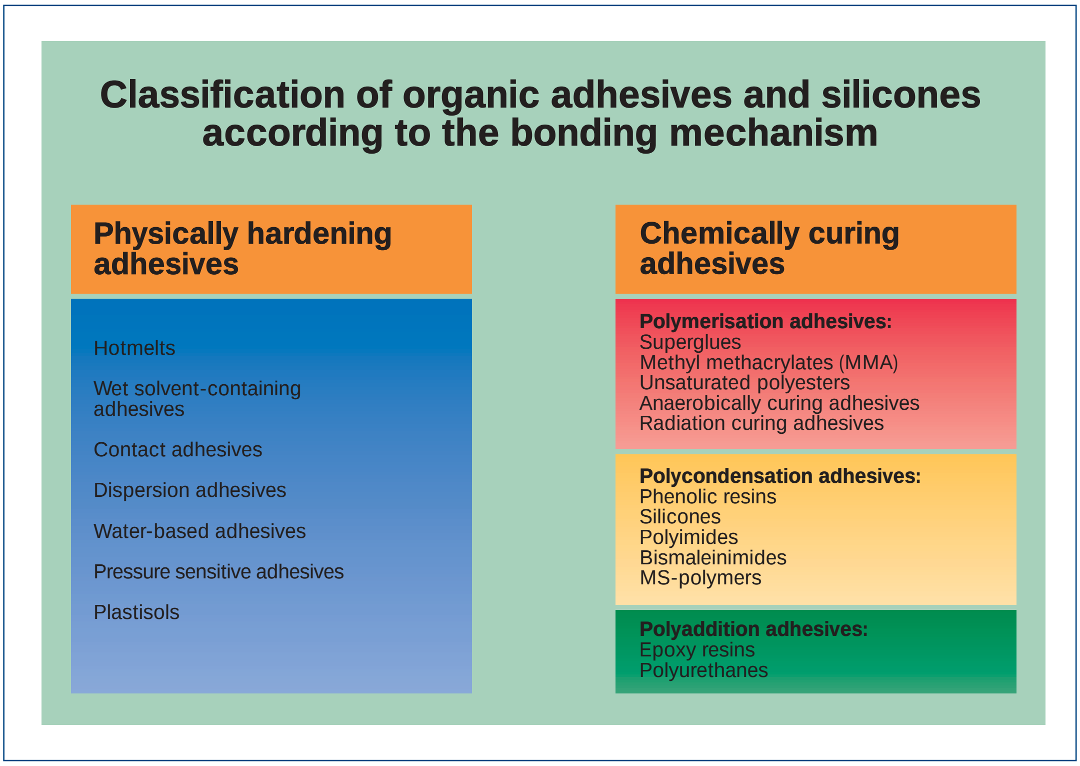


Figure 11

2.2.1 Physically hardening adhesives

These are adhesives which on application are already present in their final chemical state *(Figure 12)*. Only polymers that can be liquefied can be used: namely thermoplastics that can be melted or soluble thermoplastics. Although poorly crosslinked elastomers with good swelling properties are strictly speaking insoluble, they can however nevertheless still be used in certain cases. It suffices if they swell enough for the surfaces to be wetted.

Physically hardening adhesives

Description	Bonding mechanism	Base raw materials	Area of application
Hotmelts	Solidification of the melt	Ethylene / vinyl acetate copolymers, polyamides, polyesters, etc.	Packaging industry, printing industry, textiles, shoe-making and woodwork industries, car manufacturing, electrical engineering.
Wet solvent-containing adhesives	Evaporation of solvent	Polymeric vinyl compounds, polymethyl methacrylate, natural and synthetic rubber, etc.	Printing and packaging industries, bonding PVC pipes, adhesives used in the home
Contact adhesives		Polychloroprene, butadiene-acrylonitrile rubber, etc.	Floor coverings, mattress and shoe manufacture, car manufacturing
Dispersion adhesives	Evaporation of water	Non water-soluble polymers of vinyl acetate, also in combination with co-monomers, polyacrylates, etc.	Packaging industry, shoe-making industry, food industry, woodwork industry
Other water-based adhesives		Glutin, casein, dextrin, methyl cellulose, polyvinyl alcohol, etc.	Paper, wallpaper
Pressure sensitive adhesives	Via surface contact of tacky layers	Special polyacrylates, polyvinyl ether, natural rubber, etc.	Adhesive tapes for handicraft work and industrial use, plasters, sticky labels
Plastisols	Sol-gel process on heating	PVC and plasticisers	Vehicle bodywork construction

Figure 12

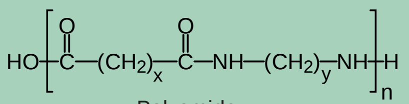
Hotmelts

Various polymers can be used as hotmelts *(Figure 13)*. In a heated state the polymers are liquid, and can hence be processed, but on cooling they solidify. Hotmelts used by industry can be in the form of blocks, rods, granulate, powder and film at room temperature. They are applied to the substrate surface as a melt. The adhesive is applied by rolling or spraying and joining is carried out immediately after application or after reheating the solidified layer. Alternatively the solid adhesive can be laid on the substrate as a film or net and then hot-pressed. In general the joining step requires the application of pressure. A feature of hotmelts is that on cooling they very rapidly build up their internal strength.

A natural hotmelt familiar to everyone is beeswax which bees use as a building material *(see section 1.3)*. Bond strengths between 15 and 35 MPa can be achieved with industrial hotmelts. They do however have a tendency to undergo creep *(see Glossary)* when subjected to continuous stress or high temperatures. On the plus side, these adhesives can be used to create thermally detachable and also redetachable bonded joints due to their thermoplastic structure. The bonded joint must however not be heated up to its melting temperature range because the adhesive loses strength at considerably lower temperatures in the so-called “softening region”. The processing temperature can be varied within a certain range *(Figure 13)* and depends on the desired viscosity of the adhesive for the particular application. The viscosity of the melt determines the application properties of the adhesive. In general a low viscosity facilitates wetting.

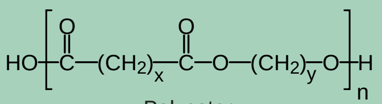
Hotmelts are used in industry for a wide range of applications. The packaging industry (manufacture of packaging from paper, cardboard and sheet metal) is one of the major users. Hotmelts are also used in the printing industry for bonding the spines of books, in the textile industry for bonding appliqué and in the shoe-making industry for bonding for example shoe soles. The wood processing industry uses hotmelts for veneer surrounds and edging. The car manufacturing industry employs hotmelts for a host of applications including bonding insulating and cushioning materials, bonding headlight covers into metal frames and for wheel covers. The electronics industry also uses hotmelts, for example for bonding coil windings and coil ends *(Figure 14)*.

Base materials for hotmelt polymers



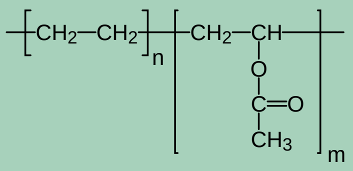
$$HO\!-\!\left[\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_x\!-\!\overset{O}{\overset{\|}{C}}\!-\!NH\!-\!(CH_2)_y\!-\!NH\right]_n\!-\!H$$

Polyamide



$$HO\!-\!\left[\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_x\!-\!\overset{O}{\overset{\|}{C}}\!-\!O\!-\!(CH_2)_y\!-\!O\right]_n\!-\!H$$

Polyester



$$\left[CH_2\!-\!CH_2\right]_n\left[CH_2\!-\!\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{\underset{O}{|}}{CH}\right]_m$$

Ethylene - vinyl acetate copolymer (EVA)

Base material	Softening range (°C)	Viscosity of the melt (Pa s)	Application temperature (°C)
Polyamide (PA)	95–175	1–20	120–240
Polyester	50–230	20–2000	150–240
Ethylene - vinyl acetate copolymer (EVA)	90–200	20–10000	max. 200

Figure 13

Application using hotmelt guns

Furniture-making industry

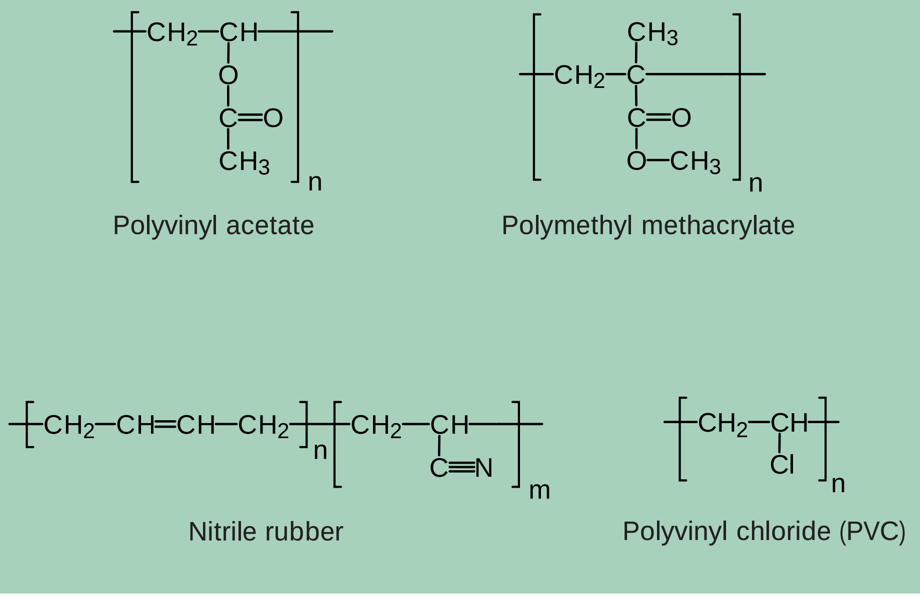
Packaging industry

Electronics industry

Figure 14

Solvent-containing wet adhesives

The “trick” for applying this class of adhesive is to use organic solvents in which the thermoplastic polymers are present *(Figure 15)*. The solvent content of such adhesives is generally in the 75-85% range. After application the solvent evaporates, so allowing the macromolecules to build up cohesion and so bond the adhesive. The development of Van der Waal interactions and the intertwining of the chains of the thermoplastic ensure that the polymer molecules cohere with one another. This class of adhesives has good wetting properties on many substrates, especially on substrates that are permeable to the solvent. The performance of the adhesives varies depending on the range of possible raw materials from which wet adhesives are manufactured. The procedure for processing wet adhesives is indicated by time intervals and adhesive manufacturers provide this information on their data sheets. The **minimum drying time** indicated for a wet adhesive is the period of time for which the adhesive must be left, after application, until some of the solvent has evaporated. This minimum drying time before joining the substrates even has to be observed for substrates that are permeable to



Base materials for wet solvent-containing adhesives

Polyvinyl acetate

Polymethyl methacrylate

Nitrile rubber

Polyvinyl chloride (PVC)

Figure 15

the solvent. Following this there is the **wet life** or **open time**. This is the time period for which the applied wet adhesive can remain on the substrate without impairment of the final strength of the bond. If the wet life is exceeded and the actual joining of the substrates is carried out after expiry of the wet life then this results in weakening of the bond. Wet adhesives have a low initial strength which slowly increases up to hand strength and then reaches its final strength. High shear strengths *(see Glossary)* cannot be achieved with this type of adhesive. Due to their thermoplastic nature, wet adhesives only have limited resistance to deformation under the influence of heat. In addition, they by nature react sensitively with solvents and when subjected to loads have a tendency to undergo creep. In industry these adhesives are mostly used for bonding paper and cardboard as well as for diffusion-bonding (solution welding and cold welding) of soluble thermoplastics (e.g. PVC). For environmental reasons, the trend in adhesive development is however shifting away from solvent-containing adhesives to solvent-free systems.

Contact adhesives

Contact adhesives are mixtures of soluble elastomers and resins in the form of a solution in an organic solvent or as a dispersion in water. The “processing trick” is the same as used for wet adhesives: The solvent evaporates and the adhesive solidifies. The different names used for these two classes of adhesives signify their distinguishing features: Whilst “wet adhesives” form a “wet” film of adhesive and the solvent only evaporates during the bonding process, contact adhesives essentially bond in the “dry” state. The adhesive is applied to both substrates and the solvent is allowed to almost fully evaporate before the substrates are joined. Water, an environmentally friendly solvent used in some contact adhesives, has up until now not been able to replace organic solvents in all applications because of the sensitivity of the bonding process to moisture.

Common raw materials used for contact adhesives are polychloroprene, butadiene-styrene rubber and butadiene-acrylonitrile rubber in organic solvents and also aqueous acrylate dispersions. The indicated evaporation time for the solvent describes the period of time after which the applied adhesive is apparently dry to touch but still contains residual solvent. Joining is then carried out under as high a pressure as possible – there is now contact between the substrates and the adhesive polymers diffuse into each other. The data sheets give information about the contact life, namely the period of time that can elapse before joining the substrates without adversely affecting the final strength of the bond. This time is limited by the onset of crystallisation in the adhesive film that causes the polymers to lose their ability to form adhesive bonds with the substrates. When joining substrates using contact adhesives, it is not the duration of the pressing that is important but rather the contact pressure (at least 0.5 MPa) which determines the strength of the bond. The strength of this bond is determined by Van der Waal forces and intertwining of the molecules between the polymer layers. Although contact adhesives in general form hand-tight bonds immediately, high shearing strengths cannot be achieved. The bonds have high flexibility and this can be adjusted within a certain range. However, they only have limited resistance to deformation under thermal stress and react sensitively to solvents and to dispersions in water. Their tendency to undergo creep at high temperatures when subjected to loads can be suppressed to a certain extent. An important area of application of contact adhesives used to be for bonding PVC and parquet floor coverings. In many parts of Europe these adhesives have now largely been replaced by solvent-free systems. However, contact adhesives are still used in the car manufacturing industry and for the production of mattresses and shoes due to the high flexibility of the bonds and their ability to give relatively high initial bond strengths.

Dispersion adhesives

Dispersion adhesives *(Table 4)* are heterogeneous systems comprising a solid polymer phase and an aqueous phase, with a solids content of between 40 and 70%. In section 1.3 it was mentioned how paper wasps use this type of adhesive for nest building and how the adhesive particles are prevented from bonding prematurely by the digestive secretion, which later evaporates to set the adhesive.

In industrially manufactured dispersion adhesives *(Figure 16)* the individual adhesive particles are kept in suspension in the water by auxiliary materials and emulsifiers. They are hence present in a liquid state that can be processed. With dispersion adhesives the bonding process takes place slowly as a result of the water being lost, either by evaporation or absorption by the substrates. As a consequence of this water loss, the concentration of the polymer particles increases. These particles become closer and closer to one another until they flow into each other. This process is called “film formation” *(Figure 17)*. For dispersion adhesives the open time, namely period of time for which the adhesive can remain on the substrate after application without adversely affecting the final strength of the bond, is determined by the temperature, the thickness of the adhesive film and the absorption properties of the substrates. The substrates are then pressed against each other, generally for a few minutes (depending on the temperature). Before further processing, the post-curing time, which is also dependent on the temperature, must be observed.

High lap shear strengths *(see Glossary)* cannot be attained with dispersion adhesives. Due to their thermoplastic nature they only have limited dimensional stability under the influence of heat. Due to the presence of embedded emulsifiers they are also sensitive to moisture and when subjected to loads they have a tendency to undergo creep. They bonds are however very flexible and this flexibility can be adjusted to a certain extent. Dispersion adhesives are especially suitable for bonding high-area laminate systems made of water-permeable materials. For this reason these adhesives are often used in the paper processing industry, in the packaging sector and in furniture-making. The summary that follows gives an overview of the many areas of application of dispersion adhesives and the polymers that are used *(Table 4)*.

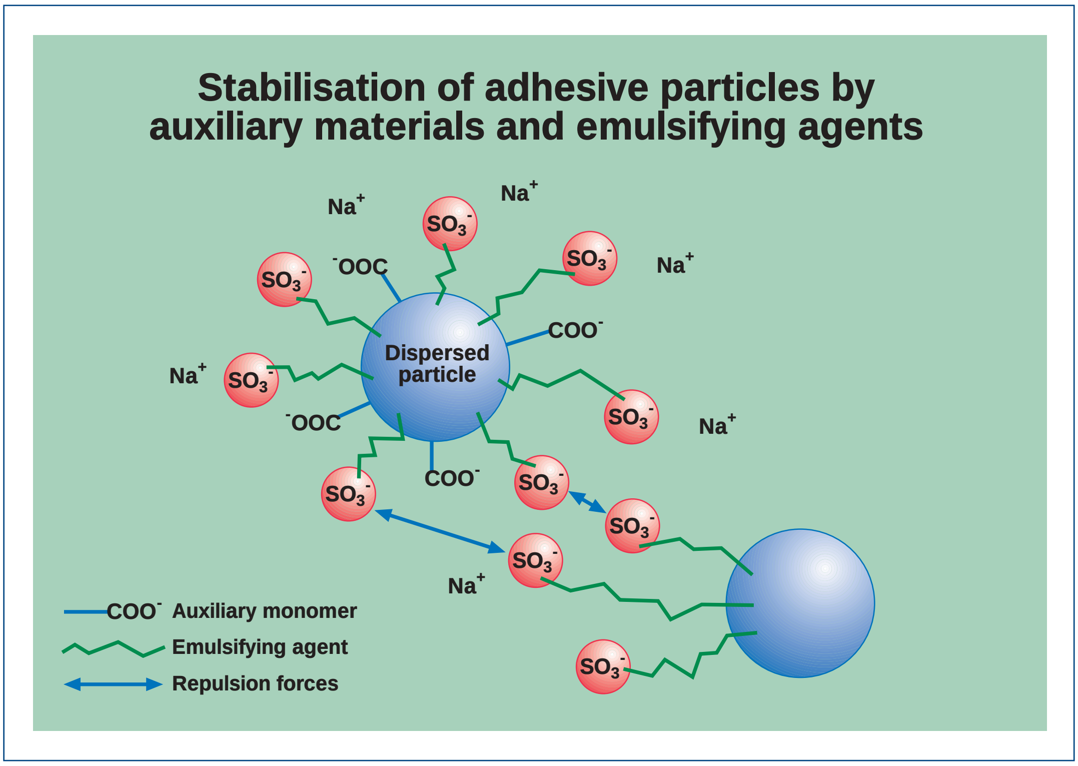


Figure 16

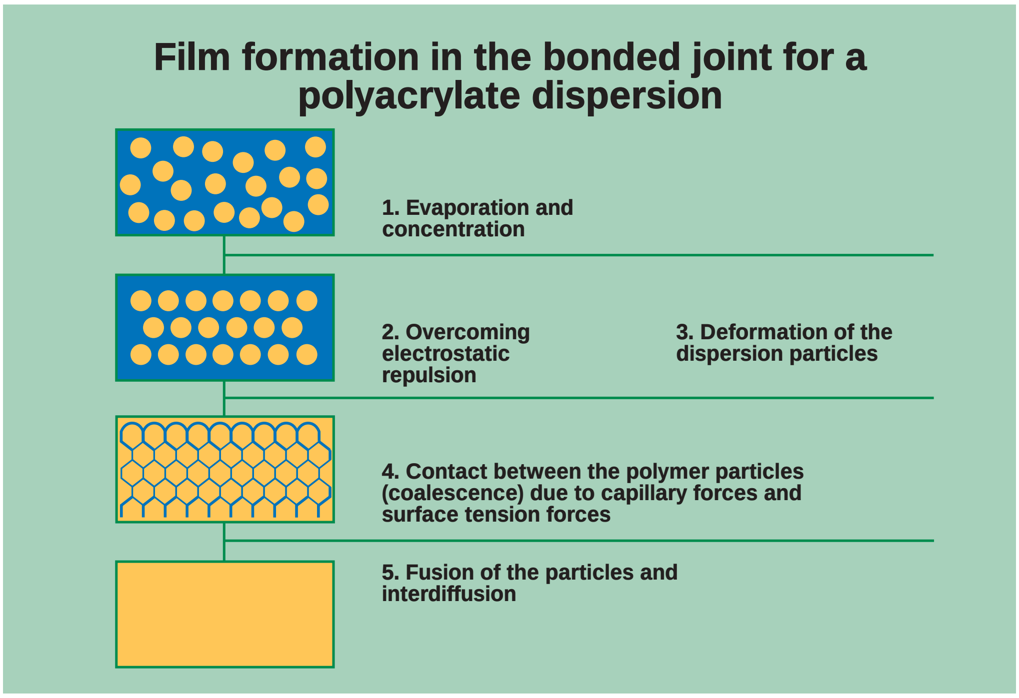


Figure 17

Dispersion adhesives

Polyvinyl acetate	Good adhesion to cellulose-containing substrates such as wood and paper. Primarily used for wood adhesives.
Vinyl acetate copolymers	Good adhesion to many polar plastics.
Polyacrylates	Good aging properties and resistance to media. Primarily used for pressure sensitive adhesives (labels, adhesive tapes), permanent adhesives (e.g. for tiles and floor and wall coverings) and laminating adhesives (e.g. glossy films).
Polyvinylidene chloride	Physiologically harmless and hence preferred for laminating adhesives used for food packaging applications.
Styrene-butadiene copolymers	Laminating adhesives (e.g. aluminium foil on paper).
Polyurethanes	Usually very good adhesion to many substrates and high adhesion strengths. Applications in the shoe-making industry and for film lamination.
Polychloroprene	High elasticity and adhesion strength. Primarily used in the shoe-making industry.
Rubber latexes	(e.g. chloroprene latex). Alternative to solvent-containing contact adhesives.

Table 4

Water-based adhesives

The group of water-based adhesives comprises four sub-groups *(Table 5)*: Adhesives based on animal connective tissue protein (glutin glues), natural plant products, the group of casein glues and adhesives containing polyvinyl alcohol (PVAL) as the raw material. With water-based adhesives, the formation of the adhesive film occurs by evaporation of the water or by absorption of the water by the substrates. Some plant glues and the casein glues have the special feature that the base raw materials are insoluble in cold water and have to be dissolved in alkaline media (sodium hydroxide solution, ammonia). The following overview shows a selection of different components of water-based adhesives and their most common areas of application.

Pressure sensitive adhesives

From a chemical standpoint, pressure sensitive adhesives are ready-to-use adhesives and are highly viscous. In general they are applied as a film to a flexible support material (adhesive tape or labels). The special feature of these adhesives is that they do not solidify to form a solid material, but remain viscous. As such they have a special place within the group of adhesives that bond via a physical mechanism. For manufacturing pressure sensitive adhesive systems, the adhesives can be dissolved in organic solvents (e.g. natural rubbers, acrylates), can be present as aqueous dispersions (e.g. acrylate dispersions) or can be solvent-free melts (pressure sensitive melts). These different pressure sensitive adhesives are however formulated similarly: they all contain the base polymer

Other water-based adhesives

Type of adhesive	Origin of the base raw material	Area of application
Glutin adhesives		
Skin adhesives	Raw skin waste and tissue	Bonding paper
Fish adhesive	Fish skin	Gummed adhesive strips
Based on natural plant products		
Starch adhesive	Maize, potatoes, rice	Bonding paper
Methyl cellulose	Casein: cellulose and wood	Wallpaper paste
Casein adhesive	Protein component of milk	Bottle labelling
PVAL adhesives	Saponification product of polyvinyl acetate or other polyvinyl esters	Bonding paper, cardboard, wood; base material for moisture-activated bonding

Table 5

(the cohesion determining component), adhesive resin and plasticiser (the adhesion determining components), plus additives to confer special properties.

A wide range of base polymers and additives (adhesive resins, plasticisers, antioxidants) are currently employed in pressure sensitive adhesives *(see Figure 18)*. The stereo-chemistry of the polymers does not have a noteworthy effect on the strengths of the resulting bonds. The term “pressure sensitive adhesive” must be understood to mean that in contrast to other adhesives there is immediate adhesion and cohesion when substrates are joined using these adhesives. In order to promote wetting of the substrate surface by the adhesive a contact pressure of ca. 0.2 MPa is necessary (hence the term “pressure sensitive adhesives” – PSA). If inadequate pressure is applied or the processing temperature is too low (viscosity increases), this can cause bonding faults such as bubbles or detachment. As with other adhesives, the actual adhesion when using pressure sensitive adhesives arises due to intermolecular interactions. However with pressure sensitive adhesives there is still a viscous liquid state in the final bond. That is why the viscosity has a direct effect on the cohesion strength of the relevant pressure sensitive adhesive. A distinction is made here between detachable and permanent adhesives. On detaching a pressure sensitive adhesive (e.g. adhesive tape) from a surface, the adhesion between the adhesive and the surface is not disturbed, rather there is a rupture in the near surface cohesion zone of the adhesive. For that reason, residues of the adhesive remain on the surface of the substrate

Rubbers used in pressure sensitive adhesives

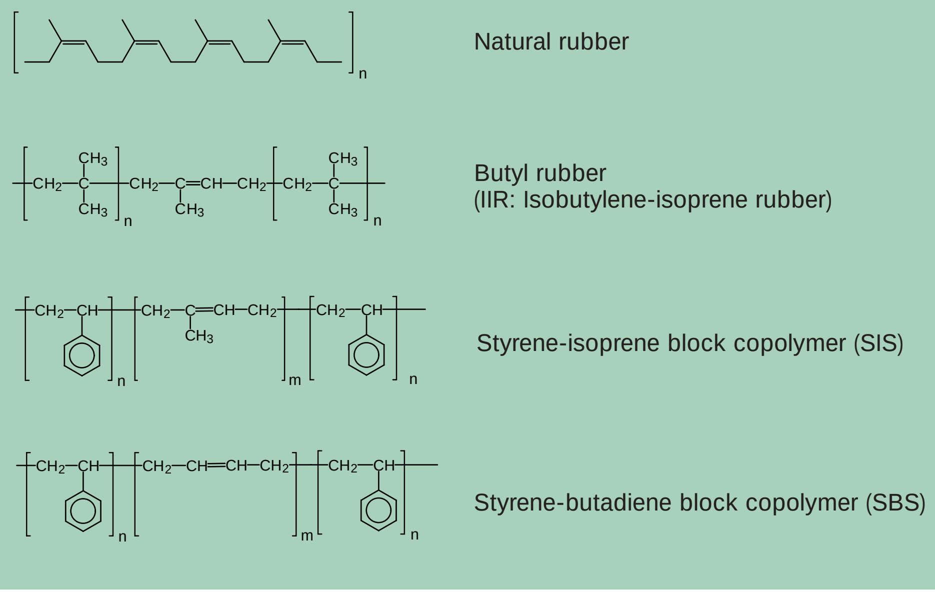


Figure 18

(e.g. bits of labels on windows). If an adhesive tape is covered with a lower viscosity pressure sensitive adhesive, its cohesion strength is low and it can be detached again. However, high final strengths cannot be achieved here. A characteristic feature is however that a relatively high initial adhesion is quickly attained because wetting processes take place quickly in low viscosity systems.

In contrast, rapid initial bonding is not possible for higher viscosity systems. Such adhesives require longer to fully wet the substrate surface. Due to the high viscosity there is higher cohesion with higher final strengths. For these reasons these systems are used to give permanent bonding. As rough surfaces make wetting more difficult and retard the wetting process, especially for high viscous pressure sensitive adhesives, the substrates to be bonded should ideally have smooth surfaces. As many pressure sensitive adhesives (especially the natural rubber adhesives and silicones) have very low surface tension, no pretreatment other than cleaning the surface of the substrate is usually required – bonds made with pressure sensitive adhesives are also “self-adhesive” on most plastic surfaces.

The peel resistance and shear strength of pressure sensitive adhesives decrease when the temperature is increased. Pressure sensitive adhesives also exhibit a tendency to undergo creep when subjected to loads. Of all the various types of adhesives, pressure sensitive adhesives are used for the most varied array of everyday applications. This is due to their characteristic properties *(see Glossary, Pressure sensitive adhesives, Table 7)* and covers applications as diverse as plasters, sticky labels and various types of adhesive tapes for handicraft work and industrial purposes *(Figure 19)*.

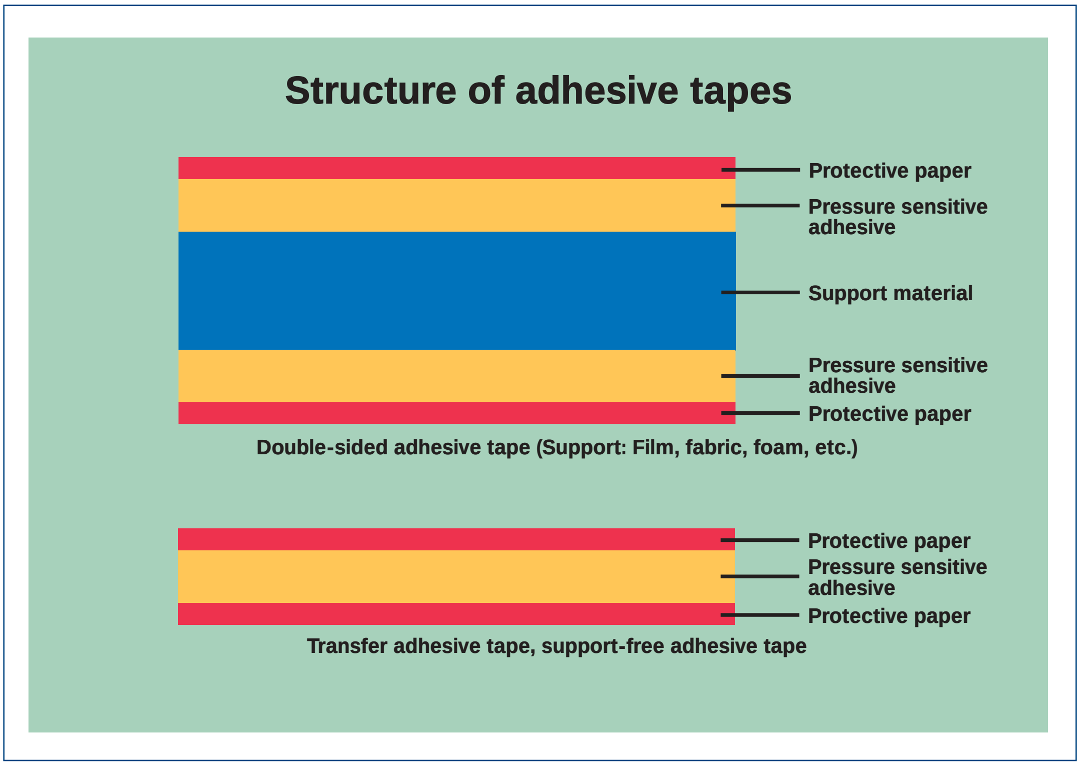


Figure 19

Plastisols

Plastisole Plastisols are 1-component adhesives that are applied as a paste to the substrate. The pastes in turn consist of two admixed components: PVC particles and plasticiser *(see Glossary)*. The solid PVC particles are dispersed in the highly viscous plasticiser in a ratio that can vary from 1:1 up to 4:1. In order to bond the adhesive, the applied adhesive is heated so that the thermoplastic PVC swells and can take up the plasticiser. This step involves a purely physical sol-gel process *(Figure 20)*. The two-phase system (sol) converts to a single-phase system (gel) by incorporating the plasticiser in the swollen polymer. This process only occurs at a temperature between 150 and 180°C, and results in an adhesive film consisting of a plasticised polymer. Plastisols have high flexibility and good peel resistance. They do however have the disadvantage that they are sensitive to lap shear stress and they also tend to undergo creep when subjected to loads but for normal applications as an adhesive sealant this has no adverse effects. Being thermoplastics, they by nature only have limited resistance to heat. If overheated, for example during spot welding, there is also the risk of liberating hydrochloric acid. A typical area of application for plastisols is in vehicle body construction. Besides their bonding function here, they are also serve to seal joints against moisture, to dampen vibrations and to increase the rigidity of the body. Plastisols can also be used to bond non-pretreated metal sheets as they have the ability to take up oil. On the down side, PVC plastisols give rise to environmental problems (PVC issue) when recycling the bonded components with the consequence that

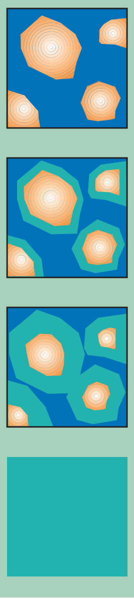


Figure 20

they are being replaced to an ever greater extent by alternative adhesives, e.g. adhesives based on epoxy resins.

2.2.2 Chemically curing adhesives

The different types of chemically curing adhesives (reactive adhesives) are described below. They are classified into three groups depending on the basic nature of the reactions involved *(Figure 21)*. In order to ensure that the adhesive only actually cures in the bonded joint, the manufacturers have had to develop a processing technique which enables the chemical reaction that forms the solid adhesive to be blocked or suppressed for a sufficient period of time to allow the adhesive to get to its final intended place, namely the bonded joint. The exact processing technique depends on the curing mechanism of the various adhesives: Adhesives which after mixing with their reaction partners spontaneously react, i.e. at room temperature, are sold as 2-component (2-C) adhesives. They are present as "resin" and "hardener" in separate containers and are hence physically apart. They are only mixed together to form the adhesive a short time before application.

Chemically curing adhesives

Description	**Curing mechanism**	**Base raw materials**	**Areas of application**
Cyanoacrylates	Polymerisation	Cyanoacrylates	Bonding small components, bonding all types of glass, fabric adhesive, spray-on bandage
Methyl methacrylates		Methyl methacrylates	Bonding plastics in the car and rail vehicle manufacturing industries
Anaerobically curing adhesives		Diacrylates of diols	Engines, electric motors, securing screws, shaft-cam connections
Radiation curing adhesives		Epoxy acrylates, polyester acrylates	Bonding glass and transparent plastics, dental technology
Phenol-formaldehyde resins		Phenols, formaldehyde	Wood materials, bonding brake and clutch linings, structural bonding of aluminium in aircraft manufacture
Silicones	Polycondensation	Polyorganosiloxanes	Seals, car manufacturing, electrical engineering; special applications in aeronautics and aerospace technology
Polyimides		Aromatic tetracarboxylic acid anhydrides and aromatic diamines	Bonding metals in aeronautics and aerospace technology
Epoxy resin adhesives		Oligomeric diepoxides and polyamines or polyamidoamines	Structural adhesive in car and aircraft manufacture, vehicle bodywork construction, electronics, bonding fibre-reinforced plastics, repair work
Polyurethanes	Polyaddition	Di-functional and sometimes tri-functional isocyanates, polyols	Vehicle bodywork construction, bonding materials with very different load and temperature expansion properties, bonding panes of glass in car manufacture

Figure 21

With single-component adhesives (1-C), the adhesive components are premixed in their final proportions. They are however chemically blocked: As long as they are not subjected to the specific conditions which activate the hardener they will not bond. They require either high temperature or substances or media (light, humidity) from the surroundings to initiate the curing mechanism. The containers in which this type of adhesive are transported and stored must be carefully chosen to prevent any undesired reactions.

Polymerisation adhesives

Cyanoacrylates (superglues)

In everyday parlance, cyanoacrylates are termed “superglues”. This term describes very clearly the dominant feature of this class of adhesives. Within a few seconds, hand-tight bonds can be realised with these adhesives. Their final strength is however only reached after several hours. From a chemical point of view superglues are 1-C reactive adhesives based on cyanoacrylates. The special structure of cyanoacrylates also explains the high speed at which the curing reaction starts *(Figure 22)*. The cyano and ester groups exert a strong electrophilic effect which promotes attack by nucleophilic substances, e.g. amines, and stabilises the resulting carbanion. Hydroxide ions, resulting from the dissociation of water, or amines, which are present in primers, can attack and initiate an anionic polymerisation reaction *(Figure 23)*. The curing of this type of adhesive can be triggered by either a humidity of between 50 and 70%, by moisture present on the substrate surfaces or by contact with basic surfaces. However, if acid is added or acid surfaces are present, the necessary concentration of nucleophilic hydroxide ions is so much reduced that the curing of the superglues is slowed down. Strong acids cause protonation of the carbanion and result in immediate termination of the chain reaction. Although weak acids can also cause termination, their nucleophilic conjugated bases can initiate new polymerisation reactions. In a neutral or basic medium the reaction runs until all monomer molecules have been used up. The behaviour of cyanoacrylates to water is however ambivalent: Although they require water to cure, too high humidity can cause detachment of the bond. The reaction mechanism involved here is thought to be base catalysed hydrolysis of the cyanoacrylate polymer *(Figure 24)*. Formaldehyde can indeed be detected as the reaction product of the hydrolysis. Also giving credence to the postulated mechanism is the increase of the reaction rate by two orders of magnitude when the pH is increased from 7 to 8, from which it can be concluded that the reaction is initiated by hydroxide ions. Besides their relatively high strength, other typical properties of superglues are their brittleness, low flexibility and being thermoplastics they only possess limited resistance to heat. In addition, non-cured superglues are usually very thin liquids, meaning that only gap widths *(see Glossary)* of ca. 0.1 mm can be bridged using this class of adhesives. For wider gaps there is an additional problem, related to the curing mechanism of cyanoacrylates. When higher adhesive

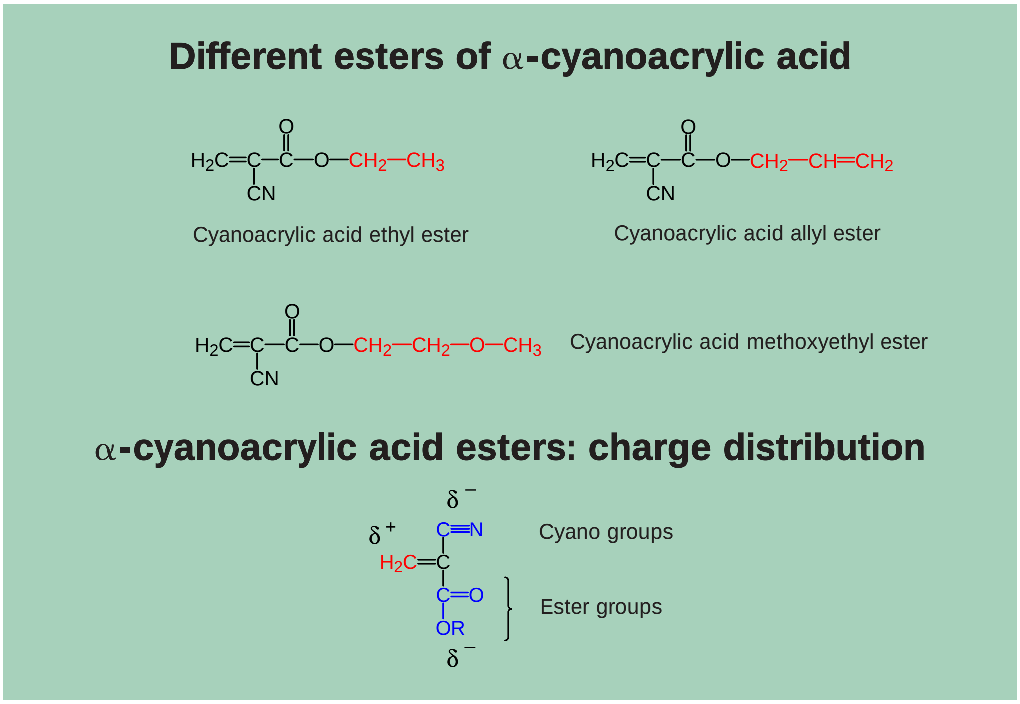


Figure 22

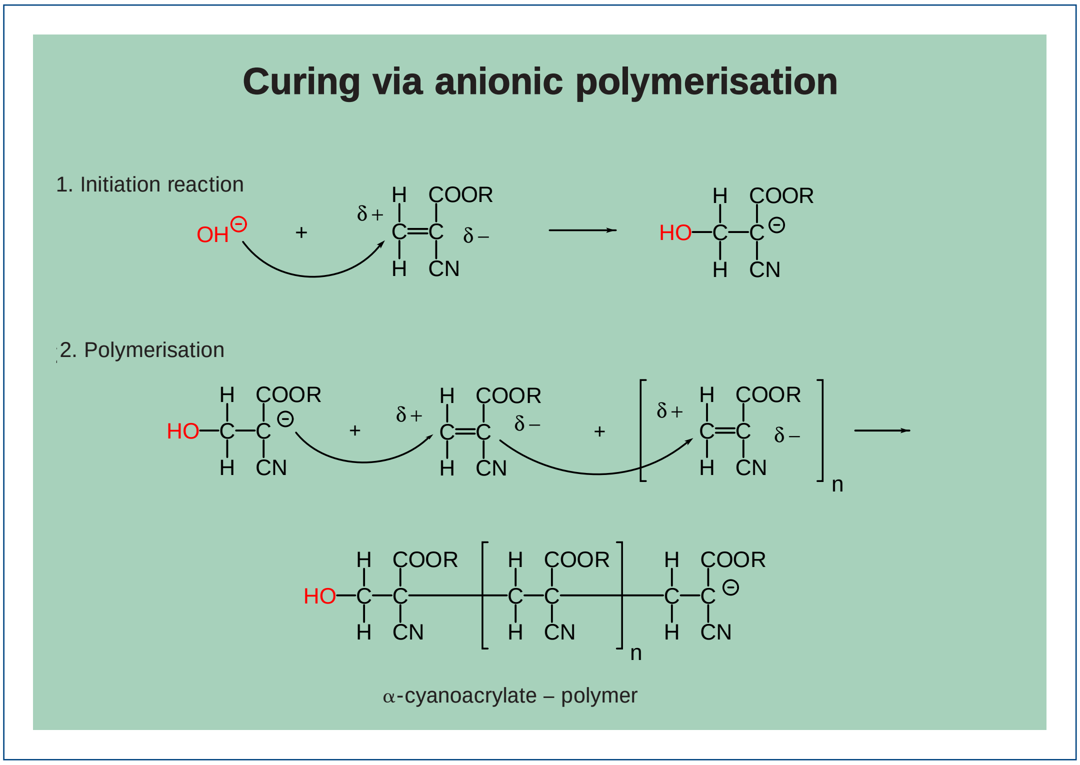


Figure 23

film thicknesses are used, the required moisture does not penetrate far enough into the bonded joint, so causing the polymerisation to terminate. The result is an adhesive that cannot fully cure. The areas of application of superglues are very diverse. Superglues are suitable for bonding many combinations of materials and are in general used for bonding small components. Superglues are popular for bonding all types of glass. On highly alkaline glass there is however the risk of shock curing. Stress in the adhesive film can reduce the strength of the bond. The same effect can be caused by high humidity (> 80%). In addition to many applications in optics, microelectronics and vehicle technology, there will in the future be a growing and extremely diverse spectrum of applications for special superglues in the area of medical technology, e.g. as a textile adhesive and for spray-on bandages.

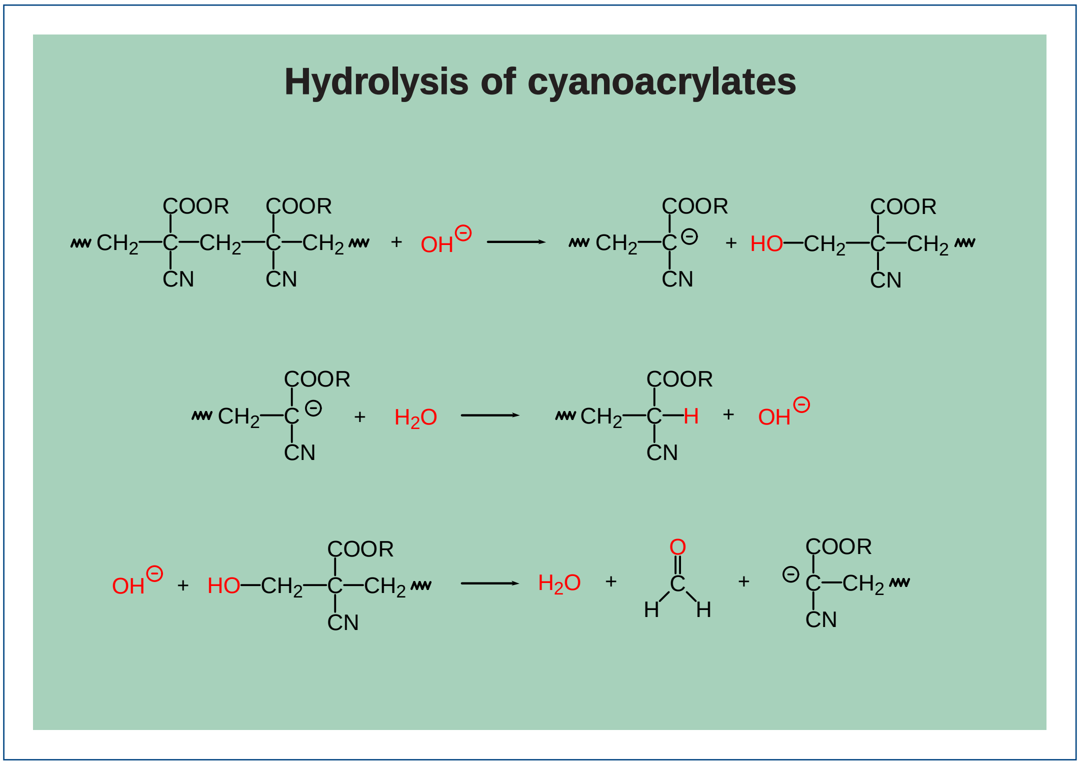


Figure 24

Methyl methacrylates (MMA)

Methyl methacrylates are reactive adhesives based on methyl methacrylate (methacrylic methyl ester). A hardener, dibenzoyl peroxide (typically added as a radical-former and N,N-dimethyl-p-toluidine (typically added as an accelerator) are also present. The curing of the reactive system comprising MMA monomers, radical-former (3 to 5%) and accelerator occurs via a radical chain polymerisation mechanism *(Figure 25)*. If the fraction of hardener is greater than 5%, the strength of the adhesive slightly decreases. If the fraction of hardener is lower than 3%, the curing time increases considerably but this is accompanied by only a slight increase in the bond strength. With MMA adhesives, lap shear strengths (before aging) up to greater than 30 MPa can be achieved and in many cases strengths of over 5 MPa are attained after just 5 minutes. At room temperature the final strength is reached after ca. 12 to 24 hours. Increasing the curing temperature accelerates the process but the final strength is adversely affected. MMA adhesives cure as thermoplastics. They can withstand temperatures between -50°C and ca. 100°C, and even up to 180°C for short periods. They possess good bonding properties to many different plastic surfaces and are relatively insensitive to surfaces that contain a certain amount of oil/grease. Depending on the viscosity of the adhesive, this type of adhesive can be used to bridge larger gap widths. The elasticity and flexibility of the cured adhesive can be adjusted within certain limits. An interesting feature is the differing processing conditions used for MMA adhesives. Besides the techniques normally used for 2-C adhesives (adhesive application using twin cartridges, processing by direct addition of the hardener), with MMA adhesives the different components can each be applied separately to one of the substrates. The actual curing reaction then only takes place in the bonded joint after bringing the substrates together. This so avoids having to mix difficult mixing ratios (for example, resin:hardener 100:3) and prevents a very short pot life *(see Glossary)* having to be closely complied with in an industrial production environment which would clearly give rise to problems. MMA adhesives are used for bonding plastics to each other and for bonding metals to plastics. Classic applications for this type of adhesive are in the car manufacturing industry and in the rail vehicle manufacturing industry.

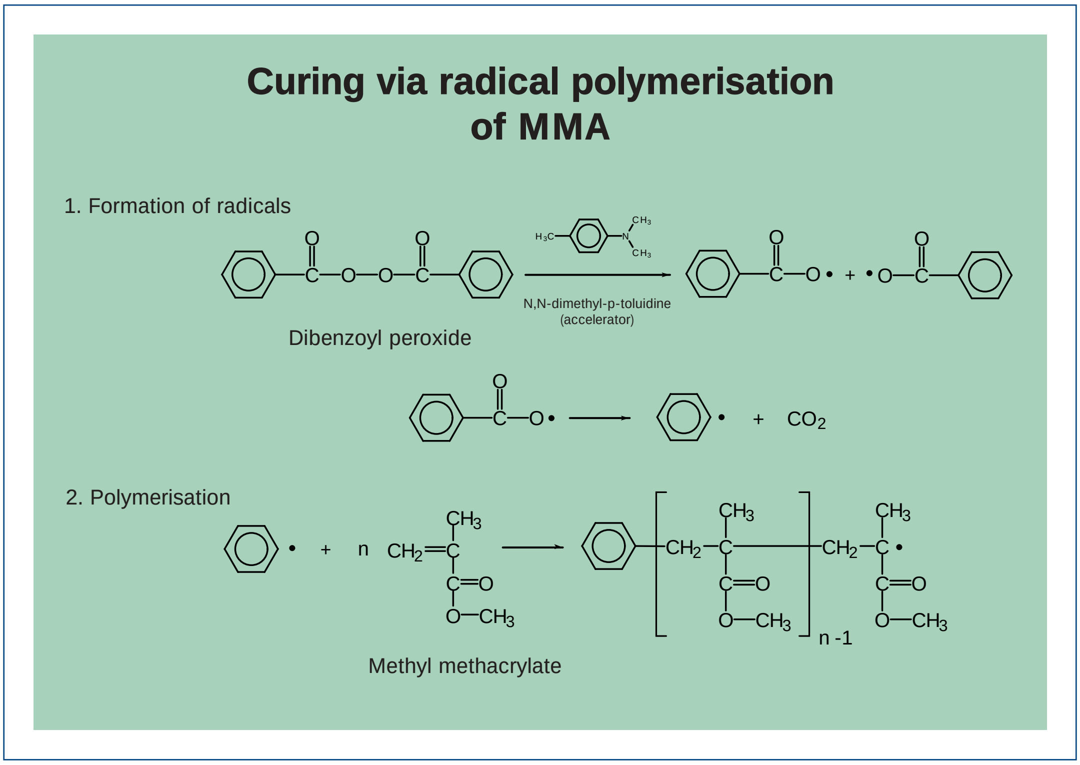


Figure 25

Adhesives that cure under anaerobic conditions

These 1-C adhesives are based on dimethyl acrylates and cure under anaerobic conditions, namely in the absence of oxygen. After application of the adhesive there is an oxygen-free environment in the joint gap if the geometry of the substrates is such that this results in the exclusion of oxygen. In order to then set the curing reaction in motion, contact with a metal is required (copper or iron). An accelerator is necessary if the substrates are copper-free and iron-free. So that the adhesive does not cure prematurely, the adhesive in its container must remain in contact with oxygen up until the time it is used. This is achieved using air-permeable plastic bottles which are only half filled and which, prior to filling, are flushed with oxygen.

A frequently used raw material for anaerobically curing adhesives is tetraethyleneglycol dimethacrylate (abbreviated to TEGMA). Cohesion development for anaerobically curing adhesives occurs via a radical polymerisation mechanism *(Figure 26)*. This reaction is inhibited by oxygen, whereby TEGMA radicals react with oxygen and so form passive TEGMA-peroxide radicals. The adhesive is present in the manufacturer's container in this state. When the adhesive is applied at a later time and exposed to oxygen, the hardener components become active. This is a complex system comprising radical-formers (e.g. cumene hydroperoxide), accelerator (e.g. N,N-dimethyl-p-toluidine) and saccharin which is used as a metal complexing agent and reducing agent for metal ions. The reaction between the saccharin and N,N-dimethyl-p-toluidine *(Figure 27)* consumes any remaining oxygen in the adhesive and in the bonded joint. An aminal is produced. This in turn dissolves metal ions from the substrate surface and reduces these to a lower oxidation state. The latter then catalyse the degradation of the radical-former into active radicals. This reaction is a part-reaction of the overall curing mechanism of anaerobic adhesives *(Figure 27)*. The aminal is the key reagent here. The activated radicals start the polymer chain reaction. As the reaction is cyclic, the constant generation of the aminal

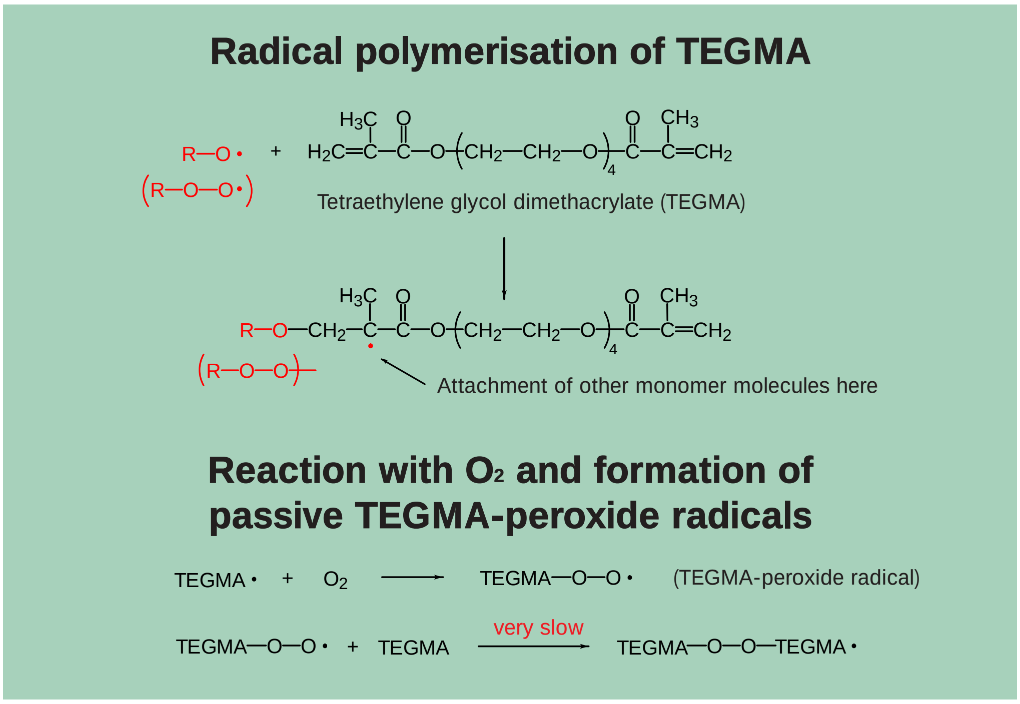


Figure 26

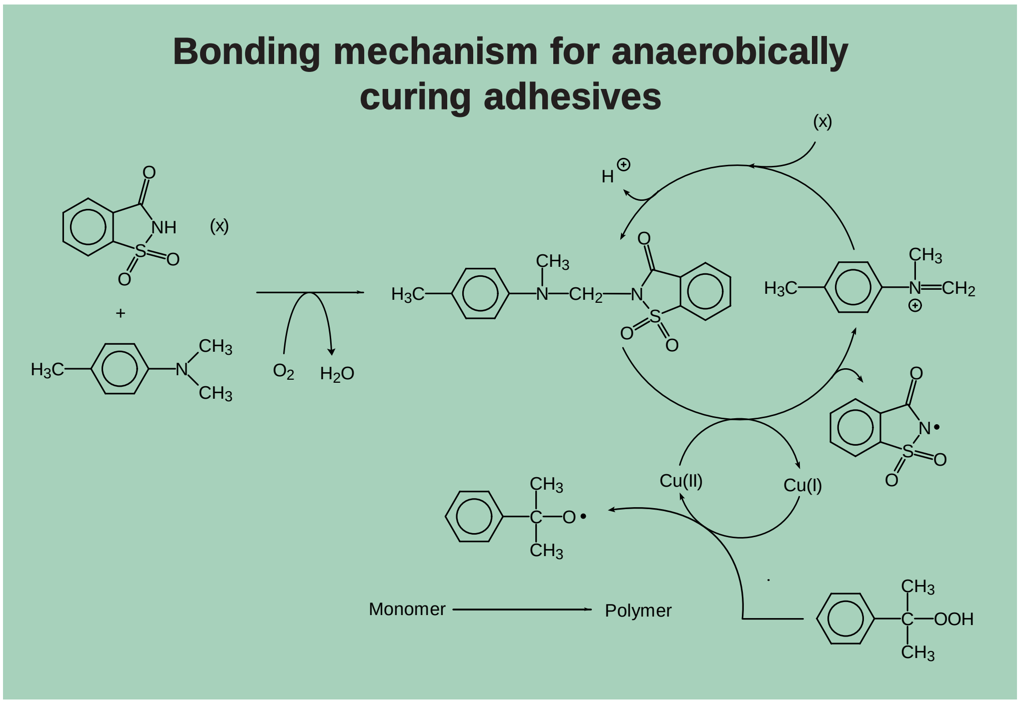
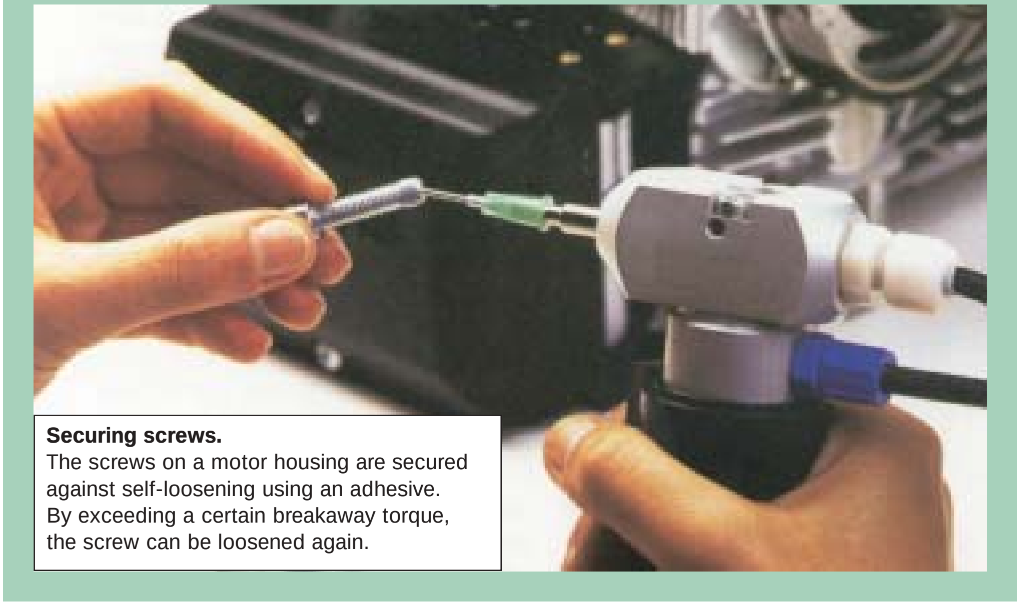


Figure 27

via the above-described reaction steps guarantees the high number of active radicals that are necessary for effective curing of the adhesive in the bonded joint. Anaerobically curing adhesives are themosets and the resulting bonds hence have high strength and high resistance to heat. Substrates joined using very high strength anaerobically curing adhesives can only be detached at temperatures between 300 and 400°C. These bonded joints are however very brittle and are hence not suitable for flexible substrates. Curing occurs exclusively in the joined area and only relatively small gap widths can be bridged (maximum gap: ca. 0.1 mm).

Besides their bonding function, anaerobically curing adhesives are often simultaneously used for their sealing properties because they are very resistant to oils, solvents and moisture. All these properties make this type of adhesive suitable for mounting engines in the vehicle manufacturing industry. Other typical areas of application are for securing screws and for bonding rotationally symmetric substrates, e.g. in electric motors *(Figure 28)*.

Securing screws with anaerobically curing adhesives



Securing screws.
The screws on a motor housing are secured against self-loosening using an adhesive. By exceeding a certain breakaway torque, the screw can be loosened again.

Figure 28

Radiation curing adhesives

These adhesives are 1-C systems whereby the curing is triggered by light. Radiation curing adhesives require no high temperatures, no solvents and no particularly complex equipment to be cured. All that is needed are light waves of defined wavelength. The curing times range from as little as 1 second up to several minutes.

There is a precondition for using radiation curing adhesives: At least one of the substrates must be permeable to light. Radiation curing adhesives based on polyurethanes, polyesters, polyethers, silicones and other substances are available. These adhesives cure by means of a radical polymerisation reaction involving the acrylate groups. Chain growth is initiated by a UV/VIS primary photochemical reaction induced by photo-initiators. The curing process for these adhesive does not merely depend on the wavelength of the light. Optimum cohesion also depends on the dose of radiation that is required to give adequate crosslinking of the adhesive.

Once solidified, radiation curing adhesives are usually thermoplastics. However occasionally they are thermosets. The degree of crosslinking can be adjusted by carefully choosing the raw materials in the adhesive. The choice of raw materials also determines the elasticity and the deformability of the cured adhesive. Initial lap shear strengths of up to ca. 25 MPa can be achieved. They resulting bonds are suitable for exposure to continuous temperatures of from -30°C up to a maximum of 120°C. For short times the bonds can withstand temperatures up to 180°C. Radiation curing adhesives are chiefly used for bonding glass (optics, glass design) *(Figure 29)*. These adhesives are however also used for joining transparent plastics and as a liquid seal for metal/plastic casings. They are also being increasingly used in dental technology *(see page 61)*.

Glass design and glass structures

Figure 29

Adhesives that cure via polycondensation

Phenol-formaldehyde resins

Phenol-formaldehyde adhesives (usually called phenolic resins for short) cure at temperatures between 100 and 140°C depending on the composition of the adhesive. The mechanism of these reactive adhesives involves a reaction between formaldehyde and phenol under alkaline conditions to form an addition product: a so-called resol *(Figure 30)*. This reaction has already reached completion in the ready-to-use adhesive.

This resol is cured in the bonded joint, liberating water to form a thermoset (condensation reaction) *(Figure 31)*. As the curing process requires temperatures above 100°C, the liberated water is present in gaseous form. In order to avoid foaming, phenolic resins are cured under contact pressures of up to 0.8 MPa.

Pure phenolic resins are very brittle and sensitive to peel stress *(see Glossary)*. That is why they usually

Precondensation of phenol and formaldehyde

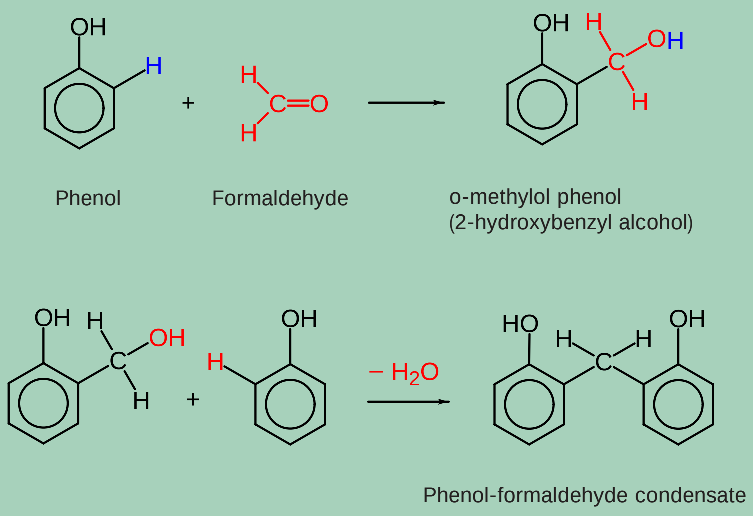
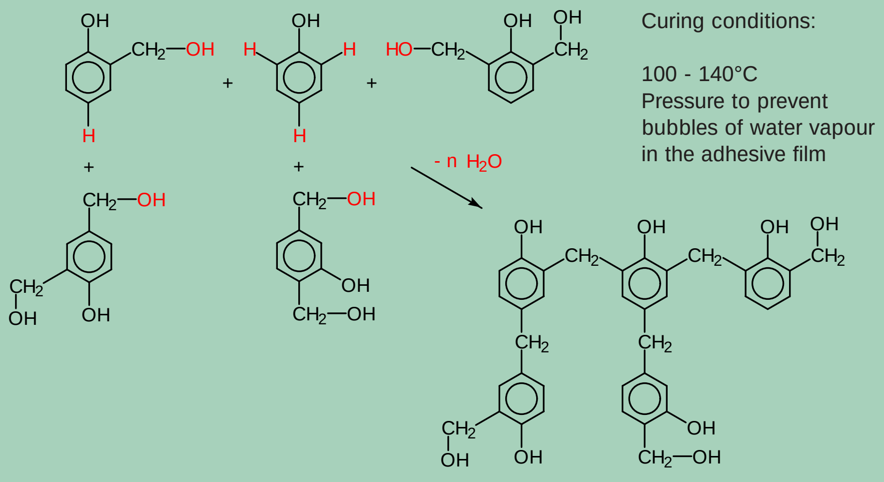


Figure 30

Curing reaction for a phenol-formaldehyde resin



Curing conditions:

100 - 140°C
Pressure to prevent
bubbles of water vapour
in the adhesive film

Figure 31

contain additives to increase the elasticity, e.g. synthetic rubber. Modified phenolic resin adhesives generally give high bond stability and bonds with good mechanical properties. Phenolic resins have very good adhesion and long-term stability on oxidatively etched aluminium surfaces. They also have good temperature stability up to ca. 250°C. In addition to using phenol as the starting monomer for the condensation reaction with formaldehyde, phenol derivatives, e.g. resorcinol (m-dihydroxybenzene) are also employed in adhesives. Resorcinol-formaldehyde resins have a higher degree of crosslinking than other phenolic resin adhesives and due to this have greater resistance to water and weathering effects. They are mostly used for wood structures that have to be resistant to water and weathering (boat adhesives).

In general phenolic resins are preferred when the adhesive film is exposed to high temperatures. A classic application is the bonding of brake and clutch linings *(Figure 32)*. Other typical application areas for this type of adhesive are in aircraft manufacture *(see section 3.4)*, for the structural bonding of aluminium and in the furniture-making industry. From a quantitative point of view, the biggest use of phenolic resins is for bonding wood in the furniture-making industry.

Brake linings

Figure 32

Silicones

The silicones have a special position within the group of “organic” adhesives. This position is special because their molecular framework consists of silicon and oxygen atoms. This gives the silicones special properties. Unlike any other organic adhesive, the silicones remain highly elastic at low temperatures (-70 to -90°C) and their other properties also remain essentially unaltered. The reason for this high elasticity is the high degree of chain mobility in the silicone polymers. The very different angles of the Si-O-Si (143°) and O-Si-O (110°) bonds prevent there being a linear chain structure and make it difficult for Van der Waal forces to act between the chains *(Figure 33)*. As a result, the individual polymer chains can move easily, namely the adhesive is elastic.

Silicones also have very good temperature stability (-100°C up to 200°C continuous exposure; up to 300°C for short periods). The reason for this is the higher bond energies of silicon-oxygen bonds (ca. 370 kJ/mol) compared to carbon-carbon bonds (ca. 350 kJ/mol). A further advantage of silicon-oxygen chains, compared to carbon-carbon chains, is their resistance to UV light. Under the influence of UV light, part of the airborne oxygen becomes active (radicals, O_3). The carbon chain of truly organic adhesives is attacked by this active oxygen at defective positions. The carbon oxidises and the chain is destroyed. Such attack is not possible with silicon-oxygen chains because the silicon is already present in an oxidised state. Silicones are also virtually inert to other aggressive chemical substances and have excellent resistance to moisture and weathering. Bonds made with silicones can however only be subjected to small mechanical loads (initial lap shear strength usually less than 1 MPa). That’s why they are chiefly used as sealants. Due to their low surface tension they can in general not be lacquered or coated. Silicones are also susceptible to mould. They are used for bonding metal when the low bonding strength is offset by the higher flexibility and resistance at low temperatures.

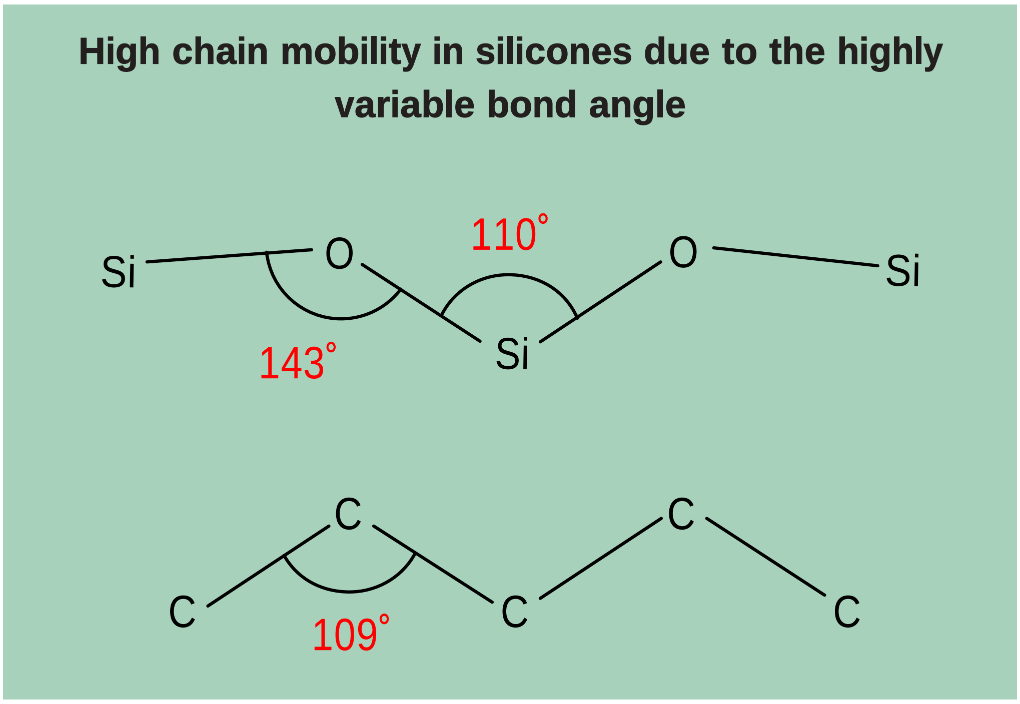
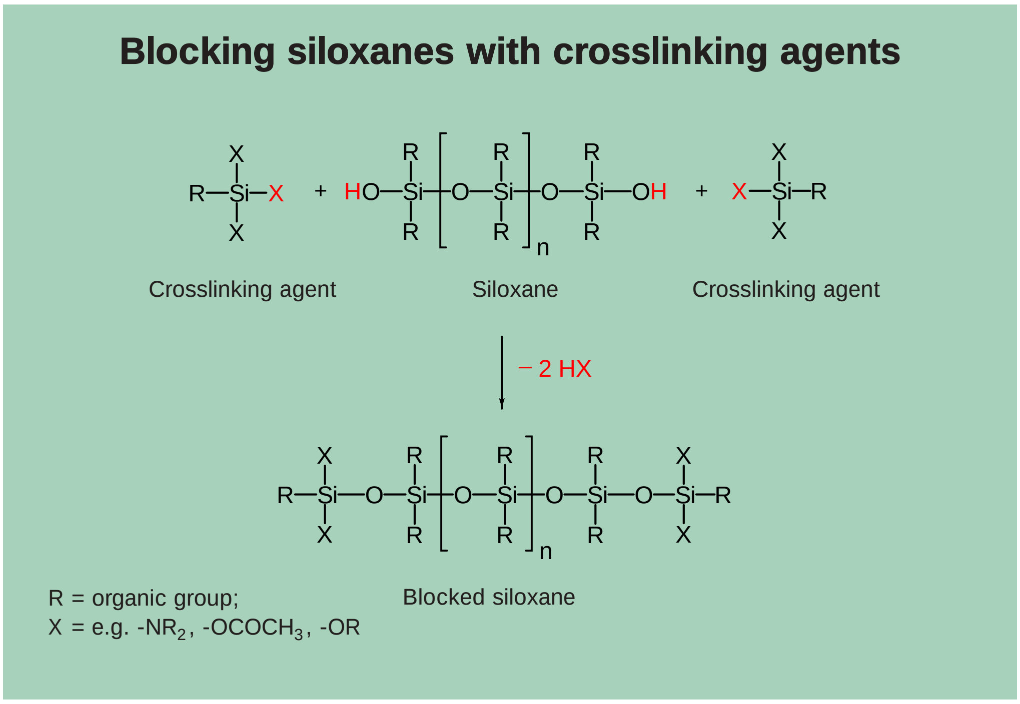


Figure 33

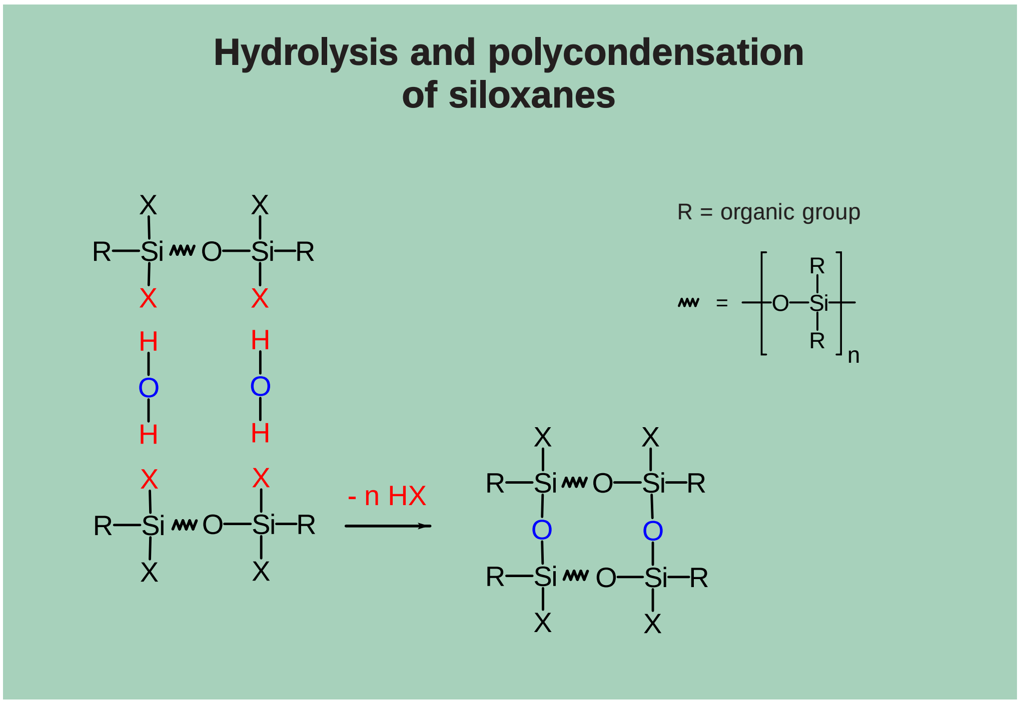
Silicones are available as 1-C and 2-C systems. Both systems cure by polycondensation – 1-C systems are initiated by moisture, 2-C systems by reaction of hydroxy polysiloxanes with a silicic acid ester. Polysiloxanes are the basis of these reactive adhesives. The condensates that are released depend on the hardener that is used. With acidic hardeners (crosslinking agents), acids are released. With basic crosslinking agents, amines are released. With neutral hardeners, oximes or alcohols are released.

Depending on their specifications, **1-C silicone adhesives** require a humidity of 5% to 95% to cure, namely to initiate and propagate the chemical crosslinking process. In the ready-to-use reactive adhesive, the terminal hydroxyl groups on the polydimethylsiloxane molecules are blocked by crosslinking agents *(Figure 34)*. Besides the presence of humidity, a temperature of between 5 and 40°C is required to crosslink the adhesive. The siloxanes crosslink via hydrolysis followed by polycondensation reactions *(Figure 35)*. Complete crosslinking and curing depend on the thickness of the adhesive film and this can take several days. The onset of curing is indicated by formation of a skin. For an adhesive film thickness of a few millimetres the adhesive generally fully cures in 24 hours. The areas of application of 1-C silicones depend on the hardener that is used. Acid-crosslinked systems are chiefly used to give moisture-resistant bonds for glass and ceramics, e.g. for sealing joins for sanitary applications. Before bonding metals, the risk of acid corrosion when using this type of silicone must be evaluated. Before bonding plastics, the risk of stress crack formation from the acetic acid that is produced must be assessed. Alkaline-crosslinked systems are particularly suitable for bonds and seals on concrete, plaster, brickwork and metals. However, yellowing may arise from the released amines. This problem does not occur for neutral-crosslinked systems. The latter are suitable for bonding glass, concrete, plaster and artificial and natural stone. Crosslinking systems that release alcohol are especially suitable for metal-plastic bonds when it is desired to avoid stress cracks. In general, the range of applications of 1-C silicone adhesives is extensive, ranging from the manufacture of irons via car manufacturing and electrical engineering right through to special applications in aeronautics and aerospace technology.


Blocking siloxanes with crosslinking agents

R = organic group;
X = e.g. $-NR_2$, $-OCOCH_3$, $-OR$

Figure 34


Hydrolysis and polycondensation of siloxanes

R = organic group

Figure 35

2-C silicone adhesives by comparison are used for mass production, e.g. in electronics and the electrical industry as well as in the production of household appliances and in the car industry, when adhesive film thicknesses of over 6 mm are required or for large bonding areas. This type of silicone adhesive is used when the available humidity in the air does not suffice for the curing process to run to completion. These adhesives are based on hydroxy polysiloxanes and crosslinking occurs via a silicic acid ester, and for example a tin catalyst *(Figure 36)*. The curing reaction can take up to 24 hours and is dependent on the pH, catalyst concentration and the raw materials that are present. Although 1-C systems can be processed straight from the container using standard pumps, the components of 2-C silicone adhesives must be brought together and mixed. This procedure must be carried out extremely carefully. Firstly, no air that can adversely affect the curing process must be introduced into the mixture whilst stirring. Secondly, the mixture must not be stirred too rapidly. The adverse effect of over-rapid mixing is that too much heat is added and the adhesive cures prematurely *(see Glossary, Pot life)*.

The attractive forces between the individual polymer chains is very difficult to disrupt and hence polyimides melt at a considerably higher temperature. The data in *Table 6* illustrates the effect of the molecular structure of polymers on their melting range.

The manufacture of industrial polyimides is carried out by reacting the anhydrides of 4-basic acids (e.g. pyromellitic anhydride) with aromatic diamines (e.g. diaminodiphenyl oxide) *(see Figure 37)*. The intermediate product is a polyamido carboxylic acid, formed by addition of the aromatic amine to the carboxylic acid anhydride via cleavage of the anhydride ring. This intermediate product is soluble in polar solvents and can be dispersed in water. The adhesive is applied in this form and after joining the substrates it is cured in an autoclave at temperatures between 230 and 350°C and with a contact pressure of between 0.8 and 1 MPa. Special polyimides are further cured for up to 16 hours at 400°C.

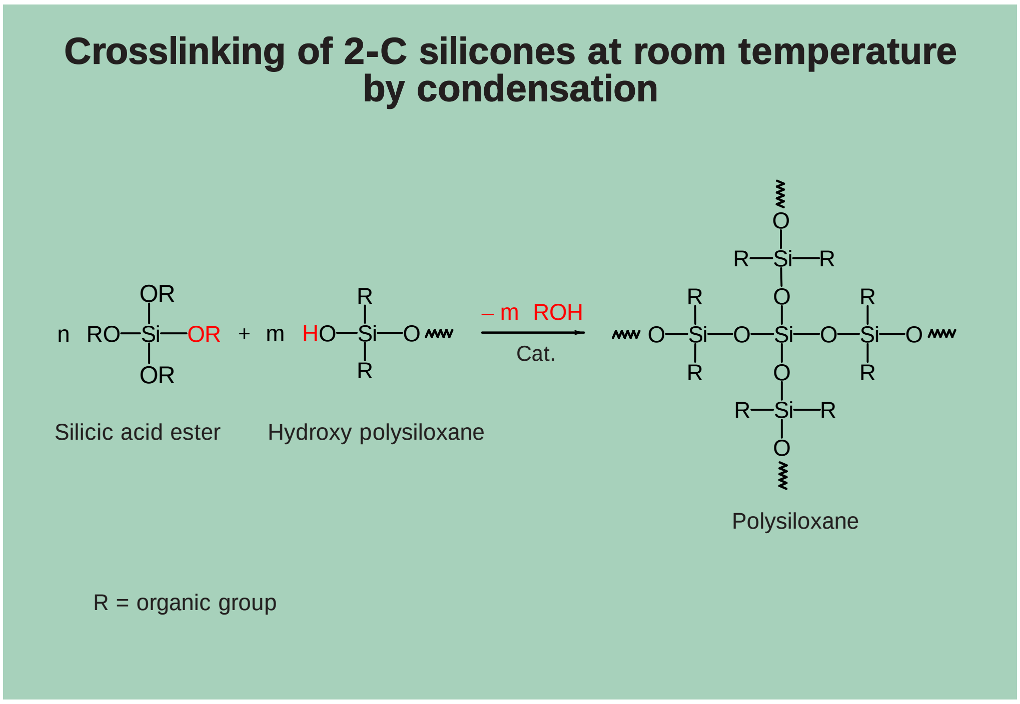


Figure 36

Polyimides

Polyimides possess a special feature. Although they have a linear non-crosslinked polymer structure and are hence thermoplastics, they are difficult to melt and are virtually insoluble. The reason for this is the aromatic and heterocyclic ring structure of the polymer units. This complex chain structure significantly reduces the mobility of the polymer chains, even at high temperatures.

1-C polyimides belong to the class of high temperature resistant reactive adhesives. The resulting bonds can withstand continuous temperatures of up to ca. 320°C and can even withstand temperatures up to 500°C for short periods. Polyimides are hence the preferred adhesives for high-quality, heat-resistant metal bonds for aeronautic and aerospace applications. Bonds created using polyimides have high bond strength and low flexibility. They are however sensitive to moisture.

Effect of the molecular structure on the melting range

Molecular structure	Example	Melting range in°C
Linear chain molecule	Polyethylene	110 to 130
Chain molecule with short side chains	Polypropylene	160 to 165
Linear chain molecule with hetero-atoms	Polyamide-6,6	220 to 240
Linear chain molecule with aromatic ring structures	Polyethylene terephthalate	250 to 260
Linear aromatic ring structure	Polysulphone	260 to 320
Linear aromatic and heterocyclic ring structure	Polyimide	380 to 400

Table 6

Manufacture and curing of polyimides

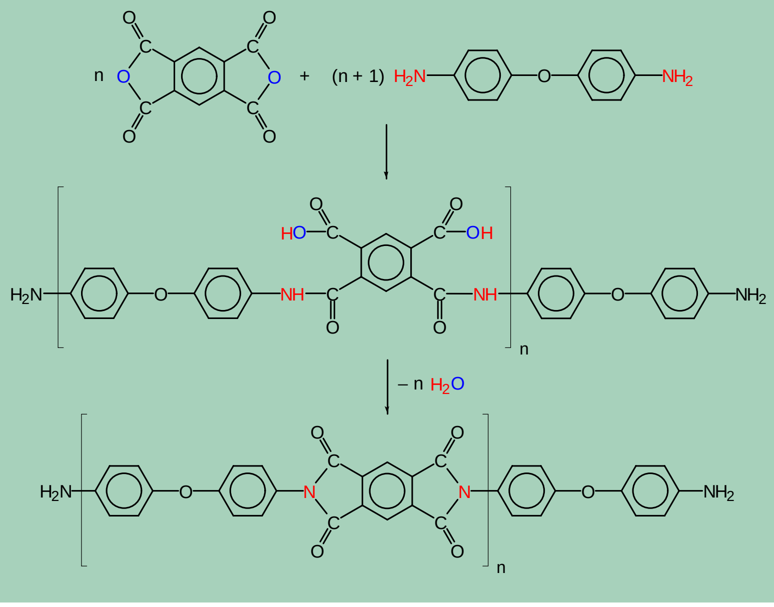


Figure 37

Adhesives that cure via polyaddition

Epoxy resins

Epoxy resins are extensively used and are available in a variety of adhesive systems: hot curing 1-C, cold curing 2-C and reactive hot melts. The cold curing 2-C epoxy resin systems are described here. The two components are the resin (prepolymer based on bisphenol A) and the hardener (polyamines or polyamido amines). These systems cure at room temperature in a period ranging from a few hours up to a few days *(Figure 38)*. The curing time can however be foreshortened by heating and this also results in an increase in the strength and stability of the bond. The curing process starts immediately the two components are brought together and mixed. These 2-C systems are however relatively sensitive to mixing errors. An important term of relevance to 2-C reactive adhesives is the so-called “pot life” or usage time. This describes the period of time, after the adhesive components have been brought together and mixed, during which the mixed adhesive can still be processed and applied. This depends on the rate at which the curing reaction proceeds.

The pot life elapses when the adhesive has become too viscous to effectively wet the surface of the substrate. Once the pot life has expired, the adhesive cannot be used because adhesive forces can no longer optimally develop. The higher the temperature, the faster the curing reaction and hence the shorter the pot life. The rule of thumb here is that a temperature change of +10°C doubles the reaction rate and a change of -10°C halves the reaction rate (based on the Arrhenius equation). All curing reactions are exothermic. When large amounts of materials have been prepared, the heat that is produced cannot dissipate as quickly to the surroundings as is the case when smaller quantities of adhesive are involved. The mixture in the “pot” can hence become very hot, so reducing the pot life. The pot life is hence dependent on:

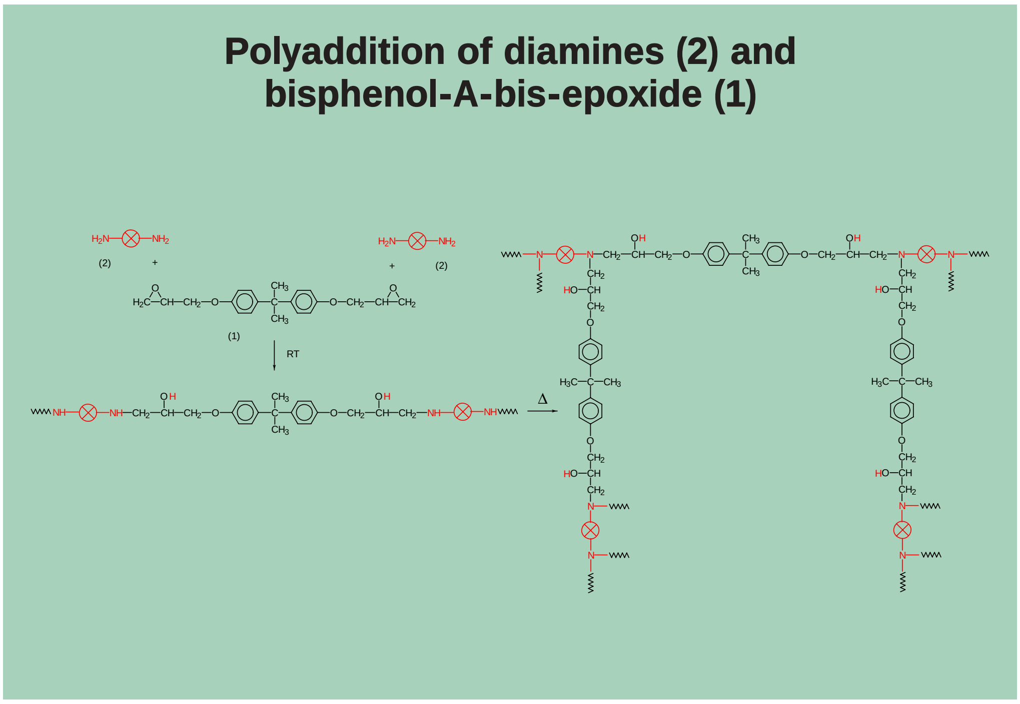

Polyaddition of diamines (2) and bisphenol-A-bis-epoxide (1)

Figure 38

1. The intrinsic curing rate of the adhesive;
2. The temperature of the surroundings;
3. The quantity of adhesive that has been prepared.

With regard to the whole course of the curing reaction, there is a point of inflection at the “gel point” of the adhesive *(Figure 39)*. This is the point at which the already viscous adhesive finally becomes a solid. However only at a significantly later time does it reach its final strength and only then can the system be subjected to full loads. If the temperature is now increased, the final strength is reached sooner and is somewhat higher. The latter is because the higher particle mobility allows the crosslinking reactions can take place more favourably and a higher crosslinking density is attained. At lower temperatures the reverse occurs and the stage can be reached when the reactions become too slow for curing to take place. Epoxy resin based systems are the most widely used structural adhesives. They are encountered everywhere – in the car manufacturing industry, aircraft manufacturing industry, building sector and in the home. In microelectronics they are used with additives (Ag powder) as electrically conducting adhesives. They are also used a matrix resin to bond fibre-reinforced plastics. If, for example, aluminium oxide powder (Al_2O_3) is added, they have heat-conducting properties. The major advantage of epoxy resins is that they are suitable for bonding metals and also provide good adhesion on many plastics. In general, they have very high resistance to physical and chemical influences and in addition they have high long-term stability because they only have a limited tendency to undergo creep. Depending on the type, they can withstand continuous temperatures from 100°C up to a maximum of 200°C. All epoxy resins cure as thermosets, and this explains their relatively low flexibility and high strength. Using special hot curing, high strength 1-C epoxy resin adhesives it is even possible to structurally bond oiled, non-pretreated metal sheets (vehicle bodywork construction) so making them self-supporting - an application of bonding technology that today is still not possible with any other type of adhesive, with the exception of hot curing 1-C polyurethane adhesives.

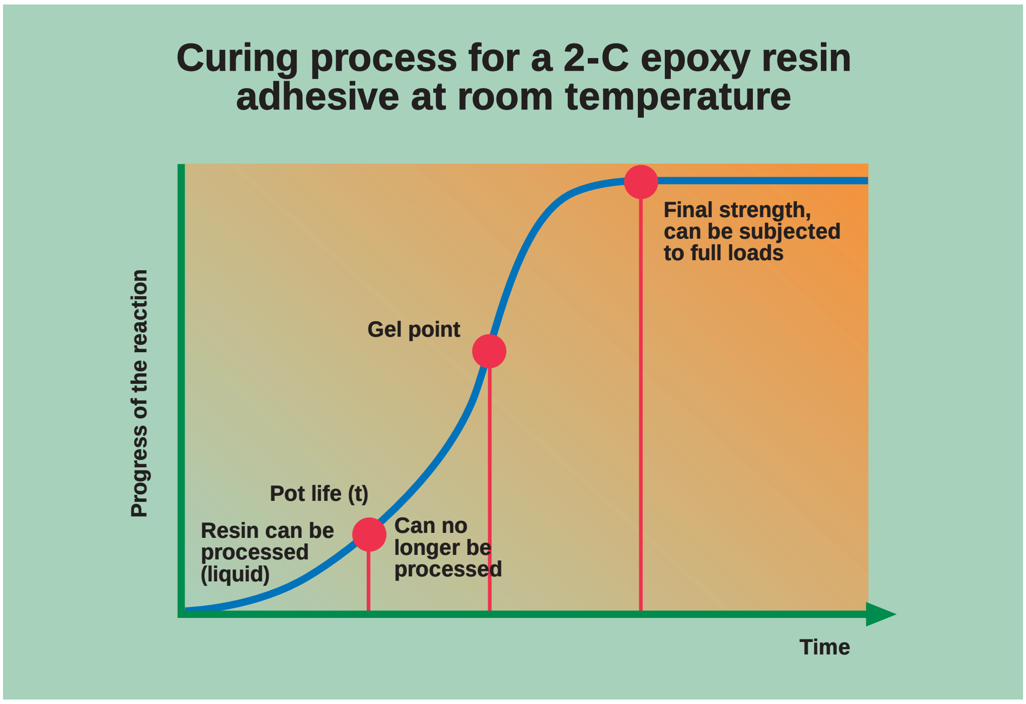


Figure 39

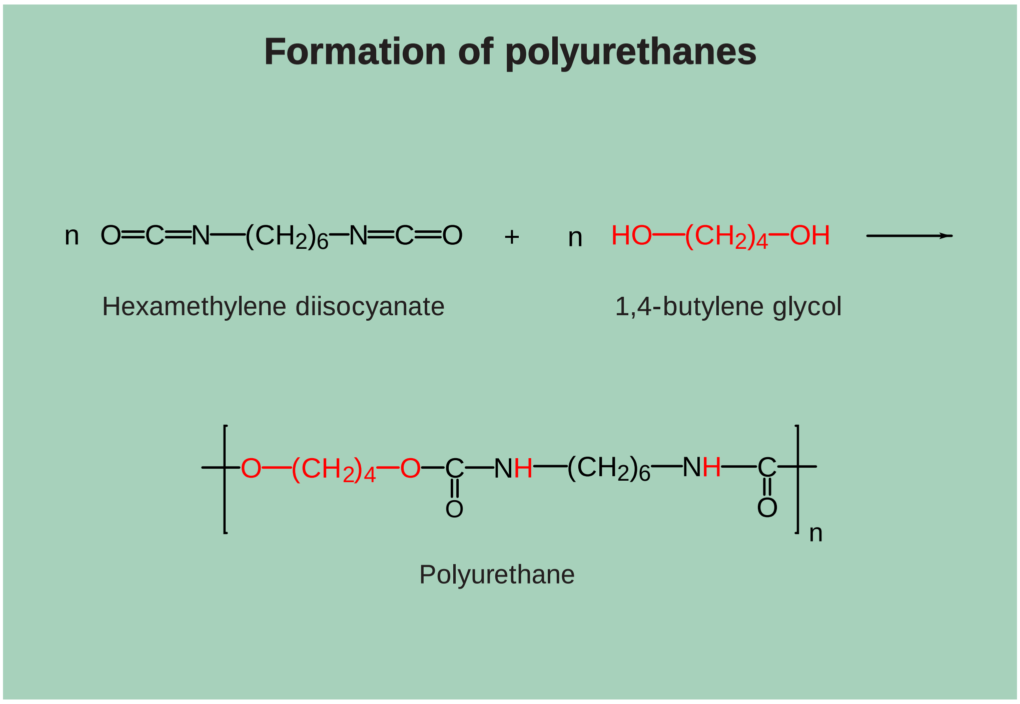
Polyurethanes

Just as for the epoxy resin adhesives, users can choose between different reactive polyurethane systems. Polyurethane adhesives (PUR) are available as cold curing 2-C systems, hot curing 1-C systems and moisture curing 1-C systems (where a polycondensation reaction takes place as the first part of the curing process and the addition reaction takes place in a second step), and reactive 1-C PUR hotmelts (for which there is second crosslinking stage induced by moisture, heat or a combination of both). These systems can cure to form elastomers or thermosets. The degree of crosslinking and hence the bond strength are determined by the various raw materials in the adhesives.

In the **2-C systems** the curing process is initiated by bringing together and mixing the resin (polyglycols or PUR prepolymer with terminal OH groups) and hardener (modified isocyanate) *(Figures 40, 41)*. At room temperature the curing can take from a few hours up to several days. This process can however be accelerated by heating and this also increases the strength of the bond. After curing, the adhesive film of 2-C systems ranges from tough and hard to rubber-like and flexible depending on the raw materials used.

Hot curing 1-C systems consist of PUR prepolymers with terminal hydroxyl groups and chemically blocked isocyanate hardeners. The isocyanate groups are capped with phenol *(Figure 42)* and form phenylcarbamine acid ester groups. The temperature required for cleavage can be decreased by employing suitable catalysts. For example, for a dimeric TDI prepolymer (Desmodur TT) there is cleavage at 120°C but this is reduced to room temperature when a phosphine catalyst is used. Hot curing 1-C systems require a temperature of 100 to 200°C to cure, with the duration varying from a few minutes to several hours depending on the actual temperature employed. Bonds formed using PUR adhesives are generally tough and hard and of high strength, but still elastic. The heat employed for curing 1-C PUR adhesives liberates isocyanate compounds from the system, some of which can be a health hazard. Hence suitable ventilation is required.

The **moisture curing 1-C systems** are viscous adhesives that consist of non-volatile PUR prepolymers having isocyanate end-groups. These systems require moisture to trigger the curing reaction. A portion of the isocyanate groups on the prepolymer are converted to amino groups. A small quantity of carbon dioxide is released but this has no effect on the bonding process. The amine groups then react with the remaining isocyanate groups and so cure the adhesive system *(Figure 43)*. This reaction can take place in a temperature range from 5 to 40°C, with a relative humidity of 40 to 70% being required. There are also so-called booster systems commercially available that function using a moisture-containing gel. These accelerate the curing and the curing is now independent of the level of the air humidity. With 1-C systems, the moisture-dependent curing of the adhesive film (that is based on the formation of urea linkages) takes place from outside to inside at a rate of a few millimetres per day. When processing adhesives, the so-called “skinning time” must be heeded, namely the time after which the adhesive solidifies on its surface (forms a “skin”) and wetting of the second substrate is no longer possible. Once this has occurred, adhesive interactions can no longer occur. In its cured state the adhesive is elastic and flexible and this is why moisture curing 1-C PUR systems are



Formation of polyurethanes

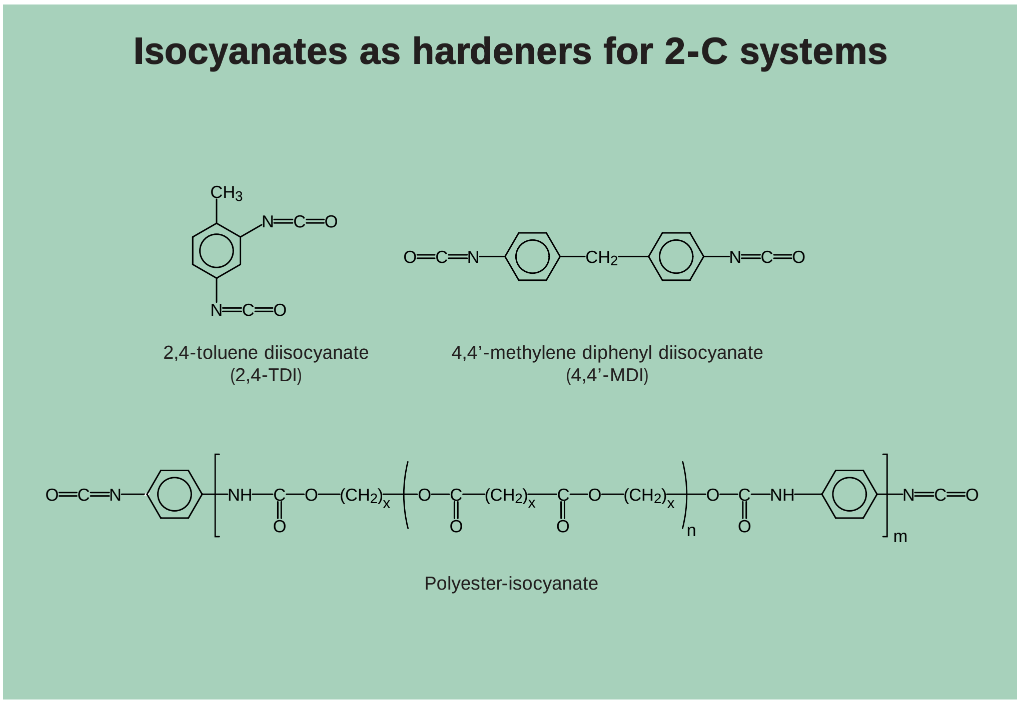
$$n\ O{=}C{=}N{-}(CH_2)_6{-}N{=}C{=}O \quad + \quad n\ HO{-}(CH_2)_4{-}OH \longrightarrow$$

Hexamethylene diisocyanate

1,4-butylene glycol

Polyurethane

Figure 40



Isocyanates as hardeners for 2-C systems

2,4-toluene diisocyanate
(2,4-TDI)

4,4’-methylene diphenyl diisocyanate
(4,4’-MDI)

Polyester-isocyanate

Figure 41

used where materials with widely differing elongation under loads and differing temperature expansion behaviour have to be joined. An example is the bonding of glass-fibre reinforced plastics (GFP) to steel, and aluminium wall and floor plates to steel supports. Figure 44 shows a high-speed ferry in which the polycarbonate window panes were bonded to the aluminium ship structure using these adhesives.

Reactive PUR hotmelts cure by a combination of physical and chemical processes *(Figure 45)*. The chemical secondary crosslinking can be triggered by heat, humidity or both. Systems in which moisture triggers the secondary crosslinking consist of high molecular weight, “meltable” polyurethanes with terminal isocyanate groups that can be activated by moisture. In contrast, systems in which heat triggers the secondary crosslinking have blocked isocyanate groups which become available when heat is supplied. Reactive PUR hotmelts cure as elastomers and the adhesive film is hence rubbery and plastic. Reactive PUR hotmelts even

Unblocking an isocyanate by heating

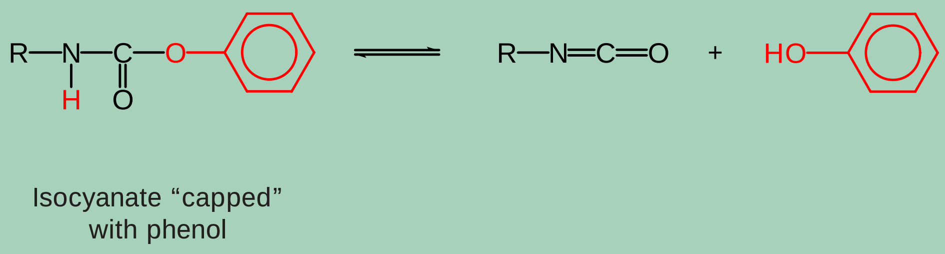


Figure 42

Activation of the isocyanate group containing prepolymer by moisture

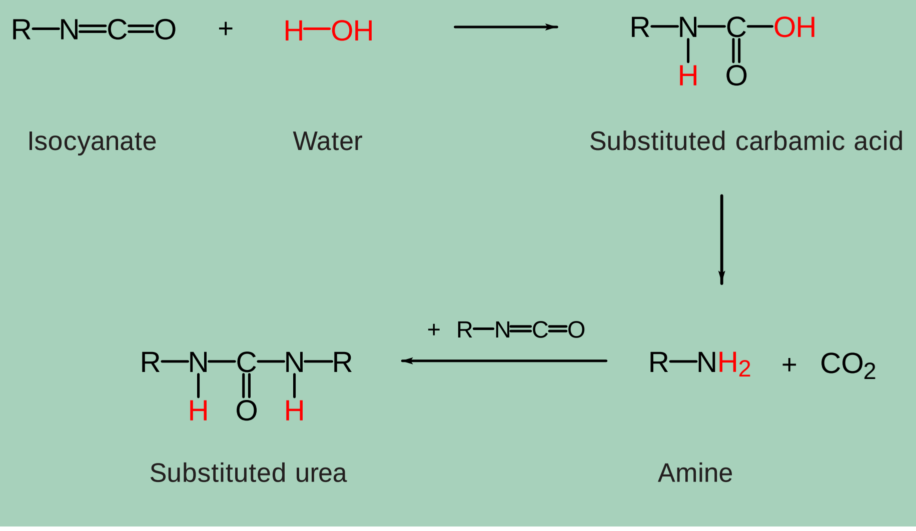


Figure 43

bond well on oiled metal sheets (vehicle bodywork construction), namely a surface to which most other adhesives would not be able to bond. Reactive PUR hotmelts have the big advantage that they can be applied at very low temperatures (50 to 100°C).

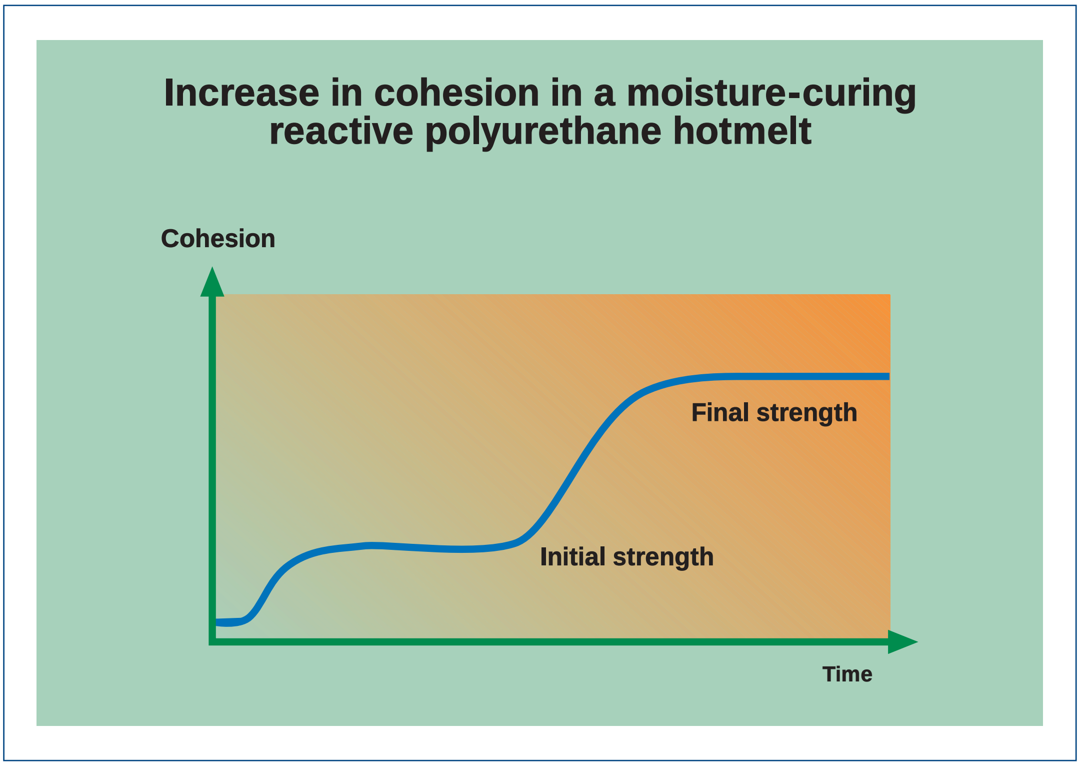
In contrast, standard hotmelts can only be applied at higher temperatures (120 to 240°C). When being processed the PUR adhesive is thermoplastic. On cooling there is rapid development of the initial bond strength, meaning the substrates can be rapidly affixed for further processing. The final strength is reached later.

The properties of polyurethanes in the cured state differ depending on their degree of crosslinking. With rubbery and flexible systems, very high elastic deformability can be attained. With a maximum elongation at fracture of over 600% this is only surpassed by the silicones *(see page 38, Silicones)*.

These adhesives allow thick adhesive films to be applied and they can be coated. Their low lap shear strength of below 6 MPa is from a design point of view compensated by using large bond areas. They are resistant to the effects of moisture and UV light and continuous use at temperatures in a range from ca. 40 to 100°C presents no problem.

High-speed ferry

Figure 44



Increase in cohesion in a moisture-curing reactive polyurethane hotmelt

Figure 45

Outlook

The array of adhesives that have been described is further increased by the fact that the properties of the different types of adhesives can be varied by modifying the components of an adhesive. Even adhesives that have different curing mechanisms are combined, for example reactive hotmelts which are applied in a first step like normal thermoplastic hotmelts and are then crosslinked via chemical reactions to form elastomers or thermosets. The same is true for reactive dispersion adhesives, reactive adhesive tapes and UV curing cyanoacrylates. The latter cure to form thermoplastics in a first step triggered by moisture and are then crosslinked to form thermosets in a second step triggered by UV light. These developments show that the borders between the individual classes of adhesives are becoming indistinct. The driving force behind development work is simply the ever more demanding requirements for new applications, for example bonds with improved temperature stability or new additional functions (electrical conductivity, elasticity, etc.). In all today's development work in the area of bonding technology there is an ever increasing shift away from solvent-containing adhesives to solvent-free systems. Just as with all other plastics, the emission of hazardous substances from adhesives is continually being reduced.

2.3 Fundamentals of bond design

Bonding technology is a systemic joining technique that is based on a variety of interrelated processes. Besides the properties of the adhesive film, substrate materials and the stresses and loads on the joint, the fundamental importance for a bond to be effective is its geometric design. Flaws in bonded structures are a common occurrence because key basic principles of bond design have been neglected. Even in the design phase of a component, special relationships must be taken into account. The principle requirement on a bond is to transmit forces and be able to withstand the stresses caused by these forces for a long period of time. When designing bonds, two key requirements must be met in order to create a bond having good long-term stability (meaning in particular resistance to moisture): Firstly, a sufficiently large area must be available for bonding and secondly measures must be taken to prevent mechanical loads causing stress peaks in the bond.

Bonds can essentially be subjected to the following stresses *(Figure 46)*:

(a) Peel stress;
(b) Shear stress;
(c) Lap shear stress
(d) Tensile stress;
(e) Compressive stress;
(f) Torsional stress.

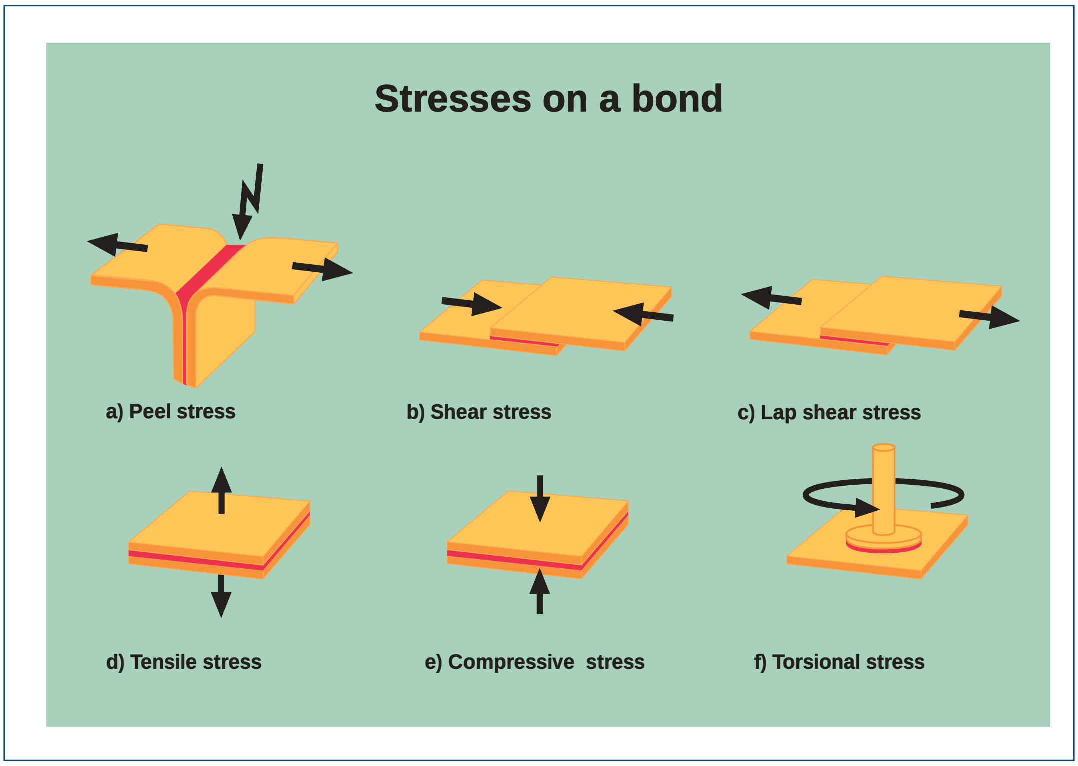


Figure 46

Peel stress leads to near line-form, high stress on the adhesive in the bonded joint. This is often many times higher than the final strength of most adhesives.

Being a planar joining technique, bonds must be designed to withstand shear stress. The substrates are pulled apart parallel to the bonding surface, meaning that the entire bonding area is subject to stress. In general, the bonding area of bonded joints can be increased such that the stresses can be distributed over an area so large that the point collapse load is not exceeded.

Tensile stresses act vertically to the plane of the joint. From a design point of view they are only considered in exceptional cases because increasing the bonding area to increase the mechanical loads than can be withstood, which is relatively simple for bonds that are subjected to shear stress, is often not possible.

Bonded joints are not sensitive to compressive stress.

The behaviour of bonded joints under torsional stress is similar to their behaviour under lap shear stress.

2.4 Testing bonded joints

The choice of test method depends on the properties of the bonded joint in question. Bond strengths are determined using the lap shear test, peeling resistance using the floating roller peel test or T-peel test and adhesion behaviour using for example the wedge test. In order to obtain information about the long-term stability of bonds, the samples are equilibrated under the likely conditions of the actual surroundings (equilibration under hot humid conditions, sweating test, salt spray test, cataplasma test, stability test under changing climatic conditions) and are then subjected to mechanical tests.

In the mechanical tests the bonded joints are loaded to the point of fracture. The nature of the fracture (adhesive fracture, cohesive fracture, substrate fracture or a combination of these) provides information about the quality of the bond and about any potential production errors. Regarding tests on samples equilibrated under controlled conditions, a cohesive fracture indicates that the adhesion remained stable despite the influences acting on the bond (e.g. moisture). In contrast, an adhesive fracture indicates that the bond has failed at its most sensitive point, the adhesion. This may indicate incompatibility between the substrate material and adhesive, inadequate surface pretreatment and/or processing/application errors. Possible processing/application errors are:

- Pot life / skinning time exceeded;
- Surface too cold;
- Adhesive too cold;
- Adhesive stored for too long;
- Mixing errors.

Lap shear test in accordance with DIN EN 1465
The lap shear test is the most commonly used standard test for determining the strength of medium-strength and high-strength bonds. The bond strength of bonded single lap joints on subjecting the substrates to loads is determined by lap shear forces in the direction of the bonded joint. In accordance with the standard, the overlap corresponds to a width of 25 mm and a length of 12.5 mm. Each sample must be measured individually. To do this, a sample is clamped in the self-aligning jaws of the test unit so that the force acts in the centre of the bonded layer *(Figure 47)*.

In accordance with the standard, the test is carried out in such a way that the period of time for separation of the substrates is 65 ± 20 s, with the speed of movement of the jaws being constant. The highest force F_{max} that acts can then be read from the force gauge and recorded. The bond strength τ_B in N/mm^2 (MPa) is then calculated using the following equation:

$$\tau_B = \frac{F_{max}}{A} = \frac{F_{max}}{L_{Ü} \cdot b}$$

where:

F_{max} = highest force in N
$L_{Ü}$ = overlap length in mm
b = average sample width in mm
A = bonded area in mm^2

Wedge test in accordance with DIN 65448
The wedge test is one of the few test methods that allows testing of the quality of bonds under the influence of mechanical, chemical and media loads. In order to carry out the wedge test two metal sheets of a prescribed thickness and pretreated under production conditions are bonded to each other. A wedge is driven into the bond and the end of the crack that is produced is marked. Thereafter the prepared sample is equilibrated under hot humid conditions (e.g. 75 minutes at 50°C and 95% humidity) or in water. The bond which is under stress from the wedge is possibly forced further apart. After being equilibrated the progress of the crack is marked and measured, the bonded area is separated and the surface of fracture is evaluated. The advantage of this test compared to the lap shear test is the fact that results are obtained relatively quickly and direct information is obtained about the effect of aging conditions on the adhesive layer when it is exposed to mechanical loads *(Figure 48)*.

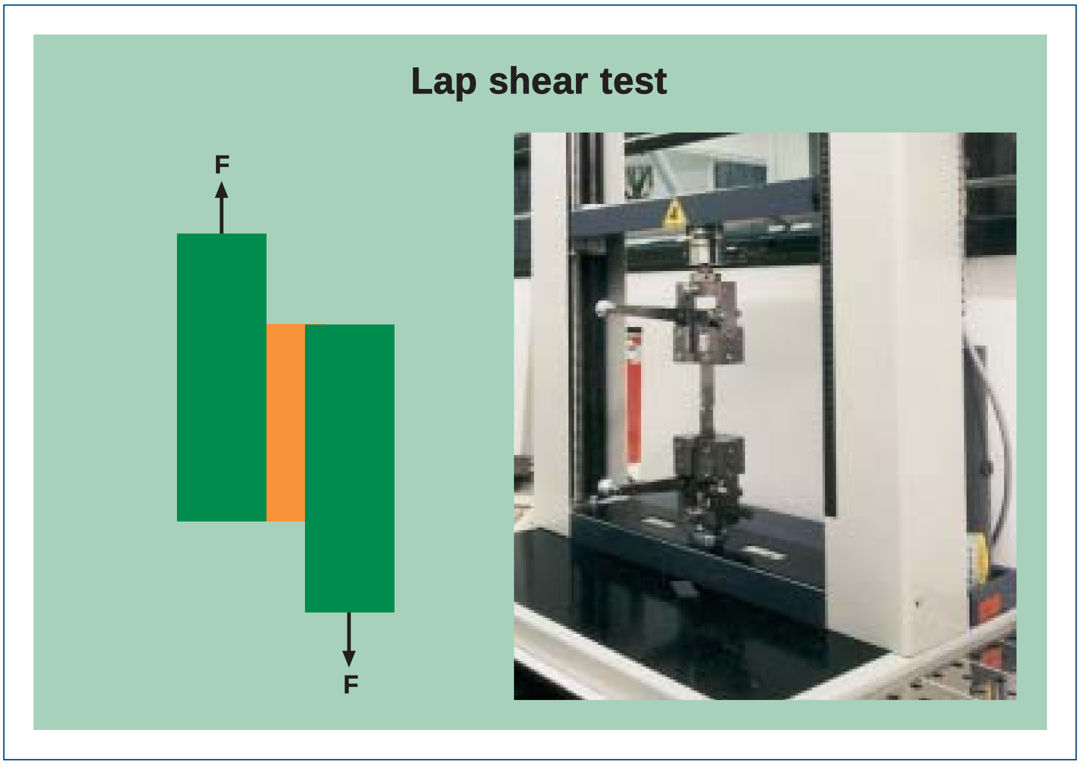


Figure 47

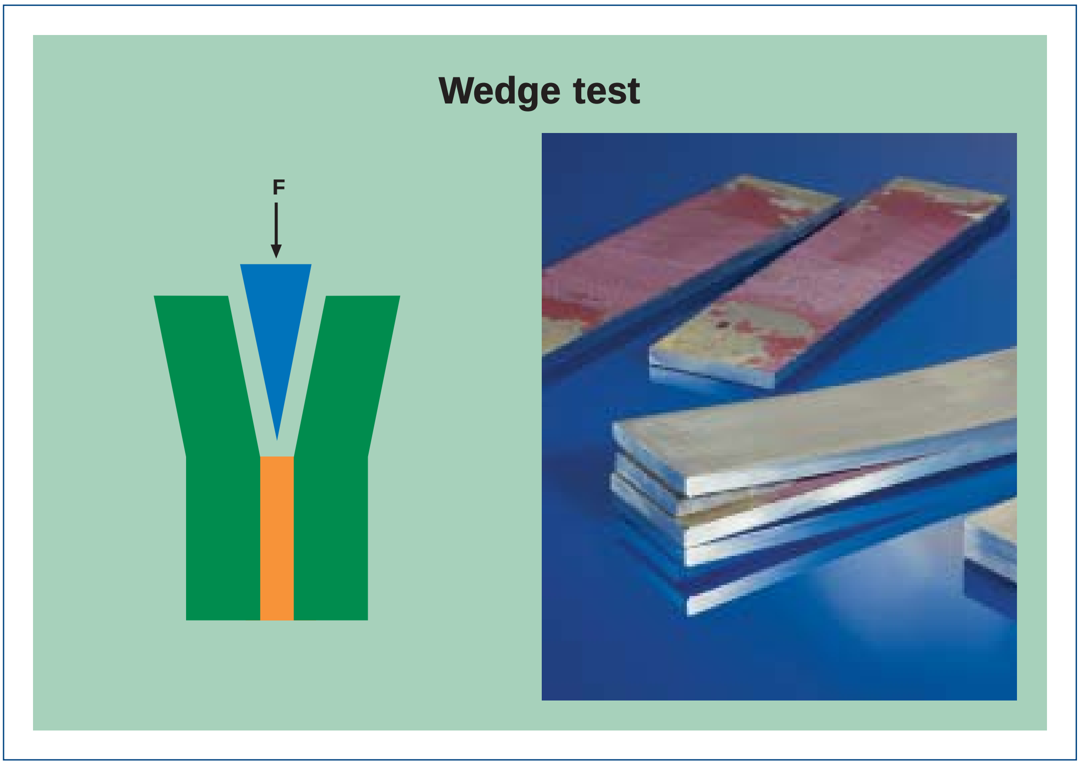
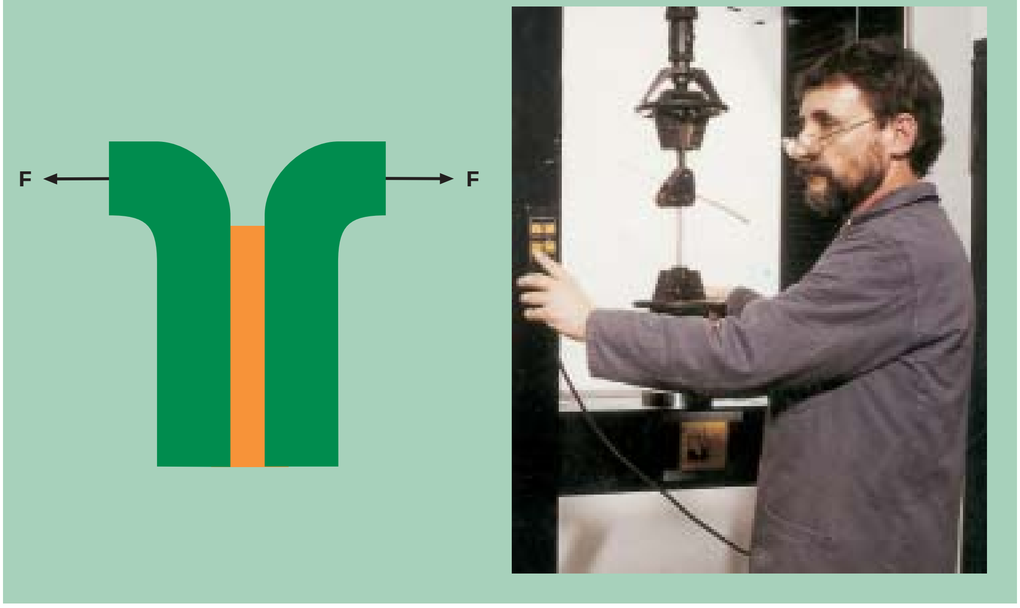


Figure 48

Peel test
Peel tests determine the resistance of bonded joints to peeling forces. They are chiefly used for comparative evaluation of adhesives and surface treatment methods because they are very sensitive at discerning differences in the adhesion and cohesion behaviour in the adhesive film. To carry out these tests, samples are subjected to tensile forces on their non-bonded sides until the adhesive film tears and both halves of the sample are apart. The force required to do this is recorded as is the change in distance between the clamp grips. The result of a peel test is a peel diagram. The fracture pattern provides information about the stability of the adhesion *(Figure 49)*.



Peel test

Figure 49

3.1 Bonding wood

In woodwork, and in particular in the furniture-making industry, polyvinyl acetate dispersion adhesives have long superseded the carpentry adhesives based on animal proteins that were used thousand of years ago. Condensation resins (urea, melamine, phenolic and resorcinol-formaldehyde resins) have made possible the development of new wood-based materials such as plywood, chipboard and laminated composites (resorcinol/phenol-formaldehyde resins) for building construction *(Figure 50)*. Melamine-formaldehyde resins are used in conjunction with special papers for manufacturing decorative boards for laminating wood for furniture manufacture. Polyurethane adhesives that cure by exposure to moisture are currently of growing importance for the manufacture of chipboard, due to the fact that they represent formaldehyde-free alternatives to the aforementioned polycondensation resins; In addition, they are being increasingly used for bonding wooden construction elements. As with adhesives in many areas of technology, wood adhesives are also tending to become 100% systems; They combine simple application with rapid curing. Hotmelts have proved particularly useful as adhesives for assembly work and for bonding decorative edging. The application of PUR hotmelts, which cure via the influence of moisture, is very much on the increase for the structural bonding of wood and for joining wood with a host of other materials. This type of adhesive involves two different curing mechanisms: The solidification of the hotmelt on cooling means that the components are rapidly affixed. The chemical curing which then follows, involving the crosslinking of molecules, leads to high-strength bonds *(see page 46)*.

Roof construction from wooden laminate composites

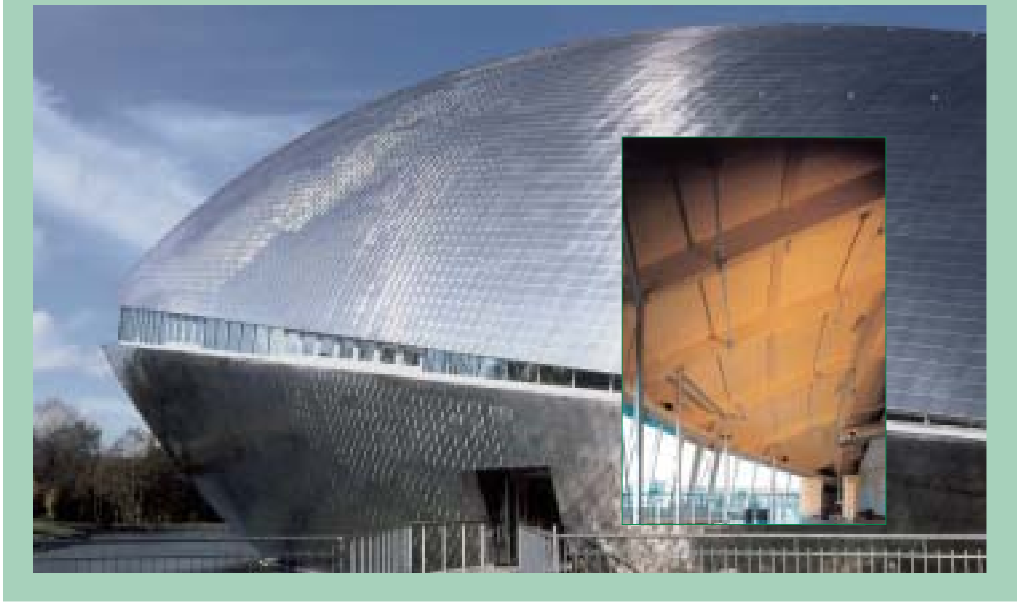


Figure 50

3.2 Bonding metal sheets in vehicle bodywork construction

Car bodies largely comprise steel sheets having a thickness of 0.6 to 0.8 mm. The trend in modern car bodies is towards a flatter design with as little wind resistance as possible, low weight and hence ultimately reduced fuel consumption. Flat components such as the bonnet and boot, and also door and roof panels, are affixed to ridge-like struts and are hence stiffened. The most common method for joining bodywork components, namely spot welding, cannot be used on the flat visible sides because this would result in unsightly points and these would require time-consuming work (filling) to repair. The use of adhesives to solve this problem was introduced about 40 years ago – adhesives are used to join the components together and the number of welding points was reduced to a small number at the edges. The bonding process had to be introduced into the relevant production line sequence *(Figure 51)*. The construction of car bodies puts extremely high demands on structural bonding technology: Special surface pretreatment of the metal sheets, which is essential for creating high-strength bonds having high stability, is not possible on a mass production line. In addition, the substrates are also still coated with corrosion protection oils during the production process. These can only be removed before the final process step.

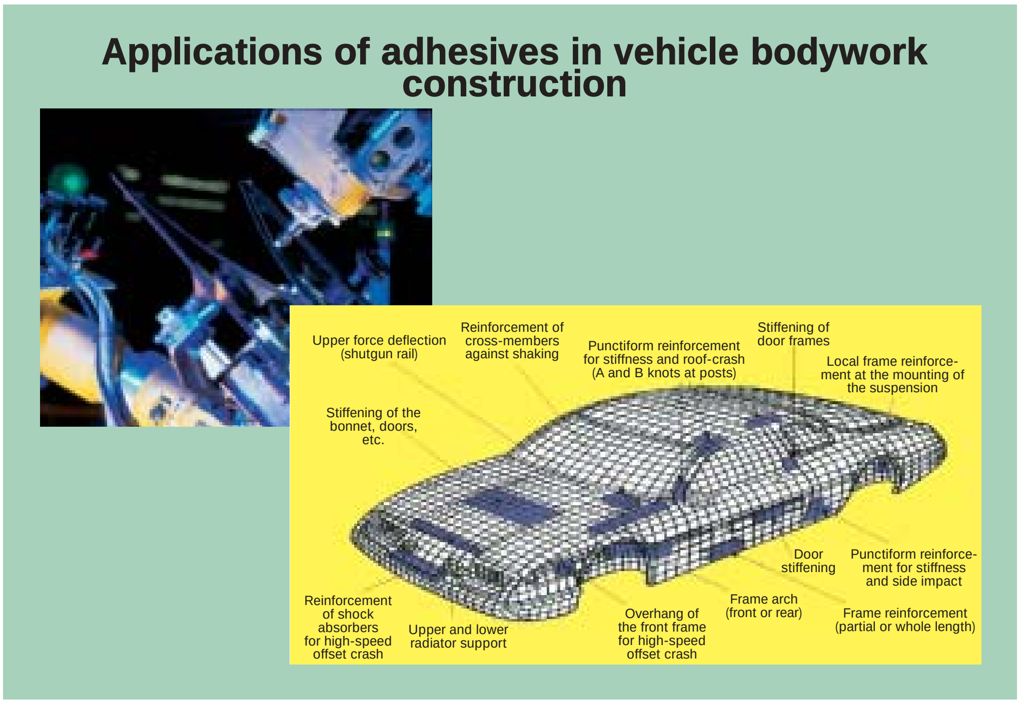


Figure 51

Key requirements of adhesives for use in vehicle bodywork construction are as follows:

- Ability to form structural bonds with defined properties over the lifetime of the component under operating loads;
- Stability at 170 to 230°C for ca. 30 minutes during the painting/lacquering process;
- Resistance to running and washing away in the non-cured state;
- Ability to be processed automatically;
- Ability to penetrate for spot-welds as crack stoppers.

Only hot curing adhesives meet the abovementioned requirements. The adhesives specially developed for these applications (curing at 180 to 230°C) are formulated in such a way that in the non-cured state up to 20 weight percent of oil can be taken up via dissolution. However, in practice when using the adhesive, so much oil is forced away by the adhesive that immediate initial bonding of the adhesive is usually guaranteed. The remaining oil is taken up by the adhesive and forms part of the adhesive film.

The high temperatures accelerate the dissolution of the oil by the adhesive. The oil is essentially uniformly distributed in the cured adhesive film and does not diffuse back to the surface.

Crash tests make clear that the alternating fatigue strength and the energy absorption, even after aging, can be considerably improved by using adhesives for some of the joints, compared to wholly spot-welded constructions. The current state-of-the-art involves a combination of bonding and spot welding, so-called spot-weld bonding, and this is used on a large scale for vehicle bodywork construction.

The following adhesives are used for bonding sheet metal in vehicle bodywork construction: Plastisol adhesives, essentially filler-containing pastes comprising powder-form PVC, plasticisers and adhesion promoters. For special applications, single component hot curing epoxy resin adhesives are used.

Example applications: Stiffening and flange seams on bonnets and boots, doors and roof structures.

3.3 Bonding panes of glass into car bodywork - direct glazing

The panes of glass are fitted after painting and lacquering the car bodywork. In days gone by, the front and rear windscreens were fitted into the bodywork using a profile made of an elastomer that surrounded the glass. A cord-like tacky elastomer sealant was then applied to improve the seal.

Since the start of the 1970s, so-called direct glazing has been increasingly used *(Figure 52)*. Moisture curing 1-C polyurethane adhesives, or alternatively MS polymers (modified siloxanes), are used for this. Besides providing an excellent seal, the advantages of this technology are that larger panes of glass can be used and this reduces the overall weight of the car bodywork. This is because the glass panes become a structural material due to the adhesive curing as an elastomer. The rigidity of the structure therefore increases and this so allows thinner metal sheets to be employed.

Figure 52

3.4 Lightweight design for aircraft, rail vehicle and container manufacture

Aircraft manufacture

For several decades now, bonding has been one of the most important joining techniques in aircraft manufacture. The specific reasons for this include the fact that bonds have lifetimes of up to 30 years, high resistance to dynamic loads and media and resistance to extreme, and sometimes very rapid, temperature changes, from sub-zero temperatures in the stratosphere to ground-level temperatures in desert climates.

The application of bonding technology in aircraft manufacture allows extremely lightweight design due to the consequent use of light metal alloys, fibre-reinforced plastics and so-called sandwich components. Bonding is used for internal structures for manufacturing structures with lightweight honeycomb sheets *(Figure 53)*. It is also used for creating high stress joints, so-called primary structures, for example for the external stiffening of sheet metal of differing geometric size, for sandwich structures made of aluminium or plastic honeycombs with bonded on veneers and for bonding stacks of sheets. The Airbus vertical tail is an example of this. It is composed of an aluminium lattice framework and veneers made of carbon-fibre reinforced epoxy resin adhesive. The individual components of the veneers are pre-cured and the whole component is bonded in an autoclave.

In the aircraft manufacturing industry, it is mainly epoxy resin adhesives, especially prefabricated films with a curing temperature of at least 120°C, that are used for bonding sheet and sandwich components. The lap shear strengths that can be attained are about 20 MPa (static) and 1 MPa (dynamic). The effect of peel forces is avoided by choice of design. However, a peel resistance of about 4 N/mm is sought for assurance.

Rail vehicle manufacture

In rail vehicle manufacture, new components such as those made from glass-fibre reinforced plastic (GFRP) have resulted in enormous weight reduction and have transformed the production process. ADtranz regional trains *(Figure 54)* are manufactured using a frame structure consisting of tensile and compression struts in a triangular arrangement. This is the lightest design for bearing structures. Due to the frame structure, it is not necessary to weld on metal sheets to take up the shear stresses. There are only tensile and compressive forces in the struts. In order to enclose the frame, large outer skin elements are bonded to the supporting metal structure using moisture curing 1-C polyurethane adhesives. No complex straightening and filling work is required, as is the case when welding is used to attach the metallic outer skin elements. The GFRP elements that are used for the outer skin have a sandwich structure and hence provide good thermal insulation and have very good acoustic properties. As no heat distortion occurs, contrary to when welding, the outer skin gives the rail vehicle a

Figure 53

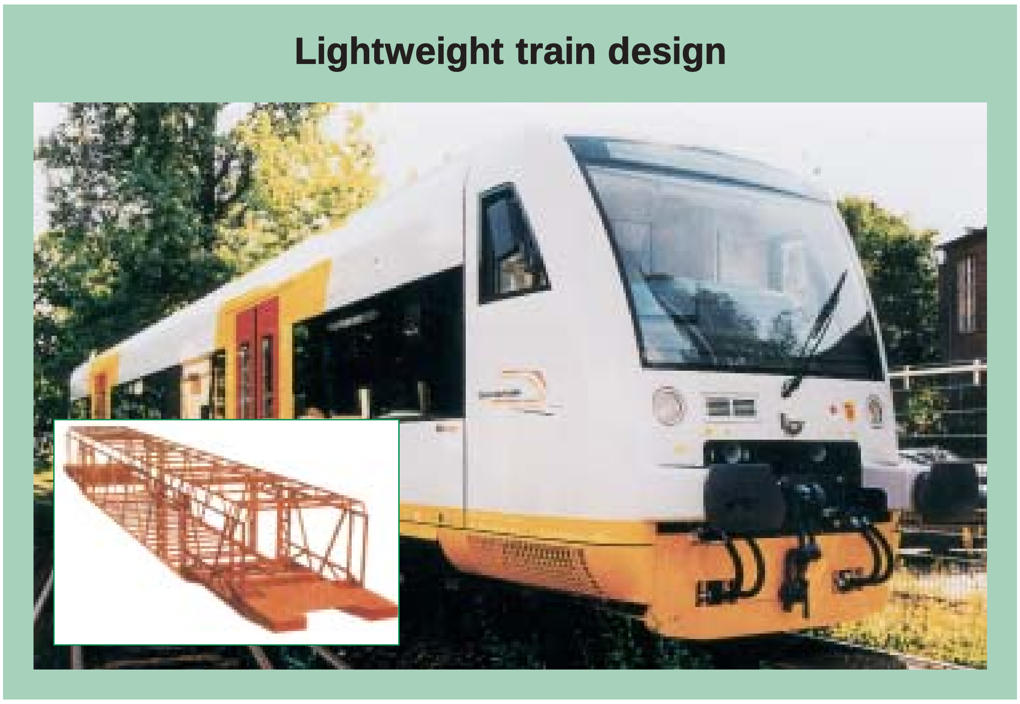


Figure 54

ready painted/lacquered, level, smooth and flush outer surface with no additional work having to be undertaken.

Joining a metallic framework structure with components made of fibre reinforced composite plastic can only be economically and reliably achieved using bonding technology. In order to compensate the different linear deformations of the structure and outer skin when they are exposed to heat, a highly elastic, thick film of adhesive is used. The resulting bonds have high strengths, even when subjected to repeated temperature fluctuations in the range between -40°C and +80°C and under impact-like stress. They also have very good resistance to aging, even in moist environments. The thickness of the bonded joint varies between 4 and 18 mm. This depends on the size of the components, which can be up to 8.5 metres long and therefore subject the bonded joint to very high shearing deformation. Another advantage of this type of structure is the high damping and the positive effect this has on the dynamic operating characteristics and ride comfort.

All in all, these regional trains are about 25% lighter than comparable conventional trains, and they also have improved ride characteristics, lower production costs and reduced energy requirements for operation.

Construction of containers

Sandwich panels are widely used for constructing containers and refrigerated containers. These panels are made by bonding core materials such as plastic foams, sheets made of mineral materials or honeycomb sheets to cover plates made of aluminium or glass-fibre reinforced plastic. Low and medium viscosity epoxy resin adhesives are used for this purpose and decorative panels also being bonded using such adhesives. Of late, MS polymers are also being increasingly used for this. They have good adhesion without prior application of a primer (even on lacquered/painted surfaces) and they have universal application because of their good elastic properties and high UV stability *(Figure 55)*.

Application of adhesives in container construction

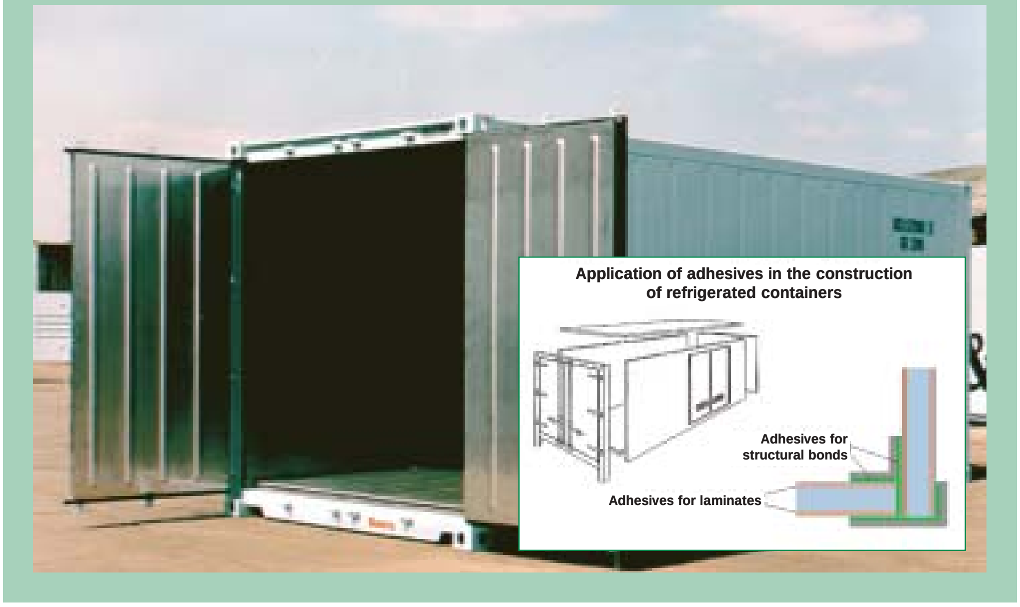


Figure 55

3.5 Electronics/electrical engineering

Electronic circuits

From the very outset, the rapid developments in the area of electronics have involved ever smaller components and ever greater circuit complexity. The continuing miniaturisation has not only resulted in smaller components but also components that are more sensitive to heat. For cost reasons, it was also necessary to reconsider the methods used to assemble printed circuit boards (PCBs). The solution to these problems was advanced bonding technology. Adhesives have hence taken over many tasks in the assembly of electronic circuits. Besides being used for mechanical attachment, they also function as for example electrical conductors and insulators. Today, many electronic components are fixed in their intended positions with adhesives, prior to soldering *(Figure 56)*.

Localised adhesive application on a PCB

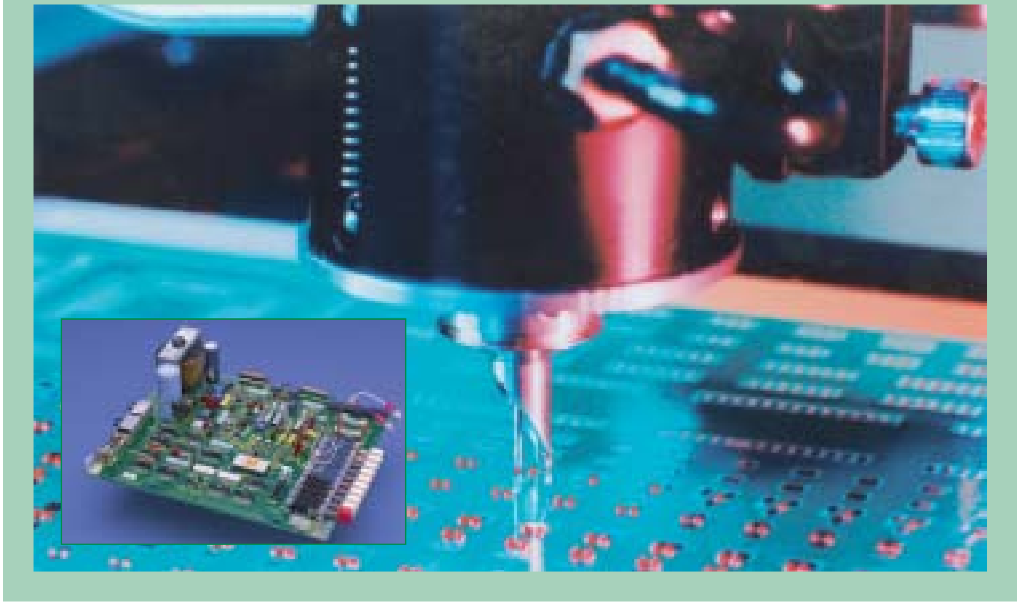


Figure 56

Single-component paste-like epoxy resin adhesives are used. These adhesives bond in 3 minutes at 120°C. Acrylate adhesives are used to a lesser extent. The latter are pre-cured by UV light to allow rapid fixing. Their final strength is then developed by applying heat.

Electrically conducting adhesives are normally epoxy resin adhesives containing a very small amount of ionic contaminants. To a lesser extent special polyimide adhesives are also used. In both cases these adhesives contain 70 to 80 weight percent of very fine silver powder. They are used when components cannot be soldered due to their sensitivity to heat, especially when repairs are being carried out. In addition, adhesives with heat conducting properties (e.g. adhesives containing high amounts of aluminium oxide) are growing in importance due to the increasing requirements on the heat management of circuits.

Manufacture of Digital Versatile Discs (DVD)
Unlike a Compact Disc (CD), a DVD has a sandwich construction and is namely a bonded object. Various designs are possible, with information storage on one or both sides. UV curing acrylate

Bonding of Digital Versatile Discs (DVD)

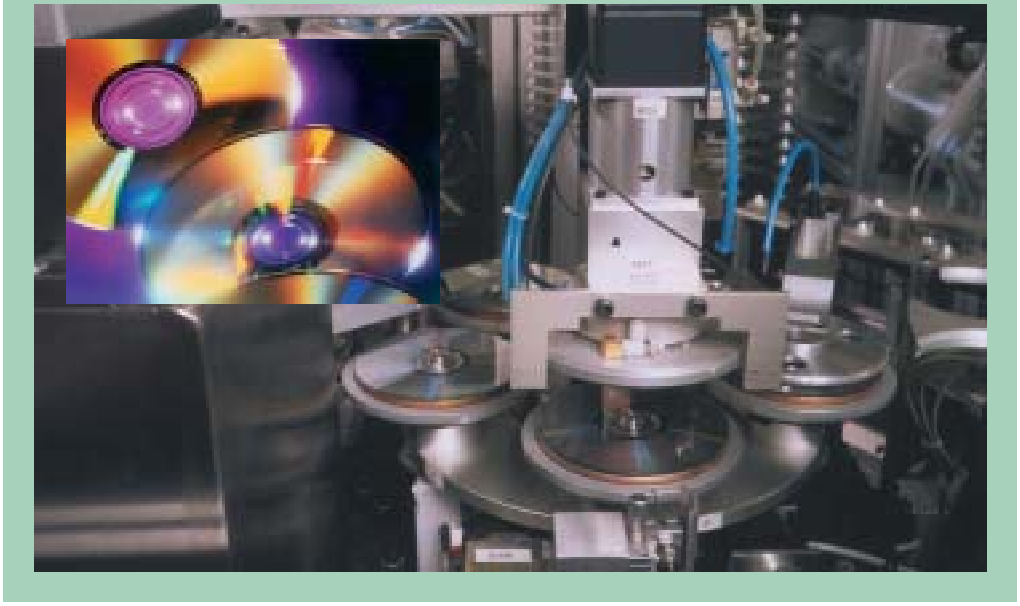


Figure 57

adhesives are used for bonding the DVD components. These adhesives bond under the influence of UV light in a few seconds and besides having high optical purity the bonds have very good long-term stability under warm humid conditions. Special hotmelts based on thermoplastic elastomers are also gaining in importance in this field *(Figure 57)*.

Electric motors
A whole host of electrical devices, from kitchen appliances to CD-players and video cameras, contain electric motors. These mass-produced motors are expected to have precise synchronisation and a long lifetime. Adhesives are nowadays indispensable in motor assembly, for example for connecting the armature and shaft, for connecting the commutator and shaft, for attaching ball-bearings and for securing screws in position *(Figure 58)*. The preferred type of adhesive for this is an anaerobically curing acrylate adhesive, namely an acrylate adhesive that cures when oxygen is excluded.

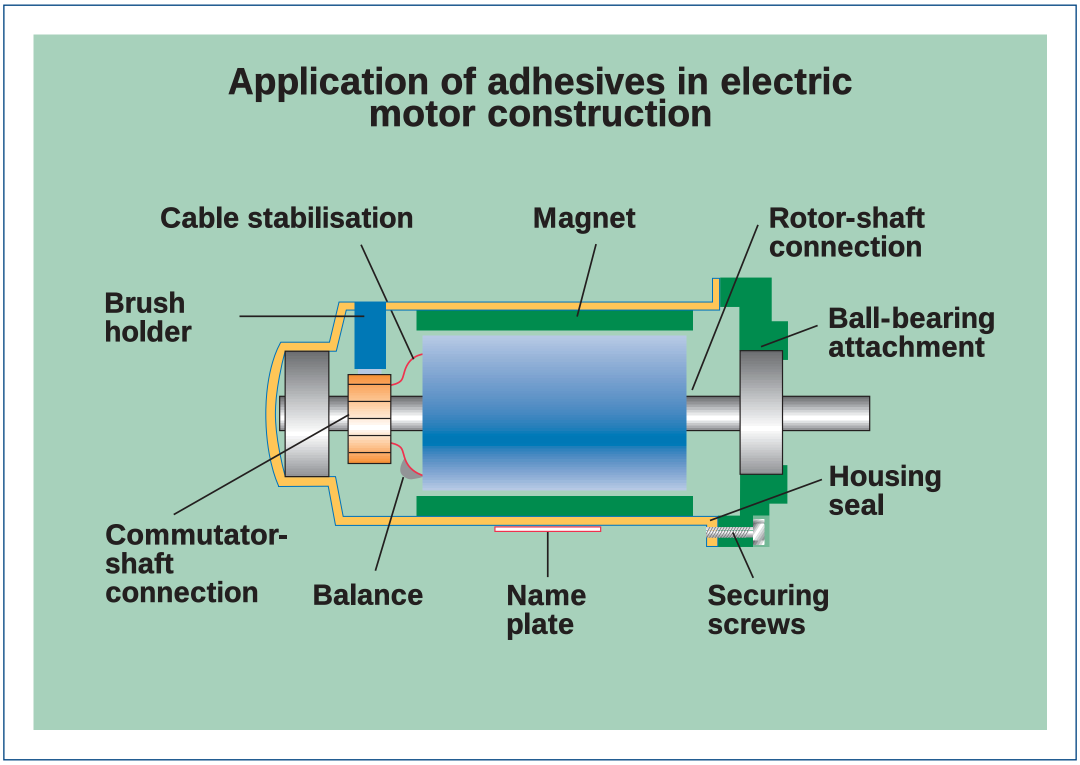


Figure 58

3.6 Adhesives for packaging materials

An extremely high proportion of all industrial products are sold in packaging – either due to stability requirements for storage and transport or for aesthetic reasons. Although normal envelopes and paper bags consist of just a single layer of material, most packaging materials used nowadays are in fact different materials laminated together *(Figure 59)*.

By laminating cardboard with paper, in particular high gloss paper, it is possible to put product information on the cardboard and give the product a commercially alluring appearance. Adhesives based on starch, dextrin and glutin, and also polyvinyl acetate dispersions, are used for this purpose.

Important requirements on overprinted packaging materials, in particular the various types of packaging materials used for foods, are their strength, stability to heat and impermeability to moisture, oxygen and aromas. These properties along with desired appearance can usually only be obtained by combining different materials. Laminated films can be manufactured from polyester (PETP, PBTP), polyamides, polyethylene, polypropylene, cellophane, paper, polyvinyl chloride, polyvinylidene fluoride, polyimides, aluminium and a few other materials. Metallic foils are also often used. Solvent-containing adhesives based on polyurethane are used for laminating films; the most recent developments in this area however involve solvent-free systems, so-called high-solid products and adhesives based on aqueous polyurethane dispersions. For application using automatic packaging machinery, high requirements are put on the constancy of the adhesive properties, especially with regards to its viscosity stability. Dispersion adhesives and hotmelts are used to seal packaging (e.g. folding cartons, packets).

Laminated films: finished products

Figure 59

3.7 Adhesives in medical applications

The use of adhesives in medical applications was for a long time restricted to the manufacture of self-adhesive bandages (plasters, self-adhesive strips of fabric, etc.) *(Figure 60)*. The first pressure sensitive adhesives used for this were based on natural rubber. This was in part later superseded by synthetic rubbers (e.g. polyisoprene, polyisobutylene). In the middle of the 20th century, pressure sensitive adhesives based on polyacrylic acid esters became increasingly important, both for general use and for bandage materials.

Adhesives are today employed in diverse areas of medicine, replacing traditional methods with “friendlier” processes. In many cases, for example, stitches can be avoided by applying special cyanoacrylate adhesives to quickly close skin wounds. An advantage here is that the whole wound can be

Examples of self-adhesive bandages

Figure 60

covered, so largely suppressing secondary bleeding and the risk of infection. Cyanoacrylic acid butyl ester is normally preferred over the methyl and ethyl esters because it cures more slowly and the polymerisation produces less heat; It also causes less tissue irritation. By and large, this adhesive is only used for relatively small wounds and occasionally in vascular surgery. In heart surgery, fibrin (made from fibrinogen), a soluble protein recovered from blood, is a key sealing agent having a haemostatic effect. Compared to cyanoacrylates, fibrin is gentler to body tissue but before use it must undergo a special treatment to prevent germs being spread. The use of methacrylate based adhesives has been a great success in orthopaedics for anchoring hip socket implants to the bone. There are currently no other types of adhesive used for this application. The adhesive products comprise a) a powder component (a mixture of polymethyl methacrylate and a polymerisation initiator) and b) a liquid component (whose main components are methyl methacrylate and a polymerisation accelerator). Although this type of adhesive puts a not inconsiderable stress on bone and tissue due to the strong heat development, hip and knee implants anchored using this adhesive are in 90 percent of cases functional for about 15 years *(Figure 61)*.

In dentistry, fillings based on UV curing acrylates have largely replaced traditional filling materials such as amalgam. The products have a long open time (the period during which they can be used after mixing) and bond in just a minute or so when exposed to UV light.

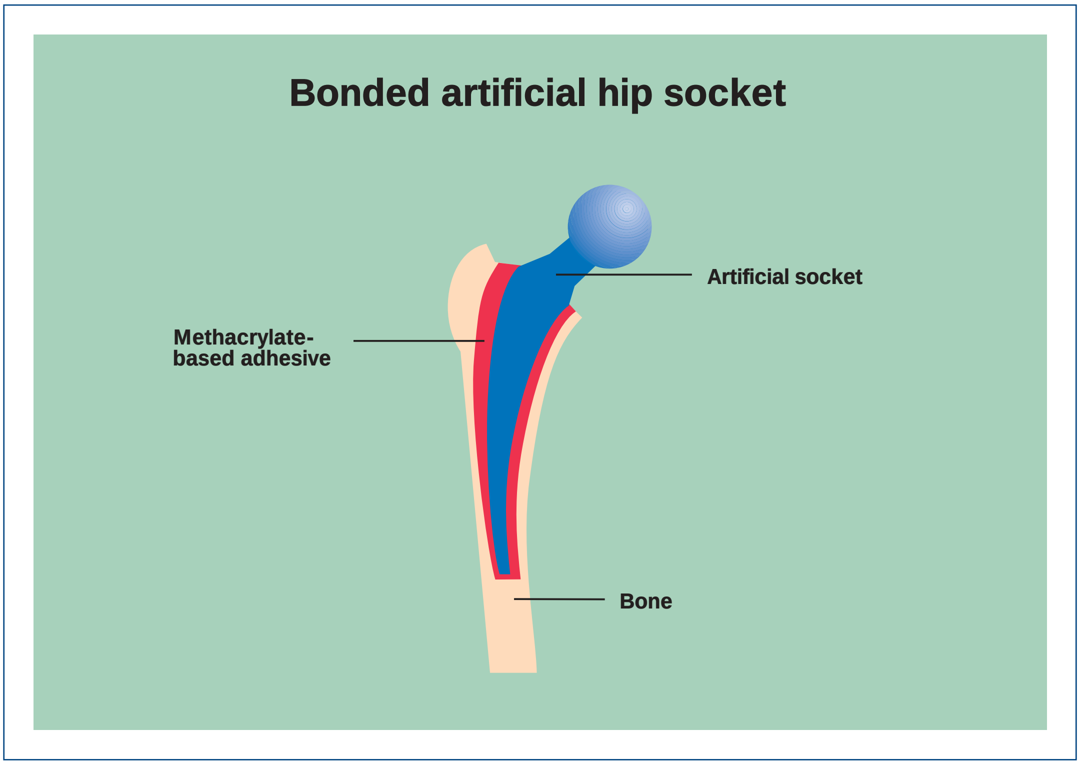


Figure 61

4 Work, health and environmental protection when using adhesives

The handling of raw materials and products in a responsible way throughout their lifecycle, namely from their manufacture via the usage stage right through to recycling and disposal, is nowadays a generally recognised principle. For some time now, the development and manufacture of adhesives in Germany has been carried out following the “Responsible Care” and “Sustainable Development” guidelines of the VCI (Verband der Chemischen Industrie) *(Figure 62)*. This specifically means that health protection and environmental compatibility considerations are taken into account when devloping and manufacturing new adhesives. This has consequences for the composition of the adhesives, the product design, the recommendations for application of the adhesive and the purpose of use and for the recycling of the product after it has been used.

The three dimensions of sustainable development

Sustainable Development is a concept which mankind must adopt to ensure a responsible future. The concept has **environmental, economic** and **social dimensions.**

We pledge today to leave behind a world worth living in for future generations.

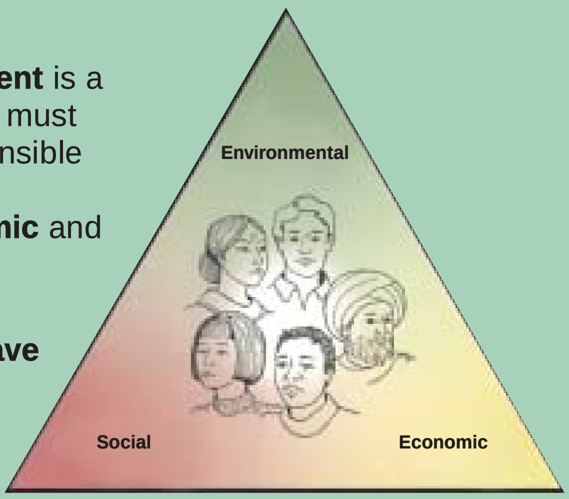


Figure 62

4.1 Health protection

The aim of health protection is to protect people against hazards and exposure. “Work protection” is used to describe protection in commercial and industrial work environments whilst “consumer protection” refers to private users.

4.1.1 Work protection

Industrial and commercial users of adhesives require special protection because they work on daily basis with adhesives, often for many hours a day. In addition to hazards associated with the physical properties of adhesives such as flammability, explosiveness and burns when using hotmelts, it is in particular chemical effects such as toxicity, skin irritation, acid burns and allergies which have to be avoided. This is achieved by equipping the workplace (workplace guidelines) with air replenishment systems and local extractors, personal protection equipment such as work clothing, gloves, and safety glasses and by ensuring that hygiene regulations are adhered to, for example thorough washing of the skin before breaks and at the end of work and refraining from eating, drinking and smoking in the workplace. Safety officers monitor compliance with these safety measures. Personnel who work with adhesives undergo regular training on matters relating to work safety and environmental protection. If special risks are involved, then personnel undergo regular medical examinations.

4.1.2 Consumer protection

Although in a professional work environment possible hazards can be efficiently managed using suitable protective measures, even in situations where there is long-term use, the situation is different for private individuals using adhesives at home where no special protective measures are taken. Different requirements are hence put on these adhesives. This is also so because private users, unlike industrial users, generally have no knowledge of the properties and potential hazards of products. That is why only relatively few of all the known types of adhesives are available to private users, and even then only small amounts are made available in the form of tubes, cartridges and tins. On the other hand, private users do not use adhesives every day, but rather only occasionally, and even then only in limited quantities and for limited periods of time. As such, the protective measures described for industrial users are generally neither possible nor necessary. It is nevertheless essential that the safety information given on the small packages is observed, as well as basic principles of work hygiene.

4.1.3 Health risks

The area of toxicology *(see Glossary)* is concerned with issues relating to the effects of chemical compounds and mixtures of chemicals. Assessing the health risk is a multi-step process. The first step is sound assessment of possible undesirable properties of substances *(Hazard potential, see Glossary)* based on recorded data. In the second step, the quantities of material involved and the nature and degree of any possible contact are determined *(Exposure, see Glossary)*. It is then investigated whether an undesired effect of a material can be caused as a result of this contact. There is no health risk for people if there is no contact with the undesired material. The risk assessment determines whether and to what extent there is a health risk to people as a result of the relevant hazard potential of the substance and the nature and degree of exposure *(Figure 63)*. Although the exposure can for example be reduced by automated processing (e.g. robots) or by taking suitable protective measures (e.g. gloves, extraction of vapours, safety glasses, etc.), the hazard potential is a fundamental property of a substance or formulation (mixture of substances). The hazard potential generally decreases when the fraction of hazardous material present is lower. Small amounts of a hazardous substance can often be present without the product having to be accordingly labelled *(Classification, see Glossary)*. The physico-chemical properties of the substance, the nature and degree of exposure and the ability of the substance to get into the body determine the relevant amount and the resulting dose that can be taken up by the body. In general there is no undesired effect below a certain dose. The dose level determines whether and to what degree a substance can harm a person's health. The risk to human health is determined from the hazard potential of the substance and the exposure (opportunity for contact).

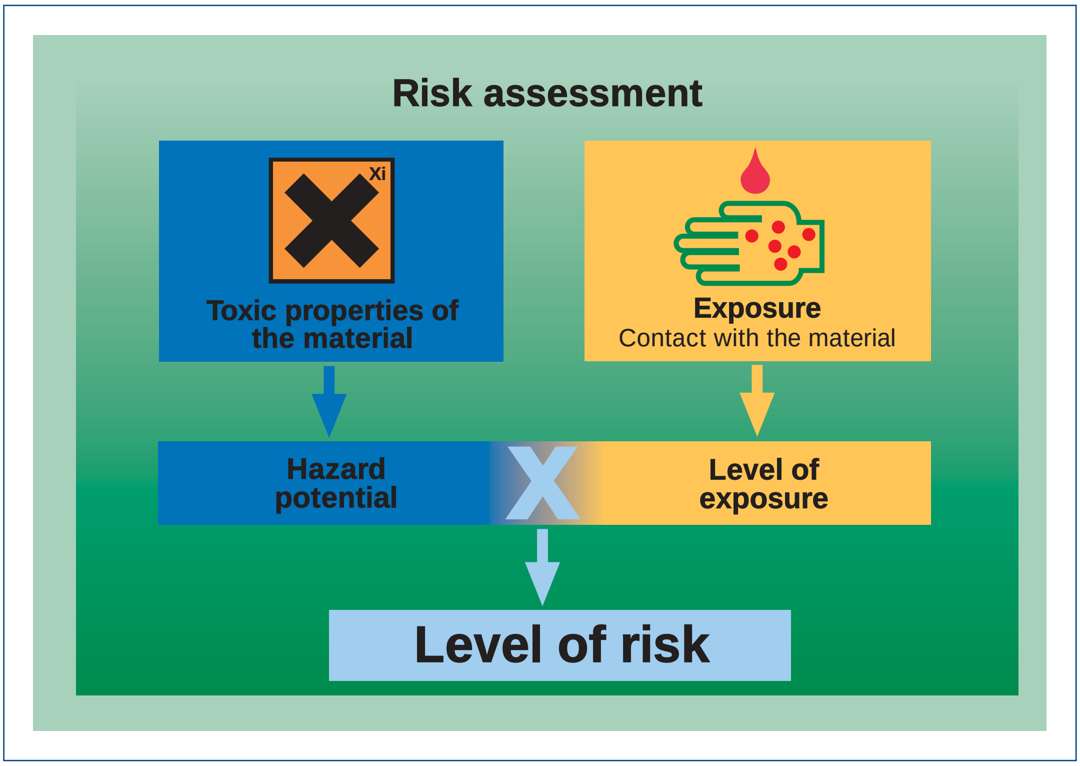


Figure 63

4.1.4 Health protection when using adhesives – examples of toxicological assessment

Of the many different types of adhesives, those discussed below are those that are also commonly used in the household:

4.1.4.1 Physically hardening adhesives

The active components are mainly solid polymers and resins. For application these must be converted to a liquid form. This can either be carried out by users by means of heating (hotmelts) or can be carried out by adhesive manufacturers by dissolving the components in organic solvents or dispersing the components in water. The dry, fully-aired adhesive is generally unreactive and biologically inert. There is hence usually no health hazard. In contrast, there is a potential health hazard from auxiliary components, such as organic solvents, that are present in some of these adhesives. These can make up as much as 80% of the weight of the adhesive product.

Hotmelts

These adhesives contain largely polymers and resins and only small amounts of auxiliary materials. There is virtually never a health hazard. When applying these adhesives manually, there is the risk of burns and users must protect themselves against this. During heating, small amounts of auxiliary materials, contaminants and cleavage products can be liberated, but these are insignificant when small amounts of adhesive are being processed. In an industrial or commercial environment, an extraction system is recommended due to the larger quantities being used and the longer working times with the adhesives.

Solvent-containing adhesives (e.g. contact adhesives)

In these adhesives the polymers and resins are dissolved in organic solvents. The hazard potential is determined by the nature of the solvent (e.g. flammability, irritation potential). Due to the high volatility of the solvents, exposure by inhalation of the vapours is the biggest problem. For most solvents the maximum concentration at the workplace and limiting factors are laid down (Workplace limit value, see Glossary). Due to the small amounts of adhesive used by private users, these limit values are generally not reached or are only exceeded for a very short time.

Dispersion adhesives (e.g. PVA / wood adhesive)

In the adhesives the organic solvents are replaced by water and suitable polymers are dispersed in the water. There are hence no potential health hazards from organic solvents. However, water-based adhesives are sensitive to attack by micro-organisms (e.g. mould formation). For that reason dispersion adhesives contain small amounts of preservatives for protection purposes. The potential health hazard is the triggering of allergic skin reactions, for example allergic reactions triggered by natural polymers such as natural rubber and non-modified colophony resins. The risk of sensitisation in non-allergic people is generally extremely low due to the very small amounts of preservatives in the adhesives. Skin contact is here the exposure issue. Depending on the mode of application, skin contact may be unavoidable, as for example when using wallpaper pastes. However, here the concentration of preservatives is reduced as a result of mixing with water. As even wearing protective gloves for a long time can lead to skin irritation (caused for example by constant sweating), it is worth considering whether the very low risk of direct skin contact causing an allergic reaction justifies wearing protective gloves.

Pressure sensitive adhesives

Private users only come into contact with these adhesives in the form of self-adhesive articles such as labels, adhesive tape, etc. As such these adhesives represent no hazard to private users in practice. Such articles are manufactured industrially using adhesives in the form of solutions, but mostly using dispersions and melts.

4.1.4.2 Chemically curing adhesives

The chemically reactive monomers/oligomers and hardeners and crosslinking agents determine the potential health hazard of these products. Once fully cured, the adhesive polymers are in general non-hazardous. Exposure and risk considerations hence only apply for the time period up until the adhesives have fully cured.

Superglues (cyanoacrylate adhesives)

This group of adhesives reacts with water from the surroundings or water on the substrate. As private individuals only usually use small drops when applying the adhesive, the potential health hazard here is that if there is contact with the eyes or splashes of adhesive enter the eye then undesired bonding can take place (can gradually be dissolved using a soap solution). When being used industrially and commercially, possible irritation caused by the cyanoacrylate monomer, thermal effects and the rapid polymerisation reaction have to be taken into consideration. Increasing the humidity prevents irritation of the respiratory tract. Cyanacrylates must be specifically labelled, as laid down by the German Ordinance on Hazardous Substances. When carrying out major bonding tasks, not only is it recommended to adjust the humidity of the air but also to wear safety glasses and protective gloves.

Silicone adhesive sealants

Silicones react with water. Depending on the type of silicone, this reaction releases either acetic acid or alcohols. The acetic acid can be clearly sensed by the nose before any irritation begins. In general the slowly released amounts are so small that they present no health risk, especially in the case of private users. Old formulations of neutral silicones which release butanone oxime must be labelled, but they are only used nowadays for special applications.

Epoxy resin adhesives
Epoxy resins are widely used by hobbyists and in home DIY because of their good bonding properties, for example for bonding glass, ceramics or metals. This is particularly because the supplied twin-nozzled container allows even the smallest quantities to be dispensed and then mixed. Liquid epoxy resins, and also crosslinking agents, irritate the skin and eyes and cause skin hypersensitivity. As such, hobbyists should avoid epoxy resin adhesives contacting the skin. For the industrial application of epoxy resins, safety glasses and suitable gloves must be worn. Epoxy resins having a molecular weight up to 700 must be labelled: Xi-R36/38-43. Monomer and oligomer epoxy resins up to a chain length of 3 n are irritating to the skin and eyes and cause skin hypersensitivity.

4.1.5 Selecting an adhesive

For private use there are no legal requirements. The selection of an adhesive is left largely to the experience of users and the recommendations of manufacturers. For commercial users, and in particular for industry, the selection of a suitable adhesive system for a particular application must be based on the technical requirements and the potential health hazard. In a situation where two adhesives are equally suitable, the one providing the lower potential health hazard must be chosen. If using an adhesive which does represent a potential health hazard is unavoidable for technical reasons, the exposure must be limited by taking suitable measures, that may even include automating the process, such that a risk to health is prevented. Safe working with adhesives is guaranteed by observing this regulation and the other regulations described in this section. Adhesive manufacturers provide support here by providing information in the form of technical data sheets and safety sheets. If necessary, users should contact the adhesive manufacturers directly. As is clear from the iterations in this section, adhesive manufacturers make considerable efforts to protect the health of both private and professional users of their products. It must be mentioned here that from a quantity point of view only a small number of adhesives have to be classified as hazardous formulations.

Private users complying with the safety instructions given on containers and industrial workers complying with relevant company regulations in their production facilities serve to protect people in accordance with the motto: “Prevention is better than cure”.

4.2 Environmental protection in adhesive bonding technology

Environmental issues have gained increasing importance over recent decades. The following is an example of a positive contribution to the environment: The car manufacturing industry uses up to 40 kg of adhesive sealants in each vehicle. The man objective of this is to save energy in the form of fuel by means of so-called “lightweight design”, whereby less weight has to be moved over the lifetime of the car and so resources are saved (e.g. 3-litre car). On the other hand, the adhesives in this same example could burden the environment if there are residues left over from the application and any cleaning. At the end of the lifecycle of the car, the adhesive that was used must not adversely affect the recycling process and must be disposed of in accordance with regulations. In order to determine the effects on the environment, an environmental assessment is carried out. The expected concentration in the environment is calculated using a model. Simultaneously, the concentration at which no harm is expected to environmental organisms is determined. The calculation models and determination methods are laid down in international standards. An adverse effect on or harm to the environment can be excluded with certainty if the Predicted Environmental Concentration (PEC) is less than the predicted concentration for which no harm to environmental organisms occurs (Predicted No-Effect Concentration - PNEC), taking into account safety factors.

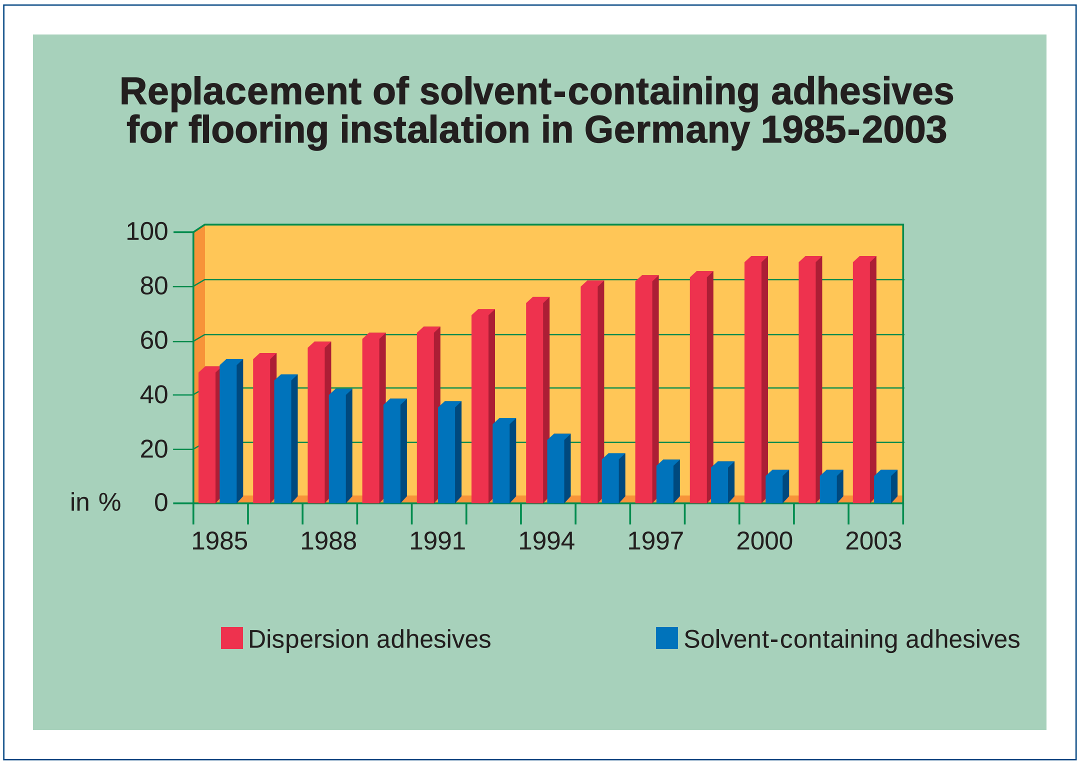
4.2.1 Air

The emission of organic solvents is detrimental to air quality. As such, considerable efforts have been made by the adhesives industry over many years to switch to low-solvent adhesives and where possible solvent-free adhesives. There has been considerable success, and this has also been beneficial for health protection. Bonding is today only responsible for less than 3% of all the solvent emissions in Europe. The few large-scale applications in industry operate with solvent-recovery plants. A typical example is the construction industry in Germany. In 1985 the fraction of solvent-containing adhesives was still about 50%, but by 2003 this was less than 10% and falling. Dispersion adhesives have largely replaced these solvent-containing adhesives *(Figure 64)*.

4.2.2 Water

With dispersion adhesives there is a particular risk of contaminating surface waters. Organic polymers and prepolymers, although not easy to biodegrade, can be removed in biological treatment plants with the excess sludge. The use of these adhesives in handicraft work, in the home and for DIY work normally results in only relatively small amounts of adhesive ending up in large amounts of wastewater (communal treatment works). As polymers usually have low toxicity for water organisms and due to the

Figure 64



very low concentrations of adhesives in the wastewater, an adverse effect on the treatment plant and adjacent surface waters (outfall) is not expected in this case. In industry, residual adhesive and rinse water must be disposed of in accordance with waste legislation.

4.2.3 Soil

When used by private individuals, liquid adhesive residues are usually collected in the hazardous waste collection boxes, but are also often disposed of with the rest of the household waste. The amounts involved here are however small. For industrial and commercial users, disposal must be carried out in accordance with the so-called waste code numbers (to be found on the safety sheets), which determine how the waste is disposed. Adhesive residues are normally disposed of as landfill or incinerated. Regarding the latter, specific contamination of the air by the incineration plants is not expected. The energy used in the manufacture of the adhesives can be partially recovered here.

4.2.4 Examples of assessing the environmental impact of adhesives

4.2.4.1 Production of adhesives and adhesives in industrial use

In industry, residues of cured adhesives and also non-crosslinked and liquid adhesives occur as waste. The former, as solid materials, are either directly passed on as waste for disposal, or are preferably passed on for recycling. In the least favourable environmental scenario they are disposed of as landfill. They are however usually recycled, either via composting or for energy recovery via incineration. Depending on how they have been treated, liquid adhesives are discharged with the wastewater and are either directly passed to a treatment plant or, if necessary, passed to a treatment plant after undergoing a specific pretreatment. There they are biodegraded or removed.

4.2.4.2 Use of adhesives in the homes of end-users

Adhesives used in the home have to be considered in different groups:

- Solid adhesive waste from the home such as hardened paper or wood glue is usually disposed of with the rest of the household waste.
- Water is usually used to remove water-soluble, hardened adhesives in the home, for example for removing wallpaper paste. This adhesive-containing water is disposed of with the household wastewater via the water treatment plant. The adhesive components, e.g. cellulose derivatives, which are dissolved to varying extents, can easily be eliminated under real environmental conditions, meaning that only very small amounts enter the outfall (river). When composting is used for recycling, cellulose decomposes slowly but thoroughly - as known for plant materials.
- Adhesives used in the home, e.g. roofing adhesives, or around the home, e.g. for the car, are exposed to processes that can wash out the adhesive, e.g. rain. This means that a small amount of adhesive ends up in drain water and then directly enters surface waters.

Considering all the adhesives that are in use, the expected environmental concentration (PEC) is determined. The most unfavourable scenario is assumed in order to ensure that all conceivable possibilities have been taken into account *(Figure 65)*.

4.2.5 Outlook

Adhesives as a whole do not represent a major environmental problem. Nevertheless, cured and non-recyclable residues as well as excess adhesive from applications are waste materials. These materials not only have to be disposed of, but also represent an unnecessary use of materials and resources. The principle of recyclable design, made possible by having detachable bonded joints, will be important in the future. Besides technologies for separating bonded materials, a further challenge of bonding technology will be resource-friendly optimisation of production and application processes. It will be necessary to incorporate non-removable adhesive into future recycling processes. This will mean that the adhesive to be used for manufacturing a component will have to be customised to the recycling process at the end of the component's lifetime.

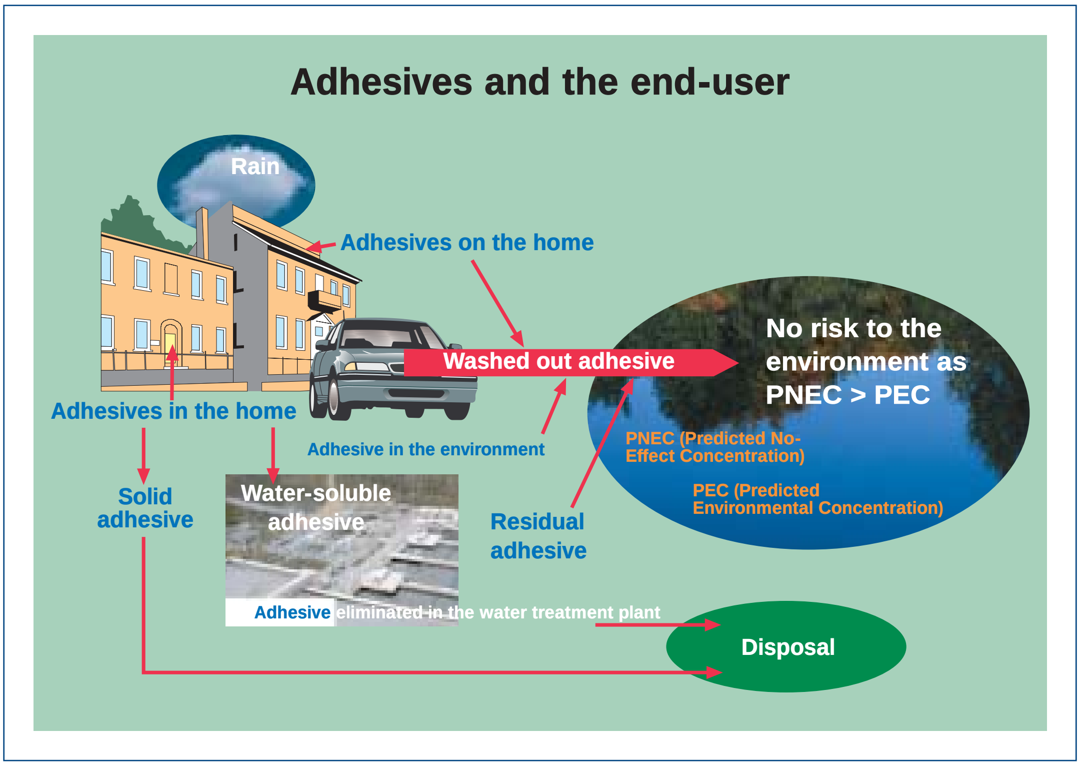


Figure 65

Experiment 1: Most adhesives are composed of organic raw materials (carbon determination)

Equipment: Safety glasses, test tubes, test tube clamps, spatula, Bunsen burner, knife.

Chemicals/materials: Adhesive samples such as wood glue e.g. Ponal® or Uhucoll®; wallpaper paste e.g. Metylan® or Glutolin®; hotmelt e.g. Pattex® cartridges or Uhu® adhesive cartridges.

Safety information: Do not use solvent-containing adhesives labelled "F" "(highly) flammable"! Ensure there is good ventilation in the working area! Do not inhale vapours! Vapours that are produced can ignite! Wear safety glasses!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the packaging of the adhesives to the work sheets!

Individual adhesive samples are added to a test tube so that there is about 1/2 cm in the test tube. The adhesive is then heated strongly in the Bunsen burner flame.

Further experiment: Mix solid adhesive (e.g. hotmelt or wallpaper paste) with copper (II) oxide and put this mixture in a test tube (Supremax®). Heat strongly. Pass the liberated vapours into chalk water (solution of $Ca(OH)_2$ in water). **Note:** On cooling down, the chalk water must not get into the hot test tube! First remove the chalk water, then terminate the heating!

Experiment 2: Adhesives consist of macromolecules (Tyndall effect)

Equipment: 2 glass beakers (250 ml, high-sided), 2 glass stirring rods, torch, piece of card (size A5, black), scissors, spatula.

Chemicals/materials: Universal adhesive e.g. Uhu®; Pritt® or Tesa® multi-purpose adhesive; wallpaper paste e.g. Metylan® or Glutolin®; water.

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the packaging of the adhesive to the work sheets!

Fill a beaker with water up to about 1 cm from the top. Then add 5 spatula tips of wallpaper paste and stir well. Leave to swell for a few minutes. Roll the card into the shape of a funnel and bond it with multi-purpose adhesive so that there is an opening of ca. 1 cm diameter. Then darken the room and shine the light of the torch through the funnel opening. The glass beaker with the wallpaper paste is then placed in the beam of the torch.

As a blank, the experiment is repeated with a beaker full of water.

Experiment 3: How adhesives work (principle of adhesion)

Equipment: 2 smoothly ground glass plates (cover plates, thickness ca. 1.0 cm, diameter ca. 12 cm) each with a handle in the centre of the non-ground side, two glass plates with a rough surface but otherwise as above, glass beaker (250 ml), pipette.

Chemicals/materials: Water, oil (edible oil or similar).

Note: The surfaces of the glass plates must not be touched by the fingers or hands. The surfaces must not be contaminated!

Experimental procedure: The glass beaker is filled with water. The whole surface of a smoothly ground cover plate is wetted with water using the pipette. The second smoothly ground cover plate is then carefully placed on top of this. Now try and separate the plates from each other by pulling vertically.

Experiment 3a: One of the two smoothly ground cover plates is coated with oil. The other smoothly ground plate is then wetted with water. Carefully place the plates together. Now try and separate the plates from each other by pulling vertically.

Experiment 3b: Repeat experiment 3 with the roughened glass plates.

Experiment 4: Wetting of material surfaces – surface tension

Equipment: Glass beaker (250 ml), pipette, aluminium sheet (surface not degreased), aluminium sheet (surface degreased and roughened), PVC sheet, PE sheet.

Chemicals/materials: Water.

Note: The surfaces must not be touched by the fingers or hands.

Experimental procedure: The glass beaker is filled with water. Using the pipette, water is carefully dropped onto the surfaces of the different materials.

Experiment 5: Manufacture of a casein adhesive

Equipment: Safety glasses, protective gloves, glass beaker (250 ml), glass stirring rod, balance, measuring cylinder, pegs, brush.

Chemicals/materials: Casein (acid casein), dilute sodium hydroxide solution (ca. 4% solution), piece of plywood or similar (ca. 10 cm x 2.5 cm x 0.5 cm).

Safety information: Sodium hydroxide causes burns! Wear safety glasses and protective gloves!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) for sodium hydroxide as indicated in the German Ordinance on Hazardous Substances to the work sheets. Place 25 ml diluted sodium hydroxide in a glass beaker and dissolve 10 g casein in this whilst stirring. Leave to swell for a few minutes! Before application, the adhesive can if necessary be made easier to use by adding water. Bonding tests are now carried out on the pieces of wood. The bonded points can be affixed using pegs until the adhesive has fully bonded.

Experiment 6: Manufacture of starch glue (I)

Equipment: 2 glass beakers (250 ml, wide type), glass stirring rod, Bunsen burner, tripod, wire gauze, measuring cylinder, balance, spatula, brush.

Chemicals/materials: Maize starch or similar, salicylic acid, writing paper.

Experimental procedure: A paste is made using 10 g starch and 10 ml water. 120 ml water are heated to boiling point and the paste is dissolved in this with stirring. A spatula tip of salicylic acid is then added. Various bonding experiments with paper can now be carried out.

Experiment 7: Manufacture of starch glue (II)

Equipment: Safety glasses, protective gloves, glass beaker (250 ml), glass stirring rod, measuring cylinder, balance, brush.

Chemicals/materials: Sodium hydroxide solution (ca. 7%), hydrochloric acid (10%), starch powder, water, universal indicator paper, writing paper, paper glue e.g. Pritt® stick, Uhu® stick or Tesa® stick.

Safety information: Acids and bases cause burns! Wear safety glasses and protective gloves!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) to the work sheets. For the chemicals use the information from the German Ordinance on Hazardous Substances. For the adhesives use the information provided on the packaging.

First of all a 20% starch suspension is prepared (about 50 ml). Dilute sodium hydroxide is added to this with stirring until a viscous solution results. This is then neutralised with hydrochloric acid. The starch glue is used for carrying out bonding tests on paper. These tests are repeated using industrially manufactured adhesives (e.g. the abovementioned sticks of adhesive). The results are then compared.

Experiment 8: Manufacture of a methyl cellulose solution

Equipment: 3 glass beakers (100 ml), 3 glass stirring rods, spatula.

Chemicals/materials: Methyl cellulose e.g. Metylan® or Glutolin®, water, acetone, ethyl acetate.

Safety information: Acetone and ethyl acetate are highly flammable! Extinguish all flames!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) for the solvents as indicated in the German Ordinance on Hazardous Substances to the work sheets.

A glass beaker is 1/3 filled with water. 5 spatulas of methyl cellulose are added and the mixture is thoroughly stirred. Wait 15 to 20 minutes. The experiment is repeated with the other solvents.

Experiment 9: Hotmelts – properties and application

Equipment: Adhesive gun e.g. Pattex® Supermatik, Uhu® gun or guns from Bosch®, Black & Decker® or Steinel®, thermometer.

Chemicals/materials: Thin aluminium foil, pieces of wood (ca. 10 cm x 2.5 cm x 0.5 cm), cartridge of hotmelt e.g. Pattex® or Uhu®.

Safety information: Do not touch the liquid adhesive with the fingers! Risk of burns!

Experimental procedure: The bulb of the themometer is carefully wrapped in thin aluminium foil (for protection for the thermometer). Hotmelt cartridges are placed in the adhesive gun for melting. **Note:** Heed the processing instructions!

The temperature of the adhesive after exiting from the nozzle is measured. The liquid adhesive is applied to a piece of wood and this is joined to another piece of wood. In a sequence, different amounts of adhesive are applied to pieces of wood and the cooling of the adhesive is monitored using the thermometer. If necessary, the adhesive must be reheated for a short time so that the thermometer can be removed from the melt. The strengths of the bonds are tested by hand (separation test).

Experiment 9a: Liquid hotmelt is applied to pieces of wood and a waiting time of 1, 1.5 and 2 minutes is observed before joining with other pieces of wood. After about 30 minutes the strengths of the bonds are tested by hand.

Experiment 10: Adhesives can contain organic solvents

Equipment: Magnesia cup, test tube, test tube clamp, Bunsen burner.

Chemicals/materials: Solvent-containing adhesive e.g. Pattex® or Uhu® Greenit.

Safety information: Ensure there is good ventilation in the working area! Work in a fume cupboard!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the packaging of the adhesive to the work sheets!

a) A little solvent-containing adhesive (ca. 3 g) is dropped onto the magnesia cup and this is held in the Bunsen flame using the clamp, in order to ignite the adhesive.

b) A little adhesive (ca. 3 g) is added to the test tube. This is held in the Bunsen flame and gently heated. The objective here is to try and ignite the escaping vapours.

Experiment 11: Dissolved plastics as adhesives

Equipment: 4 test tubes, test tube rack, 4 small labels, pencil or similar, 4 cork stoppers, 2 glass plates, knife or pliers, brush.

Chemicals/materials: Polystyrene (PS), polymethyl methacrylate (PMMA), acetone or butyl acetate.

Safety information: Acetone and ethyl acetate are highly flammable! Extinguish all flames!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) for the solvents as indicated in the German Ordinance on Hazardous Substances to the work sheets!

1. Manufacture of the adhesive
About 2 cm of solvent are placed in each of the four test tubes. About 3 pea-sized pieces of the plastic are then added to each test tube. Two of the test tubes are made up using polystyrene, the other two with polymethyl methacrylate. The test tubes are labelled accordingly. They are sealed with the stoppers and left to stand until the next day. They are then shaken a little and if necessary diluted with the corresponding solvent. The two different adhesives from two of the test tubes are now poured onto the two glass plates and the solvent is allowed to evaporate in the fume cupboard.

2. Bonding
The plastic that remains behind is separated from the glass plates, cut into pieces and bonded with the corresponding adhesive that was kept in reserve. Adhesive that is no longer required is also poured onto glass plates and the solvent is allowed to evaporate in a fume cupboard.

Experiment 12: A simple multi-purpose adhesive

Equipment: Glass beaker (100 ml), glass stirring rod, balance, measuring cylinder.

Chemicals/materials: Polyvinyl acetate (PVAC), ethyl acetate, paper, cardboard, material off-cuts:
Pieces of plastic ca. 10 cm x 2.5 cm x 0.08 cm
Pieces of wood ca. 10 cm x 2.5 cm x 0.08 cm
Pieces of metal ca. 10 cm x 2.5 cm x 0.08 cm

Safety information: Ethyl acetate is highly flammable! Extinguish all flames! Carry out the experiment in a fume cupboard!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) for ethyl acetate as indicated in the German Ordinance on Hazardous Substances to the work sheets!

Place 30 ml ethyl acetate in the glass beaker and dissolve 8 g polyvinyl acetate in this with stirring. It may be necessary to first of all leave this to swell a little. Bonding experiments are carried out with various materials.

Experiment 13: Determination of polyvinyl acetate in wood glue

Equipment: Safety glasses, 3 test tubes, test tube clamp, test tube rack, Bunsen burner, spatula, anti-bumping granules.

Chemicals/materials: Wood glue e.g. Ponal® or Uhucoll®, polyvinyl acetate (PVAC) powder, dilute sodium hydroxide solution (ca. 1%), iron III chloride, distilled water.

Safety information: Sodium hydroxide causes burns! Wear safety glasses! Risk of bumping! Use anti-bumping granules!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) to the work sheets. For the chemicals use the information from the German Ordinance on Hazardous Substances. For the adhesives use the information provided on the packaging.

The first test tube is about 1/3 filled with distilled water. A spatula tip of wood glue is added and this is dissolved by gentle shaking. Then a spatula tip of iron III chloride is added and the mixture is shaken briefly again.

The second test tube is about 1/3 filled with dilute sodium hydroxide solution. A spatula of wood glue and anti-bumping granules are added to this. The mixture is gently shaken and then heated for a short time in the Bunsen flame. After cooling this is mixed with a spatula tip of iron III chloride.

This experiment is repeated with polyvinyl acetate.

Experiment 14: Preparation and testing of a polyvinyl alcohol adhesive

Equipment: Glass beaker (100 ml), glass stirring rod, tripod, Bunsen burner, wire gauze, thermometer (up to 100°C), measuring cylinder, balance, brush.

Chemicals/materials: Polyvinyl alcohol (PVA), strips of paper, water.

Experimental procedure: 50 ml water are heated in the beaker to 85°C. About 3 g polyvinyl alcohol are then added with stirring. The resulting adhesive is applied thinly to paper and various bonding tests are carried out.

Experiment 15: Mechanism and properties of superglues

Equipment: Knife.

Chemicals/materials: Superglues (cyanoacrylates) e.g. Pattex® Blitz adhesive, Uhu® superglue or Loctite® universal adhesive, small flat pieces of plastic (PVC*, PMMA* or ABS*) ca. 10 cm x 2.5 cm x 0.08 cm, pieces of rubber, e.g. cut from a rubber cord, small plates of metal (Al, Fe) not degreased ca. 10 cm x 2.5 cm x 0.08 cm, small plates of metal (Al, Fe) degreased (size as above), acetone.

Safety information: Be careful when working with superglues! Superglues can cause the skin to stick together! Heed the instructions given on the packaging! Keep acetone at the ready! Ensure there is good ventilation in the working area! Note: Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) to the work sheets. For the solvents use the information from the German Ordinance on Hazardous Substances. For the adhesives use the information provided on the packaging.

Apply 1 drop of superglue to a piece of plastic, place another piece of plastic on top and firmly press them together. Repeat this procedure for pieces of rubber and pieces of metal.

Test the strengths of the joints, in particular noting the difference between the degreased and non-degreased pieces of metal. The strengths are tested after 1, 3, 10 and 30 minutes and after 24 hours.

Experiment 16: Mechanism and application of epoxy resin adhesives

Equipment: Safety glasses, protective gloves, mixing tray, cardboard or thick polyethylene sheet, stirring rod, pegs.

Chemicals/materials: Epoxy resin adhesive e.g. Pattex® Kraft-Mix resin or Uhu® plus resin, cold-hardener e.g. Pattex® Kraft-Mix hardener or Uhu® plus hardener, small pieces of plastic (not polyethylene or polypropylene!) ca. 10 cm x 2.5 cm x 0.08 cm, small metal plates ca. 10 cm x 2.5 cm x 0.08 cm, sandpaper, petrol (for degreasing).

Safety information: Heed the manufacturer's instructions! Avoid contact with the skin! Ensure there is good ventilation in the working area! Do not inhale vapours! Petrol is highly flammable! Extinguish all flames! Note: Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) to the work sheets. For the petrol, use the information from the German Ordinance on Hazardous Substances. For the adhesives use the information provided on the packaging.

First of all, roughen and degrease the surfaces of the materials. Then thoroughly mix the indicated amounts of epoxy resin and hardener in the mixing tray on the cardboard or thick polyethylene sheet. Apply a thin film of adhesive to the substrates and join the substrates together. Overlap length: 1.2 cm. The bonded areas are fixed in position using for example pegs. Heed the curing time! After curing, test the strength of the bonds by hand. **Note:** Protect the hands using a rag.

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* PVC = polyvinyl chloride
PMMA = polymethyl methacrylate (acrylic glass)
ABS = acrylonitrile-butadiene-styrene copolymer

Experiment 17: Preparing and testing polyurethane adhesives

Equipment: Safety glasses, protective gloves, cardboard beaker, glass stirring rod, aluminium foil or polyethylene film, balance, stopwatch.

Chemicals/materials: Diisocyanate e.g. Pattex® Montage filler-adhesive hardener, polyalcohol resin e.g. Pattex® Montage filler-adhesive resin, small flat pieces of plastic with a roughened surface (not polyethylene or polypropylene!) ca. 10 cm x 2.5 cm x 0.08 cm, sandpaper.

Safety information: Pattex® Montage filler-adhesive contains diisocyanates. Heed the manufacturer's instructions! Avoid contact with the eyes, mucous membranes and skin! Keep away from children. In the event of eye contact, flush the eyes thoroughly with water and consult a doctor. In the event of skin contact, wash the skin with excess water. Use aluminium foil or polyethylene film as the working surface. Note: Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the adhesive packaging to the work sheets.

The resin and hardener are mixed in the given proportions (2:1) on the indicated working surface and stirred thoroughly. Then apply a thin film of adhesive to the surfaces of two pieces of plastic, place the two surfaces together (overlap length: 1.2 cm) and press firmly for a short time. If necessary, keep in place using pegs. Then allow the adhesive to cure. The pot life of the resin/hardener mixture is 8-10 minutes. The curing time is ca. 5 hours. After curing, try and separate the substrates by hand. **Note:** Protect the hands using a rag.

Experiment 18: Melamine resin adhesive

Equipment: Safety glasses, protective gloves, test tube, test tube clamp, test tube rack, Bunsen burner, mini-press or iron, drying cabinet, measuring cylinder, balance, glass stirring rod.

Chemicals/materials: Melamine (2,4,6-triamino-1,3,5-triazine), formaldehyde solution (35%), dilute sodium hydroxide solution (ca. 4%), dilute sulphuric acid (ca. 2%), indicator paper, strips of wood veneer.

Safety information: Wear safety glasses and protective gloves when working with sodium hydroxide, sulphuric acid and formaldehyde! Formaldehyde is thought to be carcinogenic! Work in the fume cupboard! **Note:** Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) for the above-mentioned chemicals from the German Ordinance on Hazardous Substances to the work sheets.

5 ml of a weakly alkaline formaldehyde solution (pH value 7-8) are placed in a test tube and 2.5 g melamine are added. This is then heated under a gentle flame until the melamine has dissolved and the mixture has become slightly viscous. After cooling, the mixture is acidified using dilute sulphuric acid (pH ca. 6) and reheated again for a short time until the mixture becomes viscous. Strips of veneer wood are coated with the adhesive and placed against each other in the press. Then they are pressed thoroughly together. The adhesive is allowed to cure at 130°C in the drying cabinet. The pressing and curing can also be carried out using a hot iron (use the linen setting).

Experiment 19: Urea resin adhesive

Equipment: Safety glasses, protective gloves, measuring cylinder, balance, test tube, test tube clamp, test tube rack, glass stirring rod, brush, pipette, Bunsen burner, anti-bumping granules, mini-press or iron, glass beaker (400 or 500 ml), drying cabinet.

Chemicals/materials: Urea, formaldehyde solution (35%), dilute sodium hydroxide solution (ca. 4%), ammonium chloride solution (saturated), strips of wood veneer, small flat pieces of wood.

Safety information: Wear safety glasses and protective gloves when working with sodium hydroxide and formaldehyde solutions! Formaldehyde is thought to be carcinogenic! Work in the fume cupboard! Take care when heating! Bumping possible! Use anti-bumping granules! Note: Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) for the abovementioned chemicals from the German Ordinance on Hazardous Substances to the work sheets.

3 g urea are placed in a test tube and 3 ml formaldehyde solution are added. The urea is dissolved by heating. Then add 1 or 2 anti-bumping granules and ca. 15-20 drops of dilute sodium hydroxide solution. This mixture is then gently heated with simultaneous careful shaking until the liquid becomes viscous. A strip of wood veneer is coated with the resulting adhesive A small piece of wood is soaked with ammonium chloride solution. The two substrates are placed in the press with the areas to be bonded facing each other and then firmly pressed together. The adhesive is allowed to cure at 120 to 130°C in the drying cabinet. The pressing and curing can also be carried out using a hot iron (use the linen setting).

Experiment 20: Determining the open time of contact adhesives

Equipment: Spreader, scissors, ruler, pencil, stopwatch, weight (1 kg).

Materials: Contact adhesive e.g. Pattex® Kraft adhesive or Uhu® Greenit, drawing card (DIN A5), small flat pieces of rubber.

Safety information: Extinguish all flames! Ventilate the working area thoroughly!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the adhesive packaging to the work sheets.

Using the ruler and pencil, the drawing card is divided into 5 mm wide strips. A thin film of adhesive (thickness ca. 300 µm) is applied using the spreader. After evaporation of the solvent (10-15 minutes), a strip is cut off at 15 minute intervals and this strip is halved. The two halves are crossed together and a 1 kg weight is placed on the joint for 10 seconds. It is then attempted to separate the two halves. The open time of the contact adhesive expires as soon as it is possible to separate the halves without the material tearing.

Experiment 21: Testing the initial strength of contact adhesives

Equipment: Spreader (e.g. from a DIY shop), wallpaper roller, chisel, vice.

Materials: Laminated board ca. 12 cm x 12 cm, chipboard ca. 12 cm x 12 cm, the surfaces must be free of dust and grease.
Contact adhesive e.g. Pattex® Kraft adhesive, Pattex® transparent or Uhu® Greenit, multi-purpose adhesive.

Safety information: Extinguish all flames! Ventilate the working area thoroughly! Take care when working with the chisel! Note: Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the adhesive packaging to the work sheets.

The contact adhesive is applied using a toothed spatula to the reverse side of the laminated board and the chipboard. After leaving in the air for about 15 minutes the substrates are joined and pressed together by rolling the roller across the bonded laminated board with as high a pressure as possible. The bonded parts are placed in a vice. It is then attempted to separate the parts using the chisel. The experiment is repeated with a multipurpose adhesive.

Experiment 22: Strength of water-based dispersion adhesives for wood as a function of the curing time

Equipment: Brush, pegs, ruler, stopwatch.

Materials: Wood adhesive e.g. Ponal® express or Uhucoll®, multi-purpose adhesive e.g. Uhu® or Tesa® multi-purpose adhesive, small flat pieces of wood ca. 10 cm x 2.5 cm x 0.5 cm.

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the adhesive packaging to the work sheets.

Wood adhesive is applied to three small flat pieces of wood at the intended bonding positions (overlap length: 1.2 cm) and then joined with other small pieces of wood. After joining, the pieces of wood are held in position with pegs. The strength of each bond is measured after 10-20-30 minutes, 3 hours and 1 day by hand and in a tensile testing device. The experiment is repeated using a multi-purpose adhesive and the results are compared.

Experiment 23: Reactive adhesives (pot life, heat of reaction)

Equipment: Thermometer (up to 250°C), glass stirring rod, stopwatch, mixing tray with spoon.

Materials: Pattex® Stabilit Express, Uhu® Plus Schnellfest, aluminium foil, paper tissues.

Safety information: Heed the manufacturer's instructions and hazard symbols indicated on the packaging! Extinguish all flames! Ventilate the working area thoroughly! Due to the higher rate of reaction at elevated temperatures, this experiment must only be undertaken with small amounts of adhesive! **Note:** Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the adhesive packaging to the work sheets.

The tip of the thermometer is wrapped in aluminium foil. Two spoons of hardener powder (Pattex® Stabilit Express) are placed in the mixing tray. This is filled up to the edge with resin (ca. 3 g) and then thoroughly stirred until a homogenous mixture is obtained. The thermometer is placed in the mixture and after ca. 3 minutes the reading is noted. In order to determine for how long the mixture can be used after mixing, a glass stirring rod is placed in the mixture at 1 minute intervals and then removed again. In between each use, the glass rod is cleaned using a paper tissue. Shortly before the mixture becomes hard the temperature is measured again. The experiment is repeated using Uhu® Plus Schnellfest.

Experiment 24: Securing screws with anaerobically curing adhesive

Equipment: Safety glasses, protective gloves.

Chemicals/materials: Anaerobically curing adhesive (medium strength) e.g. Loctite 542 or DELO ML 5327, anaerobically curing adhesive (medium strength) e.g. Loctite 5331 or DELO ML 5198, steel screws and nuts of different size, stainless steel screws and nuts of different size, spanner, butyl acetate (for degreasing).

Safety information: Heed the manufacturer's instructions! Avoid contact with the skin! Ventilate the working area thoroughly! Vapours are flammable! Extinguish all flames! **Note:** Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the adhesive packaging to the work sheets.

The screws and nuts are first of all degreased using butyl acetate. 2 or 3 drops of adhesive are placed on the thread of each screw and the matching nuts are screwed on a few turns. After leaving for 5 minutes, it is carefully checked by hand at regular intervals whether the adhesive has started to secure the nut. At least one of each material/adhesive combination is allowed to cure for 24 hours and the bond is then tested using a suitable spanner.

Experiment 25: Moisture curing 1-C polyurethane adhesives

Equipment: Safety glasses, protective gloves, plastic working surface.

Chemicals/materials: Moisture curing 1-C polyurethane adhesive e.g. Sikaflex 255, 500 ml cartridges (adhesive), cartridge gun (manual), plastic working surface (e.g. 50 x 50 cm).

Safety information: Heed the manufacturer's instructions! Avoid contact with the skin! Ventilate the working area thoroughly! **Note:** Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the adhesive packaging to the work sheets.

4 beads of adhesive (1 cm high, ca. 2 cm width) and each about 20 cm long are put on the working surface. As the beads cure, the beads are cut through with a knife on a daily basis in order to determine the skinning time and the progress of the curing. The room temperature and the relative humidity of the air are also recorded each day.

Experiment 26: Moisture curing 1-C silicones

Equipment: Safety glasses, protective gloves, steel sheets, stainless steel sheets, plates made of glass or transparent plastic, plastic working surface.

Chemicals/materials: 1-C silicone (that releases acetic acid). 1-C silicone (crosslinking with neutral hardener), steel sheets (ca. 20 x 100 mm), stainless steel sheets (ca. 20 x 100 mm), plates made of glass or transparent plastic (ca. 200 x 100 mm), butyl acetate (for degreasing/cleaning), test inks.

Safety information: Heed the manufacturer's instructions! Avoid contact with the skin! Ventilate the working area thoroughly! Note: Do not allow the experiment to be carried out by school pupils under 12 years of age!

Experimental procedure: Transfer the hazard symbols as well as risk statements (R-phrases) and safety recommendations (S-phrases) from the adhesive packaging to the work sheets.

A thin bead of the acetic acid releasing silicone is applied to both a steel and stainless steel sheet and these are joined to transparent sheets. The two silicones are also applied to further stainless sheets and allowed to cure in the open. Using test inks, the ability to coat the cured silicones is tested and the results are recorded.

Information about the experiments

Experiment 1: The carbon that is present in most adhesives is released as carbon dioxide and this can be identified by the clouding of the chalk water (formation of highly insoluble calcium carbonate). This demonstrates that adhesives contain organic compounds.

Experiment 2: When adhesives are dispersed in solvents (here water), the macromolecules can be identified by light scattering. This phenomenon, also known as the Tyndall Effect, only occurs for macromolecules having molecular weight greater than 104.

Experiment 3: The smoothly ground glass plates can only be separated by using a lot of force. They are "bonded", with water as the "adhesive". Water of course contains no macromolecules. There are strong attractive forces between the water molecules (see experiment 4: Surface Tension) but these only have very limited range. The free mobility of the small water molecules means the two plates can be moved relatively easily in a direction parallel to the plane of contact and can ultimately be separated.

Experiment 4: Of all the materials here, polyethylene has the lowest surface energy and is difficult to bond without being pretreated.

Experiment 5: Casein rapidly swells in an alkaline solution. A viscous mass forms: adhesive. By adding for example aluminium sulphate, the stability in water can be increased.

Experiment 6: Starch swells in hot water. A paste results which thickens further on cooling and possibly has to be diluted with water. Salicylic acid is used as a preservative.

Experiment 7: A similar effect is observed to that in experiment 6. As excess alkali can adversely affect the substrate, the mixture has to be neutralised.

Experiment 8: Methyl cellulose is an ether. It is manufactured by partial methylation of the hydroxyl groups of cellulose. Methyl cellulose dissolves in water but not in the other organic solvents used here.

Experiment 9: Hotmelts are based on thermoplastic polymers. They become liquid when heated and solid again on cooling without undergoing any chemical change.

Experiment 10: The volatile solvent burns first of all (blue-yellow flame) and then the raw material burns (yellow, sooty flame).

Experiment 11: By evaporating the solvent, the relevant plastic is joined again. The adhesive bonds.

Experiment 12: Polyvinyl acetate is a base raw material for industrially manufactured multi-purpose adhesives. Mixtures of ethyl acetate, acetone and sometimes ethanol are commonly used to dissolve the polyvinyl acetate.

Experiment 13: The brown-beige colour of PVAC wood adhesive and the hexa-aqua iron (III) complex is seen in the test tube. This experiment serves as the control. The polyvinyl acetate is saponified using the sodium hydroxide solution. There is development of an intense red-brown coloration in test tubes 2 and 3 due to the presence of the iron (III) - acetate complex.

Experiment 14: Polyvinyl alcohol is a thermoplastic polymer that is manufactured by alkaline saponification of polyvinyl acetate. As polyvinyl alcohol often still contains some acetyl groups it is generally only poorly soluble in cold water.

Experiment 15: The curing of cyanoacrylate adhesives is due to polymerisation and this is triggered by hydroxide ions or basic substances. It is important here to stress the importance of handling superglues in the correct way: Avoid contact with the skin. If there is contact with the skin, remove fresh spots of adhesive with acetone. Remove cured adhesive with soapy water. Do not inhale vapours (see also the information sheet entitled “Information about first aid and accident procedures when working with cyanoacrylate adhesives (superglues)” published by the Industrieverband Klebstoffe e.V., Düsseldorf).

Experiment 16: Epoxy resins are produced by reacting aromatic dihydroxy compounds with epichlorohydrine. First of all viscous resins having a linear structure are formed via polyaddition. By adding amines or polyamido amines, the resins are crosslinked via further polyaddition reactions and hence cure.

Experiment 17: This adhesive also cures via a polyaddition reaction.

Experiment 18: The overall reaction occurs in steps: Hexamethylol melamine forms as one of the intermediate products. Pressure and heat cause the formation of ether bridges (with the cleavage of water) and this condenses to form a crosslinked melamine resin which then cures.

Experiment 19: This reaction also occurs in steps: Methylol urea forms first of all. Linear and then crosslinked urea resin molecules then form with cleavage of water molecules. Ammonium chloride accelerates the reaction: Ammonium chloride is acidic in an aqueous solution. The hydrogen ions catalyse the curing step.

Experiment 23: There is a rise in temperature on curing, namely the reaction is exothermic.

Experiment 24: Anaerobically curing adhesives cure by contact with metal ions in the absence of oxygen. The screws permit an ideal polymerisation reaction to take place. The curing on stainless steel is slower and/or incomplete due to the closed chromium oxide surface layer (passivating layer). The necessary contact with metal ions ($Fe^{2}+/Fe^{3+}$) either does not occur or occurs to an insufficient degree. If necessary, heat (20 minutes / 120°C). If a secured screw cannot be detached using a spanner at room temperature, heat to ca. 150°C and then detach (softening of the adhesive).

Experiment 25: The moisture in the air causes the terminal isocyanate groups to convert to amino groups and the latter react with the remaining isocyanate groups and cure the adhesive as an elastomer. The curing is anisotropic, namely from outside to inside, and this can be proven by cutting through the beads of adhesive. By varying the temperature and humidity of the air, the curing and rate of curing can be adjusted.

Experiment 26: The acetic acid releasing silicone causes corrosion on the steel sheet. Due to their low surface tension, silicones are difficult to paint and coat.

1-C adhesive
Single-component adhesive. This is an adhesive that cures under the influence of temperature, light, moisture or exclusion of air and as such requires no second component to be added. For that reason, 1-C adhesives do not have to be mixed prior to application. A 1-C adhesive is hence supplied in a single container.

2-C adhesive
Two-component adhesive. This is an adhesive that has to be mixed with other substances in order to trigger its adhesive function. For that reason, 2-C adhesives are supplied in at least 2 containers and in general must be mixed prior to application.

Adhesion
Bonding forces between the surface of the substrate and the adhesive film. These surface adhesive forces are decisive for the strength of the bond in conjunction with the internal forces in the bond (cohesiveness). Example: A water droplet adhering to a window pane is stopped from falling by a force (adhesive force).

Application
Application or use of an adhesive during the bonding process.

Application temperature
The temperature of the adhesive and temperature of the surroundings when applying the adhesive.

Cataplasma test
For this test the sample is in a closed atmosphere so that the corrosion products that are formed cannot be removed. The bonded sample is wrapped in aluminium foil with a water-soaked pad of cotton-wool and this is sealed air-tight in a polyethylene film. The sample is then subjected to the following test cycle:
21 days storage at 70°C;
16 days storage at -30°C.
The bond strength is determined two hours after the end of the test cycle.

Classification/labelling
The prescribed test methods, the procedures involved, the evaluation of the data and the resulting classification and labelling of the hazard potential are laid down by law. In the European Union, the classification and labelling, the information that has to be provided for users and details of handling procedures are laid down in directives. Many substances have been classified by EU law and must be labelled accordingly. In the EU member states, the directives have been turned into national laws. Substances and formulations representing a hazard potential must be provided with hazard symbols depending on the severity and nature of the hazard *(Figure 67)*. In addition, the corresponding hazard statements (R-phrases) and safety recommendations (S-phrases) must be quoted *(Figure 68)*. Safety data sheets must be prepared for hazardous substances and formulations

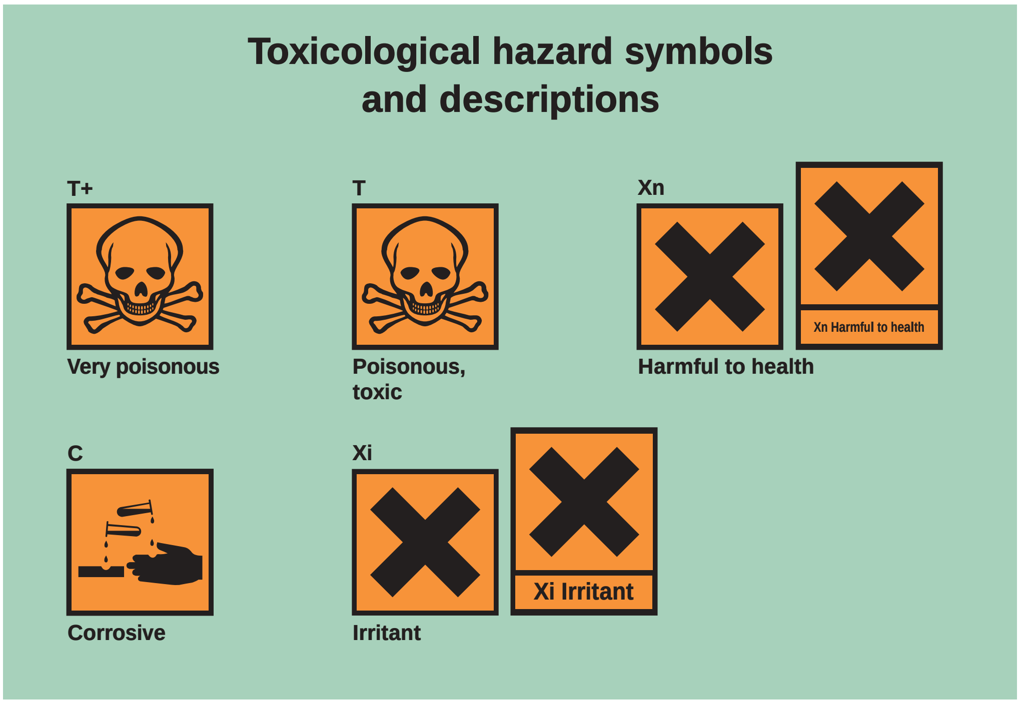
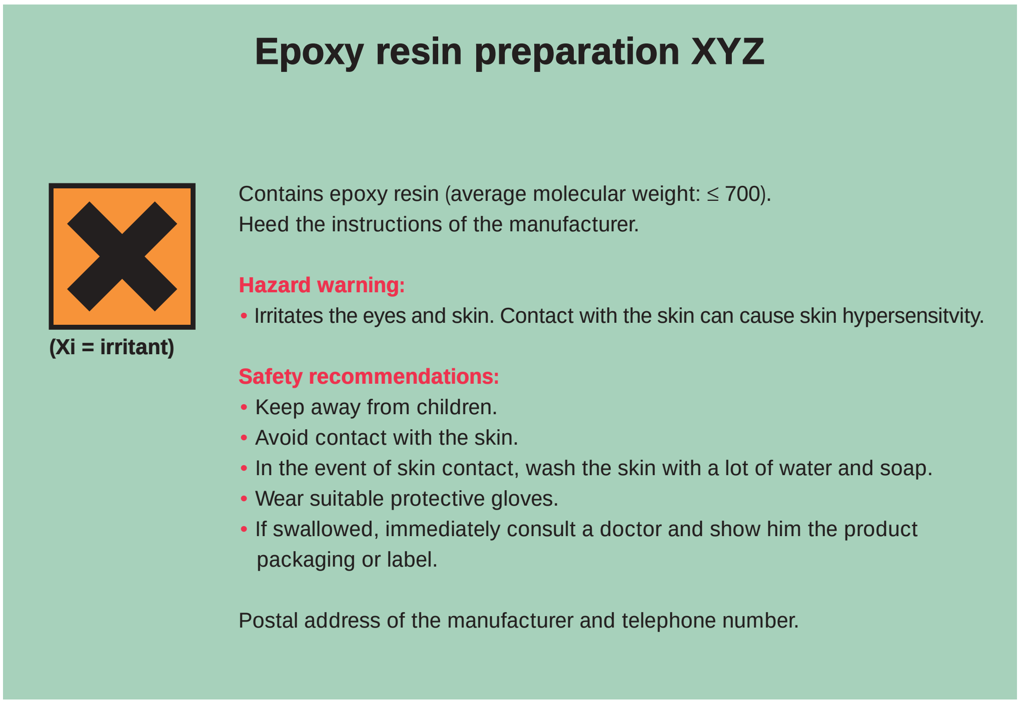


Figure 67



Epoxy resin preparation XYZ

(Xi = irritant)

Contains epoxy resin (average molecular weight: ≤ 700).
Heed the instructions of the manufacturer.

Hazard warning:
- Irritates the eyes and skin. Contact with the skin can cause skin hypersensitvity.

Safety recommendations:
- Keep away from children.
- Avoid contact with the skin.
- In the event of skin contact, wash the skin with a lot of water and soap.
- Wear suitable protective gloves.
- If swallowed, immediately consult a doctor and show him the product packaging or label.

Postal address of the manufacturer and telephone number.

Figure 68

and these must be made available to commercial and industrial users and trade outlets.

Cohesion
The forces that maintain the internal integrity of the adhesive. Cohesion describes how molecules keep together (polymers in the adhesive). These forces are attractive forces and the mechanical adhesion (intertwining) of the molecules and chains of large plastic molecules (polymer chains).

Continuous load capacity
Describes the stress to which a bond can be continuously subjected without adversely affecting the bond. This is significantly below the maximum (lap) shear strength. For bond design using the following adhesives, the continuous stress is taken to be the following percentages of the initial lap shear strength:
Moisture curing 1-C polyurethanes 3%;
Cold curing 2-C epoxy resin adhesives 5%;
Hot curing 1-C epoxy resin adhesives 30%.

Schematic representation of direct and indirect corona treatment

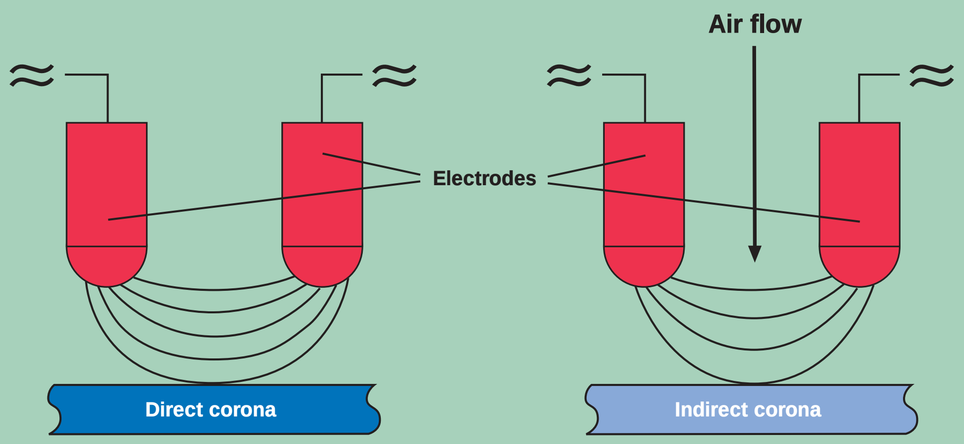


Figure 66

Corona method

A method for pretreating the surfaces of plastics: Electrons emanating from electrodes, which are “visible” by an arc, ionise molecules in the air (O_2 and N_2). Polar structures are generated on the surface of the plastic due to incorporation of these activated oxygen atoms. These polar structures improve the wetting and adhesion properties.

Creep resistance

The ability of an adhesive to be subjected to external forces over a longer period of time and not to be deformed or undergo very little deformation.

C_W value

The dimensionless resistance value (Cw) describes the air resistance of an object. This is determined by the shape of this object.

Etching

Surface pretreatment technique for metals: The substrates are treated with non-oxidising acids (hydrochloric acid, dilute sulphuric acid) as a result of which any surface layer that is present is removed, and possibly also a layer of the base raw material if etching times are long. The surface of the substrate hence becomes roughened and activated.

Exposure

A substance can enter the body by various routes, namely by swallowing, by contact with the skin (dermal) or mucous membranes (e.g. the eyes) and by inhalation (*Figure 69*). The risk of contact is dependent on the physico-chemical properties of the substance or formulation as well as on the processing and application conditions.

The most common means of contact is contact with the skin. Gases, vapours (liquids dissolved in air) and aerosols (liquid and solid particles in the air) can also come into contact with the skin via the ambient air. Gases, vapours, liquid particles and solid particles (dust) from the ambient air can be taken up by inhalation.

Gap-bridging

The ability of an adhesive to bridge a large (> 0.2 mm) gap. When cured, the adhesive must completely fill the gap.

Gas phase fluorination

A surface pretreatment method for plastics which improves the wetting properties of plastics and activates their surfaces. The substrates are subjected to a fluorine gas / nitrogen mixture (ca. 0.1 to 5% fluorine in nitrogen), enabling fluorine atoms to be incorporated into the plastic surface without disturbing the macromolecular structure.

Hazard potential

Undesired properties of substances (hazard potential) are described on the basis of toxicological tests:

- Acute toxicity, lethal dose (LD50);
- Poisoning symptoms after repeated uptake;
- Carcinogenic properties;
- Genetic damage / hereditary defects;
- Reduced fertility, foetus development disorders during pregnancy;
- Skin irritation, burns;
- Irritation of mucous membranes, e.g. the eyes and respiratory tract;
- Ability to cause allergies (sensitisation) and trigger allergic reactions.

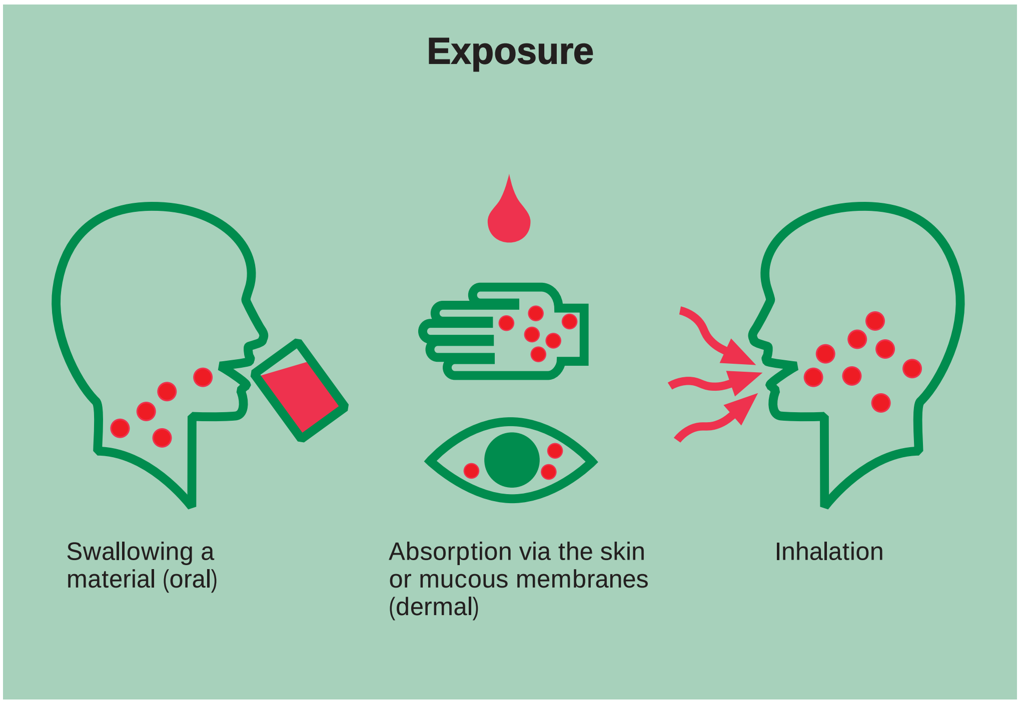


Figure 69

Lamination
Joining layers of usually high-area, flexible substrates (e.g. films, fabrics) using an adhesive to form a laminate.

Lap shear test
The lap shear strength of bonded lap joints is determined via a shear load on a single lap joint between substrates, by applying a tensile force that acts parallel to the bonded area and parallel to the main axis of the sample (DIN EN 1465). The result is the measured force or the collapse load. The highest force in N is divided by the bond area in mm^2 (identical to the shear strength; see also continuous stress).

Bond strengths in practice (lap shear strengths):

• Aeronautics and aerospace	30 to 40 MPa
• Industry, constructional	15 to 25 MPa
• Industry, non-constructional	5 to 10 MPa
• Sealants	< 5 MPa

Pressure sensitive adhesives

	Rubber solutions	Acrylate dispersions	Hotmelts	Acrylate solutions
Tackiness	+	o	o	o
Peel strength	+	o	+	o
Shear strength RT	+	+	+	+
Shear strength at elevated temperature	o	+	–	+
Punching properties	o	+	o	+
Adhesive run	o	+	o	+
UV resistance	–	+	–	+
Heat resistance	o	+	o	+
Plasticising behaviour	–	o	–	+
Colour/transparency	o	+	o	+
Low-temperature behaviour	+	o	o	o
Moisture resistance	+	o	+	+
Water resistance	+	–	+	+

\+ = excellent o = satisfactory, fulfils normal expectations
– = unsatisfactory, if this property is important for the intended application

Table 7

Low pressure plasma
See plasma techniques.

MS polymers
Modified siloxanes. They arise from the curing of alkoxy silane modified polypropylene glycols by the action of moisture accompanied by the cleavage of alcohol.

Peel stress
Line-form stresses that only act on a line (e.g. removing / peeling off a film). The resistance of bonded joints to peel forces is determined using the floating roller peel test or T-peel test in accordance with DIN EN 1464. In the roller peel test, a brittle and a flexible substrate are required. In the T-peel test two flexible substrates are required. The tests are predominantly used for comparing adhesives and bonds as well as for monitoring the suitability of surface pretreatment methods (fracture pattern analysis).

Plasma techniques
A plasma is a gas in an ionised state that is produced by continually supplying energy to the gas. In this state, portions of the gas molecules are split into positively and negatively charged particles. The number of positively and negatively charged particles in a plasma is the same, namely a plasma is electrically neutral. The alternating frequency accelerates the particles. If there is sufficient acceleration, then chemical bonds are broken on hitting the plastic surface and the surface of the plastic is chemically modified. Depending on the design of the plasma technique (working gas, pressure, energy), surfaces can cleaned (plasma cleaning), activated (plasma activation) or coated (plasma polymerisation). Plasma pretreatment is commonly carried out on polymeric materials but can be used on metals for plasma-cleaning and plasma-polymer coating. A distinction is generally made between non-thermal techniques (low pressure and low temperature plasmas) and thermal techniques (high temperature plasmas). Low pressure plasma techniques are mainly used for surface pretreatment. Application temperatures are typically from ca. 30°C up to 100°C. Plasma pretreatment only affects the near-surface region down to a depth of a few nanometres.

Plasticiser
Term for inert liquid or solid organic substances having a low vapour pressure. Mainly esters by chemical nature. They physically interact with polymers (no chemical reaction), predominantly due to their dissolution and swelling behaviour.

Plasticisers enable the physical properties of the polymers to be customised, for example lower freezing temperature, improved ability to be shaped, improved elastic properties, lower hardness (see also DIN 55945). An ideal plasticiser should be odourless, colourless, resistant to light, cold and heat, be as involatile as possible, not be harmful to health, have low flammability, be able to be mixed with polymers and auxiliary materials and have good gelling properties. Another property of plasticisers that has to be considered is their ability to migrate. Of major importance for the physiological safety of food packaging is that the plasticisers have restricted migration.

Plasticisation
This means shifting the thermoplastic region to a lower temperature – either by copolymerisation (internal plasticisation) or by adding plasticisers (external plasticisation).The latter is the method chiefly used in practice. Here, the polar groups of the small, mobile plasticiser interact with the polar groups on the polymers (exceptions: polyolefin, rubber). As a result, the polymer chains become looser and more mobile. At the same time, the softness and elongation of the plastic increase. The terms hinge plasticisers and shield plasticisers are also used. The oxygen atoms of in particular -COOR groups have a polar effect (i.e. are dipole-forming) and hence dicarboxylic acid esters are especially suitable as plasticisers. Phosphorus and sulphur atoms are also involved in some plasticisers (see also DIN 7723 for abbreviations for plasticisers).

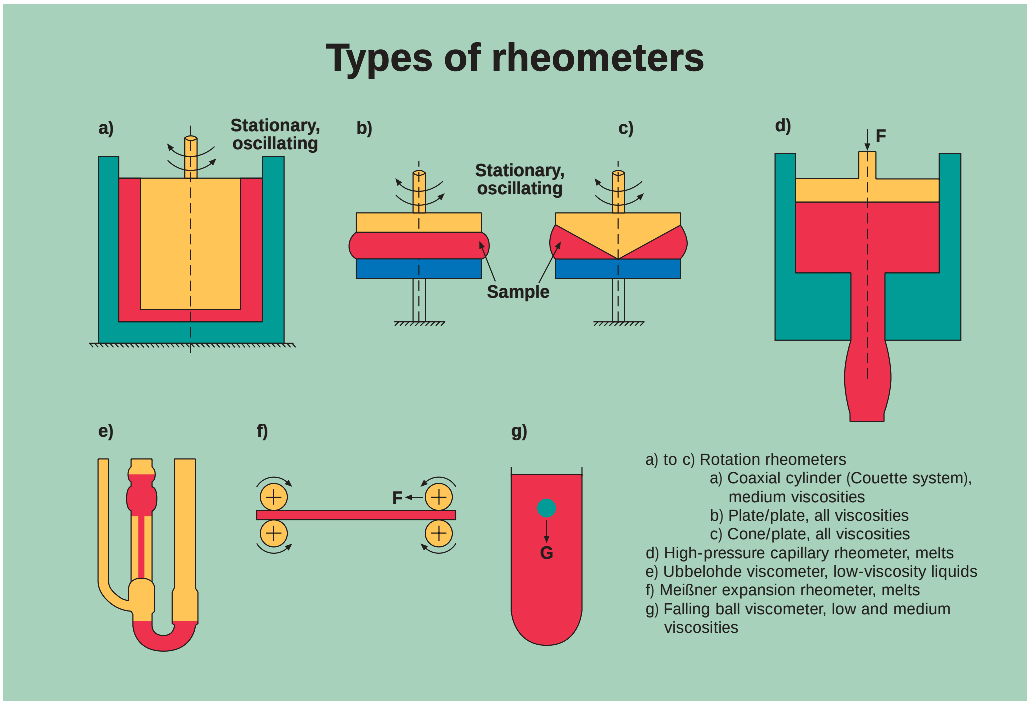
Plastisols
An adhesive in which PVC components are dispersed in a liquid plasticiser. The temperature is increased to ca. 150-160°C to cure the adhesive. The plasticiser absorbs the PVC powder and the adhesive hardens.

Pot life
The period of time during which a reactive adhesive can be usefully applied after having been mixed (application period). It depends on the rate of curing and this in turn depends on external boundary conditions (temperature and quantity of adhesive mixed up). In order to create effective bonds, the pot life must be strictly adhered to. Once the pot life has elapsed the adhesive is too viscous to provide optimum wetting.

Primers
Special formulations (for example highly diluted 10-20% solutions of the adhesive that is to be later used) which are applied to the newly treated surfaces. Objective: Improved wetting of the substrates and also protection against contaminants. This also improves the adhesion properties of the adhesive and aging processes are retarded.

PUR
Abbreviation for polyurethane.

Rheometer
A device for determining the viscosity (a special type of viscometer). Figure 70 shows different types of rheometer.



a) to c) Rotation rheometers
a) Coaxial cylinder (Couette system), medium viscosities
b) Plate/plate, all viscosities
c) Cone/plate, all viscosities
d) High-pressure capillary rheometer, melts
e) Ubbelohde viscometer, low-viscosity liquids
f) Meißner expansion rheometer, melts
g) Falling ball viscometer, low and medium viscosities

Figure 70

Shear strength
This is the maximum shear stress, i.e. shearing force per unit surface area, which a bond can withstand. This is obtained by dividing the maximum force in N (load at fracture) by the bond area in mm^2. It is determined in accordance with DIN EN 1465 (compare with lap shear strength; see also continuous stress).

Silicone
A term coined by the F.S. Kipping, an American chemist, for polymers in which silicon atoms are linked via oxygen atoms (chain-like or network-like), with the residual bonds on the silicon atoms being saturated with hydrocarbon residues. Depending on the degree of crosslinking, a distinction is made between silicon oils (linear), silicone rubbers (slightly crosslinked) and silicone resins (highly crosslinked).

Siloxanes
A systematic term for silicon-oxygen bonds. Polyorganosiloxanes are usually referred to as silicones in technical fields.

Spot welding
Electrical resistance welding technique. In resistance welding, the heat generated by passing an electric current through a resistance is utilised, e.g. current passage between two sheets. In spot welding, individual points are welded, not whole seams as in conventional welding.

Spot-weld bonding
Spot-weld bonding is the standard joining technique used in car bodywork construction. A 1-C epoxy resin adhesive is applied first of all. The component is then spot-welded and the adhesive together with the paint is cured at the end of the production process.

Substrates
Solid objects that are joined or have to be joined with each other.

Tensile strength
The tensile strength gives the maximum tensile stress, namely tensile force per unit surface area, which a material or bond can withstand. The critical tensile stress results in fracture. The fracture strength is given in MPa.

Test methods
Test methods are selected depending on the properties of the bonded joint under study: Initial bond strengths can be determined by purely mechanical tests (e.g. lap shear test, peel test, wedge test). If, however, it is desired to test the long-term stability of a bonded joint, then a combination of storage (under simulated ambient conditions) followed by mechanical testing must be carried out.

Thixotropy
Description for the phenomenon whereby gels become liquid on applying mechanical forces (e.g. stirring, shaking, ultra-sound), but return to their original form again when the mechanical forces no longer act. Modern, non-drip paints are thixotropic: They are easy to apply and are readily liquid whilst brushing the paint on. When in a state of rest, they are however much more viscous meaning that there are no drops and running of the paint. This is achieved by applying so-called thixotropic agents (e.g. bentonite, kaolin, alginic acid and especially grades of SiO_2).

Toxicology
Although the physical properties of materials (e.g. flammability, explosiveness, self-ignition) can result in there being specific hazards (fire, deflagration, explosion), it is the task of toxicology to study, recognise and assess the harmful effects of chemical substances or mixtures of chemical substances on life. The first step is to make a well-substantiated assessment of possible undesired effects. Only a sufficiently high dose of a substance causes effects in the body. The lowest dose that can trigger effects is called the threshold value. Most effects are threshold-dependent. For the few effects that are not threshold-dependent, special measures to minimise risks have to be undertaken. The second step is to consider what level of contact there will be with products. This takes into account the conditions of the intended application and also possible improper use. To draw up a safety assessment all this information is collated. If there is a sufficient safety margin between the threshold value and the level of contact then a product is considered to be safe.

Viscosity
The flow properties and internal stress of substances. Viscosity is given in mPa s. A small value indicates a thin, low-viscosity liquid (e.g. water, 1 mPa s). A high value indicates a thick, high-viscosity liquid (e.g. thick oil, ca. 2000 mPa s).

Wood laminate composite
Different layers of wood are bonded (laminated) with each other. Due to the low density of the individual layers, they can be bent and laminated in this shape. This allows new designs.

Workplace limit value
An independent body of experts has set down upper limits for exposure to a range of substances at the workplace (maximum workplace concentration). These limits particularly concern gases, volatile substances (present as vapours in ambient air), aerosols and dust. These concentration limits have been set at such a level that compliance with the limit values is deemed to exclude there being any risk to health. The maximum workplace concentrations are made into statutory limit values in air by the TRGS (Technische Regeln für Gefahrstoffe-/ Technical Regulations for Hazardous Substances).

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