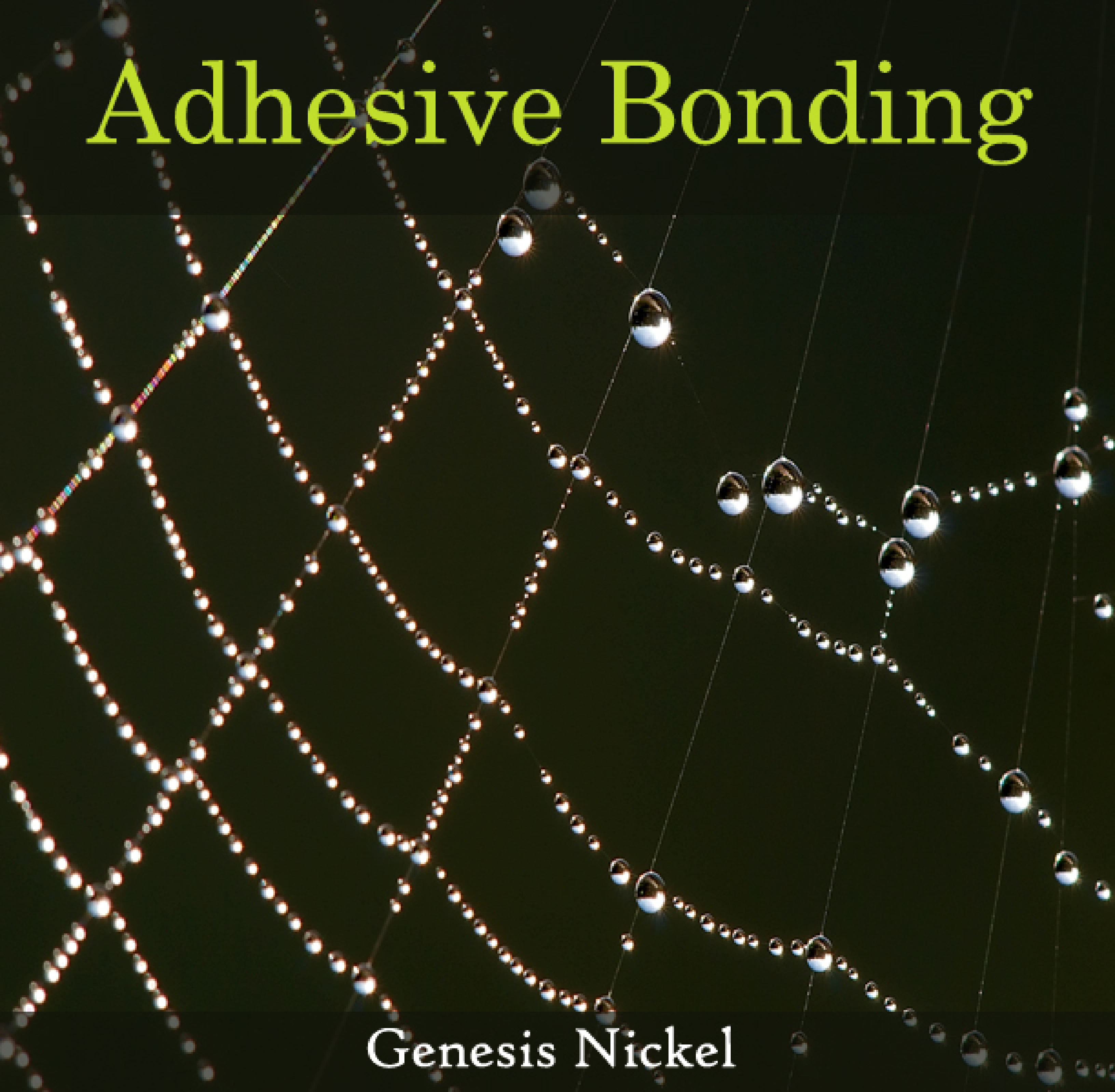
Adhesive Bonding



Genesis Nickel

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Adhesion

Dew drops adhering to a spider web

Adhesion is any attraction process between dissimilar molecular species that can potentially bring them in "direct contact". By contrast, cohesion takes place between similar molecules.

Adhesion is the tendency of dissimilar particles and/or surfaces to cling to one another (cohesion refers to the tendency of similar or identical particles/surfaces to cling to one another). The forces that cause adhesion and cohesion can be divided into several different types. The intermolecular forces responsible for the function of various kinds of stickers and sticky tape fall into the categories of chemical adhesion, dispersive adhesion, and diffusive adhesion.

Surface energy

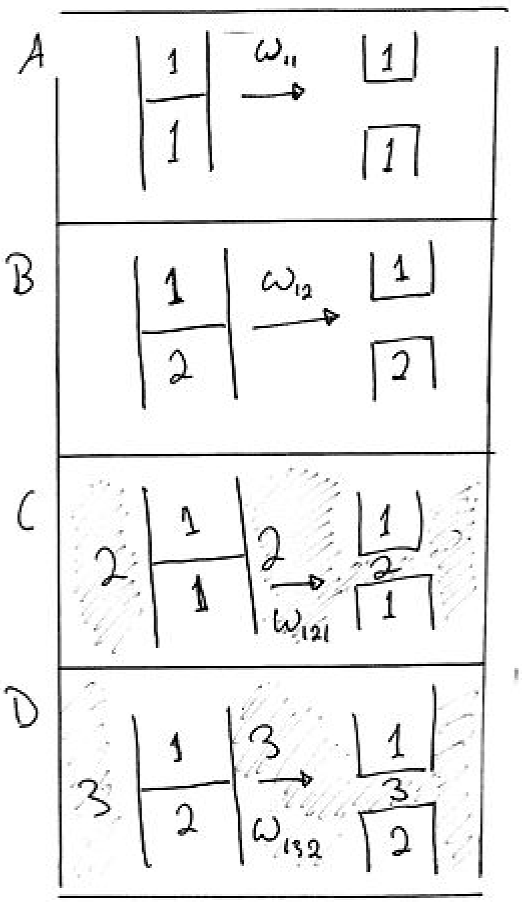


Figure 2 Diagram of various cases of cleavage, with each unique species labeled. **A**-$\gamma = (1/2)W_{11}$ **B**-$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}$ **C**-$\gamma_{12} = (1/2)W_{121} = (1/2)W_{212}$ **D**-$W_{12} + W_{33} - W_{13} - W_{23} = W_{132}$.

Surface energy is conventionally defined as the work that is required to build a unit area of a particular surface. Another way to view the surface energy is to relate it to the work required to cleave a bulk sample, creating two surfaces. If the new surfaces are identical, the surface energy γ of each surface is equal to half the work of cleavage, W:

$\gamma = (1/2)W_{11}$

If the surfaces are unequal, the Young-Dupré equation applies: $W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}$ where γ_1 and γ_2 are the surface energies of the two new surfaces, and γ_{12} is the interfacial tension.

We can also use this methodology to discuss cleavage that happens in another medium: $\gamma_{12} = (1/2)W_{121} = (1/2)W_{212}$. These two energy quantities refer to the energy that is needed to cleave one species into two pieces while it is contained in a medium of the other species. Likewise for a three species system: $\gamma_{13} + \gamma_{23} - \gamma_{12} = W_{12} + W_{33} - W_{13} - W_{23} = W_{132}$, where W_{132} is the energy of cleaving species 1 from species 2 in a medium of species 3.

A basic understanding of the terminology of cleavage energy, surface energy, and surface tension is very helpful for understanding the physical state and the events that happen at a given surface, but as discussed below, the theory of these variables also yields some interesting effects that concern the practicality of adhesive surfaces in relation to their surroundings.

Mechanisms of adhesion

Cohesion causes water to form drops, surface tension causes them to be nearly spherical, and adhesion keeps the drops in place.

Water droplets are flatter on a Hibiscus flower which shows better adhesion

Five mechanisms of adhesion have been proposed to explain why one material sticks to another:

Mechanical adhesion

Adhesive materials fill the voids or pores of the surfaces and hold surfaces together by interlocking. Sewing forms a large scale mechanical bond, velcro forms one on a medium scale, and some textile adhesives form one at a small scale.

Chemical adhesion

Two materials may form a compound at the join. The strongest joins are where atoms of the two materials swap (ionic bonding) or share (covalent bonding) outer electrons. A weaker bond is formed if a Hydrogen atom in one molecule is attracted to an atom of

Nitrogen, Oxygen, or Fluorine in another molecule, a phenomenon called Hydrogen bonding.

Chemical adhesion occurs when the surface atoms of two separate surfaces form ionic, covalent, or hydrogen bonds. The engineering principle behind chemical adhesion in this sense is fairly straight forward: if surface molecules can bond, then the surfaces will be bonded together by a network of these bonds. It bears mentioning that these attractive ionic and covalent forces are effective over only very small distances – less than a nanometer. This means in general not only that surfaces with the potential for chemical bonding need to be brought very close together, but also that these bonds are fairly brittle, since the surfaces then need to be *kept* close together..

Dispersive adhesion

In dispersive adhesion, also known as physisorption, two materials are held together by van der Waals forces: the attraction between two molecules, each of which has a regions of slight positive and negative charge. In the simple case, such molecules are therefore polar with respect to average charge density, although in larger or more complex molecules, there may be multiple "poles" or regions of greater positive or negative charge. These positive and negative poles may be a permanent property of a molecule (Keesom forces) or a transient effect which can occur in any molecule, as the random movement of electrons within the molecules may result in a temporary concentration of electrons in one region (London forces).

In surface science, the term "adhesion" almost always refers to dispersive adhesion. In a typical solid-liquid-gas system (such as a drop of liquid on a solid surrounded by air) the contact angle is used to quantify adhesiveness. In the cases where the contact angle is low, more adhesion is present. This is due to a larger surface area between the liquid and solid and results in higher surface energy. The work of adhesion explains the interactive force between the liquid and solid phases and the Young-Dupre equation is used to calculate the Work of Adhesion. The contact angle of the three-phase system is a function not only of dispersive adhesion (interaction between the molecules in the liquid and the molecules in the solid) but also cohesion (interaction between the liquid molecules themselves). Strong adhesion and weak cohesion results in a high degree of wetting, a lyophilic condition with low measured contact angles. Conversely, weak adhesion and strong cohesion results in lyophobic conditions with high measured contact angles and poor wetting.

London dispersion forces are particularly useful for the function of adhesive devices, because they don't require either surface to have any permanent polarity. They were described in the 1930s by Fritz London, and have been observed by many researchers. Dispersive forces are a consequence of statistical quantum mechanics. London theorized that attractive forces between molecules that cannot be explained by ionic or covalent interaction can be caused by polar moments within molecules. Multipoles could account for attraction between molecules having permanent multipole moments that participate in electrostatic interaction. However, experimental data showed that many of the compounds observed to experience van der Waals forces had no multipoles at all. London suggested that momentary dipoles are induced purely by virtue of molecules being in proximity to one another. By solving the quantum mechanical system of two electrons as harmonic oscillators at some finite distance from one another, being displaced about their respective rest positions and interacting with each others fields, London showed that the energy of this system is given by:

$$E = 3h\nu - \frac{3}{4}\frac{(h\nu\ \alpha^{2})}{R^{6}}$$

While the first term is simply the zero-point energy, the negative second term describes an attractive force between neighboring oscillators. The same argument can also be extended to a large number of coupled oscillators, and thus skirts issues that would negate the large scale attractive effects of permanent dipoles; cancelling through symmetry, in particular. The additive nature of the dispersion effect has another useful consequence. Consider a single such dispersive dipole, referred to as the origin dipole. Since any origin dipole is inherently oriented so as to be attracted to the adjacent dipoles it induces, while the other, more distant dipoles are not correlated with the original dipole by any phase relation (thus on average contributing nothing), there is a net attractive force in a bulk of such particles. Since we are discussing identical particles, this is called cohesive force.

When discussing adhesion, this theory needs to be converted into terms relating to surfaces. If there is a net attractive energy of cohesion in a bulk of similar molecules, then cleaving this bulk to produce two surfaces will yield surfaces with a dispersive surface energy, since the form of the energy remain the same. This theory provides a basis for the existence of van der Waals forces at the surface, which exist between any molecules having electrons. These forces are easily observed through the spontaneous jumping of smooth surfaces into contact. Smooth surfaces of mica, gold, various polymers and solid gelatin solutions do not stay apart when their separating becomes small enough – on the order of 1-10 nm. The equation describing these attractions was predicted in the 1930s by De Boer and Hamaker:

$$\frac{P}{area} = \frac{-A}{(24\pi\ z^{3})}$$

Where P is the force (negative for attraction), z is the separation distance, and A is a material specific constant called the Hamaker constant.

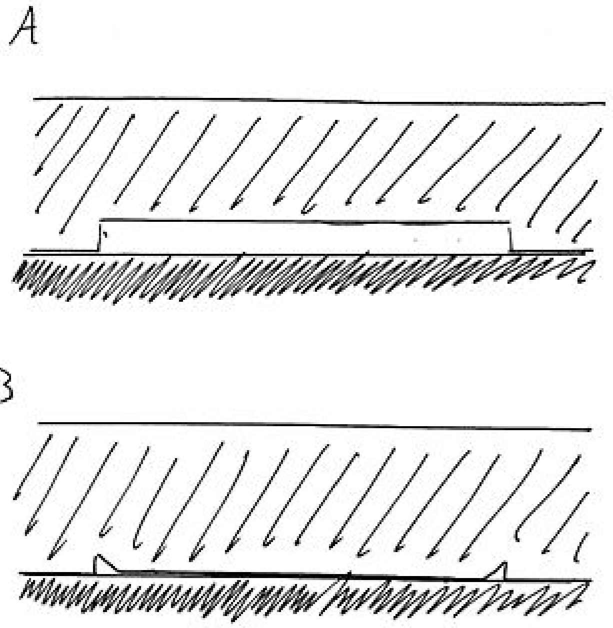


Figure 3 The two stages of PDMS microstructure collapse due to van der Waals attractions. The PDMS stamp is indicated by the hatched region, and the substrate is indicated by the shaded region. A) The PDMS stamp is placed on a substrate with the "roof" elevated. B) Van der Waals attractions make roof collapse energetically favorable for PDMS stamp.

The effect is also apparent in experiments where a Polydimethylsiloxane (PDMS) stamp is made with small periodic post structures. The surface with the posts is placed face down on a smooth surface, such that the surface area in between each post is elevated above the smooth surface, like a roof supported by columns. Because of these attractive dispersive forces between the PDMS and the smooth substrate, the elevated surface – or “roof” – collapses down onto the substrate without any external force aside from the van der Waals attraction.. Simple smooth polymer surfaces – without any microstructures –

are commonly used for these dispersive adhesive properties. Decals and stickers that adhere to glass without using any chemical adhesives are fairly common as toys and decorations and useful as removable labels because they do not rapidly lose their adhesive properties, as do sticky tapes that use adhesive chemical compounds.

It is important to note that these forces also act over very small distances. 99% of the work necessary to break van der Waals bonds is done once surfaces are pulled more than a nanometer apart. As a result of this limited motion in both the van der Waals and ionic/covalent bonding situations, practical effectiveness of adhesion due to either or both of these interactions leaves much to be desired. Once a crack is initiated, it propagates easily along the interface because of the brittle nature of the interfacial bonds.

As an additional consequence, increasing surface area often does little to enhance the strength of the adhesion in this situation. This follows from the aforementioned crack failure – the stress at the interface is not uniformly distributed, but rather concentrated at the area of failure.

Electrostatic adhesion

Some conducting materials may pass electrons to form a difference in electrical charge at the join. This results in a structure similar to a capacitor and creates an attractive electrostatic force between the materials.

Diffusive adhesion

Some materials may merge at the joint by diffusion. This may occur when the molecules of both materials are mobile and soluble in each other. This would be particularly effective with polymer chains where one end of the molecule diffuses into the other material. It is also the mechanism involved in sintering. When metal or ceramic powders are pressed together and heated, atoms diffuse from one particle to the next. This joins the particles into one.

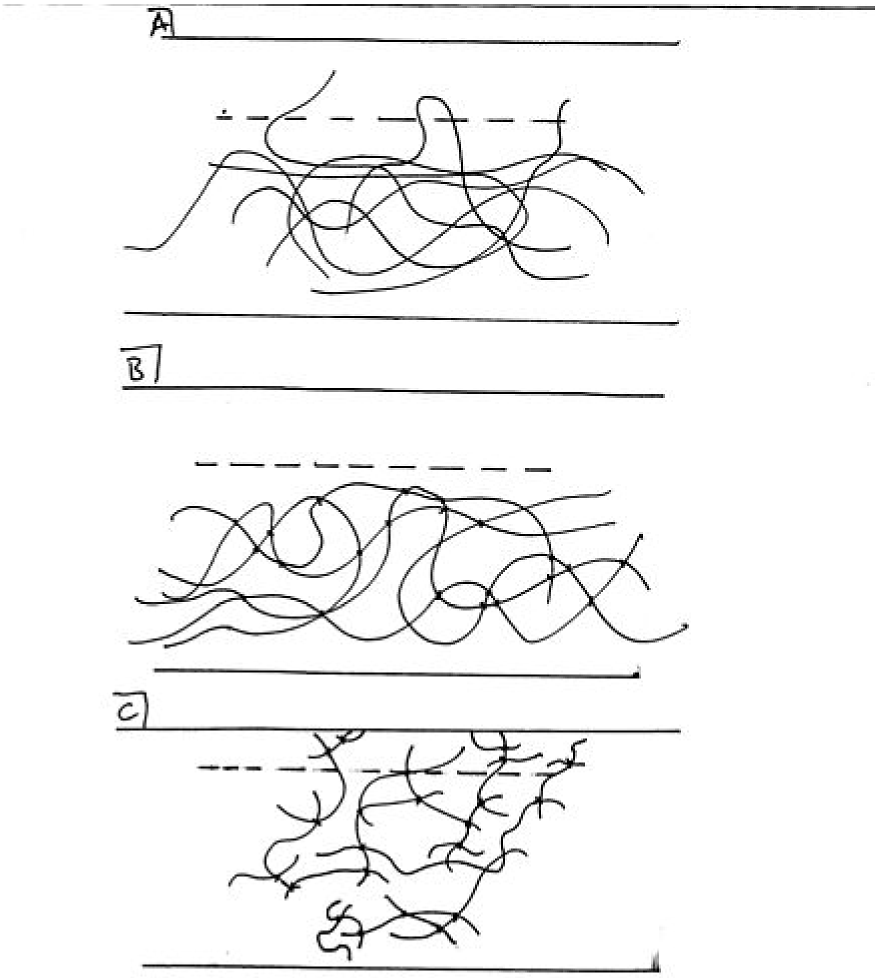


Figure 4 The interface is indicated by the dotted line. A)Uncross-linked polymers are somewhat free to diffuse across the interface. One loop and two distal tails are seen diffusing. B) Cross-linked polymers not free enough to diffuse. C)"Scissed" polymers very free, with many tails extending across the interface.

Diffusive forces are somewhat like mechanical tethering at the molecular level. Diffusive bonding occurs when species from one surface penetrate into an adjacent surface while still being bound to the phase of their surface of origin. One instructive example is that of polymer-on-polymer surfaces. Diffusive bonding in polymer-on-polymer surfaces is the result of sections of polymer chains from one surface interdigitating with those of an adjacent surface. The freedom of movement of the polymers ha s a strong effect on their ability to interdigitate, and hence, on diffusive bonding. For example, cross-linked polymers are less capable of diffusion and interdigitation because they are bonded together at many points of contact, and are not free to twist into the adjacent surface. Uncrosslinked polymers, on the other hand are freer to wander into the adjacent phase by extending tails and loops across the interface.

Another circumstance under which diffusive bonding occurs is “scission”. Chain scission is the cutting up of polymer chains, resulting in a higher concentration of distal tails. The heightened concentration of these chain ends gives rise to a heightened concentration of polymer tails extending across the interface. Scission is easily achieved by ultraviolet irradiation in the presence of oxygen gas, which suggests that adhesive devices employing diffusive bonding actually benefit from prolonged exposure to heat/light and air. The longer such a device is exposed to these conditions, the more tails are scissed and branch out across the interface.

Once across the interface, the tails and loops form whatever bonds are favorable. In the case of polymer-on-polymer surfaces, this means more van der Waals forces. While these may be brittle, they are quite strong when a large network of these bonds is formed. The outermost layer of each surface plays a crucial role in the adhesive properties of such interfaces, as even a tiny amount of interdigitation - as little as one or two tails of 1.25 angstrom length - can increase the van der Waals bonds by an order of magnitude.

Strength

The strength of the adhesion between two materials depends on which of the above mechanisms occur between the two materials, and the surface area over which the two materials contact. Materials that wet against each other tend to have a larger contact area than those that do not. Wetting depends on the surface energy of the materials.

Low surface energy materials such as polyethylene, polypropylene, polytetrafluoroethylene, and Delrin are difficult to bond without special surface preparation.

Other effects

In concert with the primary surface forces described above, there are several circumstantial effects in play. While the forces themselves each contribute to the magnitude of the adhesion between the surfaces, the following play a crucial role in the overall strength and reliability of an adhesive device.

Stringing

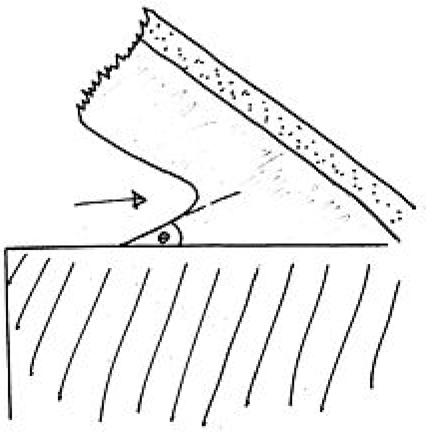


Figure 5 Fingering process. The hatched area is the receiving substrate, the dotted strip is the tape, and the shaded area in between is the adhesive chemical layer. The arrow indicates the direction of propagation for the fracture.

Stringing is perhaps the most crucial of these effects, and is often seen on adhesive tapes. Stringing occurs when a separation of two surfaces is beginning and molecules at the interface bridge out across the gap, rather than cracking like the interface itself. The most significant consequence of this effect is the restraint of the crack. By providing the otherwise brittle interfacial bonds with some flexibility, the molecules that are stringing across the gap can stop the crack from propagating. Another way to understand this phenomenon is by comparing it to the stress concentration at the point of failure mentioned earlier. Since the stress is now spread out over some area, the stress at any given point has less of a chance of overwhelming the total adhesive force between the surfaces. If failure does occur at an interface containing a viscoelastic adhesive agent, and a crack does propagate, it happens by a gradual process called “fingering”, rather than a rapid, brittle fracture. Stringing can apply to both the diffusive bonding regime and the chemical bonding regime. The strings of molecules bridging across the gap would either be the molecules that had earlier diffused across the interface or the viscoelastic adhesive, provided that there was a significant volume of it at the interface.

Microstructures

Technologically advanced adhesive devices sometimes make use of microstructures on surfaces, such as the periodic posts described above. These are biomimetic technologies inspired by the adhesive abilities of the feet of various arthropods and vertebrates (most notably, geckos). By intermixing periodic breaks into smooth, adhesive surfaces, the interface acquires valuable crack-arresting properties. Because crack initiation requires much greater stress than does crack propagation, surfaces like these are much harder to separate, as a new crack has to be restarted every time the next individual microstructure is reached.

Hysteresis

Hysteresis, in this case, refers to the restructuring of the adhesive interface over some period of time, with the result being that the work needed to separate two surfaces is greater than the work that was gained by bringing them together ($W > \gamma_1 + \gamma_2$). For the most part, this is a phenomenon associated with diffusive bonding. The more time is given for a pair of surfaces exhibiting diffusive bonding to restructure, the more diffusion will occur, the stronger the adhesion will become. The aforementioned reaction of certain polymer-on-polymer surfaces to ultraviolet radiation and oxygen gas is an instance of hysteresis, but it will also happen over time without those factors.

In addition to being able to observe hysteresis by determining if $W > \gamma_1 + \gamma_2$ is true, one can also find evidence of it by performing “stop-start” measurements. In these experiments, two surfaces slide against one another continuously and occasionally stopped for some measured amount of time. Results from experiments on polymer-on-polymer surfaces show that if the stopping time is short enough, resumption of smooth sliding is easy. If, however, the stopping time exceeds some limit, there is an initial increase of resistance to motion, indicating that the stopping time was sufficient for the surfaces to restructure.

Wettability and Adsorption

We can also characterize some atmospheric effects on the functionality of adhesive devices by following the theory of surface energy and interfacial tension. We know that $\gamma_{12} = (1/2)W_{121} = (1/2)\ W_{212}$ (figure 2). If γ_{12} is high, then each species finds it favorable to cohere while in contact with a foreign species, rather than dissociate and mix with the other. If this is true, then it follows that when the interfacial tension is high, the force of adhesion is weak, since each species does not find it favorable to bond to the other. Since we know that the interfacial tension of a liquid and a solid is directly related to the liquids wettability (relative to the solid), we can also extrapolate that cohesion increases in non-wetting liquids, and decreases in wetting liquids. One example that verifies this is polydimethyl siloxane rubber, which has a work of self-adhesion of 43.6 mJ/m^2 in air, 74 mJ/m^2 in water (a nonwetting liquid) and 6 mJ/m^2 in methanol (a wetting liquid).

This argument can be extended to the idea that when a surface is in a medium with which binding is favorable, it will be less likely to adhere to another surface, since the medium is taking up the potential sites on the surface that would otherwise be available to adhere to another surface. Naturally this applies very strongly to wetting liquids, but also to gas molecules that could adsorb onto the surface in question, thereby occupying potential adhesion sites. This last point is actually fairly intuitive: Leaving an adhesive exposed to air too long gets it dirty, and its adhesive strength will decrease. We can also observe this experimentally: When mica is cleaved in air, its cleavage energy, W_{121} or $W_{\text{mica/air/mica}}$, is smaller than the cleavage energy in vacuum, $W_{\text{mica/vac/mica}}$, by a factor of 13.

Chapter- 2

Adhesive

Nitrocellulose adhesive outside a tube

An **adhesive**, or **glue**, is a mixture in a liquid or semi-liquid state that adheres or bonds items together. Adhesives may come from either natural or synthetic sources. The types of materials that can be bonded are vast but they are especially useful for bonding thin materials. Adhesives cure (harden) by either evaporating a solvent or by chemical reactions that occur between two or more constituents.

Adhesives are advantageous for joining thin or dissimilar materials, minimizing weight, and when a vibration dampening joint is needed. A disadvantage to adhesives is that they do not form an instantaneous joint, unlike most other joining processes, because the adhesive needs time to cure.

The earliest known date for a simple glue is 200,000 BC and for a compound glue 70,000 BC.

History

The oldest known adhesive, dated to approximately 200,000 BC, is from spear stone flakes glued to a wood with birch-bark-tar, which was found in central Italy. The use of compound glues to haft stone spears into wood dates back to round 70,000 BC. Evidence for this has been found in Sibudu Cave, South Africa and the compound glues used were made from plant gum and red ochre. The Tyrolean Iceman had weapons fixed together with the aid of birch-bark-tar glue.

6000-year-old ceramics show evidence of adhesives based upon animal glues made by rendering animal products such as horse teeth. During the times of Babylonia, tar-like glue was used for gluing statues. The Egyptians made much use of animal glues to adhere furniture, ivory, and papyrus. The Mongols also used adhesives to make their short bows, and the Native Americans of the eastern United States used a mixture of spruce gum and fat as adhesives to fashion waterproof seams in their birchbark canoes.

In medieval Europe, egg whites were used as glue to decorate parchments with gold leaf. The first actual glue factory was founded in Holland in the early 18th century. In the 1750s, the English introduced fish glue. As the modern world evolved, several other patented materials, such as bones, starch, fish skins and isinglass, and casein, were introduced as alternative materials for glue manufacture. Modern glues have improved flexibility, toughness, curing rate, and chemical resistance.

In the late 19th century in Switzerland, casein was first used as a wood glue. Today, it is seen to be used to glue grocery bags.

Types

Adhesives are typically organized by the method of adhesion. These are then organized into reactive and non-reactive adhesives, which refers to if the adhesive chemically reacts to harden. Alternatively they can be organized by whether the raw stock is of natural, or synthetic origin, or by their starting physical phase.

Non-reactive adhesives

Drying adhesives

There are two types of adhesives that harden by drying: *solvent based adhesives* and *polymer dispersion adhesives*, also known as *emulsion adhesives*.

Solvent based adhesives are a mixture of ingredients (typically polymers) dissolved in a solvent. White glue, contact adhesives and rubber cements are members of the *drying adhesive* family. As the solvent evaporates, the adhesive hardens. Depending on the chemical composition of the adhesive, they will adhere to different materials to greater or lesser degrees.

Polymer dispersion adhesives are milky-white dispersions often based on polyvinyl acetate (PVAc). Used extensively in the woodworking and packaging industries. Also used with fabrics and fabric-based components, and in engineered products such as loudspeaker cones.

Pressure sensitive adhesives

Pressure sensitive adhesives (PSA) form a bond by the application of light pressure to marry the adhesive with the adherend. They are designed with a balance between flow and resistance to flow. The bond forms because the adhesive is soft enough to flow (i.e. "wet") the adherend. The bond has strength because the adhesive is hard enough to resist flow when stress is applied to the bond. Once the adhesive and the adherend are in close proximity, molecular interactions, such as van der Waals forces, become involved in the bond, contributing significantly to its ultimate strength.

PSAs are designed for either permanent or removable applications. Examples of permanent applications include safety labels for power equipment, foil tape for HVAC duct work, automotive interior trim assembly, and sound/vibration damping films. Some high performance permanent PSAs exhibit high adhesion values and can support kilograms of weight per square centimeter of contact area, even at elevated temperature. Permanent PSAs may be initially removable (for example to recover mislabeled goods) and build adhesion to a permanent bond after several hours or days.

Removable adhesives are designed to form a temporary bond, and ideally can be removed after months or years without leaving residue on the adherend. Removable adhesives are used in applications such as surface protection films, masking tapes, bookmark and note papers, price marking labels, promotional graphics materials, and for skin contact (wound care dressings, EKG electrodes, athletic tape, analgesic and transdermal drug patches, etc.). Some removable adhesives are designed to repeatedly stick and unstick. They have low adhesion and generally can not support much weight.

Pressure sensitive adhesives are manufactured with either a liquid carrier or in 100% solid form. Articles are made from liquid PSAs by coating the adhesive and drying off the solvent or water carrier. They may be further heated to initiate a cross-linking reaction and increase molecular weight. 100% solid PSAs may be low viscosity polymers that are coated and then reacted with radiation to increase molecular weight and form the adhesive; or they may be high viscosity materials that are heated to reduce viscosity enough to allow coating, and then cooled to their final form. Major raw material for PSA's are acrylate based polymers.

Contact adhesives

Contact adhesives are used in strong bonds with high shear-resistance like laminates, such as bonding Formica to a wooden counter, and in footwear, as in attaching outsoles to uppers.

Natural rubber and polychloroprene (Neoprene) are commonly used contact adhesives. Both of these elastomers undergo strain crystallization.

Contact adhesives must be applied to both surfaces and allowed some time to dry before the two surfaces are pushed together. Some contact adhesives require as long as 24 hours to dry before the surfaces are to be held together. Once the surfaces are pushed together, the bond forms very quickly. It is usually not necessary to apply pressure for a long time, so there is less need for clamps.

Hot adhesives

A glue gun, an example of a hot adhesive

Hot adhesives, also known as *hot melt adhesives*, are simply thermoplastics applied in molten form (in the 65-180 C range) which solidify on cooling to form strong bonds between a wide range of materials. Ethylene-vinyl acetate based hot-melts are particularly popular for crafts because of their ease of use and the wide range of common materials they can join. A glue gun (shown at right) is one method of applying hot adhesives. The glue gun melts the solid adhesive then allows the liquid to pass through its barrel onto the material, where it solidifies.

Thermoplastic glue may have been invented around 1940 by Procter & Gamble as a solution to water-based adhesives commonly used in packaging at that time failing in humid climates, causing packages to open and become damaged.

Reactive adhesives

Multi-part adhesives

Multi-component adhesives harden by mixing two or more components which chemically react. This reaction causes polymers to cross-link into acrylics, urethanes, and epoxies.

There are several commercial combinations of multi - component adhesives in use in industry. Some of these combinations are:

- Polyester resin - polyurethane resin
- Polyols - polyurethane resin
- Acrylic polymers - polyurethane resins

The individual components of a multi-component adhesive are not adhesive by nature. The individual components react with each other after being mixed and show full adhesion only on curing. The multi-component resins can be either solvent-based or solvent-less. The solvents present in the adhesives is a medium for the polyester or the polyurethane resin. The solvent is dried during the curing process.

One-part adhesives

One-part adhesives harden via a chemical reaction with an external energy source, such as radiation, heat, and moisture.

Ultraviolet (UV) *light curing adhesives*, also known as *light curing materials* (LCM), have become popular within the manufacturing sector due to their rapid curing time and strong bond strength. Light curing adhesives can cure in as little as a second and many formulations can bond dissimilar substrates (materials) and withstand harsh temperatures. These qualities make UV curing adhesives essential to the manufacturing of items in many industrial markets such as electronics, telecommunications, medical, aerospace, glass, and optical. Unlike traditional adhesives, UV light curing adhesives not only bond materials together but they can also be used to seal and coat products. They are generally acrylic based.

Heat curing adhesives consist of a pre-made mixture of two or more components. When heat is applied the components react and cross-link. This type of adhesive includes epoxies, urethanes, and polyimides.

Moisture curing adhesives cure when they react with moisture present on the substrate surface or in the air. This type of adhesive includes cyanoacrylates and urethanes.

Natural adhesives

Natural adhesives are made from organic sources such as vegetable matter, starch (dextrin), natural resins or from animals e.g. casein or animal glue. They are often referred to as bioadhesives. One example is a simple paste made by cooking flour in water. Animal glues are traditionally used in bookbinding, wood joining, and many other areas but now are largely replaced by synthetic glues. Casein are mainly used in glass bottle labelling. Starch based adhesives are used in corrugated board production and paper sack production, paper tube winding, wall paper adhesives. Another form of natural adhesive is blood albumen (made from protein component of blood), which is used in the plywood industry. Animal glue remains the preferred glue of the luthier. Casein based glues are made by precipitating casein from milk protein using the acetic acid from vinegar. This forms curds, which are neutralized with a base, such as sodium bicarbonate (baking soda), to cause them to unclump and become a thicker plastic-like substance.

Synthetic adhesives

Synthetic adhesives are based on elastomers, thermoplastics, emulsions, and thermosets. Examples of thermosetting adhesives are: epoxy, polyurethane, cyanoacrylate and acrylic polymers.

Application

Applicators of different adhesives are designed according to the adhesive being used and the size of the area to which the adhesive will be applied. The adhesive is applied to either one or both of the materials being bonded. The pieces are aligned and pressure is added to aid in adhesion and rid the bond of air bubbles.

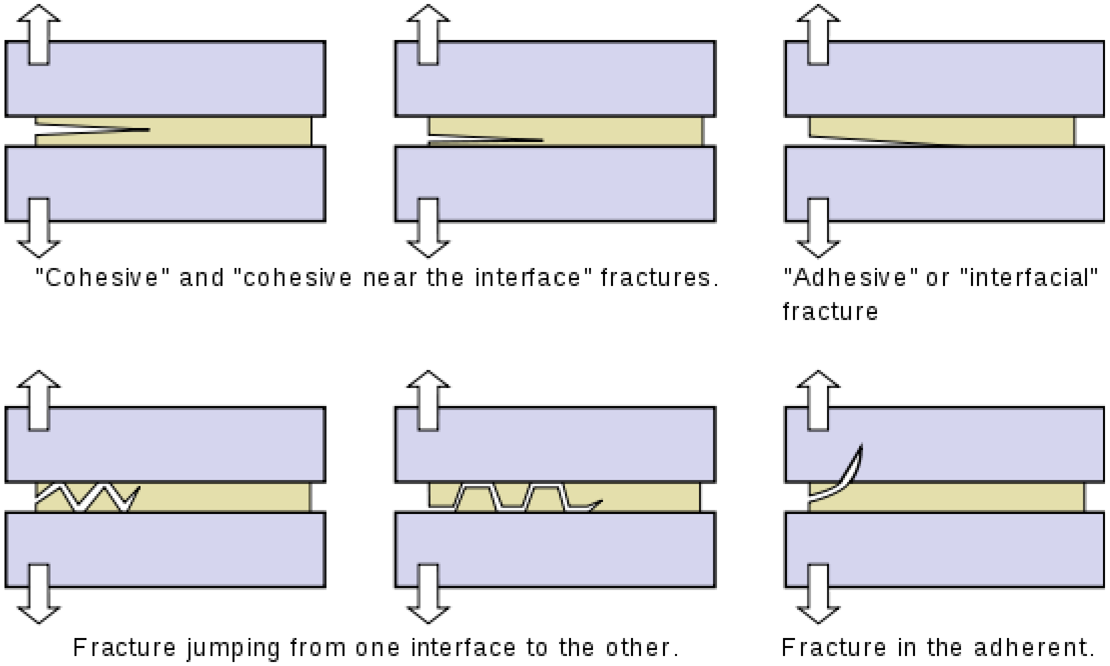
Common ways of applying an adhesive include brushes, rollers, using films or pellets, spray guns and applicator guns (*e.g.*, caulk gun). All of these can be done manually or can be automated into a machine.

Mechanisms of adhesion

Adhesion, the attachment between adhesive and substrate may occur either by mechanical means, in which the adhesive works its way into small pores of the substrate, or by one of several chemical mechanisms. The strength of adhesion depends on many factors, including the means by which it occurs.

In some cases, an actual chemical bond occurs between adhesive and substrate. In others, electrostatic forces, as in static electricity, hold the substances together. A third mechanism involves the van der Waals forces that develop between molecules. A fourth means involves the moisture-aided diffusion of the glue into the substrate, followed by hardening.

Failure of the adhesive joint



"Cohesive" and "cohesive near the interface" fractures.

"Adhesive" or "interfacial" fracture

Fracture jumping from one interface to the other.

Fracture in the adherent.

Failure of the adhesive joint can occur in different locations

There are several factors that could contribute to the failure of two adhered surfaces. Sunlight and heat may weaken the adhesive. Solvents can deteriorate or dissolve adhesive. Physical stresses may also cause the separation of surfaces. When subjected to loading, debonding may occur at different locations in the adhesive joint. The major fracture types are the following:

Cohesive fracture

Cohesive fracture is obtained if a crack propagates in the bulk polymer which constitutes the adhesive. In this case the surfaces of both adherents after debonding will be covered by fractured adhesive. The crack may propagate in the centre of the layer or near an interface. For this last case, the cohesive fracture can be said to be “cohesive near the interface”. Most quality control standards consider a good adhesive bond to be cohesive.

Interfacial fracture

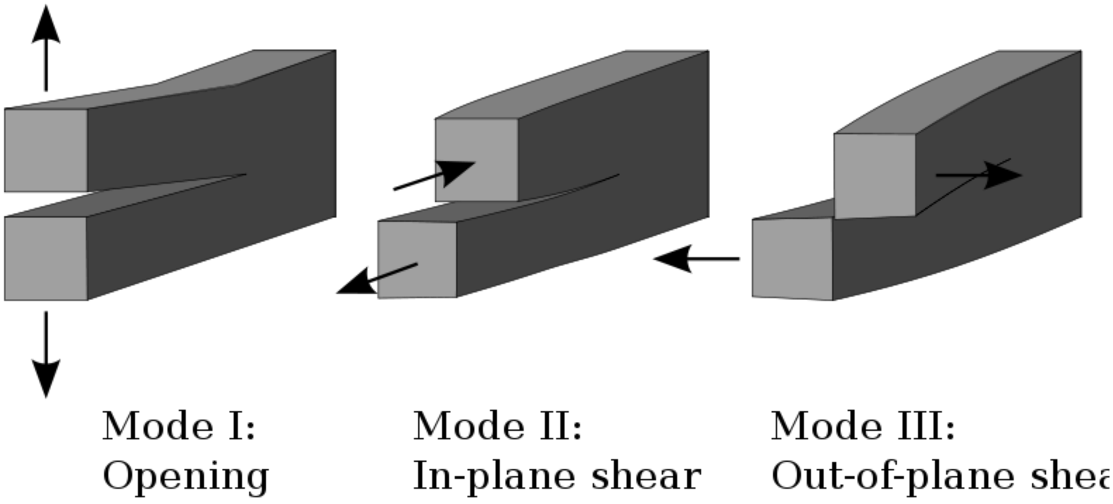
The fracture is *adhesive* or *interfacial* when debonding occurs between the adhesive and the adherent. In most cases, the occurrence of interfacial fracture for a given adhesive goes along with a smaller fracture toughness. The interfacial character of a fracture surface is usually to identify the precise location of the crack path in the interphase.

Other types of fracture

Other types of fracture include:

- The *mixed* type, which occurs if the crack propagates at some spots in a cohesive and in others in an interfacial manner. Mixed fracture surfaces can be characterised by a certain percentage of adhesive and cohesive areas.
- The *alternating crack path* type which occurs if the cracks jumps from one interface to the other. This type of fracture appears in the presence of tensile pre-stresses in the adhesive layer.
- Fracture can also occur in the adherent if the adhesive is tougher than the adherent. In this case the adhesive remains intact and is still bonded to one substrate and remnants of the other. For example, when one removes a price label, adhesive usually remains on the label and the surface. This is cohesive failure. If, however, a layer of paper remains stuck to the surface, the adhesive has not failed. Another example is when someone tries to pull apart Oreo cookies and all the filling remains on one side; this is an adhesive failure, rather than a cohesive failure.

Design of adhesive joints



Modes of failure

As a general design rule, the material properties of the object need to be greater than the forces anticipated during its use. (i.e. geometry, loads, etc.). The engineering work will consist of having a good model to evaluate the function. For most adhesive joints, this can be achieved using fracture mechanics. Concepts such as the stress concentration factor and the strain energy release rate can be used to predict failure. In such models, the behavior of the adhesive layer itself is neglected and only the adherents are considered.

Failure will also very much depend on the opening *mode* of the joint.

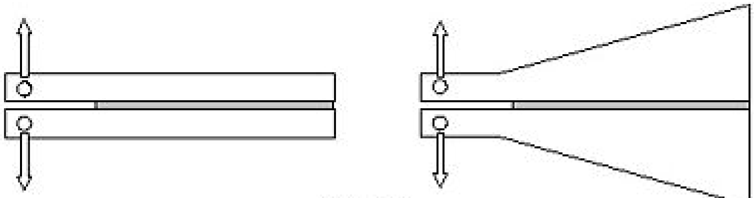
- *Mode I* is an opening or tensile mode where the loadings are normal to the crack.
- *Mode II* is a sliding or in-plane shear mode where the crack surfaces slide over one another in direction perpendicular to the leading edge of the crack. This is typically the mode for which the adhesive exhibits the highest resistance to fracture.
- *Mode III* is a tearing or antiplane shear mode.

As the loads are usually fixed, an acceptable design will result from combination of a material selection procedure and geometry modifications, if possible. In adhesively bonded structures, the global geometry and loads are fixed by structural considerations and the design procedure focuses on the material properties of the adhesive and on local changes on the geometry.

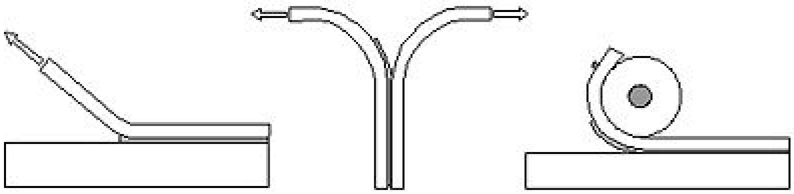
Increasing the joint resistance is usually obtained by designing its geometry so that:

- The bonded zone is large
- It is mainly loaded in mode II
- Stable crack propagation will follow the appearance of a local failure.

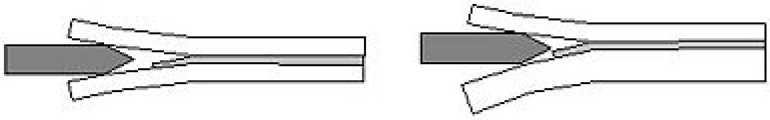
Testing the resistance of the adhesive



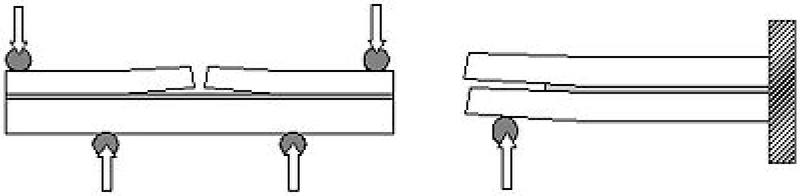
Double cantilever Beam (DCB) and Tapered Double Cantilever Beam (TDCB) tests



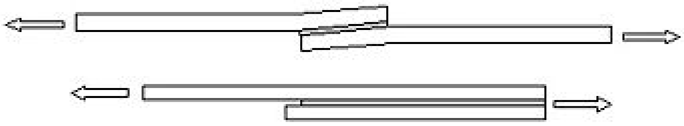
Peel tests



Wedge tests



MMDB and End Notch Flexure (ENF) tests



Symmetrical and Dissymetrical Crack Lap Shear tests (CLS and DLS)

Testing devices

A wide range of testing devices have been devised to evaluate the fracture resistance of bonded structures in pure mode I, pure mode II or in mixed mode. Most of these devices are beam type specimens. We will very shortly review the most popular:

- *Double cantilever beam tests* (DCB) measure the mode I fracture resistance of adhesives in a fracture mechanics framework. These tests consist in opening an assembly of two beams by applying a force at the ends of the two beams. The test is unstable (i.e. the crack propagates along the entire specimen once a critical load is attained) and a modified version of this test characterised by a non constant inertia was proposed called the *tapered double cantilever beam* (TDCB) specimen.
- *Peel tests* measure the fracture resistance of a thin layer bonded on a thick substrate or of two layers bonded together. They consist in measuring the force needed for tearing an adherent layer from a substrate or for tearing two adherent layers one from another. Whereas the structure is not symmetrical, various mode mixities can be introduced in these tests. This is one of the more common methods of evaluating paper strength in library and archival preservation.
- *Wedge tests* measure the mode I dominated fracture resistance of adhesives used to bond thin plates. These tests consist in inserting a wedge in between two bonded plates. A critical energy release rate can be derived from the crack length during testing. This test is a mode I test but some mode II component can be introduced by bonding plates of different thicknesses.
- *Mixed-mode delaminating beam tests* (MMDB) consist in a bonded bilayer with two starting cracks loaded on four points. The test presents roughly the same amount of mode I and mode II with a slight dependence on the ratio of the two layer thicknesses.
- *End notch flexure tests* consist in two bonded beams built-in on one side and loaded by a force on the other. As no normal opening is allowed, this device allows testing in essentially mode II condition.
- *Crack lap shear tests* (CLS) are application-oriented fracture resistance tests. They consist in two plates bonded on a limited length and loaded in tension on both ends. The test can be either symmetrical or dis-symmetrical. In the first case two cracks can be initiated and in the second only one crack can propagate.

Chapter- 3

Dispersive Adhesion and Wetting

Dispersive adhesion

Dispersive adhesion, also called adsorptive adhesion, is a mechanism for adhesion which attributes attractive forces between two materials to intermolecular interactions between molecules of each material. This mechanism is widely viewed as the most important of the five mechanisms of adhesion due to its presence in every type of adhesive system and relative strength.

Source of dispersive adhesion attractions

The source of adhesive forces, according to the dispersive adhesion mechanism, is the weak interactions that occur between molecules close together. These interactions include London dispersion forces, Keesom forces, Debye forces and hydrogen bonds. Taken on an individual basis, these attractions are not very strong, but when summed over the bulk of a material, can become significant.

London dispersion

London dispersion forces arise from instantaneous dipoles between two nonpolar molecules close together. The random nature of electron orbit allows moments in which the charge distribution in a molecule is unevenly distributed, allowing an attraction to another molecule with a temporary dipole. A larger molecule allows for a larger dipole, and thus will have stronger dispersion forces.

Keesom

Keesom forces, also known as dipole-dipole interactions, result from two molecules that have a permanent dipole due to electronegativity differences between atoms in the molecule. This dipole causes a coulombic attraction between the two molecules.

Debye

Debye forces, or dipole-induced dipole interactions, can also play a role in dispersive adhesion. These come about when a nonpolar molecule becomes temporarily polarized due to interactions with a nearby polar molecule. This “induced dipole” in the nonpolar molecule then is attracted to the permanent dipole, yielding a Debye attraction.

Hydrogen Bonding

Sometimes grouped into the chemical mechanism of adhesion, hydrogen bonding can increase adhesive strength by the dispersive mechanism. Hydrogen bonding occurs between molecules with a hydrogen atom attached to a small, electronegative atom such as fluorine, oxygen or nitrogen. This bond is naturally polar, with the hydrogen atom gaining a slight positive charge and the other atom becoming slightly negative. Two molecules, or even two functional groups on one large molecule, may then be attracted to each other via Keesom forces.

Factors affecting adhesion strength

The strength of adhesion by the dispersive mechanism depends on a variety of factors including: chemical structure of the molecules involved in the adhesive system, the degree to which coatings wet each other, and the surface roughness at the interface.

Chemical composition

The chemical structure of the materials involved in a given adhesive system plays a large role in the adhesion of the system as a whole because the structure determines the type and strength of the intermolecular interactions present. All things equal, larger molecules, which experience higher dispersion forces, will have a larger adhesive strength than smaller molecules of the same basic chemical fingerprint. Similarly, polar molecules will have Keesom and Debye forces not experienced by nonpolar molecules of similar size. Compounds which can hydrogen bond across the adhesive interface will have even greater adhesive strength.

Roughness

Surface roughness can also affect the adhesive strength. Surfaces with roughness on the scale of 1-2 micrometres can yield better wetting because they have a larger surface area. Thus, more intermolecular interactions at closer distances can arise, yielding stronger attractions and larger adhesive strength. Once the roughness becomes larger, on the order of 10 micrometres, the coating can no longer wet effectively, resulting in less contact area and a smaller adhesive strength.

Systems dominated by dispersive adhesion

All materials, even those not usually classified as adhesives, experience an attraction to other materials, due simply to dispersion forces. In many situations these attractions are trivial; however, dispersive adhesion plays a dominant role in various adhesive systems, especially when multiple forms of intermolecular attractions, as described above, are present. It has been shown by experimental methods that the dispersive mechanism of adhesion plays a large role in the overall adhesion in polymeric systems in particular.

Wetting

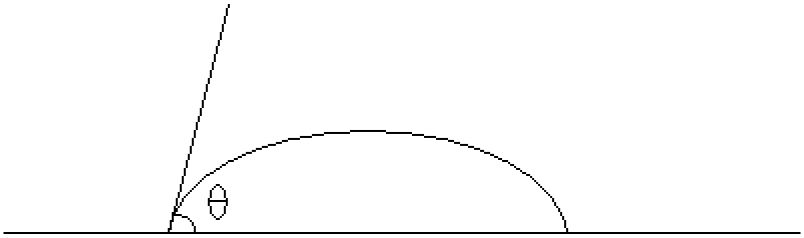
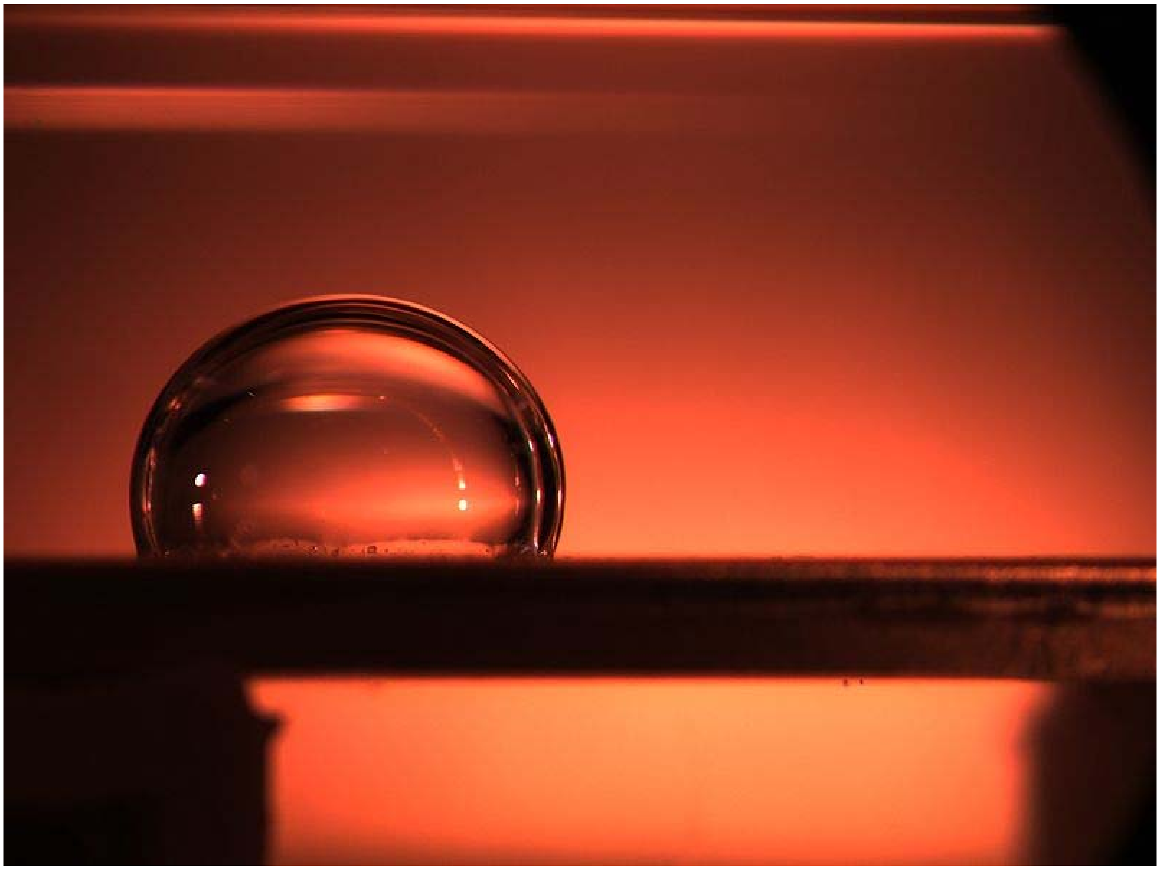
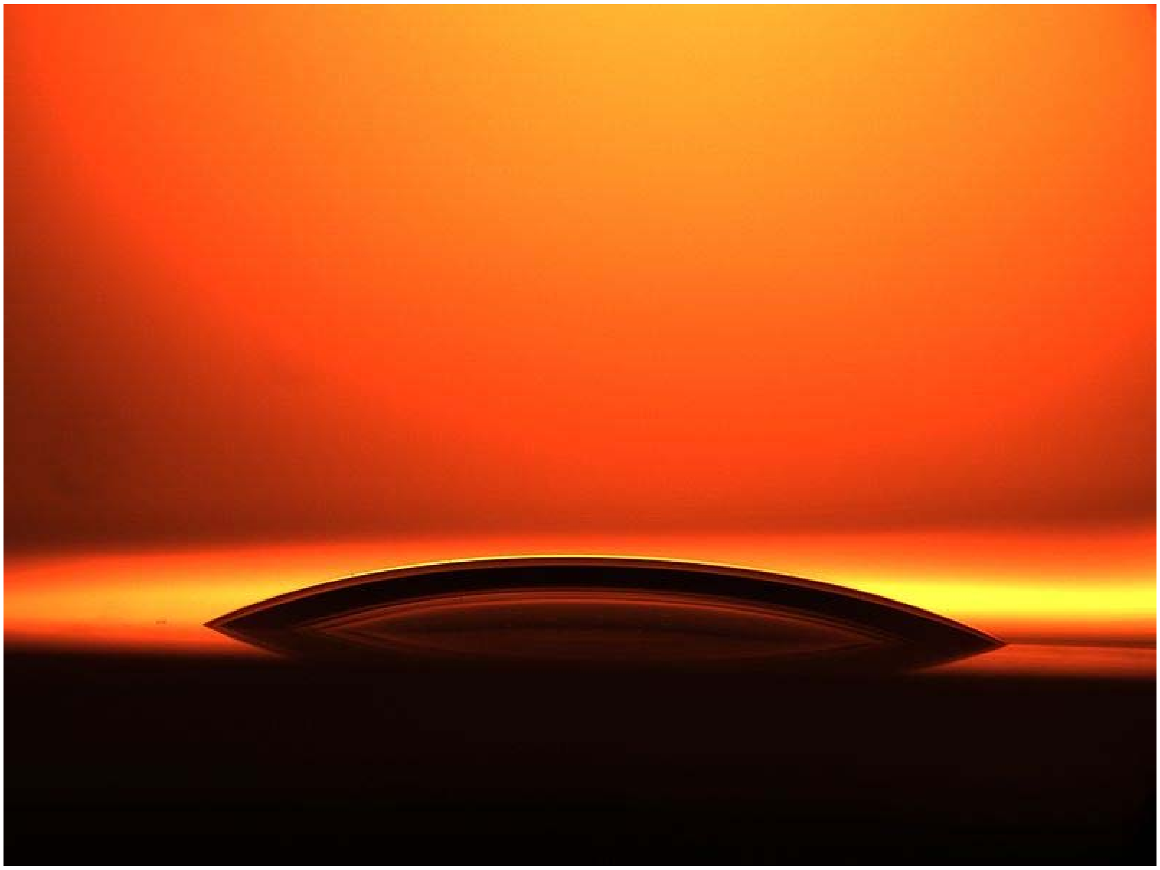


Figure 1: Droplet of water on an ideal surface



Water droplet immersed in oil and resting on a brass surface



Same fluids as above, but resting on a glass surface

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by a force balance between adhesive and cohesive forces.

Wetting is important in the bonding or adherence of two materials. Wetting and the surface forces that control wetting are also responsible for other related effects, including so-called capillary effects. Regardless of the amount of wetting, the shape of a liquid drop on a rigid surface is roughly a truncated sphere. Various degrees of wetting are summarized in the table.

Explanation

Adhesive forces between a liquid and solid cause a liquid drop to spread across the surface. Cohesive forces within the liquid cause the drop to ball up and avoid contact with the surface.

Contact angle	**Degree of wetting**	**Strength of:**	
		Sol./Liq. interactions	**Liq./Liq. interactions**
$\theta = 0$	Perfect wetting	strong	weak
$0 < \theta < 90°$	high wettability	strong	strong
		weak	weak
$90° \leq \theta < 180°$	low wettability	weak	strong
$\theta = 180°$	perfectly non-wetting	weak	strong

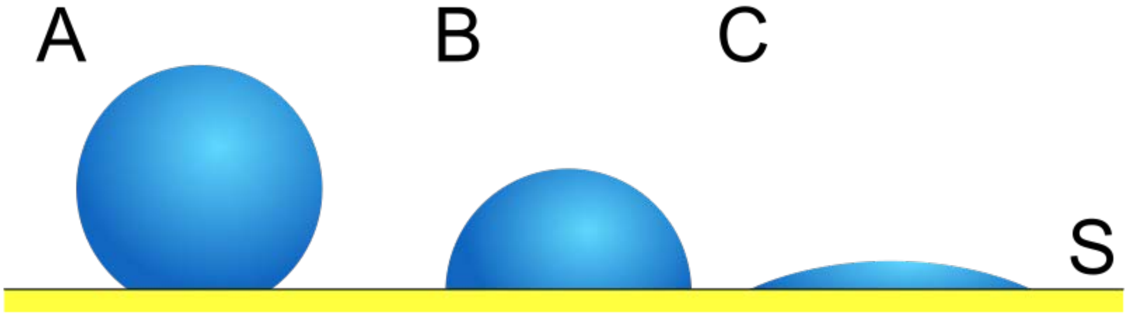


Figure 2: Wetting of different fluids. *A* shows a fluid with very little wetting, while *C* shows a fluid with more wetting. *A* has a large contact angle, and *C* has a small contact angle.

The contact angle (θ), as seen in Figure 1, is the angle at which the liquid-vapor interface meets the solid-liquid interface. The contact angle is determined by the resultant between adhesive and cohesive forces. The tendency of a drop to spread out over a flat, solid surface increases as the contact angle decreases. Thus, the contact angle provides an inverse measure of wettability.

A contact angle less than 90° (low contact angle) usually indicates that wetting of the surface is very favorable, and the fluid will spread over a large area of the surface. Contact angles greater than 90° (high contact angle) generally means that wetting of the surface is unfavorable so the fluid will minimize contact with the surface and form a compact liquid droplet.

For water, a wettable surface may also be termed hydrophilic and a non-wettable surface hydrophobic. Superhydrophobic surfaces have contact angles greater than 150°, showing almost no contact between the liquid drop and the surface. This is sometimes referred to as the "Lotus effect". The table describes varying contact angles and their corresponding solid/liquid and liquid/liquid interactions. For non-water liquids, the term lyophilic is used for low contact angle conditions and lyophobic is used when higher contact angles result. Similarly, the terms omniphobic and omniphilic apply to both polar and apolar liquids.

High energy vs. low energy surfaces

There are two main types of solid surfaces with which liquids can interact. Traditionally, solid surfaces have been divided into high energy solids and low energy types. The relative energy of a solid has to do with the bulk nature of the solid itself. Solids such as metals, glasses, and ceramics are known as 'hard solids' because the chemical bonds that hold them together (e.g. covalent, ionic, or metallic) are very strong. Thus, it takes a large input of energy to break these solids so they are termed “high energy.” Most molecular liquids achieve complete wetting with high-energy surfaces.

The other type of solids is weak molecular crystals (e.g. fluorocarbons, hydrocarbons, etc.) where the molecules are held together essentially by physical forces (e.g. van der waals and hydrogen bonds). Since these solids are held together by weak forces it would take a very low input of energy to break them, and thus, they are termed “low energy.” Depending on the type of liquid chosen, low-energy surfaces can permit either complete or partial wetting.

Wetting of low energy surfaces

Low-energy surfaces primarily interact with liquids through dispersion (van der waals) forces. Zisman had several key findings in the work that he did:

- Zisman observed that cos θ increases linearly as the surface tension (γ_{LV}) of the liquid decreased. Thus, he was able to establish a rectilinear relation between cos θ and the surface tension (γ_{LV}) for various organic liquids.

A surface is more wettable when γ_{LV} is low and when θ is low. He termed the intercept of these lines when the $\cos\theta = 1$, as the critical surface tension (γ_c) of that surface. This critical surface tension is an important parameter because it is a characteristic of only the solid.

Knowing the critical surface tension of a solid, it is possible to predict the wettability of the surface.

- The wettability of a surface is determined by the outermost chemical groups of the solid.
- Differences in wettability between surfaces that are similar in structure are due to differences in packing of the atoms. For instance, if a surface has branched chains, it will have poorer packing than a surface with straight chains.

Ideal solid surfaces

An ideal solid surface is one that is flat, rigid, perfectly smooth, chemically homogeneous, and has zero contact angle hysteresis. Zero hysteresis implies that the advancing and receding contact angles are equal. In other words, there is only one thermodynamically stable contact angle. When a drop of liquid is placed on such a surface, the characteristic contact angle is formed as depicted in Fig. 1. Furthermore, on an ideal surface the drop will return to its original shape if it is disturbed. The following derivations apply only to ideal solid surfaces. In other words, they are only valid for the state in which the interfaces are not moving and the phase boundary line exists in equilibrium.

Minimization of energy, three phases

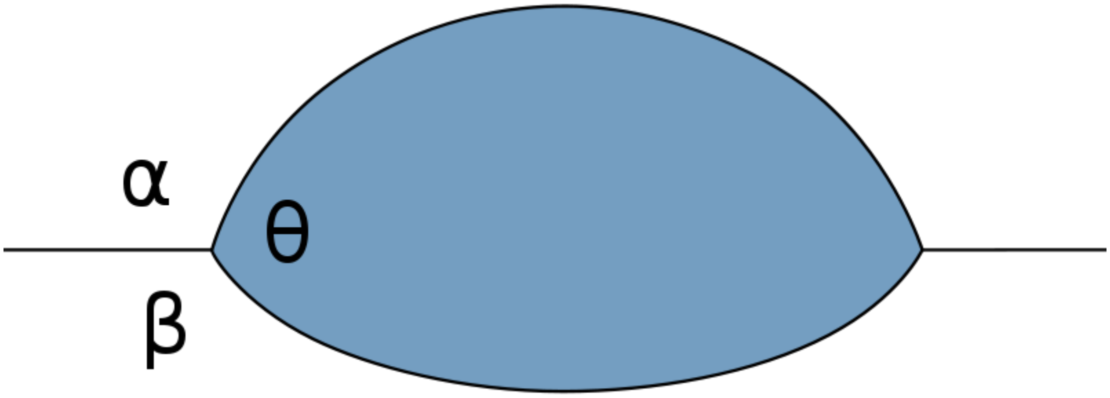


Figure 3: Coexistence of 3 fluid phases in mutual contact. α, β, and θ represent both the labels of the phases and the contact angles.

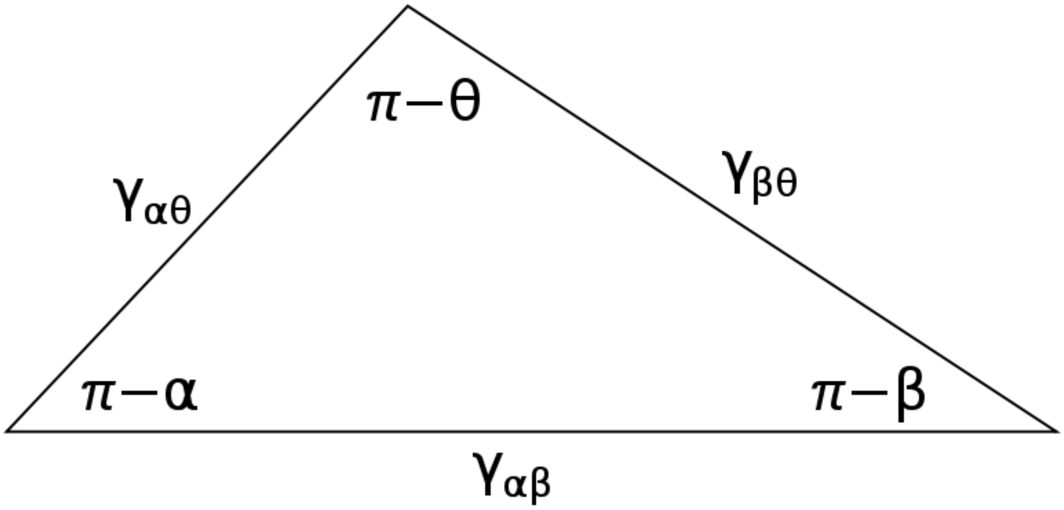


Figure 4: Neumann's triangle relating the surface energies and contact angles of 3 fluid phases coexisting in static equilibrium, as depicted in Figure 3.

Figure 3 shows the line of contact where three phases meet. In equilibrium, the net force per unit length acting along the boundary line between the three phases must be zero. The components of net force in the direction along each of the interfaces are given by:

$$\begin{aligned}\gamma_{\alpha\theta} + \gamma_{\theta\beta}\cos\theta + \gamma_{\alpha\beta}\cos\alpha &= 0\\ \gamma_{\alpha\theta}\cos\theta + \gamma_{\theta\beta} + \gamma_{\alpha\beta}\cos\beta &= 0\end{aligned}$$

$$\gamma_{\alpha\theta}\cos\alpha + \gamma_{\theta\beta}\cos\beta + \gamma_{\alpha\beta} = 0$$

where α, β, and θ are the angles shown and γ_{ij} is the surface energy between the two indicated phases. These relations can also be expressed by an analog to a triangle known as Neumann's triangle, shown in Figure 4. Neumann's triangle is consistent with the geometrical restriction that $\alpha + \beta + \theta = 2\pi$, and applying the law of sines and law of cosines to it produce relations that describe how the interfacial angles depend on the ratios of surface energies.

Because these three surface energies form the sides of a triangle, they are constrained by the triangle inequalities, $\gamma_{ij} < \gamma_{jk} + \gamma_{ik}$ meaning that no one of the surface tensions can exceed the sum of the other two. If three fluids with surface energies that do not follow these inequalities are brought into contact, no equilibrium configuration consistent with Figure 3 will exist.

Simplification to planar geometry, Young's relation

If the β phase is replaced by a flat rigid surface, as shown in Figure 5, then $\beta = \pi$, and the second net force equation simplifies to the Young equation,

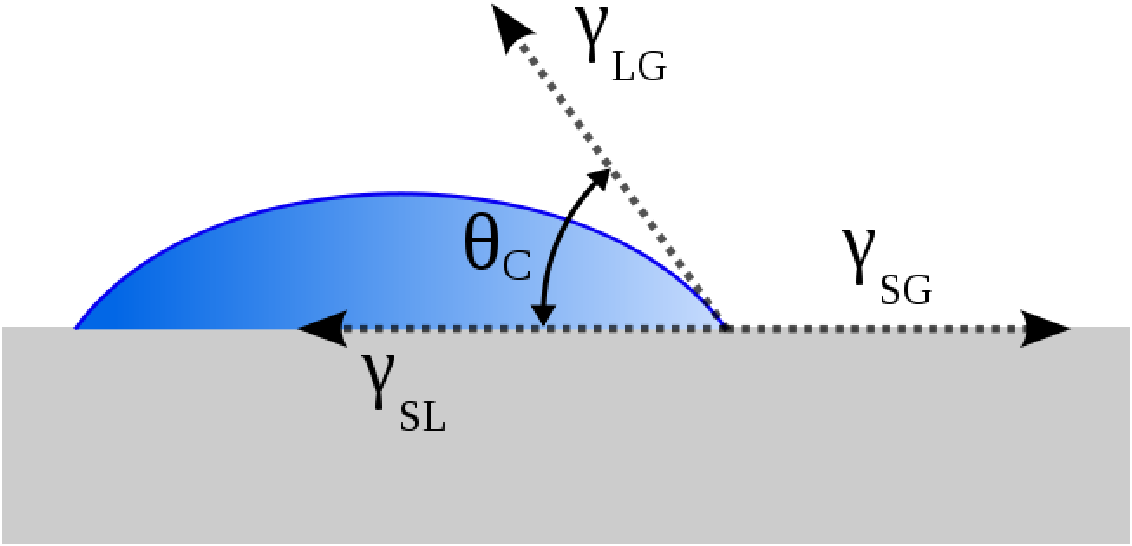


Figure 5: Contact angle of a liquid droplet wetted to a rigid solid surface.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta$$

which relates the surface tensions between the three phases: solid, liquid and gas. Subsequently this predicts the contact angle of a liquid droplet on a solid surface from knowledge of the three surface energies involved. This equation also applies if the "gas" phase is another liquid, immiscible with the droplet of the first "liquid" phase.

Real Smooth Surfaces and the Young contact angle

The Young equation mentioned above assumes a perfectly flat and rigid surface. In many cases surface are far from this ideal situation, and there are two cases that we consider here. The case or rough surfaces is discussed in the paragraph below, and the case of smooth surfaces that are still real (finitly rigid) is discussed here. Even in a perfectly smooth surface a drop will assume a wide spectrum of contact angles ranging from the so called **advancing contact angle**, θ_A, to the so called **receding contact angle**, θ_R. The equilibrium contact angle (θ_c) can be calculated from θ_A and θ_R as was shown by Tadmor as,

$$\theta_{\mathrm{c}} = \arccos\left(\frac{r_{\mathrm{A}}\cos\theta_{\mathrm{A}} + r_{\mathrm{R}}\cos\theta_{\mathrm{R}}}{r_{\mathrm{A}} + r_{\mathrm{R}}}\right)$$

where

$$r_{\mathrm{A}} = \left(\frac{\sin^3\theta_{\mathrm{A}}}{2 - 3\cos\theta_{\mathrm{A}} + \cos^3\theta_{\mathrm{A}}}\right)^{1/3} \quad ; \quad r_{\mathrm{R}} = \left(\frac{\sin^3\theta_{\mathrm{R}}}{2 - 3\cos\theta_{\mathrm{R}} + \cos^3\theta_{\mathrm{R}}}\right)^{1/3}$$

The Young–Dupre equation and Spreading Coefficient

The Young–Dupre equation dictates that neither γ_{SG} nor γ_{SL} can be larger than the sum of the other two surface energies. The consequence of this restriction is the prediction of complete wetting when $\gamma_{SG} > \gamma_{SL} + \gamma_{LG}$ and zero wetting when $\gamma_{SL} > \gamma_{SG} + \gamma_{LG}$. The lack of a solution to the Young–Dupre equation is an indicator that there is no equilibrium configuration with a contact angle between 0 and 180° for those situations.

A useful parameter for gauging wetting is the *spreading parameter S*,

$$S \ = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$$

When $S > 0$, the liquid wets the surface completely (complete wetting). When $S < 0$, there is partial wetting.

Combining the spreading parameter definition with the Young relation, we obtain the Young-Dupre equation:

$$S \ = \gamma_{LG}(\cos\theta - 1)$$

which only has physical solutions for θ when $S < 0$.

Non-ideal rough solid surfaces

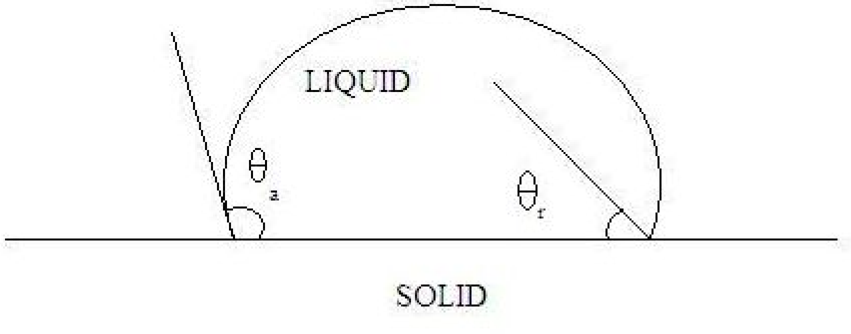


Figure 6: Schematic of advancing and receding contact angles

Unlike ideal surfaces, real surfaces do not have perfect smoothness, rigidity, or chemical homogeneity. Such deviations from ideality result in phenomena called contact-angle hysteresis. Contact-angle hysteresis is defined as the difference between the advancing (θ_a) and receding (θ_r) contact angles:

$$\mathrm{H} = \theta_a - \theta_r$$

In simpler terms, contact angle hysteresis is essentially the displacement of a contact line such as the one in figure 3, by either expansion or retraction of the droplet. Figure 6 depicts the advancing and receding contact angles. The advancing contact angle is the maximum stable angle, whereas the receding contact angle is the minimum stable angle. Contact-angle hysteresis occurs because there are many different thermodynamically stable contact angles on a non-ideal solid. These varying thermodynamically stable contact angles are known as metastable states.

Such motion of a phase boundary, involving advancing and receding contact angles, is known as dynamic wetting. When a contact line advances, covering more of the surface with liquid, the contact angle is increased and generally is related to the velocity of the contact line. If the velocity of a contact line is increased without bound, the contact angle increases, and as it approaches 180° the gas phase will become entrained in a thin layer between the liquid and solid. This is a kinetic non-equilibrium effect which results from the contact line moving at such a high speed that complete wetting cannot occur.

A well known departure from ideality is when the surface of interest has a rough texture. The rough texture of a surface can fall into one of two categories: homogeneous or heterogeneous. A homogeneous wetting regime is where the liquid fills in the roughness grooves of a surface. On the other hand, a heterogeneous wetting regime is where the surface is a composite of two types of patches. An important example of such a composite surface is one composed of patches of both air and solid. Such surfaces have varied effects on the contact angles of wetting liquids. Cassie-Baxter and Wenzel are the two main models that attempt describe the wetting of textured surfaces. However, these equations only apply when the drop size is sufficiently large compared with the surface roughness scale.

Wenzel's model

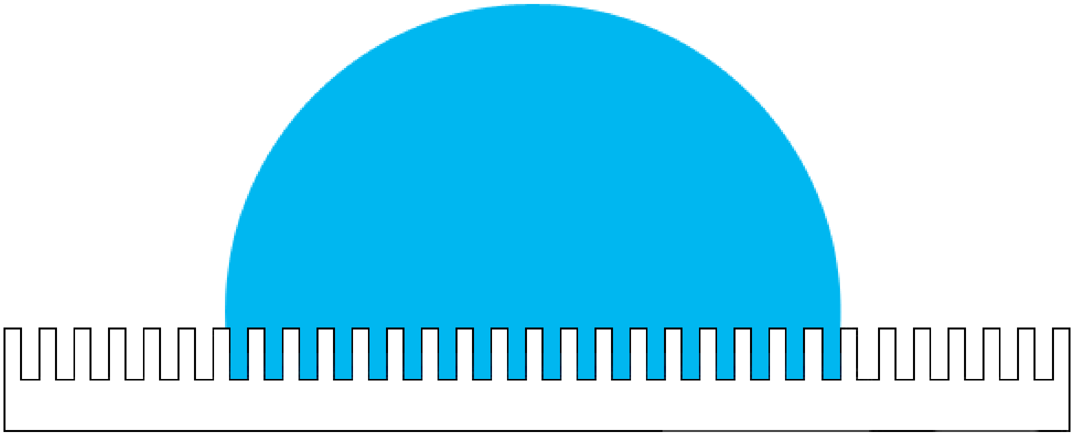


Figure 7: Wenzel model

The Wenzel model describes the homogeneous wetting regime, as seen in Figure 7, and is defined by the following equation for the contact angle on a rough surface:

$$\cos\theta^* = r\cos\theta$$

where θ^* is the apparent contact angle which corresponds to the stable equilibrium state (i.e. minimum free energy state for the system). The roughness ratio, r, is a measure of how surface roughness affects a homogeneous surface. The roughness ratio is defined as the ratio of true area of the solid surface to the apparent area.

θ is the Young contact angle as defined for an ideal surface. Although Wenzel's equation demonstrates that the contact angle of a rough surface is different from the intrinsic contact angle, it does not describe contact angle hysteresis.

Cassie–Baxter model

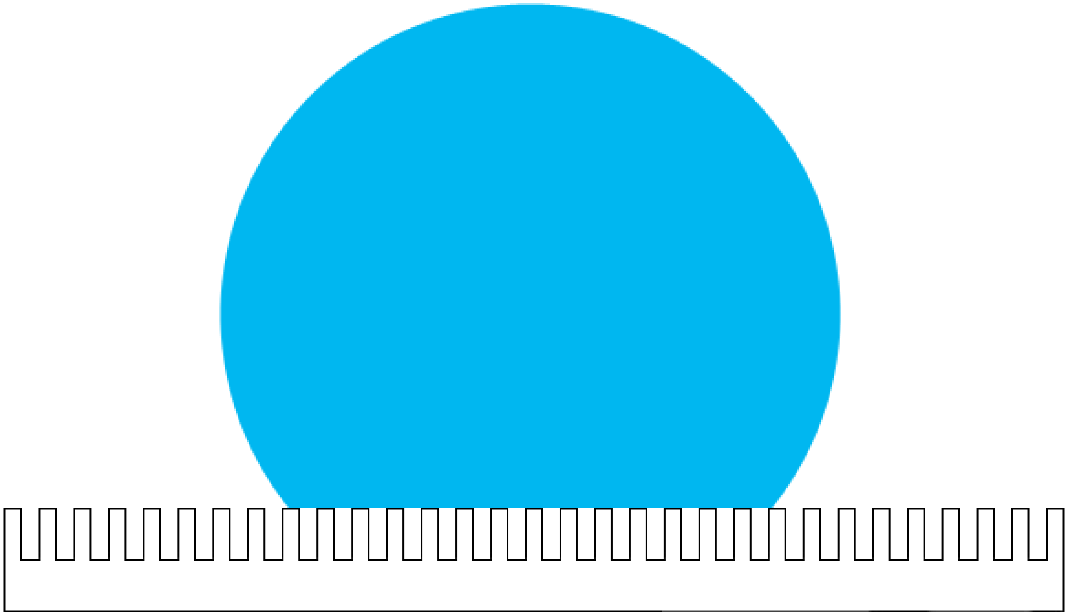


Figure 8: Cassie–Baxter Model

When dealing with a heterogeneous surface, the Wenzel model is not sufficient. A more complex model is needed to measure how the apparent contact angle changes when various materials are involved. This heterogeneous surface, like that seen in Figure 8, is explained using the Cassie-Baxter equation (Cassie's law):

$$\cos\theta^* = r_f\, f\, cos\,\theta_Y + f - 1$$

Here the r_f is the roughness ratio of the wet surface area and f is the fraction of solid surface area wet by the liquid. It is important to realize that when $f = 1$ and $r_f = r$, the Cassie–Baxter equations becomes the Wenzel equation. On the other hand, when there are many different fractions of surface roughness, each fraction of the total surface area is denoted by f_i.

A summation of all f_i equals 1 or the total surface. Cassie–Baxter can also be re-casted in the following equation:

$$\gamma\cos\theta^* = \sum_{n=1}^{N} f_i(\gamma_{\mathrm{i,sv}} - \gamma_{\mathrm{i,sl}})$$

Here γ is the Cassie-Baxter surface tension and between liquid and vapor, the $\gamma_{\mathrm{i,sv}}$ is the solid vapor surface tension of every component and $\gamma_{\mathrm{i,sl}}$ is the solid liquid surface tension of every component. A case that is worth mentioning is when the liquid drop is placed on the substrate and creates small air pockets underneath it. This case for a two component system is denoted by:

$$\gamma \cos \theta^* = f_1(\gamma_{1,\mathrm{sv}} - \gamma_{1,\mathrm{sl}}) + (1 - f_1)\gamma$$

Here the key difference to notice is that the there is no surface tension between the solid and the vapor for the second surface tension component. This is because we assume that the surface of air that is exposed is under the droplet and is the only other substrate in the system. Subsequently the equation is then expressed as (1 - *f*). Therefore the Cassie equation can be easily derived from the Cassie–Baxter equation. Experimental results regarding the surface properties of Wenzel versus Cassie–Baxter systems showed the effect of pinning for a Young angle of 180° to 90°, a region classified under the Cassie–Baxter model. This liquid air composite system is largely hydrophobic. After that point a sharp transition to the Wenzel regime was found where the drop wets the surface but no further than edges of the drop.

Precursor film

With the advent of high resolution imaging, researchers have started to obtain experimental data has led them to question the assumptions of the Cassie–Baxter equation when calculating the apparent contact angle. These groups believe that the apparent contact angle is largely dependent on the triple line. The triple line, which is in contact with the heterogeneous surface, cannot rest on the heterogeneous surface like the rest of the drop. In theory it should follow the surface imperfection. This bending in triple line is unfavorable and isn't seen in real world situations. A theory that preserves the Cassie–Baxter equation while at the same time explaining the presence of minimized energy state of the triple line hinges on the idea of a precursor film. This film of submicrometer thickness advances ahead of the motion of the droplet and is found around the triple line. Furthermore, this precursor film allows the triple line to bend and take different conformations that were originally considered unfavorable. This precursor fluid has been observed using environmental scanning electron microscopy (ESEM) in surfaces with pores formed in the bulk. With the introduction of the precursor film concept, the triple line can follow energetically feasible conformations and thereby correctly explaining the Cassie–Baxter model.

"Petal effect" vs. "lotus effect"

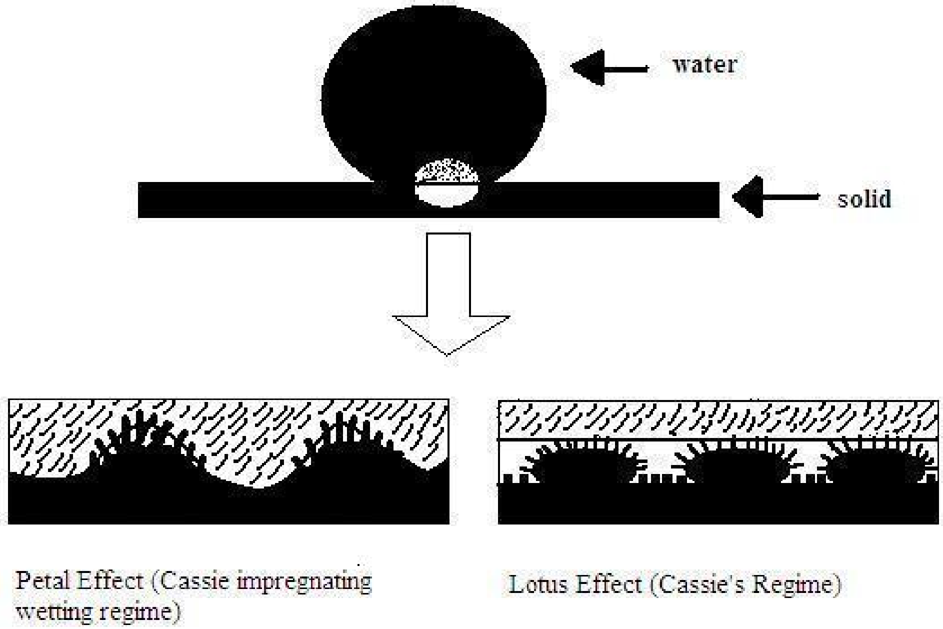


Figure 9: "Petal effect" vs. "lotus effect"

The intrinsic hydrophobicity of a surface can be enhanced by being textured with different length scales of roughness. The red rose takes advantage of this by using a hierarchy of micro- and nanostructures on each petal to provide sufficient roughness for superhydrophobicity. More specifically, each rose petal has a collection of micropapillae on the surface and each papillae, in turn, has many nanofolds. The term “petal effect” describes the fact that a water droplet on the surface of a rose petal is spherical in shape, but cannot roll off even if the petal is turned upside down. The water drops maintain their spherical shape due to the superhydrophobicity of the petal (contact angle of about 152.4°), but do not roll off because the petal surface has a high adhesive force with water.

When comparing the "petal effect" to the "lotus effect", it is important to note some striking differences. The surface structure of the lotus petal and the rose petal, as seen in Figure 9, can be used to explain the two different effects. The lotus petal has a randomly rough surface and low contact angle hysteresis, which means that the water droplet is not able to wet the microstructure spaces between the spikes. This allows air to remain inside the texture, causing a heterogeneous surface composed of both air and solid. As a result, the adhesive force between the water and the solid surface is extremely low, allowing the water to roll off easily (i.e. "self-cleaning" phenomena).

On the other hand, the rose petal's micro- and nanostructures are larger in scale than the lotus leaf, which allows the liquid film to impregnate the texture. However, as seen in Figure 9, the liquid can enter the larger scale grooves, but it cannot enter into the smaller grooves. This is known as the Cassie impregnating wetting regime. Since the liquid can wet the larger scale grooves, the adhesive force between the water and solid is very high. This explains why the water droplet will not fall off even if the petal is tilted at an angle or turned upside down. However, this effect will fail if the droplet has a volume larger than 10 µL because the balance between weight and surface tension is surpassed.

Cassie–Baxter to Wenzel transition

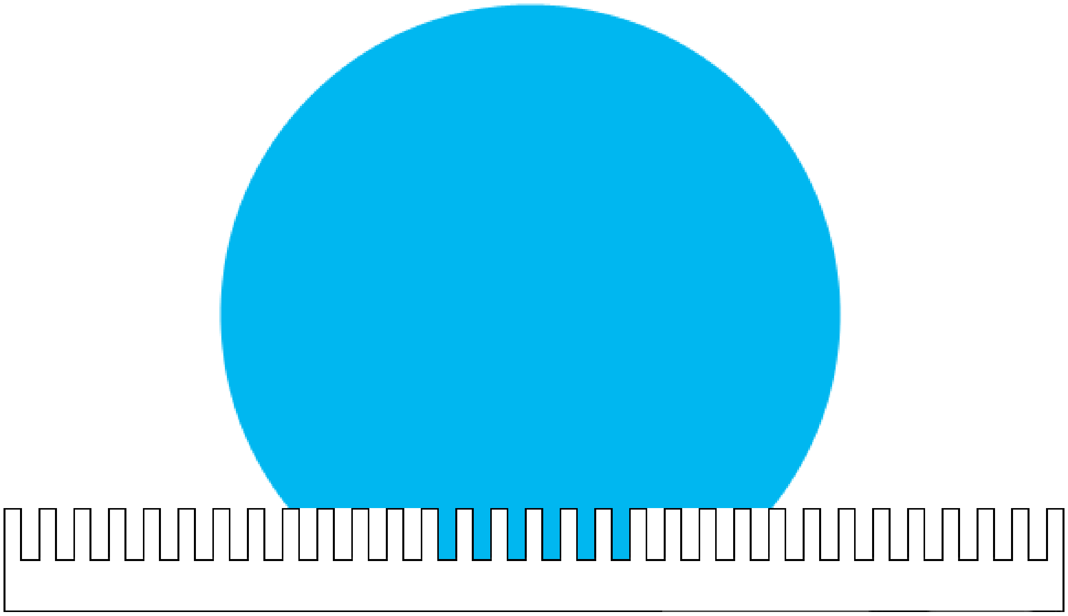


Figure 10: Mushroom state

In the Cassie–Baxter model, the drop sits on top of the textured surface with trapped air underneath. During the wetting transition from the Cassie state to the Wenzel state, the air pockets are no longer thermodynamically stable and liquid begins to nucleate from the middle of the drop, creating a "mushroom state," as seen in Figure 10. The penetration condition is given by the following equation:

$$\cos\theta_C = \frac{\phi - 1}{r - \phi}$$

where

- θ_C is the critical contact angle
- φ is the fraction of solid/liquid interface where drop is in contact with surface
- r is solid roughness (for flat surface, r = 1)

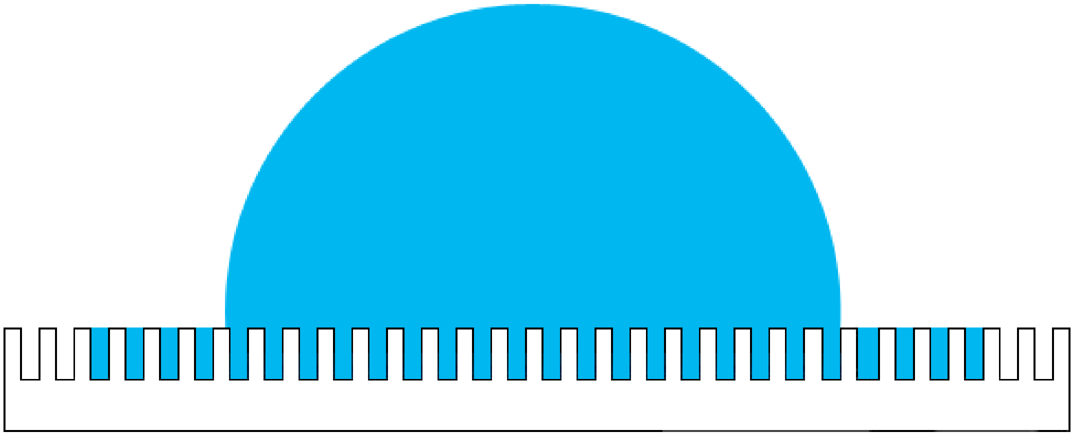


Figure 11: Penetration front spreads beyond drop

The penetration front propagates to minimize the surface energy until it reaches the edges of the drop, thus arriving at the Wenzel state. Since the solid can be considered an absorptive material due to its surface roughness, this phenomenon of spreading and imbibition is called hemi-wicking. The contact angles at which spreading/imbibition occurs are between $0 \leq \theta < \pi/2$.

The Wenzel model is valid between $\theta_C < \theta < \pi/2$. If the contact angle is less than Θ_C, the penetration front spreads beyond the drop and a liquid film forms over the surface. Figure 11 depicts the transition from the Wenzel state to the surface film state. The film smoothes the surface roughness and the Wenzel model no longer applies. In this state, the equilibrium condition and Young's relation yields:

$$\cos\theta^* = \phi\cos\theta_C + (1-\phi)$$

By fine tuning the surface roughness, it is possible achieves a transition between both super hydrophobic and super hydrophilic regions. Generally, the rougher the surface, the more hydrophobic it is.

Effect of surfactants on wetting

Many technological processes require control of liquid spreading over solid surfaces. When a drop is placed on a surface, it can completely wet, partially wet, or not wet the surface. By reducing the surface tension with surfactants, a non-wetting material can be made to become partially or completely wetting. The excess free energy (σ) of a drop on a solid surface is:

$$\sigma = \gamma S + \pi R^2 \gamma_{\mathrm{SL}} - \gamma_{\mathrm{SV}}$$

- γ is the liquid-vapor interfacial tension
- γ_{SL} is the solid-liquid interfacial tension
- γ_{SV} is the solid-vapor interfacial tension
- S is the area of liquid-vapor interface
- P is the excess pressure inside liquid
- R is the radius of droplet base

Based on this equation, the excess free energy is minimized when γ decreases, γ_{SL} decreases, or γ_{SV} increases. Surfactants are absorbed onto the liquid-vapor, solid-liquid, and solid-vapor interfaces, which modify the wetting behavior of hydrophobic materials to reduce the free energy. When surfactants are absorbed onto a hydrophobic surface, the polar head groups face into the solution with the tail pointing outward. In more hydrophobic surfaces, surfactants may form a bilayer on the solid, causing it to become more hydrophilic. The dynamic drop radius can be characterized as the drop begins to spread. Thus, the contact angle changes based on the following equation:

$$\cos\theta(t) = \cos\theta_0 + (\cos\theta_\infty - \cos\theta_0)(1 - \mathrm{e}^{\frac{-t}{\tau}})$$

- θ_0 is initial contact angle
- θ_∞ is final contact angle
- τ is the surfactant transfer time scale

As the surfactants are absorbed, the solid-vapor surface tension increases and the edges of the drop become hydrophilic. As a result, the drop spreads.

Chapter- 4

Hysteresis

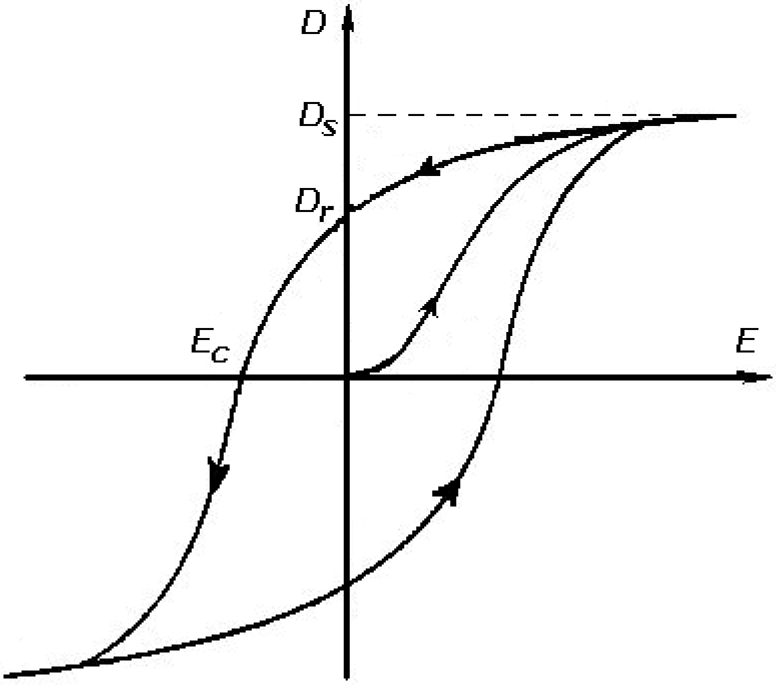


Fig. 1. Electric hysteresis loop of a ferroelectric material

Hysteresis refers to systems that may exhibit path dependence, or "rate-independent memory". In a deterministic system with no dynamics or hysteresis, it is possible to predict the system's output at an instant in time given only its input at that instant in time. In a system with hysteresis, this is not possible; the output depends in part on the internal state of system and not only on its input. There is no way to predict the system's output without looking at the history of the input (to determine the path that the input followed before it reached its current value) or inspecting the internal state of the system.

A system may be explicitly designed to exhibit hysteresis, especially in control theory. An example is the switching element of a thermostat that controls a furnace; this element has hysteresis. Schmitt triggers are examples of electronic circuits that exhibit hysteresis, in this case by introducing a positive feedback. Many physical systems naturally exhibit hysteresis. Hysteresis phenomena occur in magnetic materials, ferromagnetic materials and ferroelectric materials, as well as in the elastic, electric, and magnetic behavior of materials, in which a lag occurs between the application and the removal of a force or field and its subsequent effect. Electric hysteresis occurs when applying a varying electric field, and elastic hysteresis occurs in response to a varying force.

The word hysteresis is often used specifically to represent rate-independent state. This means that if some set of inputs $X(t)$ produce an output $Y(t)$, then the inputs $X(\alpha t)$ produce output $Y(\alpha t)$ for any $\alpha > 0$. The magnetized iron or the thermostat have this property. Not all systems with state (or, equivalently, with memory) have this property; for example, a linear low-pass filter has state, but its state is rate-dependent.

The term "hysteresis" is sometimes used in other fields, such as economics or biology, where it describes a memory, or lagging, effect.

History

The term "hysteresis" is derived from ὑστέρησις, an ancient Greek word meaning "deficiency" or "lagging behind"). It was coined by Sir James Alfred Ewing.

Some early work on describing hysteresis in mechanical systems was performed by James Clerk Maxwell. Subsequently, hysteresis models have received significant attention in the works of Preisach (Preisach model of hysteresis), Neel and Everett in connection with magnetism and absorption. A simple parametric description of various hysteresis loops may be found in ref. (with the model, substitution of rectangle, triangle or trapezoidal pulses instead of the harmonic functions also allows piecewise-linear hysteresis loops frequently used in discrete automatics to be built, see example in Fig. 4). More formal mathematical theory of systems with hysteresis was developed in 1970s by a group of Russian mathematicians led by Mark Krasnosel'skii, one of the founders of nonlinear analysis. He suggested an investigation of hysteresis phenomena using the theory of nonlinear operators.

Hysteresis was initially seen as problematic, but is now thought to be of great importance in technology. For example, the properties of hysteresis are applied when constructing non-volatile storage for computers; as hysteresis allows most superconductors to operate at the high currents needed to create strong magnetic fields. Hysteresis is also important in living systems. Many critical processes occurring in living (or dying) cells use hysteresis to help stabilize them against the various effects of random chemical fluctuations. Magnetic core losses (iron losses) in transformers are due to hysteresis.

Terminology

Rate-independent hysteresis

The memory, or lagging, effects which constitute hysteresis should not necessarily be interpreted as a simple time lag. Even relatively simple systems such as an electric circuit containing resistors and capacitors exhibit a time lag between the input and the output, but are not normally considered hysteretic. Typically there is a very short time scale over which the dynamic behavior and various related time dependences are observed. In magnetism, for example, the dynamic processes occurring on this very short time scale have been referred to as Barkhausen jumps.

Also, if observations are carried out over very long periods, creep or slow relaxation (typically toward true thermodynamic equilibrium, or other types of equilibria that depend on the nature of the system) can be noticed. This is also not normally considered to be hysteresis.

Hysteresis occurs when observations are carried out without regard for very swift dynamic phenomena or very slow relaxation phenomena and the system appears to display irreversible behavior whose rate is practically independent of the driving force rate. This rate-independent irreversible behavior is the key feature that distinguishes hysteresis from most other dynamic processes in many systems.

Hysteresis loop

If the displacement of a system with hysteresis is plotted on a graph against the applied force, the resulting curve is in the form of a loop. In contrast, the curve for a system without hysteresis is a single, not necessarily straight, line. Although the hysteresis loop depends on the material's physical properties, there is no complete theoretical description that explains the phenomenon. The family of hysteresis loops, from the results of different applied varying voltages or forces, form a closed space in three dimensions, called the hysteroid.

Manifestations

In engineering

Control systems

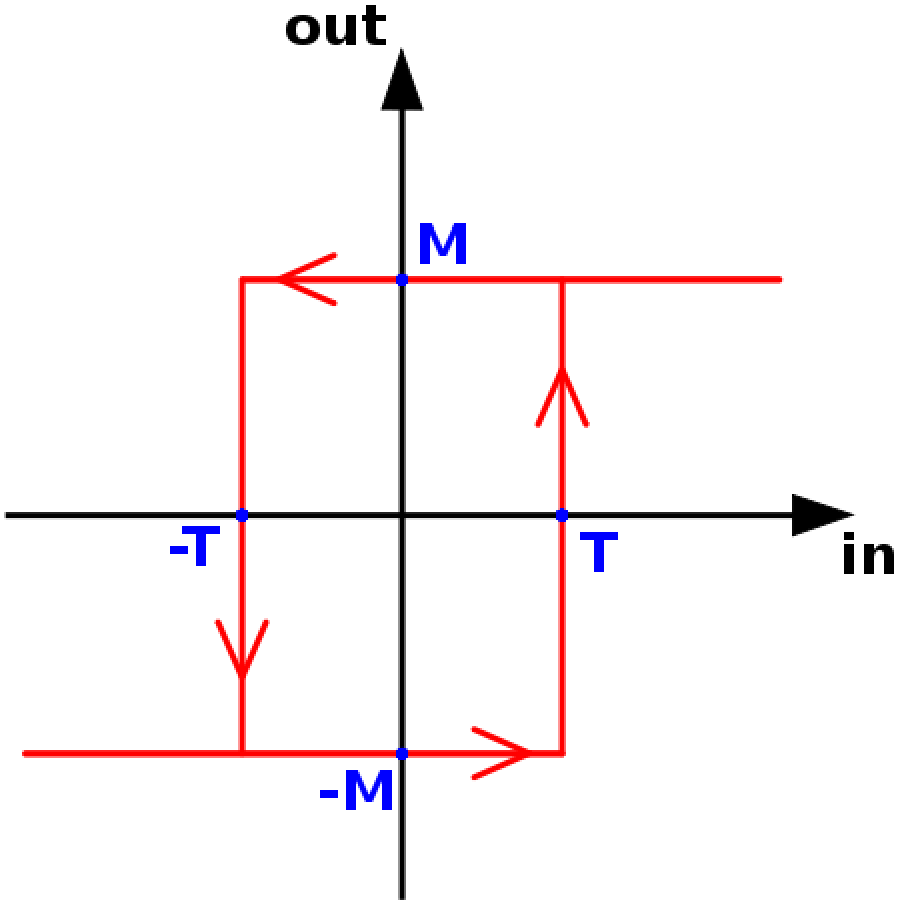


Fig. 4. Sharp hysteresis loop of a Schmitt trigger

Hysteresis can be used to filter signals so that the output reacts slowly by taking recent history into account. For example, a thermostat controlling a heater may turn the heater on when the temperature drops below A degrees, but not turn it off until the temperature rises above B degrees (e.g., if one wishes to maintain a temperature of 20 °C, then one might set the thermostat to turn the furnace on when the temperature drops below 18 °C, and turn it off when the temperature exceeds 22 °C). This thermostat has hysteresis. Thus the on/off output of the thermostat to the heater when the temperature is between A and B depends on the history of the temperature. This prevents rapid switching on and off as the temperature drifts around the set point. The furnace is either off or on, with nothing in between. The thermostat is a system; the input is the temperature, and the output is the furnace state. If the temperature is 21 °C, then it is not possible to predict whether the furnace is on or off without knowing the history of the temperature.

Similarly a pressure switch also exhibits hysteresis. Its pressure setpoints are substituted for those of temperature corresponding to a thermostat.

Electronic circuits

A Schmitt trigger is a simple electronic circuit that also exhibits this property. Often, some amount of hysteresis is intentionally added to an electronic circuit to prevent unwanted rapid switching. This and similar techniques are used to compensate for contact bounce in switches, or noise in an electrical signal.

A latching relay uses a solenoid to actuate a ratcheting motion that keeps the relay closed even if power to the relay is terminated.

Hysteresis is essential to the workings of the memristor, a circuit component which "remembers" changes in the current passing through it by changing its resistance.

User interface design

A hysteresis is sometimes intentionally added to computer algorithms. The field of user interface design has borrowed the term hysteresis to refer to times when the state of the user interface intentionally lags behind the apparent user input. For example, a menu that was drawn in response to a mouse-over event may remain on-screen for a brief moment after the mouse has moved out of the trigger region and the menu region. This allows the user to move the mouse directly to an item on the menu, even if part of that direct mouse path is outside of both the trigger region and the menu region. For instance, right-clicking on the desktop in most Windows interfaces will create a menu that exhibits this behavior.

In mechanics

Elastic hysteresis

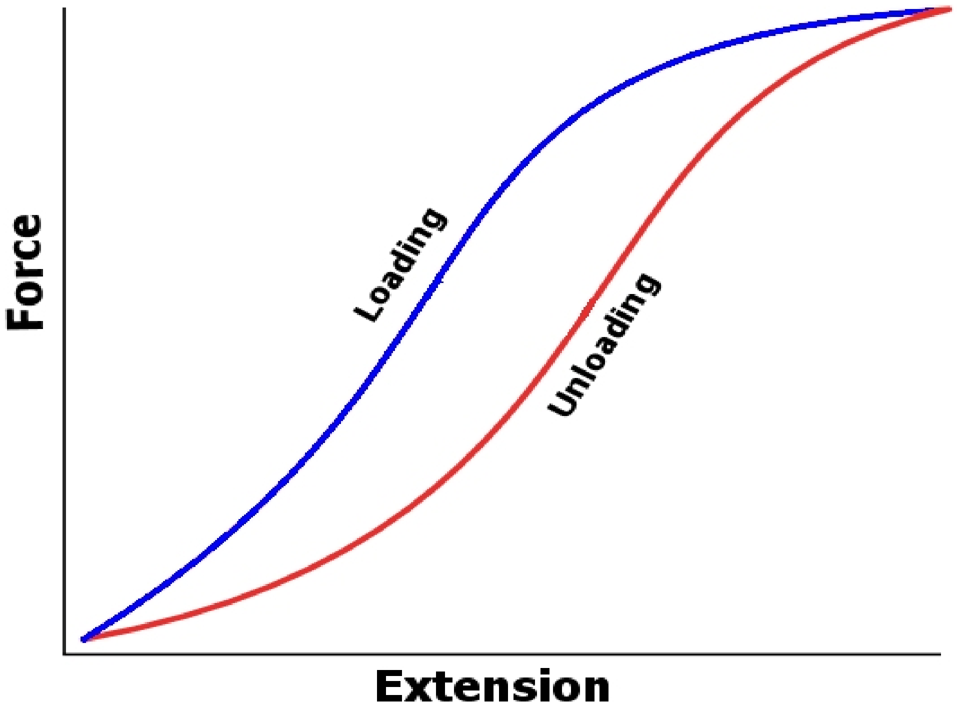


Fig. 3. Elastic hysteresis of an idealized rubber band. The area in the centre of the hysteresis loop is the energy dissipated as heat.

Elastic hysteresis was one of the first types of hysteresis to be examined.

A simple way to understand it is in terms of a rubber band with weights attached to it. If the top of a rubber band is hung on a hook and small weights are attached to the bottom of the band one at a time, it will get longer. As more weights are *loaded* onto it, the band will continue to extend because the force the weights are exerting on the band is increasing. When each weight is taken off, or *unloaded*, it will get shorter as the force is reduced. As the weights are taken off, each weight that produced a specific length as it was loaded onto the band now produces a slightly longer length as it is unloaded. This is because the band does not obey Hooke's law perfectly. The hysteresis loop of an idealized rubber band is shown in Fig. 3.

In one sense the rubber band was harder to stretch when it was being loaded than when it was being unloaded. In another sense, as one unloads the band, the cause (the force of the weights) lags behind the effect (the length) because a smaller value of weight produces the same length. In another sense more energy was required during the loading than the unloading; that energy must have gone somewhere, it was dissipated or "lost" as heat.

Elastic hysteresis is more pronounced when the loading and unloading is done quickly than when it is done slowly. Some materials such as hard metals don't show elastic hysteresis under a moderate load, whereas other hard materials like granite and marble do. Materials such as rubber exhibit a high degree of elastic hysteresis.

A word of caution: rubber behaves like a gas. When the rubber band is stretched it heats up. If it is suddenly released, the rubber cools down, very easy to perceive just by touching. So, there is a large hysteresis from the thermal exchange with the environment and a smaller hysteresis due to internal friction within the rubber. This proper, intrinsic hysteresis could be measured only if adiabatic isolation of the rubber band is imposed.

Contact angle hysteresis

The contact angle formed between a liquid and solid phase will exhibit a range of contact angles that are possible. There are two common methods for measuring this range of contact angles. The first method is referred to as the tilting base method. Once a drop is dispensed on the surface with the surface level, the surface is then tilted from 0° to 90°. As the drop is tilted, the downhill side will be in a state of imminent wetting while the uphill side will be in a state of imminent dewetting. As the tilt increases the downhill contact angle will increase and represents the advancing contact angle while the uphill side will decrease; this is the receding contact angle. The values for these angles just prior to the drop releasing will typically represent the advancing and receding contact angles. The difference between these two angles is the contact angle hysteresis. The second method, often referred to as the add/remove volume method. When the maximum liquid volume is removed from the drop without the interfacial area decreasing the receding contact angle is thus measured. When volume is added to the maximum before the interfacial area increases, this is the advancing contact angle. As with the tilt method, the difference between the advancing and receding contact angles is the contact angle hysteresis. Most researchers prefer the tilt method; the add/remove method requires that a tip or needle stay embedded in the drop which can affect the accuracy of the values, especially the receding contact angle.

Adsorption hysteresis

Hysteresis can also occur during physical adsorption processes. In this type of hysteresis, the quantity adsorbed is different when gas is being added than it is when being removed. The specific causes of adsorption hysteresis are still an active area of research, but it is linked to differences in the nucleation and evaporation mechanisms inside mesopores. These mechanisms are further complicated by effects such as cavitation and pore blocking.

In physical adsorption, hysteresis is evidence of mesoporosity-indeed, the definition of mesopores (2-50 nm) is associated with the appearance (50 nm) and disappearance (2 nm) of mesoporosity in nitrogen adsorption isotherms as a function of Kelvin radius. An adsorption isotherm showing hysteresis is said to be of Type IV (for a wetting adsorbate) or Type V (for a non-wetting adsorbate), and hysteresis loops themselves are classified according to how symmetric the loop is. Adsorption hysteresis loops also have the unusual property that it is possible to scan within a hysteresis loop by reversing the direction of adsorption while on a point on the loop. The resulting scans are called "crossing," "converging," or "returning," depending on the shape of the isotherm at this point.

Matric potential hysteresis

The relationship between matric water potential and water content is the basis of the water retention curve. Matric potential measurements (Ψ_m) are converted to volumetric water content (θ) measurements based on a site or soil specific calibration curve. Hysteresis is a source of water content measurement error. Matric potential hysteresis arises from differences in wetting behaviour causing dry medium to re-wet; that is, it depends on the saturation history of the porous medium. Hysteretic behaviour means that, for example, at a matric potential (Ψ_m) of 5 kPa, the volumetric water content (θ) of a fine sandy soil matrix could be anything between 8% to 25%.

Tensiometers are directly influenced by this type of hysteresis. Two other types of sensors used to measure soil water matric potential are also influenced by hysteresis effects within the sensor itself. Resistance blocks, both nylon and gypsum based, measure matric potential as a function of electrical resistance. The relation between the sensor's electrical resistance and sensor matric potential is hysteretic. Thermocouples measure matric potential as a function of heat dissipation. Hysteresis occurs because measured heat dissipation depends on sensor water content, and the sensor water content–matric potential relationship is hysteretic. As of 2002, only desorption curves are usually measured during calibration of soil moisture sensors. Despite the fact that it can be a source of significant error, the sensor specific effect of hysteresis is generally ignored.

In materials

Magnetic and electrical hysteresis

The phenomenon of hysteresis in ferromagnetic and ferroelectric materials can conceptually be explained as follows: a system can be divided into subsystems or domains, much larger than an atomic volume, but still microscopic. Such domains occur in ferroelectric and ferromagnetic systems, since individual dipoles tend to group with each other, forming a small isotropic region. Each of the system's domains can be shown to have a metastable state. The metastable domains can in turn have two or more substates. Such a *metastable state* fluctuates widely from domain to domain, but the average represents the configuration of lowest energy. The *hysteresis* is simply the sum of all domains, or the sum of all metastable states.

Magnetic hysteresis

Hysteresis is well known in ferromagnetic materials. When an external magnetic field is applied to a ferromagnet, the atomic dipoles align themselves with the external field.

Even when the external field is removed, part of the alignment will be retained: the material has become *magnetized*. For example, a piece of iron that is brought into a magnetic field retains some magnetization, even after the external magnetic field is removed. Once magnetized, the iron will stay magnetized indefinitely. To demagnetize the iron, it would be necessary to apply a magnetic field in the opposite direction. This is the effect that provides the element of memory in a hard disk drive.

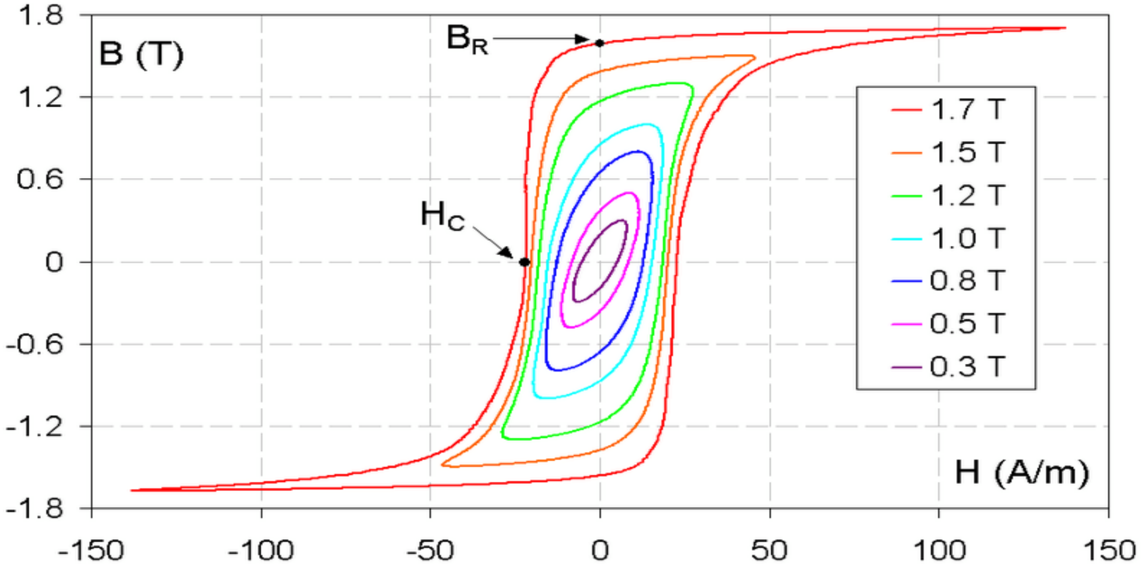


Fig. 2. A family of B-H loops for grain-oriented electrical steel in sinusoidally varying fields with amplitudes from 0.3 T to 1.7 T. B_R denotes *remanence* and H_C is the *coercivity*.

The relationship between magnetic field strength (H) and magnetic flux density (B) - Fig. 2, is not linear in such materials. If the relationship between the two is plotted for increasing levels of field strength, it will follow a curve up to a point where further increases in magnetic field strength will result in no further change in flux density. This condition is called magnetic saturation.

If the magnetic field is now reduced linearly, the plotted relationship will follow a different curve back towards zero field strength at which point it will be offset from the original curve by an amount called the *remanent flux density* or remanence.

If this relationship is plotted for all strengths of applied magnetic field the result is a sort of *S- shaped* loop. The width of the middle section of the loop describes the amount of hysteresis, related to the coercivity of the material.

Its practical effects might be, for example, to cause a relay to be slow to release due to the remaining magnetic field continuing to attract the armature when the applied electric current to the operating coil is removed.

This curve for a particular material influences the design of a magnetic circuit, This is also a very important effect in magnetic tape and other magnetic storage media like hard disks. In these materials it would seem obvious to have one polarity represent a bit, say north for 1 and south for 0. However, to change the storage from one to the other, the hysteresis effect requires the knowledge of what was already there, because the needed field will be different in each case. In order to avoid this problem, recording systems first overdrive the entire system into a known state using a process known as bias. Analog magnetic recording also uses this technique. Different materials require different biasing, which is why there is a selector switch for this on the front of most cassette recorders.

In order to minimize this effect and the energy losses associated with it, ferromagnetic substances with low coercivity and low hysteresis loss are used, like permalloy.

In many applications small hysteresis loops are driven around points in the B-H plane. Loops near the origin have a higher μ. The smaller loops the more they have a soft magnetic (lengthy) shape. As a special case, a damped AC field demagnetizes any material provided it is initially sufficiently intense.

Magnetic field hysteresis loss causes heating. This is an energy loss mechanism in power transformers and electric motors and other apparatus using ferromagnetic cores.

Electrical hysteresis

Electrical hysteresis typically occurs in ferroelectric material, where domains of polarization contribute to the total polarization. Polarization is the electrical dipole moment (either $C \cdot m^{-2}$ or $C \cdot m$).

Liquid-solid phase transitions

Hysteresis manifests itself in state transitions when melting temperature and freezing temperature do not agree. For example, agar melts at 85 °C and solidifies from 32 to 40 °C. This is to say that once agar is melted at 85 °C, it retains a liquid state until cooled to 40 °C. Therefore, from the temperatures of 40 to 85 °C, agar can be either solid or liquid, depending on which state it was before.

In biology

Cell biology and genetics

Cells undergoing cell division exhibit hysteresis in that it takes a higher concentration of cyclins to switch them from G2 phase into mitosis than to stay in mitosis once begun.

Darlington in his classic works on genetics discussed hysteresis of the chromosomes, by which he meant "failure of the external form of the chromosomes to respond immediately to the internal stresses due to changes in their molecular spiral", as they lie in a somewhat rigid medium in the limited space of the cell nucleus.

In developmental biology, cell type diversity is regulated by long range-acting signaling molecules called morphogens that pattern uniform pools of cells in a concentration- and time-dependent manner. The morphogen Sonic Hedgehog (Shh), for example, acts on limb bud and neural progenitors to induce expression of a set of homeodomain-containing transcription factors to subdivide these tissues into distinct domains. It has been shown that these tissues have a 'memory' of previous exposure to Shh. In neural tissue, this hysteresis is regulated by a homeodomain (HD) feedback circuit that amplifies Shh signaling. In this circuit, expression of Gli transcription factors, the executors of the Shh pathway, is suppressed. Glis are processed to repressor forms (GliR) in the absence of Shh, but in the presence of Shh, a proportion of Glis are maintained as full-length proteins allowed to translocate to the nucleus, where they act as activators (GliA) of transcription. By reducing Gli expression then, the HD transcription factors reduce the total amount of Gli (GliT), so a higher proportion of GliT can be stabilized as GliA for the same concentration of Shh.

Neuroscience

The property by which some neurons do not return to their basal conditions from a stimulated condition immediately after removal of the stimulus is an example of hysteresis.

Respiratory physiology

Lung hysteresis is evident when observing the compliance of a lung on inspiration versus expiration. The difference in compliance (volume/pressure) is due to the additional energy required during inspiration to recruit and inflate additional alveoli.

The transpulmonary pressure vs Volume curve of inhalation is different from the Pressure vs Volume curve of exhalation, the difference being described as hysteresis. Lung volume at any given pressure during inhalation is less than the lung volume at any given pressure during exhalation.

In economics

Economic systems can exhibit hysteresis. For example, export performance is subject to strong hysteresis effects: because of the fixed transportation costs it may take a big push to start a country's exports, but once the transition is made, not much may be required to keep them going.

Hysteresis is a hypothesized property of unemployment rates. It's possible that there is a ratchet effect, so a short-term rise in unemployment rates tends to persist. An example is the notion that inflationary policy leads to a permanently higher 'natural' rate of unemployment (NAIRU), because inflationary expectations are 'sticky' downward due to wage rigidities and imperfections in the labour market. Another channel through which hysteresis can occur is through learning by doing. Workers who lose their jobs due to a temporary shock may become permanently unemployed because they miss out on the job training and skill acquisition that normally takes place. This explanation has been invoked, by Olivier Blanchard among others, as explaining the differences in long run unemployment rates between Europe and the United States.

Hysteresis occurs in applications of game theory to economics, in models with product quality, agent honesty or corruption of various institutions. Slightly different initial conditions can lead to opposite outcomes and resulting stable "good" and "bad" equilibria.

Another area where hysteresis phenomena are found is capital controls. A developing country can ban a certain kind of capital flow (e.g. engagement with international private equity funds), but when the ban is removed, the system takes a long time to return to the pre-ban state.

Applications

Hysteresis represents states, and the characteristic curve shape is sometimes remiscent of a two-value state, also called a bistable state. The hysteresis curve really contains *infinitely* many states, but a simple application is to let the threshold regions (usually to the left and to the right) represent respectively the on and off states. In this way, the system can be regarded as bistable. Note that even if no external field is applied, the position of the hysteresis curve might change with time: it is not necessarily *stationary*; i.e. the system may not stay in exactly the same state as it had previously. The system might need new energy transfer to be stationary.

The hysteresis effect can be used when connecting complex circuits with the so-called passive matrix addressing. This scheme is praised as a technique that can be used in modern nanoelectronics, electrochrome cells, memory effect, etc. In this scheme, shortcuts are made between adjacent components and the hysteresis helps to keep the components in a particular state while the other components change states. That is, one can address all rows at the same time instead of doing each individually.

In economics, hysteresis is used extensively in the area of labor markets. According to theories based on hysteresis, economic downturns (recession) result in an individual becoming unemployed, losing his/her skills (commonly developed 'on the job'), demotivated/disillusioned, and employers may use time spent in unemployment as a screen. In times of an economic upturn or 'boom', the workers affected will not share in the prosperity, remaining Long-Term Unemployed (>52 weeks). Hysteresis has been put forward as a possible explanation for the poor unemployment performance of many economies in the 1990s. Labor market reform, and/or strong economic growth, may not therefore aid this pool of long-term unemployed, and thus specific targeted training programs are presented as a possible policy solution.

In the field of audio electronics, a noise gate often implements hysteresis intentionally to prevent the gate from "chattering" when signals close to its threshold are applied.

Small vehicle suspensions using rubber (or other elastomers) can achieve the dual function of springing and damping because rubber, unlike metal springs, has pronounced hysteresis and does not return all the absorbed compression energy on the rebound. Mountain bikes have frequently made use of elastomer suspension, as did the original Mini car.

Additional considerations

Models of hysteresis

Each subject that involves hysteresis has models that are specific to the subject. In addition, there are models that capture general features of many systems with hysteresis. An example is the Preisach model of hysteresis, which represents a hysteresis nonlinearity as a superposition of square loops called hysterons.

The Bouc-Wen model of hysteresis is often used to describe non-linear hysteretic systems. It was introduced by Bouc and extended by Wen, who demonstrated its versatibility by producing a variety of hysteretic patterns. This model is able to capture in analytical form, a range of shapes of hysteretic cycles which match the behaviour of a wide class of hysteretical systems; therefore, given its versability and mathematical tractability, the Bouc-Wen model has quickly gained popularity and has been extended and applied to a wide variety of engineering problems, including multi-degree-of-freedom (MDOF) systems, buildings, frames, bidirectional and torsional response of hysteretic systems two- and three-dimensional continua, soil liquefaction, and base isolation systems among others. The Bouc-Wen model and its variants/extensions have been used in applications of structural control, in particular in the modeling of the behaviour of magneto-rheological dampers, base isolation devices for buildings and other kinds of damping devices; it has also been in the modelling and analysis of structures built of reinforced concrete, steel, mansory and timber.

Energy

When hysteresis occurs with extensive and intensive variables, the work done on the system is the area under the hysteresis graph.

Chapter- 5

Hot-melt Adhesive

A hot glue gun loaded with a glue stick

Hot melt adhesive (**HMA**), also known as **hot glue**, is a form of thermoplastic adhesive that is commonly supplied in solid cylindrical sticks of various diameters, designed to be melted in an electric *hot glue gun*. The gun uses a continuous-duty heating element to melt the plastic glue, which may be pushed through the gun by a mechanical trigger mechanism, or directly by the user. The glue squeezed out of the heated nozzle is initially hot enough to burn and blister skin. The glue is tacky when hot, and hardens in anywhere from a few seconds to one minute. Hot melt adhesives can also be applied by dipping or spraying.

In industrial use, hot melt adhesives provide several advantages over solvent-based adhesives. Volatile organic compounds are reduced or eliminated, and the drying or curing step of manufacture is eliminated. Hot melt adhesives have long shelf life and usually can be disposed of without special precautions. Some of the disadvantages involve thermal load of the substrate, limiting use to substrates not sensitive to higher temperatures, and loss of bond strength at higher temperatures, up to complete melting of the adhesive. This can be reduced by using a reactive adhesive that after solidifying undergoes further curing e.g. by moisture (e.g. reactive urethanes and silicones), or is cured by ultraviolet radiation. Some HMAs may not be resistant to chemical attacks and weathering. HMAs do not lose thickness during solidifying; solvent-based adhesives may lose up to 50-70% of layer thickness during drying.

Glue sticks

Glue sticks are manufactured in several diameters for different glue guns. The most-used size has a diameter of 11 millimetres (0.43 in). Sticks are available in various lengths, from about 10 centimetres (3.9 in) up, although guns will take sticks of any length. Thinner 7 mm (0.28 in) sticks are also used. Hot-melt and low temperature glue sticks are available for different types of guns, and some dual-use sticks melt at low temperatures but can be used at high temperatures without degradation. Hot melt adhesives are also available as granules, powder, slats, blocks, foils, ribbons, and solutions.

For domestic use, only a few types of stick are available, and they are more or less interchangeable. For industrial use, many types of sticks are available for special purposes, with the most common diameters being 12 mm (0.47 in), 15 mm (0.59 in), and 45 mm (1.8 in). Compositions resistant to plasticizers, usually based on polyamides, are needed for gluing PVC. Sticks have different *open time* and *set time*, varying from a second or two to several minutes; the times depend on glue temperature, substrate, rate of heat loss from the glue mass, etc. A range of values of viscosity and heat resistance of the bond are available.

Important properties

The hot-melt adhesives have a number of important properties, making them suitable for different applications:

- Open time, the working time to make a bond, where the surface still retains sufficient tack, can range from seconds for fast-setting HMAs to infinity for pressure-sensitive adhesives
- Set time, time to form a bond of acceptable strength
- Bond-formation temperature, minimum temperature below which sufficient wetting of substrates do not occur
- Melt viscosity, one of the most important properties. Influences the spread of applied adhesive, and the wetting of the surfaces. Temperature-dependent, higher temperature lowers viscosity.

- Melt flow index, a value inversely proportional to the molecular weight of the base polymer. High melt flow index adhesives are easy to apply but have poor mechanical properties due to short polymer chains. Low melt flow index adhesives have better properties but are more difficult to apply.
- Surface energy, which influences wetting of different kinds of surfaces.
- Pot life stability, the degree of stability in molten state, the tendency to decompose and char. Important for industrial processing where the adhesives are molten for prolonged periods before deposition.
- Tack, the degree of surface stickiness of the adhesive; influences the strength of the bond between wetted surfaces.

Materials used

Hot glue sticks are usually based on one or more base material, with various additives. The composition is usually formulated to have glass transition temperature (onset of brittleness) below the lowest service temperature and a suitably high melt temperature. The degree of crystallization should be as high as possible but within limits of allowed shrinkage. The melt viscosity and the crystallization rate (and corresponding open time) can be tailored for the application. Faster crystallization rate usually implies higher bond strength. To reach the properties of semicrystalline polymers, amorphous polymers would require too high molecular weights and therefore unreasonably high melt viscosity; the use of amorphous polymers in hot melt adhesives is therefore usually only as modifiers and additives. Some polymers can form hydrogen bonds between the chains, forming pseudo-cross-links strengthening the polymer.

The nature of the polymer and the tackifier additive influences the nature of mutual molecular interaction and interaction with the substrate; e.g. the EVA together with terpene-phenol resin (TPR) tackifiers display acid-base interactions between the carbonyl groups of vinyl acetate and hydroxyl groups of TPR, complexes are formed between phenolic rings of TPR and hydroxyl groups on the surface of aluminium substrates, and interactions between carbonyl groups and silanol groups on surfaces of glass substrates are formed. Polar groups, hydroxyls and amine groups can form acid-base and hydrogen bonds with polar groups on substrates like paper or wood or natural fibers. Nonpolar polyolefin chains interact well with nonpolar substrates. Good wetting of the substrate is essential for forming a satisfying bond between the adhesive and the substrate. More polar compositions tend to have better adhesion due to their higher surface energy. Amorphous adhesives deform easily, tend to dissipate most of mechanical strain within their structure, passing only small loads on the adhesive-substrate interface; even a relatively weak nonpolar-nonpolar surface interaction can then form a fairly strong bond prone primarily to a cohesive failure. The distribution of molecular weights and degree of crystallinity influences the width of melting temperature range. Polymers with crystalline nature tend to be more rigid and have higher cohesive strength than the corresponding amorphous ones, but also transfer more strain to the adhesive-substrate interface. Higher molecular weight of the polymer chains provides higher tensile strength and heat resistance. Presence of unsaturated bonds makes the adhesive more susceptible to autoxidation and UV degradation and necessitates use of antioxidants and stabilizers.

The adhesives are usually clear or translucent, colorless, straw-colored, tan, or amber. Pigmented versions are also made. Materials containing polar groups, aromatic systems, and double and triple bonds tend to appear darker than non-polar fully saturated substances; when a water-clear appearance is desired, suitable polymers and additives, e.g. hydrogenated tackifying resins, have to be used.

Increase of bond strength and service temperature can be achieved by formation of cross-links in the polymer after solidification. This can be achieved by using polymers undergoing curing with residual moisture (e.g. reactive polyurethanes, silicones), exposition to ultraviolet radiation, electron irradiation, or by other methods.

Resistance to water and solvents is critical in some applications. E.g. in textile industry, resistance to dry cleaning solvents may be required. Permeability to gases and water vapor may or may not be desirable. Non-toxicity of both the base materials and additives and absence of odors is important for food packaging.

Mass consumption articles, e.g. diapers and hygienic products, necessitate development of biodegradable HMAs. Research is being performed on e.g. lactic acid polyesters, polycaprolactone with soy protein, etc.

Some of the possible base materials are:

- Ethylene-vinyl acetate (EVA) copolymers, low-performance, the low-cost and most common material for the glue sticks (e.g. the light amber colored Thermogrip GS51, GS52, and GS53). They provide sufficient strength between 30-50 °C but are limited below 60-80°C and have low creep resistance under load. The vinyl acetate monomer content is about 18–29 percent by weight of the polymer. High amounts of tackifiers and waxes are often used; an example composition is 30-40% of EVA copolymer (provides strength and toughness), 30-40% of tackifier resin (improves wetting and tack), 20-30% of wax (usually paraffin-based; reduces viscosity, alters setting speed, reduces cost), and 0.5-1% of stabilizers. Fillers can be added for special applications. Can be formulated for service temperatures ranging from -40°C to +80°C, and for both short and long open times and a wide range of melt viscosities. High stability at elevated temperatures and resistance to ultraviolet radiation, which can be further enhanced with suitable stabilizers. High vinylacetate content can serve for formulating a hot-melt pressure sensitive adhesive (HMPSA). EVA formulations are compatible with paraffin. EVA was the base for the original hot melt composition. The composition of the copolymer influences its properties; increased content of ethylene promotes adhesion to nonpolar substrates, e.g. polyethylene, while increased content of vinyl acetate promotes adhesion to polar substrates, e.g. paper. Higher ethylene content also increases mechanical strength, block resistance, and paraffin solubility. Higher vinyl acetate content provides higher flexibility, adhesion, hot tack, and better low-temperature performance. Adhesive grade EVA usually contains 14-35% vinyl acetate. Lower molecular weight chains provide lower melt viscosity, better wetting, and better adhesion to porous surfaces. Higher molecular weights provide better cohesion at elevated temperatures and better low-temperature behavior. Increased ratio of vinyl acetate lowers the crystallinity of the material, improves optical clarity, flexibility and toughness, and worsens resistance to solvents. EVA can be crosslinked by e.g. peroxides, yielding a thermosetting material. EVAs can be compounded with aromatic hydrocarbon resins. Grafting butadiene to EVA improves its adhesion. Its dielectric properties are poor due to high content of polar groups, the dielectric loss is moderately high. Polypropylene HMAs are a better choice for high-frequency electronics. EVAs are optically clearer and more gas and vapor permeable than polyolefins. Nearly half of EVA HMAs is used in packaging applications. Cryogenic grinding of EVAs can provide small, water-dispersible particles for heat-seal applications. EVA can degrade primarily by loss of loss of acetic acid and formation of a double bond in the chain, and by oxidative degradation. EVA can be compounded into a wide range of HMAs, from soft pressure-sensitive adhesives to rigid structural adhesives for furniture construction.

    - Ethylene-acrylate copolymers have lower glass transition temperature and higher adhesion even to difficult substrates than EVA. Better thermal resistance, increased adhesion to metals and glass. Suitable for low temperature use. Ethylene-vinylacetate-maleic anhydride and ethylene-acrylate-maleic anhydride terpolymers offer very high performance. Examples are ethylene *n*-butyl acrylate (EnBA), ethylene-acrylic acid (EAA) and ethylene-ethyl acetate (EEA).

- Polyolefins (PO) (polyethylene (usually LDPE but also HDPE; HDPE has higher melting point and better temperature resistance), atactic polypropylene (PP or APP), polybutene-1, oxidized polyethylene, etc.), low-performance, for difficult-to-bond plastics. Very good adhesion to polypropylene, good moisture barrier, chemical resistance against polar solvents and solutions of acids, bases, and alcohols. Longer open time in comparison with EVA and polyamides. Polyolefins have low surface energy and provide good wetting of most metals and polymers. Polyolefins made by metallocene catalyzed synthesis have narrow distribution of molecular weight and correspondingly narrow melting temperature range. Due to the relatively high crystallinity, polyethylene-based glues tend to be opaque and, depending on additives, white or yellowish. Polyethylene hot melts have high pot life stability, are not prone to charring, and are suitable for moderate temperature ranges and on porous non-flexible substrates. Nitrogen or carbon dioxide can be introduced into the melt, forming a foam which increases spreading and open time and decreases transfer of heat to the substrate, allowing use of more heat-sensitive substrates; polyethylene-based HMAs are usually used. Foamable HMAs are available on the market since 1981. Amorphous polypropylene HMAs have good dielectric properties, making them suitable for use at high frequencies. PE and APP are usually used on their own or with just a small amount of tackifiers (usually hydrocarbons) and waxes (usually paraffins or microcrystalline waxes, for lower cost, improved anti-blocking, and altered open time and softening temperature). The molecular weight of the polymer is usually lower. Lower molecular weights provide better low-temperature performance and higher flexibility, higher molecular weights increase the seal strength, hot tack, and melt viscosity.

  - Polybutene-1 and its copolymers are soft and flexible, tough, partially crystalline, and slowly crystallizing with long open times. The low temperature of recrystallization allows for stress release during formation of the bond. Good bonding to nonpolar surfaces, worse bonding to polar ones. Good for rubber substrates. Can be formulated as pressure-sensitive.
  - Amorphous polyolefin (APO/APAO) polymers are compatible with many solvents, tackifiers, waxes, and polymers; they find wide use in many adhesive applications. APO hot melts have good fuel and acid resistance, moderate heat resistance, are tacky, soft and flexible, have good adhesion and longer open times than crystalline polyolefins. APOs tend to have lower melt viscosity, better adhesion, longer open times and slow set times than comparable EVAs. Some APOs can be used alone, but often they are compounded with tackifiers, waxes, and plasticizers (e.g. mineral oil, poly-butene oil). Examples of APOs are e.g. amorphous (atactic) propylene (APP), amorphous propylene/ethylene (APE), amorphous propylene/butene (APB), amorphous propylene/hexene (APH), amorphous propylene/ethylene/butene. APP is harder than APE, which is harder than APB, which is harder than APH, in accordance with decreasing crystallinity. APOs show relatively low cohesion, the entangled polymer chains have fairly high degree of freedom of movement. Under mechanical load, most of the strain is dissipated by elongation and disentanglement of polymer chains, and only a small fraction reaches the adhesive-substrate interface. Cohesive failure is therefore a more common failure mode of APOs.
- Polyamides and polyesters, high-performance
  - Polyamides (PA), high-performance, for severe environments; high-temperature glues; typically applied at over 200 °C, but can degrade and char during processing. In molten state can somewhat degrade by atmospheric oxygen. High application temperature. High range of service temperatures, generally showing adequate bonding from -40 to 70°C; some compositions allow operation to 185°C if they do not have to carry load. Resistant to plasticizers, therefore suitable for gluing polyvinyl chloride; only polyamides derived from secondary diamines however provide a satisfying bond. Resistant to oils and gasoline. Good adhesion to many substrates, e.g. metal, wood, vinyl, ABS, and treated polyethylene and polypropylene. Some formulations are UL-approved for electrical applications requiring reduced flammability. Three groups are employed, with low, intermediate, and high molecular weight; the low MW ones are low-temperature melting and easy to apply, but have lower tensile strength, lower tensile-shear strength, and lower elongation than the high-MW ones. The high-MW ones require sophisticated extruders and are used as high-performance structural adhesives. The presence of hydrogen bonds between the polymer chains gives polyamides a high strength at even low molecular weights, in comparison with other polymers.

    Hydrogen bonds also provide retention of most of the adhesive strength up almost to the melting point; however they also make the material more susceptible to permeation of moisture in comparison with polyesters. Can be formulated as soft and tacky or as hard and rigid. Niche applications, together with polyesters taking less than 10% of total volume of hot melt adhesives market. Absorption of moisture may lead to foaming during application as water evaporates during melting, leaving voids in the adhesive layer which degrade mechanical strength. Polyamide HMAs are usually composed of a dimer acid with often two or more different diamines. The dimer acid usually presents 60-80% of the total polyamide mass, and provides amorphous nonpolar character. Linear aliphatic amines, e.g. ethylene diamine and hexamethylene diamine, provide hardness and strength. Longer chain amines, e.g. dimer amine, reduce the amount of hydrogen bonds per volume of material, resulting in lower stiffness. Polyether diamines provide good low-temperature flexibility. Piperazine and similar diamines also reduce the number of hydrogen bonds. Only polyamides based on piperazine and similar secondary amines form satisfactory bond with polyvinyl chloride; primary amines form stronger hydrogen bonds within the adhesive, secondary amines can act only as proton acceptors, don't form hydrogen bonds within the polyamide, and are therefore free to form weaker bonds with vinyl, probably with the hydrogen atom adjanced to the chlorine.
  - Polyesters, similar to the ones used for synthetic fibers. High application temperature. Synthetized from a diol and a dicarboxylic acid. The length of the diol chain has major influence to the material's properties; with increasing diol chain length the melting point increases, the crystallization rate increases, and the degree of crystallization decreases. Both the diol and acid influence the melting point. In comparison with similar polyamides, due to absence of hydrogen bonds, polyesters have lower strength and melting point, but are much more resistant to moisture, though still susceptible. In other parameters, and in applications where these factors do not play a role, polyesters and polyamides are very similar. Polyesters are often used for bonding fabrics. They can be used on their own, or blended with large amounts of additives. They are used where high tensile strength and high temperature resistance are needed. Most polyester hot melt adhesives have high degree of crystallinity. Niche applications, together with polyamides taking less than 10% of total volume of hot melt adhesives market. Water-dispersible amorphous polymers, modified by addition of sodium sulfonate groups for dispersability, were however developed for repulpable adhesives. Polyesters are often highly crystalline, leading to narrow melting temperature range, which is advantageous for high-speed bonding.
- Polyurethanes
  - Thermoplastic polyurethane (TPU) offer good adhesion to different surfaces due to presence of polar groups. Their low glass transition temperature provides flexibility at low temperatures. They are highly

    elastic and soft, with wide possible crystallization and melting point ranges. Polyurethanes consist of long linear chains with flexible, soft segments (diisocyanate-coupled low-melting polyester or polyether chains) alternating with rigid segments (diurethane bridges resulting from diisocyanate reacting with a small-molecule glycol chain extender). The rigid segments form hydrogen bonds with rigid segments of other molecules. Higher ratio of soft to hard segments provides better flexibility, elongation, and low-temperature performance, but also lower hardness, modulus, and abrasion resistance. The bonding temperature is lower than with most other HMAs, only about 50-70 °C, when the adhesive behaves as a soft rubber acting as a pressure-sensitive adhesive. The surface wetting in this amorphous state is good, and on cooling the polymer crystallizes, forming a strong flexible bond with high cohesion. Choice of a proper diisocyanate and polyol combination allows tailoring the polyuretane properties; they can be used on their own or blended with a plasticizer. Polyurethanes are compatible with most common plasticizers, and many resins.
    - Polyurethanes (PUR), or reactive urethanes, for high temperatures and high flexibility. New type of hot melt thermosetting adhesives, introduced in early 1990s. Solidification can be rapid or extended in range of several minutes; secondary curing with atmospheric or substrate moisture then continues for several hours, forming cross-links in the polymer. Excellent resistance to solvents and chemicals. Low application temperature, suitable for heat-sensitive substrates. Heat-resistant after curing, with service temperatures generally from -30°C to +150°C. Ink-solvent resistant. Often used in bookbinding, automotive, aerospace, filter and plastic bag applications. Susceptible to UV degradation causing discoloring and degradation of mechanical properties, requires blending with UV stabilizers and antioxidants. Usually based on prepolymers made of polyols and methylene diphenyl diisocyanate (MDI) or other diisocyanate, with small amount of free isocyanate groups; these groups when subjected to moisture react and cross-link. The uncured solidified "green" strength tends to be low than non-reactive HMAs, mechanical strength develops with curing. Green strength can be improved by blending the prepolymer with other polymers.
- Styrene block copolymers (SBC), also called styrene copolymer adhesives and rubber-based adhesives, have good low-temperature flexibility, high elongation, and high heat resistance. Frequently used in pressure sensitive adhesive applications, where the composition retains tack even when solidified; however non-pressure-sensitive formulations are also used. High heat resistance, good low-temperature flexibility. Lower strength than polyesters. They usually have A-B-A structure, with an elastic rubber segment between two rigid plastic endblocks. High-strength film formers as standalone, increase cohesion and viscosity as an additive. Water-resistant, soluble in some organic solvents; cross-linking improves solvent resistance. Resins associating with endblocks (cumarone-indene, α-methyl styrene, vinyl toluene, aromatic hydrocarbons, etc.) improve

adhesion and alter viscosity. Resins associating to the midblocks (aliphatic olefins, rosin esters, polyterpenes, terpene phenolics) improve adhesion, processing and pressure-sensitive properties. Addition of plasticizers reduces cost, improves pressure-sensitive tack, decrease melt viscosity, decrease hardness, and improve low-temperature flexibility. The A-B-A structure promotes a phase separation of the polymer, binding together the endblocks, with the central elastic parts acting as cross-links; SBCs do not require additional cross-linking.
    - Styrene-butadiene-styrene (SBS), used in high-strength PSA applications
    - Styrene-isoprene-styrene (SIS), used in low-viscosity high-tack PSA applications
    - Styrene-ethylene/butylene-styrene (SEBS), used in low self-adhering non-woven applications
    - Styrene-ethylene/propylene (SEP)
- Polycaprolactone with soy protein, using coconut oil as plasticizer, a biodegradable hot-melt adhesive investigated at Korea University
- Polycarbonates
- Fluoropolymers, with tackifiers and ethylene copolymer with polar groups
- Silicone rubbers, undergo cross-linking after solidification, form durable flexible UV and weather resistant silicone sealant
- Thermoplastic elastomers
- Polypyrrole (PPY), a conductive polymer, for intrinsically conducting hot melt adhesives (ICHMAs), used for EMI shielding. EVA compounded with 0.1-0.5 wt.% PPY are strongly absorbing in near infrared, allowing use as near-infrared activated adhesives.
- various other copolymers

The usual additives are:

- tackifying resins (e.g. rosins and their derivates, terpenes and modified terpenes, aliphatic, cycloaliphatic and aromatic resins (C5 aliphatic resins, C9 aromatic resins, and C5/C9 aliphatic/aromatic resins), hydrogenated hydrocarbon resins, and their mixtures, terpene-phenol resins (TPR, used often with EVAs)), up to about 40% Tackifiers tend to have low molecular weight, and glass transition and softening temperature above room temperature, providing them with suitable viscoelastic properties. Tackifiers frequently present most of both weight percentage and cost of the hot-melt adhesive.
- waxes, e.g. microcrystalline waxes, fatty amide waxes or oxidized Fischer-Tropsch waxes; increase the setting rate. One of the key components of formulations. Waxes lower the melt viscosity and can improve bond strength and temperature resistance.
- plasticizers (e.g. benzoates, e.g. 1,4-cyclohexane dimethanol dibenzoate, glyceryl tribenzoate, or pentaerythritol tetrabenzoate, phthalates, paraffin oils, polyisobutylene, chlorinated paraffins, etc.)
- antioxidants and stabilizers (e.g. hindered phenols, BHT, phosphites, phosphates, hindered aromatic amines); added in small amounts (<1%), not influencing physical properties. These compounds protect the material from degradation both

  during service life, compounding and in molten state during application. Stabilizers based on functionalized silicones have improved resistance to extraction and outgassing.
- UV stabilizers, protecting the material against degradation by ultraviolet radiation
- pigments and dyes, glitter
- biocides where hindering bacterial growth is desired
- flame retardants
- antistatic agents
- fillers, for reducing cost, adding bulk, improving cohesive strength (forming an aggregate-matrix composite material) and altering properties; e.g. calcium carbonate, barium sulfate, talc, silica, carbon black, clays (e.g. kaolin).

Fugitive glues and pressure sensitive adhesives can also be available in hot-melt form.

Additives and polymers containing unsaturated bonds are highly prone to autoxidation. Examples include rosin-based additives. antioxidants can be used for suppressing this aging mechanism.

Addition of ferromagnetic particles, hygroscopic water-retaining materials, or other materials can yield a hot melt adhesive which can be activated by microwave heating.

Addition of electrically conductive particles can yield conductive hot-melt formulations.

Glue gun specifications and usage

Glue guns come in a low-temperature and a high-temperature (hot-melt) version. Low-temperature glue guns heat up to about 250 °F (121 °C) and are well suited when high temperatures are undesirable, such as gluing lace and cloth. High-temperature guns heat up to around 380 °F (193 °C) and produce a stronger bond. *Dual guns* have a switch for both low- and high-temperature use.

In addition to bonding surfaces together, hot-melt glue can be used to fill gaps, but the properties that allow gap-filling (high viscosity, high toughness, and so on) keep it from forming an adhesive film as thin and smooth as is possible with other adhesives. (For example, a wood joint properly made with hide glue may be invisible, marked only by a difference in grain at the seam line.) Bonds must be made quickly before the glue has time to cool and harden. Usually it must be applied accurately with the glue gun, as it can not easily be spread, but it is always possible at any time to melt and spread the glue with a heat gun or a household clothes iron, which helps when bonding larger areas.

Surprisingly, hot-melt glue can be used to assemble and repair foam models as an alternative to foam-safe Cyanoacrylate or UHU POR adhesive. Due to the insulating properties of the foam the hot-melt glue stays sticky for much longer than when used on wood, metal or plastics.

Another development of glue gun technology allows the user to effectively 'spray' an area with a semi-pressure sensitive hot melt adhesive. Using compressed air to force the adhesive through the glue gun at a controlled rate and through a specially developed glue gun nozzle, a spiral pattern of adhesive is applied. The tackiness of the adhesive / open time is limited to just a few minutes, after which the adhesive will lose its tack, so coverage is limited.

Applications

- Hot melt adhesives are used to close corrugated fiberboard boxes and paperboard cartons.
- Crafts in the home
- Assembly of parts in manufacturing
- Heat sometimes allows disassembly: Points of modern arrows, hockey sticks, etc.
- Assembly and repair of foam model aircraft and other toys.
- Hot melt adhesive is used for disposable diaper construction where it is used to bond together the nonwoven material with the backsheet and the elastics.

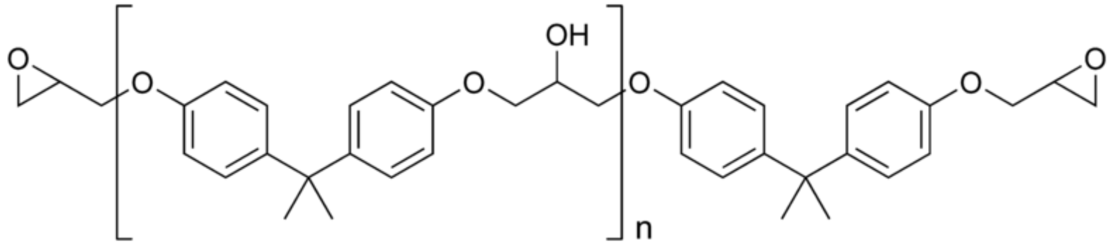
Chapter- 6

Epoxy

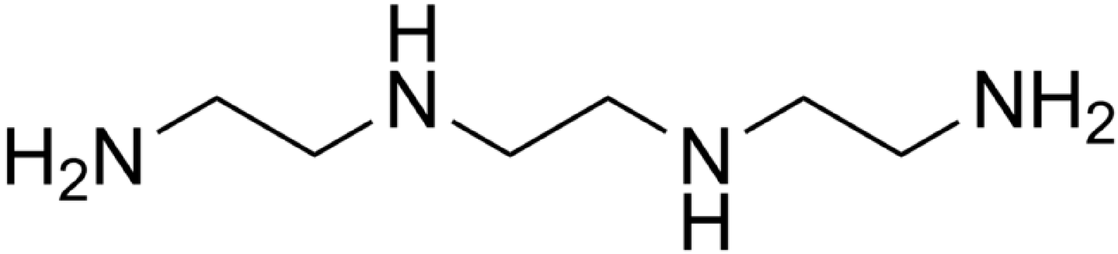
A syringe of "5-minute" epoxy

Epoxy or **polyepoxide** is a thermosetting polymer formed from reaction of an epoxide "resin" with polyamine "hardener". Epoxy has a wide range of applications, including fiber-reinforced plastic materials and general purpose adhesives.

Chemistry



Structure of unmodified epoxy prepolymer resin. *n* denotes the number of polymerized subunits and is in the range from 0 to about 25



Structure of TETA, a typical hardener. The amine (NH) groups react with the epoxide groups of the resin during polymerization.

Epoxy is a copolymer; that is, it is formed from two different chemicals. These are referred to as the "resin" and the "hardener". The resin consists of monomers or short chain polymers with an epoxide group at either end. Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A, though the latter may be replaced by similar chemicals. The hardener consists of polyamine monomers, for example Triethylenetetramine (TETA). When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond. Each NH group can react with an epoxide group, so that the resulting polymer is heavily crosslinked, and is thus rigid and strong.

The process of polymerization is called "curing", and can be controlled through temperature, choice of resin and hardener compounds, and the ratio of said compounds; the process can take minutes to hours. Some formulations benefit from heating during the cure period, whereas others simply require time, and ambient temperatures.

History

The first commercial attempts to prepare resins from epichlorohydrin were made in 1927 in the United States. Credit for the first synthesis of bisphenol-A-based epoxy resins is shared by Dr. Pierre Castan of Switzerland and Dr. S.O. Greenlee of the United States in 1936. Dr. Castan's work was licensed by Ciba, Ltd. of Switzerland, which went on to become one of the three major epoxy resin producers worldwide. Ciba's epoxy business was spun off and later sold in the late 1990s and is now the advanced materials business unit of Huntsman Corporation of the United States. Dr. Greenlee's work was for the firm of Devoe-Reynolds of the United States. Devoe-Reynolds, which was active in the early days of the epoxy resin industry, was sold to Shell Chemical (now Hexion, formerly Resolution Polymers and others).

Applications

The applications for epoxy-based materials are extensive and include coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements (although polyester, vinyl ester, and other thermosetting resins are also used for glass-reinforced plastic). The chemistry of epoxies and the range of commercially available variations allows cure polymers to be produced with a very broad range of properties. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties. Many properties of epoxies can be modified (for example silver-filled epoxies with good electrical conductivity are available, although epoxies are typically electrically insulating). Variations offering high thermal insulation, or thermal conductivity combined with high electrical resistance for electronics applications, are available.

Paints and coatings

Two part epoxy coatings were developed for heavy duty service on metal substrates and use less energy than heat-cured powder coatings. These systems use a 4:1 by volume mixing ratio, and dry quickly providing a tough, protective coating with excellent hardness. Their low volatility and water clean up makes them useful for factory cast iron, cast steel, cast aluminum applications and reduces exposure and flammability issues associated with solvent-borne coatings. They are usually used in industrial and automotive applications since they are more heat resistant than latex-based and alkyd-based paints. Epoxy paints tend to deteriorate, known as chalk out, due to UV exposure.

Polyester epoxies are used as powder coatings for washers, driers and other "white goods". Fusion Bonded Epoxy Powder Coatings (FBE) are extensively used for corrosion protection of steel pipes and fittings used in the oil and gas industry, potable water transmission pipelines (steel), concrete reinforcing rebar, *et cetera*. Epoxy coatings are also widely used as primers to improve the adhesion of automotive and marine paints especially on metal surfaces where corrosion (rusting) resistance is important. Metal cans and containers are often coated with epoxy to prevent rusting, especially for foods like tomatoes that are acidic. Epoxy resins are also used for high performance and decorative flooring applications especially terrazzo flooring, chip flooring and colored aggregate flooring.

Adhesives

Special epoxy is strong enough to withstand the forces between a surfboard fin and the fin mount. This epoxy is waterproof and capable of curing underwater. The blue-coloured epoxy on the left is still undergoing curing.

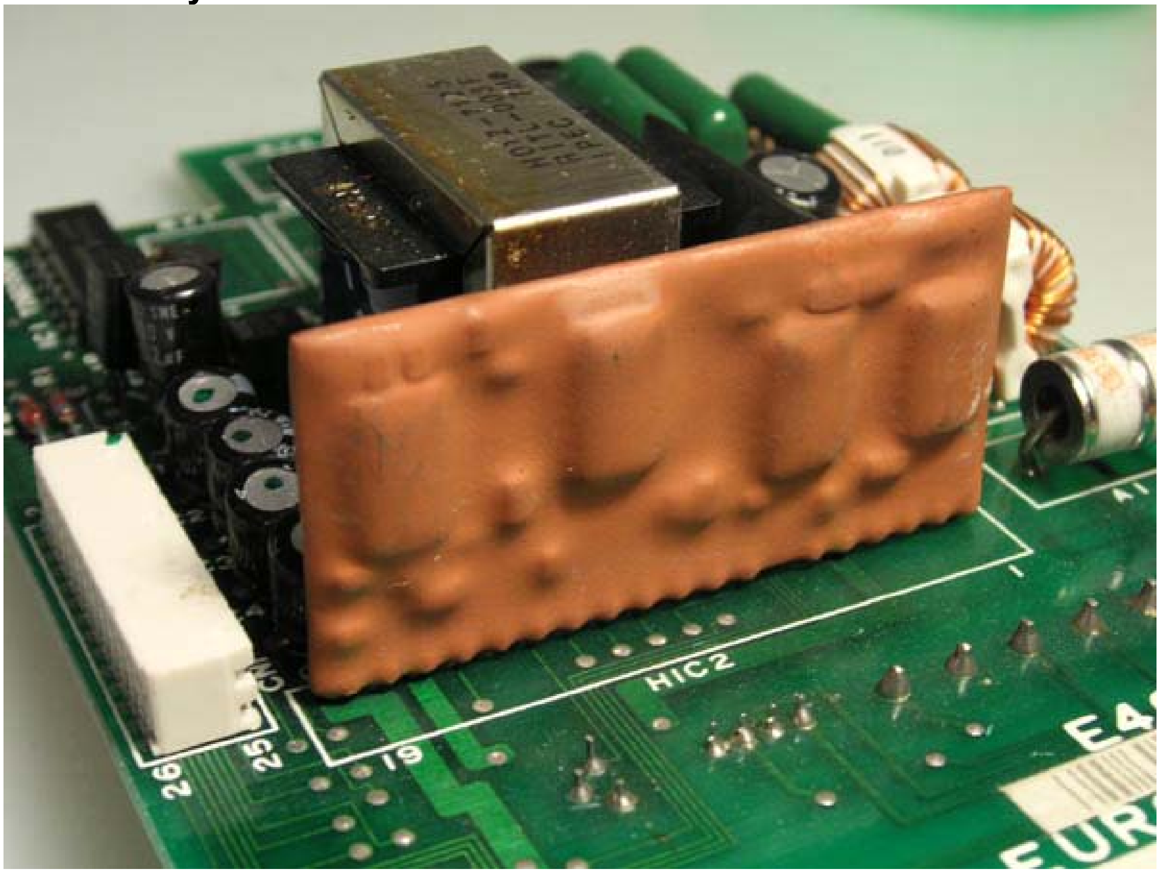
Epoxy adhesives are a major part of the class of adhesives called "structural adhesives" or "engineering adhesives" (that includes polyurethane, acrylic, cyanoacrylate, and other chemistries.) These high-performance adhesives are used in the construction of aircraft, automobiles, bicycles, boats, golf clubs, skis, snowboards, and other applications where high strength bonds are required. Epoxy adhesives can be developed to suit almost any application. They can be used as adhesives for wood, metal, glass, stone, and some plastics. They can be made flexible or rigid, transparent or opaque/colored, fast setting or slow setting. Epoxy adhesives are better in heat and chemical resistance than other common adhesives. In general, epoxy adhesives cured with heat will be more heat- and chemical-resistant than those cured at room temperature. The strength of epoxy adhesives is degraded at temperatures above 350 °F (177 °C).

Some epoxies are cured by exposure to ultraviolet light. Such epoxies are commonly used in optics, fiber optics, optoelectronics, and dentistry.

Industrial tooling and composites

Epoxy systems are used in industrial tooling applications to produce molds, master models, laminates, castings, fixtures, and other industrial production aids. This "plastic tooling" replaces metal, wood and other traditional materials, and generally improves the efficiency and either lowers the overall cost or shortens the lead-time for many industrial processes. Epoxies are also used in producing fiber-reinforced or composite parts. They are more expensive than polyester resins and vinyl ester resins, but usually produce stronger and more temperature-resistant composite parts.

Electrical systems and electronics



An epoxy encapsulated hybrid circuit on a printed circuit board.

Epoxy resin formulations are important in the electronics industry, and are employed in motors, generators, transformers, switchgear, bushings, and insulators. Epoxy resins are excellent electrical insulators and protect electrical components from short circuiting, dust and moisture. In the electronics industry epoxy resins are the primary resin used in overmolding integrated circuits, transistors and hybrid circuits, and making printed circuit boards. The largest volume type of circuit board—an "FR-4 board"—is a sandwich of layers of glass cloth bonded into a composite by an epoxy resin. Epoxy resins are used to bond copper foil to circuit board substrates, and are a component of the solder mask on many circuit boards.

Flexible epoxy resins are used for potting transformers and inductors. By using vacuum impregnation on uncured epoxy, winding-to-winding, winding-to-core, and winding-to-insulator air voids are eliminated. The cured epoxy is an electrical insulator and a much better conductor of heat than air. Transformer and inductor hot spots are greatly reduced, giving the component a stable and longer life than unpotted product.

Epoxy resins are applied using the technology of resin dispensing.

Consumer and marine applications

Epoxies are sold in hardware stores, typically as a pack containing separate resin and hardener, which must be mixed immediately before use. They are also sold in boat shops as repair resins for marine applications. Epoxies typically are not used in the outer layer of a boat because they deteriorate by exposure to UV light. They are often used during boat repair and assembly, and then over-coated with conventional or two-part polyurethane paint or marine-varnishes that provide UV protection.

There are two main areas of marine use. Because of the better mechanical properties relative to the more common polyester resins, epoxies are used for commercial manufacture of components where a high strength/weight ratio is required. The second area is that their strength, gap filling properties and excellent adhesion to many materials including timber have created a boom in amateur building projects including aircraft and boats.

Normal gelcoat formulated for use with polyester resins and vinylester resins does not adhere to epoxy surfaces, though epoxy adheres very well if applied to polyester resin surfaces. "Flocoat" that is normally used to coat the interior of polyester fibreglass yachts is also compatible with epoxies.

Epoxy materials tend to harden somewhat more gradually, while polyester materials tend to harden quickly, particularly if a lot of catalyst is used. The chemical reactions in both cases are exothermic. Large quantities of mix will generate their own heat and greatly speed the reaction, so it is usual to mix small amounts which can be used quickly.

While it is common to associate polyester resins and epoxy resins, their properties are sufficiently different that they are properly treated as distinct materials. Polyester resins are typically low strength unless used with a reinforcing material like glass fibre, are relatively brittle unless reinforced, and have low adhesion. Epoxies, by contrast, are inherently strong, somewhat flexible and have excellent adhesion. However, polyester resins are much cheaper.

Epoxy resins typically require a precise mix of two components which form a third chemical. Depending on the properties required, the ratio may be anything from 1:1 or over 10:1, but in every case they must be mixed exactly. The final product is then a precise thermo-setting plastic. Until they are mixed the two elements are relatively inert, although the 'hardeners' tend to be more chemically active and should be protected from the atmosphere and moisture. The rate of the reaction can be changed by using different hardeners, which may change the nature of the final product, or by controlling the temperature.

By contrast, polyester resins are usually made available in a 'promoted' form, such that the progress of previously-mixed resins from liquid to solid is already underway, albeit very slowly. The only variable available to the user is to change the rate of this process using a catalyst, often Methyl-Ethyl-Ketone-Peroxide (MEKP), which is very toxic. The presence of the catalyst in the final product actually detracts from the desirable properties, so that small amounts of catalyst are preferable, so long as the hardening proceeds at an acceptable pace. The rate of cure of polyesters can therefore be controlled both by the amount of catalyst and by the temperature.

As adhesives, epoxies bond in three ways: a) Mechanically, because the bonding surfaces are roughened; b) By proximity, because the cured resins are physically so close to the bonding surfaces that they are hard to separate; c) Ionically, because the epoxy resins form ionic bonds at an atomic level with the bonding surfaces. This last is substantially the strongest of the three. By contrast, polyester resins can only bond using the first two of these, which greatly reduces their utility as adhesives and in marine repair.

Aerospace applications

In the aerospace industry, epoxy is used as a structural matrix material which is then reinforced by fiber. Typical fiber reinforcements include glass, carbon, Kevlar, and boron. Epoxies are also used as a structural glue. Materials like wood, and others that are 'low-tech' are glued with epoxy resin.

Art

Epoxy resin, mixed with pigment, is used as a painting medium, by pouring layers on top of each other to form a complete picture.

Wind Energy applications

Epoxy resin is used in manufacturing the rotor blades of wind turbines. The resin is infused in the core materials, such as balsa wood or foam, and the reinforcing media, such as fabric, glass fibre or carbon fibre. The process is called VARTM, i.e. Vacuum Assisted Resin Transfer Moulding. Due to excellent properties and good finish, epoxy is the most favoured resin for composites.

Industry

As of 2006, the epoxy industry amounts to more than US$5 billion in North America and about US$15 billion worldwide. The Chinese market has been growing rapidly, and accounts for more than 30% of the total worldwide market. It is made up of approximately 50–100 manufacturers of basic or commodity epoxy resins and hardeners of which the three largest are Hexion (formerly Resolution Performance Products, formerly Shell Development Company; whose epoxy tradename is "Epon"), the Dow Chemical Company (tradename "D.E.R."), and Huntsman Corporation's Advanced Materials business unit (formerly Vantico, formerly Ciba Specialty Chemical; tradename "Araldite"). In 2007 Huntsman Corporation agreed to merge with Hexion (owned by the Apollo Group). KUKDO Chemical is one of the largest epoxy manufacturers in Asia, and recently their capacity has been increased up to 210,000 MT/Y (Korea 150,000 MT/Y, China 60,000 MT/Y and will be increased totally 300,000 MT/Y by 2009). Nanya Plastic also has the capacity of over 250,000 MT/Y (Taiwan and China), which is mostly for captive use. There are over 50 smaller epoxy manufacturers primarily producing epoxies only regionally, epoxy hardeners only, specialty epoxies, or epoxy modifiers.

These commodity epoxy manufacturers mentioned above typically do not sell epoxy resins in a form usable to smaller end users, so there is another group of companies that purchase epoxy raw materials from the major producers and then compounds (blends, modifies, or otherwise customizes) epoxy systems from these raw materials. These companies are known as "formulators". The majority of the epoxy systems sold are produced by these formulators and they comprise over 60% of the dollar value of the epoxy market. There are hundreds of ways that these formulators can modify epoxies—by adding mineral fillers (talc, silica, alumina, etc.), by adding flexibilizers, viscosity reducers, colorants, thickeners, accelerators, adhesion promoters, etc.. These modifications are made to reduce costs, to improve performance, and to improve processing convenience. As a result a typical formulator sells dozens or even thousands of formulations—each tailored to the requirements of a particular application or market.

Impacted by the global economic slump, the epoxy market size declined to $15.8 billion in 2009, almost to the level of 2005. In some regional markets it even decreased nearly 20%. The current epoxy market is experiencing positive growth as the global economy revives. With an annual growth rate of 3.5 - 4% the epoxy market is expected to reach $17.7 billion by 2012 and $21.35 by 2015. Higher growth rate is foreseen thereafter due to stronger demands from epoxy composite market and epoxy adhesive market.

Health risks

The primary risk associated with epoxy use is sensitization to the hardener, which, over time, can induce an allergic reaction. It is a main source of occupational asthma among users of plastics. Bisphenol A, which is used in epoxy resin, is a known endocrine disruptor.

Chapter- 7

Silicone

A mobile phone case made from silicone.

Silicones are inert, synthetic compounds with a wide variety of forms and uses. Typically heat-resistant and rubber-like, they are commonly used in breast implants, cookware, medical applications, sealants, adhesives, lubricants, and insulation.

Silicones are polymers that include silicon together with carbon, hydrogen, oxygen, and sometimes other chemical elements. Some common forms include silicone oil, silicone grease, silicone rubber, and silicone resin.

Properties

Some of the most useful properties of silicones can include:

- Good electrical insulation. Because silicone can be formulated to be electrically insulative or conductive, it is suitable for a wide range of electrical applications.
- Thermal stability (constancy of properties over a wide operating range of −100 to 250 °C).

- Though not a hydrophobe, the ability to repel water and form watertight seals.
- Excellent resistance to oxygen, ozone and UV light (sunlight). This has led to widespread use in the construction industry (e.g. coatings, fire protection, glazing seals), and automotive industry (external gaskets, external trim).
- Does not stick.
- Low chemical reactivity.
- Low toxicity, but does not support microbiological growth.
- High gas permeability: at room temperature (25 °C) the permeability of silicone rubber for gases like oxygen is approximately 400 times that of butyl rubber, making silicone useful for medical applications that could benefit from increased aeration. Silicone rubbers cannot be used where gas-tight seals are necessary.

History

Frederick Kipping was the chemist who pioneered the study of the organic compounds of silicon (organosilicons), and coined the term silicone.

Technical details

More precisely called polymerized siloxanes or polysiloxanes, silicones are mixed inorganic-organic polymers with the chemical formula $[R_2SiO]_n$, where R is an organic group such as methyl, ethyl, or phenyl. These materials consist of an inorganic silicon-oxygen backbone (…-Si-O-Si-O-Si-O-…) with organic side groups attached to the silicon atoms, which are four-coordinate.

In some cases organic side groups can be used to link two or more of these -Si-O- backbones together. By varying the -Si-O- chain lengths, side groups, and crosslinking, silicones can be synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic. The most common siloxane is linear polydimethylsiloxane (PDMS), a silicone oil. The second largest group of silicone materials is based on silicone resins, which are formed by branched and cage-like oligosiloxanes.

Synthesis

Silicones are synthesized from chlorosilanes, tetraethoxysilane, and related compounds. In the case of PDMS, the starting material is dimethyldichlorosilane, which reacts with water as follows:

$$n\ Si(CH_3)_2Cl_2 + n\ H_2O \rightarrow [Si(CH_3)_2O]_n + 2n\ HCl$$

During polymerization, this reaction evolves hazardous hydrogen chloride gas. For medical uses, a process was developed where the chlorine atoms in the silane precursor were replaced with acetate groups. The reaction product of the final curing process is the much less dangerous acetic acid (the one found in vinegar). As a side effect, the curing process is also much slower in this case. This is the chemistry used in many consumer applications, such as silicone caulk and adhesives.

Silane precursors with more acid-forming groups and fewer methyl groups, such as methyltrichlorosilane, can be used to introduce branches or cross-links in the polymer chain. Ideally, each molecule of such a compound becomes a branch point. This can be used to produce hard silicone resins. Similarly, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so forms the end of a siloxane chain.

Modern silicone resins are made with tetraethoxysilane, which reacts in a more mild and controllable manner than chlorosilanes.

Chemical terminology

Silicone is often mistakenly referred to as "silicon." Although silicones contain silicon atoms, they are not made up exclusively of silicon, and have completely different physical characteristics from elemental silicon.

F. S. Kipping coined the word "silicone" in 1901 to describe polydiphenylsiloxane by analogy of its *formula*, Ph_2SiO, with the formula of the ketone benzophenone, Ph_2CO (Ph stands for phenyl, C_6H_5). Kipping was well aware that polydiphenylsiloxane is polymeric whereas benzophenone is monomeric and noted that Ph_2SiO and Ph_2CO had very different chemistry.

A true *silicone group* with a double bond between oxygen and silicon does not commonly exist in nature; chemists find that the silicon atom much prefers a single bond with each of two oxygen atoms, rather than a double bond to a single atom. Polysiloxanes are still more commonly known as "silicones".

Molecules containing silicon-oxygen double bonds do exist and are called silanones. Several silanones have been studied in argon matrices and in the gas phase, but they are highly reactive. Despite their reactivity, silanones are important as intermediates in gas-phase processes such as chemical vapor deposition in microelectronics production, in the formation of ceramics by combustion, and in astrochemistry.

Uses

Aquarium joints

Glass aquarium manufacturers have used 100% silicone sealant exclusively from its inception in order to join glass plates, making aquariums of every size and shape. Glass joints made with silicone sealant can withstand a great deal of pressure, making obsolete the original aquarium construction method using angle-iron and putty. This same silicone is also used to make hinges in aquarium lids or even for minor repairs. Not all commercial silicones are safe for aquarium manufacture, nor is silicone used for the manufacture of acrylic aquariums as silicones do not have long-term adhesion to plastics.

Automotive

In the automotive field, silicone grease is typically used as a lubricant for brake components since it is stable at high temperatures, is not water-soluble and is far less likely than other lubricants to foul.

Automotive spark plug wires are often insulated by multiple layers of silicone to prevent sparks from jumping to adjacent wires, causing misfires.

Silicone tubing is sometimes used in automotive intake systems (especially for engines with forced-induction).

Sheet silicone is used to manufacture gaskets used in automotive engines, transmissions and other applications.

Automotive body manufacturing plants and paint shops must avoid the presence of all silicones, as they may cause "fish eyes," small, circular craters that appear in the finish.

Additionally, silicone compounds such as silicone rubber are used in the automotive industry for airbags as coatings and sealants. The high strength of silicone rubber makes it an optimal adhesive/sealant for high impact airbags.

Coatings

Silicone films can be applied to silica-based substrates like glass to form a covalently bonded hydrophobic coating.

Fabrics may be coated or impregnated with silicone to form a strong, waterproof composite such as silnylon.

Cookware

- As a low taint, non-toxic material, silicone can be used where contact with food is required. Silicone is becoming an important product in the cookware industry, particularly bakeware and kitchen utensils.
- It is used as an insulator in heat resistant potholders and similar, however it is more conductive of heat than the less dense fiber-based ones. Silicone oven mitts are able to withstand temperatures up to 260 °C (500 °F), and allow reaching into boiling water.
- Molds for chocolate, ice, cookies, muffins, etc.
- Some novel designs are steamer, egg boiler, vegetables cooker, cooking lids, pot handle, kitchen mats, etc.

Defoaming

Silicones are used as active compound in defoamers due to the low water solubility and good spreading properties.

Dry cleaning

Liquid silicone can be used as a dry cleaning solvent. Touted as an "environmentally friendly" alternative to the traditional perchloroethylene (or perc) solvent, the decamethylpentacyclosiloxane (D5) process has been patented by the company GreenEarth Cleaning. This significantly reduces the environmental impact of a typically high-polluting industry.

Additionally, liquid silicone is chemically inert, meaning it does not react with fabrics or dyes during the cleaning process. This reduces the amount of fading and shrinking that most dry-cleaned garments experience.

Electronics

Electronic components are sometimes encased in silicone to increase stability against mechanical and electrical shock, radiation and vibration. This is often called "potting".

Silicones are used where durability and high performance are demanded of components under hard conditions, such as in space (satellite technology). They are selected over polyurethane or epoxy encapsulation when a wide operating temperature range is required (−65 to 315 °C). Silicones also have the advantage of little exothermic heat rise during cure, low toxicity, good electrical properties and high purity.

The use of silicones in electronics is not without problems, however. Silicones are relatively expensive and can be attacked by solvents. Silicone easily migrates as either a liquid or vapor onto other components.

Silicone contamination of electrical switch contacts can lead to failures by causing an increase in contact resistance, often late in the life of the contact, well after any testing is completed. Use of silicone-based spray products in electronic devices during maintenance or repairs can cause later failures.

Firestops

Silicone foam has been used in North American buildings in an attempt to firestop openings within fire-resistance-rated wall and floor assemblies to prevent the spread of flames and smoke from one room to another.

Silicone foam firestops have been the subject of controversy and press attention due to smoke development from pyrolysis of combustible components within the foam, hydrogen gas escape, shrinkage and cracking. These problems have been exposed by whistleblower Gerald W. Brown and have led to a large number of reportable events among licensees (operators of nuclear power plants) of the Nuclear Regulatory Commission (NRC).

When properly installed, silicone-foam firestops can be fabricated for building code compliance. Advantages include flexibility and high dielectric strength. Disadvantages include combustibility (hard to extinguish) and significant smoke development.

Silicone can also be found in aircraft technology.

Lubricants

Silicone greases are used for many purposes, such as bicycle chains, airsoft gun parts and a wide range of other mechanisms. A dry-set lubricant is delivered with a solvent carrier to penetrate the mechanism. The solvent evaporates, leaving a clear film that lubricates but does not attract dirt and grit as much as a traditional "wet" lubricant.

Silicone personal lubricants are also available, for use in medical procedures or sexual activity.

Medicine

Silicone, particularly the gel form, is used in bandages and dressings, in breast implants and a variety of other medical uses.

Polydimethylsiloxane (PDMS) has been used as the hydrophobic block of amphiphilic synthetic block copolymers used to form the vesicle membrane of polymersomes.

Moldmaking

Two-part silicone systems are used to create rubber molds which can be used for production casting of resins, foams, rubber and low-temp alloys.

A mold made of silicone generally requires little or no mold release or surface preparation as most materials do not adhere to moldmaking silicone.

For experimental uses, ordinary one-part silicone can also be used, either to make molds, or to mold into shapes. Common vegetable cooking oils and petroleum jelly can be used on mating surfaces as a mold release agent.

Personal care

Silicones are ingredients in many hair conditioner, shampoo, and hair gel products. Some silicones, notably the amine functionalized amodimethicones, are excellent conditioners. They improve combability, feel, and softness, and also lessen frizz. Another silicone family, the phenyltrimethicones, are used in reflection-enhancing and color-correcting hair products, where they increase shine and glossiness (and possibly effect subtle color changes). Phenyltrimethicones, unlike the conditioning amodimethicones, have refractive indices (typically 1.46) close to that of human hair (1.54). Achieving both high-shine and excellent conditioning in one hair care product is much more difficult than simply adding two different silicones to the formulation, because amodimethicone and phenyltrimethicone interact with and dilute each other. This is one reason why modern hair care products, and cosmetics generally, are among the most highly engineered consumer cosmetic products.

Silicones are also used in some shaving products and personal lubricants. Menstrual cups and scar treatment sheets are often made of medical grade silicone for its durability, reusability, and biocompatibility. Silicone is also material of choice for soft sex toys, due to its durability, cleanability and lack of phthalates, chemicals suspected of having carcinogenic and mutagenic effects on the skin and mucous membranes.

Specific grades of silicone rubber are used widely in the production of baby bottle teats due to their cleanliness, aesthetic appearance, and low extractable content.

Silicones, often Polydimethylsiloxane, are used in scar treatment sheets. This specific crosslinking results in a flexible and soft silcone with high durability and tack.

Plumbing and building construction

The strength and reliability of silicone rubber is widely acknowledged in the construction industry.

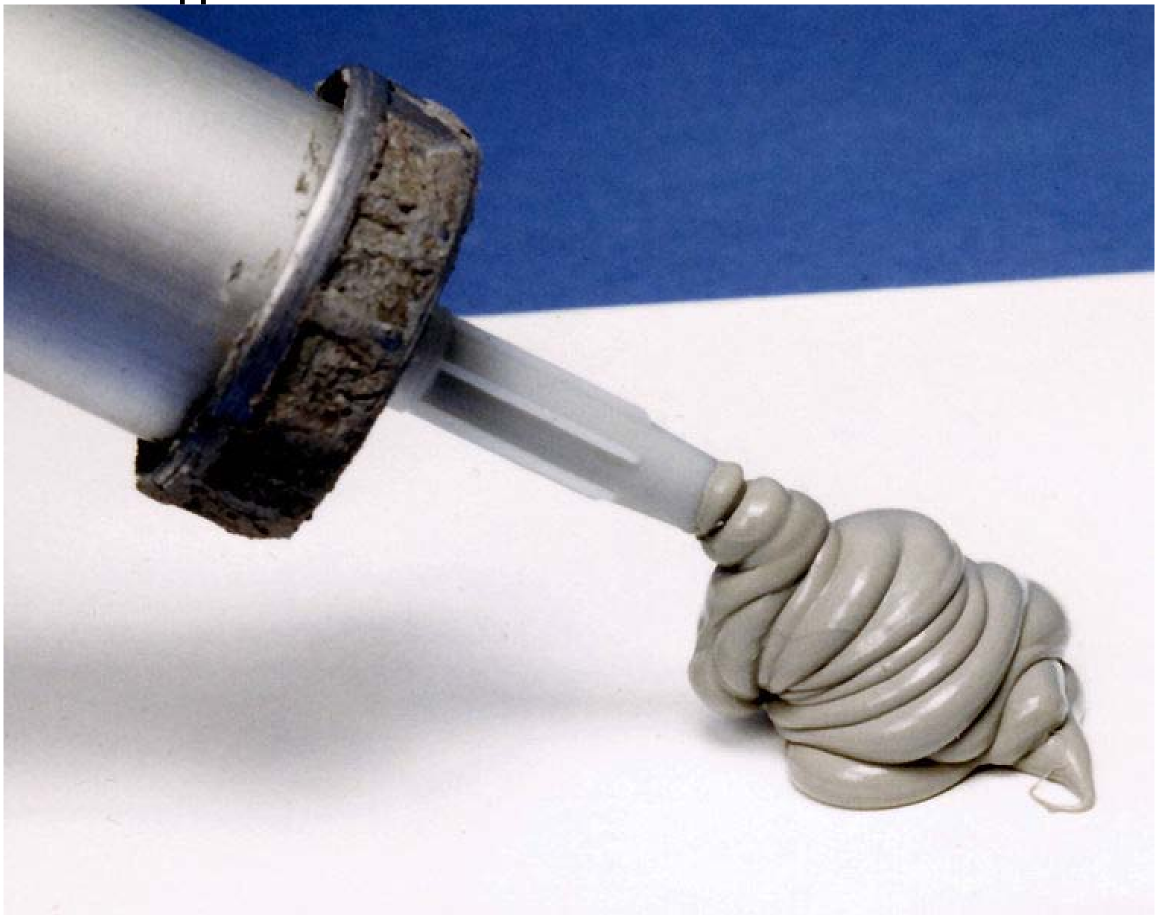
One-part silicone sealants and caulks are in common use to seal gaps, joints and crevices in buildings. One-part silicones cure by absorbing atmospheric moisture, which helps in the professional installation.

In plumbing, silicone grease is typically applied to O-rings in taps and valves. Whilst the film is extant it prevents lime from sticking to the brasswork.

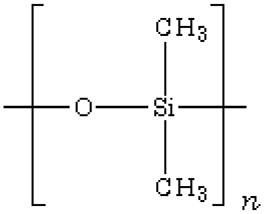
Toys

Silicone balls have become a juggler's favorite due to the high bounce back, and are used as a response system in many low response yo-yos. Silicone has the potential of replacing plastic in creating many forms of toys.

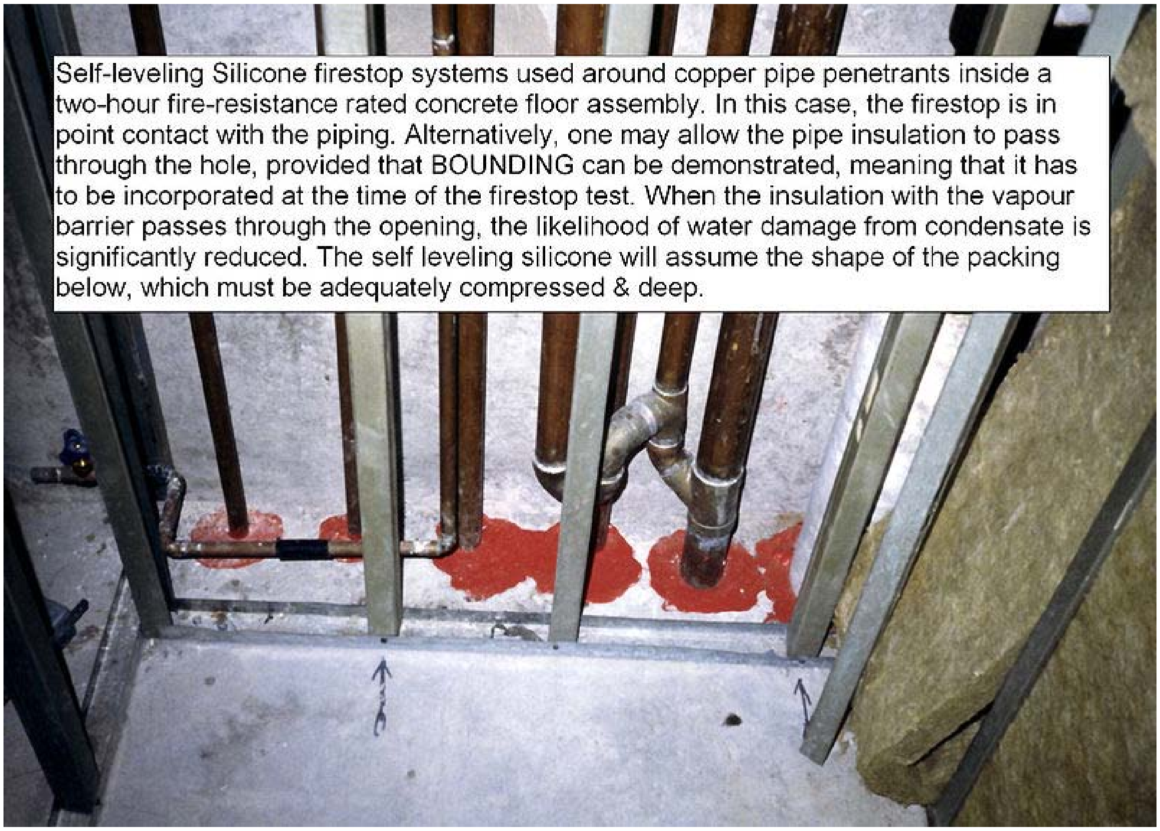
Versatile applications



Silicone caulk can be used as a basic sealant against water and air penetration

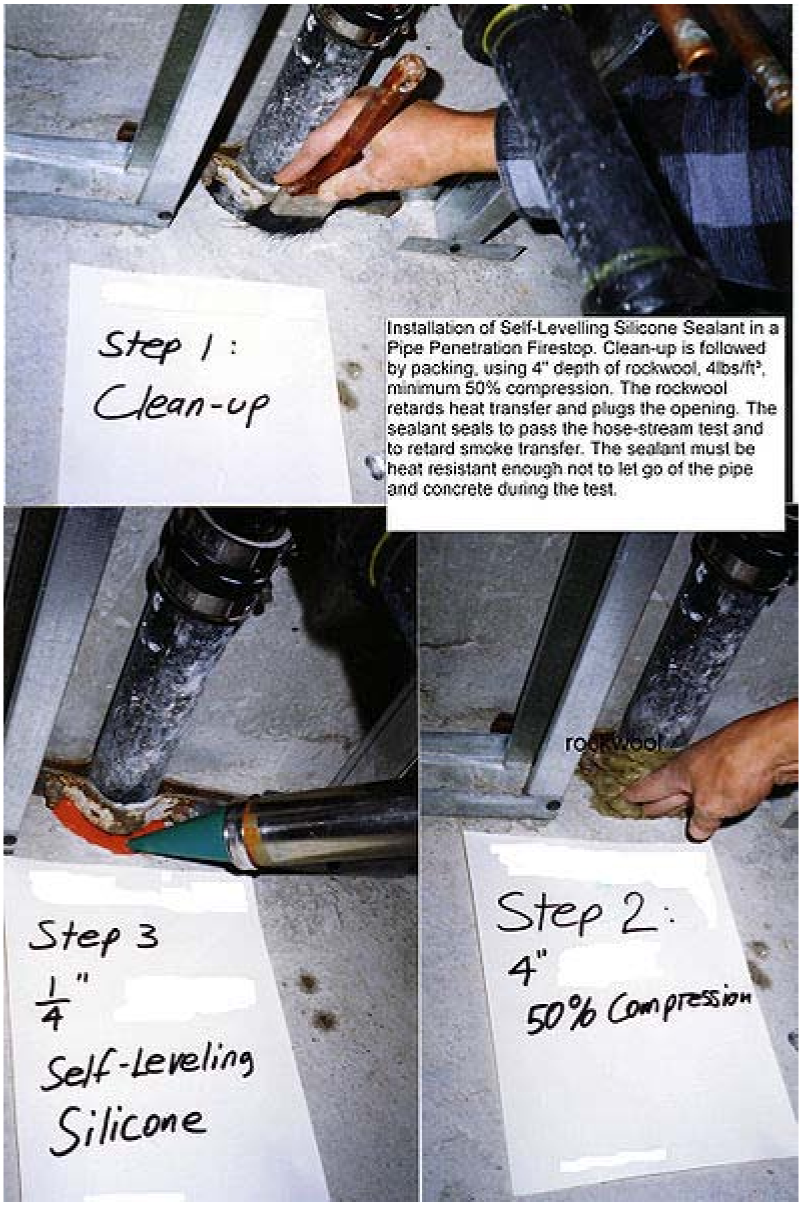


Chemical structure of polydimethylsiloxane (PDMS)



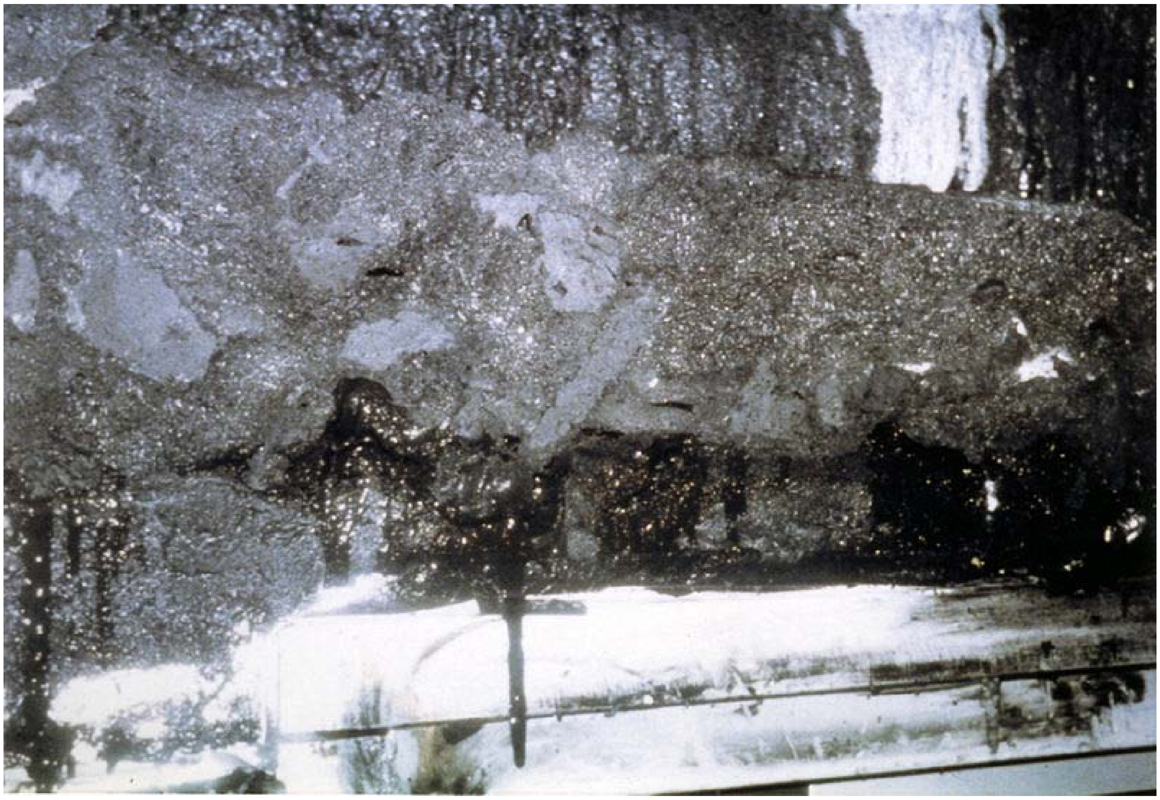
Self-leveling Silicone firestop systems used around copper pipe penetrants inside a two-hour fire-resistance rated concrete floor assembly. In this case, the firestop is in point contact with the piping. Alternatively, one may allow the pipe insulation to pass through the hole, provided that BOUNDING can be demonstrated, meaning that it has to be incorporated at the time of the firestop test. When the insulation with the vapour barrier passes through the opening, the likelihood of water damage from condensate is significantly reduced. The self leveling silicone will assume the shape of the packing below, which must be adequately compressed & deep.

Self-leveling silicone firestop system used around copper pipe through-penetrations in a two-hour fire-resistance rated concrete floor assembly



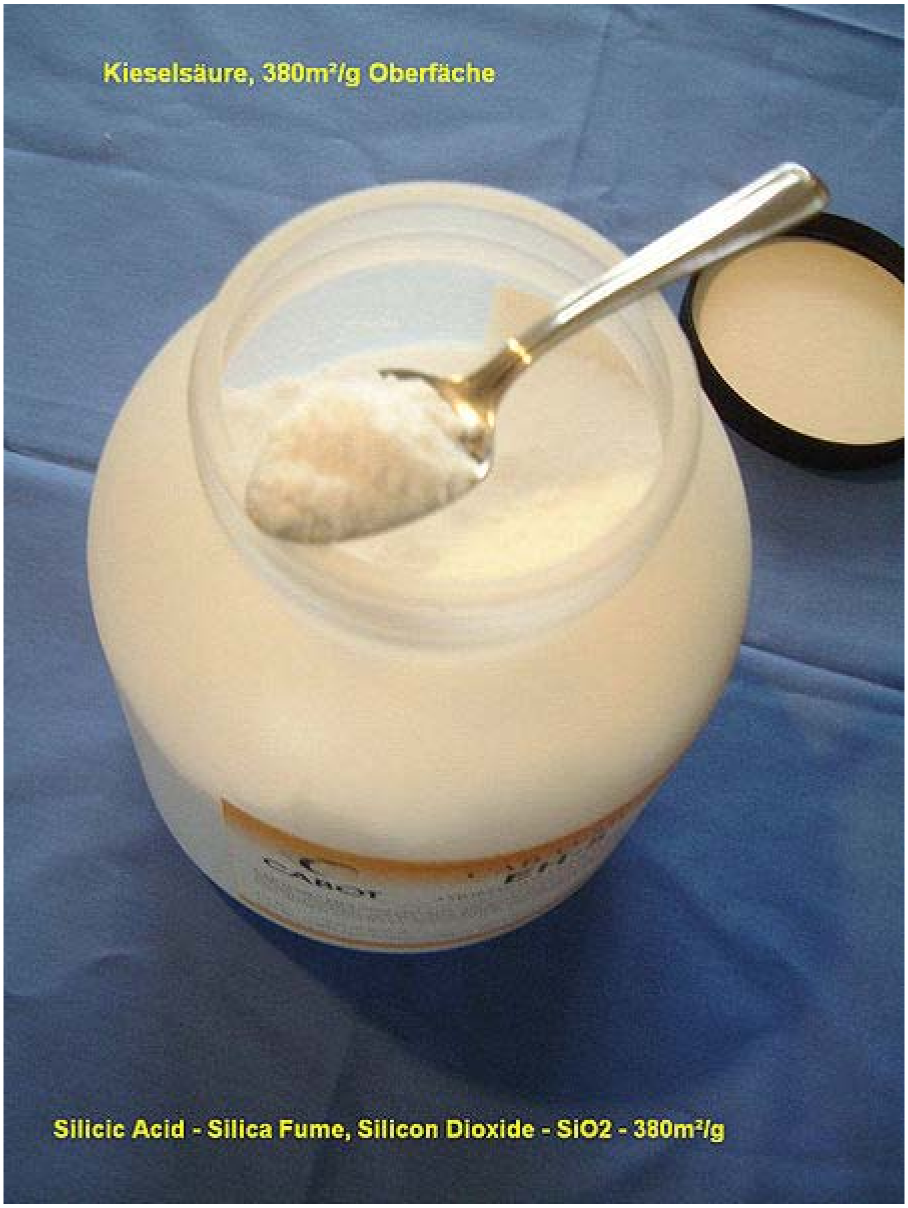
Installation of Self-Levelling Silicone Sealant in a Pipe Penetration Firestop. Clean-up is followed by packing, using 4" depth of rockwool, 4lbs/ft^3, minimum 50% compression. The rockwool retards heat transfer and plugs the opening. The sealant seals to pass the hose-stream test and to retard smoke transfer. The sealant must be heat resistant enough not to let go of the pipe and concrete during the test.

Self-levelling silicone firestop installation in mechanical service penetration in 2 hour rated concrete floor



Faulty Sakno Silicone Foam Firestop Installation in Calgary Sewage Treatment Plant in the 1980s, to seal opening above a fire door in a cast concrete fire separation.

Silicone "foamfixer" pump used to apply silicone foam firestop materials



Silicon dioxide (silica) used in the manufacture of all silicones. This is what remains when one burns silicone; burning silicone caulking or foam produces silica (as well as char) as a white powder – silica fume.

Current market

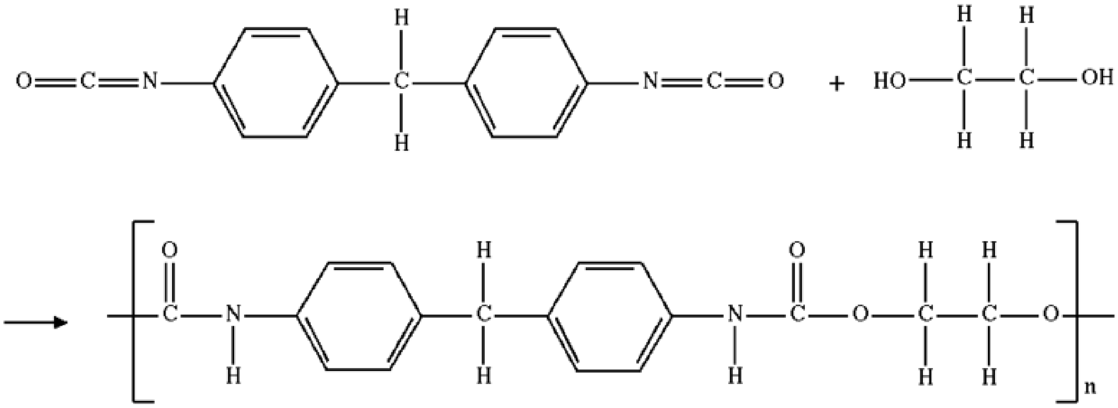
The global demand on silicones approached US$ 12.5 billion in 2008, approximately 4% up from the previous year. It continues similar growth in the following years to reach US$13.5 billion by 2010. The annual growth is expected to rebound to 7% when the economy revives, boosted by broader applications, introduction of novel products and increasing awareness of using more environmentally friendly materials.

Industry trade organizations

The leading global manufacturers of silicone base materials belong to three regional organizations: the European Silicone Center(CES) in Brussels, Belgium; the Silicone Environment Health and Safety Council(SEHSC) in Washington, USA; and the Silicone Industry Association of Japan (SIAJ) in Tokyo, Japan. A fourth organization, the Global Silicone Council (GSC) acts as an umbrella structure over the regional organizations. All four are nonprofit making and have no commercial role. Their primary mission is to promote the safety of silicones from a health, safety and environmental perspective. As the European chemical industry is getting prepared to implement the REACH legislation, CES is leading the formation of a consortium of silicones, silanes and siloxanes producers and importers to facilitate data and cost sharing.

Chapter- 8

Polyurethane



Example of synthesis of a polyurethane. Note the urethane groups -NH-(C=O)-O- linking the units of the product.

A **polyurethane** (IUPAC abbreviation **PUR**, but commonly abbreviated **PU**) is any polymer consisting of a chain of organic units joined by urethane (carbamate) links. Polyurethane polymers are formed through step-growth polymerization (also known as polyaddition) by reacting a monomer containing at least two isocyanate functional groups with another monomer containing at least two hydroxyl (alcohol) groups in the presence of a catalyst.

Polyurethanes are widely used in high resiliency flexible foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives, surface coatings and sealants, Spandex fibers, seals, gaskets, carpet underlay, and hard plastic parts (such as for electronic instruments).

Polyurethane products are often called "urethanes". They should not be confused with the specific substance urethane, also known as ethyl carbamate. Polyurethanes are neither produced from ethyl carbamate, nor do they contain it.

History

The pioneering work on polyurethane polymers was conducted by Otto Bayer and his coworkers in 1937 at the laboratories of I.G. Farben in Leverkusen, Germany. They recognized that using the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols seemed to point to special opportunities, especially when compared to already existing plastics that were made by polymerizing olefins, or by polycondensation. The new monomer combination also circumvented existing patents obtained by Wallace Carothers on polyesters. Initially, work focused on the production of fibres and flexible foams. With development constrained by World War II (when PUs were applied on a limited scale as aircraft coating), it was not until 1952 that polyisocyanates became commercially available. Commercial production of flexible polyurethane foam began in 1954, based on toluene diisocyanate (TDI) and polyester polyols. The invention of these foams (initially called *imitation swiss cheese* by the inventors) was thanks to water accidentally introduced in the reaction mix. These materials were also used to produce rigid foams, gum rubber, and elastomers. Linear fibers were produced from hexamethylene diisocyanate (HDI) and 1,4-butanediol (BDO).

The first commercially available polyether polyol, poly(tetramethylene ether) glycol, was introduced by DuPont in 1956 by polymerizing tetrahydrofuran. Less expensive polyalkylene glycols were introduced by BASF and Dow Chemical in 1957. Polyether polyols offered technical and commercial advantages such as low cost, ease of handling, and better hydrolytic stability over polyester polyols and quickly replaced them in the manufacture of polyurethane goods. Other PU pioneers were Union Carbide and Mobay, a U.S. Monsanto/Bayer joint venture. In 1960 more than 45,000 metric tons of flexible polyurethane foams were produced. As the decade progressed, the availability of chlorofluoroalkane blowing agents, inexpensive polyether polyols, and methylene diphenyl diisocyanate (MDI) heralded the development and use of polyurethane rigid foams as high performance insulation materials. Rigid foams based on polymeric MDI (PMDI) offered better thermal stability and combustion characteristics than those based on TDI. In 1967, urethane modified polyisocyanurate rigid foams were introduced, offering even better thermal stability and flammability resistance compared to low-density insulation products. During the 1960s, automotive interior safety components such as instrument and door panels were produced by back-filling thermoplastic skins with semi-rigid foam.

In 1969, Bayer exhibited an all plastic car in Düsseldorf, Germany. Parts of this car were manufactured using a new process called RIM, Reaction Injection Molding. RIM technology uses high pressure impingement of liquid reactive components followed by the rapid flow of the reaction mixture into a mold cavity. Large parts, such as automotive fascia and body panels, can be molded in this manner. Polyurethane RIM evolved into a number of different products and processes. Using diamine chain extenders and trimerization technology gave poly(urethane urea), poly(urethane isocyanurate), and polyurea RIM. The addition of fillers, such as milled glass, mica, and processed mineral fibres gave rise to reinforced RIM (RRIM), which provided improvements in flexural modulus (stiffness), reduction in coefficent of thermal expansion and thermal stability. This technology allowed production of the first plastic-body automobile in the United States, the Pontiac Fiero, in 1983. Further increases in flexural modulus were obtained by incorporating preplaced glass mats into the RIM mold cavity, also known broadly as resin injection molding (a process technology that also includes thermosetting polyester resins, epoxide resins, etc.) or more specifically for PUR systems as SRIM, or structural RIM.

Starting in the early 1980s, water-blown microcellular flexible foams were used to mold gaskets for panel and radial seal air filters in the automotive industry. Since then, increasing energy prices and the pressures to eliminate PVC plastisol from automotive applications have greatly increased market share. Costlier raw materials are offset by a significant decrease in part weight and in some cases, the elimination of metal end caps and filter housings. Highly filled polyurethane elastomers, and more recently unfilled polyurethane foams are now used in high temperature oil filter applications.

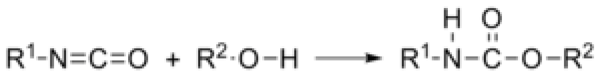
Polyurethane foam (including foam rubber) is often made by adding small amounts of volatile materials, so-called blowing agents, to the reaction mixture. These volatile chemicals yield important performance characteristics, primarily density reduction, cushioning/energy absorption and thermal insulation. In the early 1990s, because of their impact on ozone depletion, the Montreal Protocol led to the greatly reduced use of many chlorine-containing blowing agents, such as trichlorofluoromethane (CFC-11). Other haloalkanes, such as the hydrochlorofluorocarbon 1,1-dichloro-1-fluoroethane (HCFC-141b), were used as interim replacements until their phase out under the IPPC directive on greenhouse gases in 1994 and by the Volatile Organic Compounds (VOC) directive of the EU in 1997. By the late 1990s, the use of blowing agents such as carbon dioxide, pentane, 1,1,1,2-tetrafluoroethane (HFC-134a) and 1,1,1,3,3-pentafluoropropane (HFC-245fa) became more widespread in North America and the EU, although chlorinated blowing agents remained in use in many developing countries.

Building on existing polyurethane spray coating technology and polyetheramine chemistry, extensive development of two-component polyurea spray elastomers took place in the 1990s. Their fast reactivity and relative insensitivity to moisture make them useful coatings for large surface area projects, such as secondary containment, manhole and tunnel coatings, and tank liners. Excellent adhesion to concrete and steel is obtained with the proper surface treatment and primer. During the same period, new two-component polyurethane and hybrid polyurethane-polyurea elastomer technology was used to enter the marketplace of spray-in-place load bed liners and military marine applications for the U.S. Navy. Even a one-part polyurethane is specified as high durability deck coatings under MIL-PRF-32171 for the US Navy. This technique for coating creates a durable, abrasion resistant composite with the metal substrate, and eliminates corrosion and brittleness associated with drop-in thermoplastic bed liners.

The potential for polyols derived from vegetable oils to replace petrochemical-based polyols began garnering attention beginning around 2004, partly due to the rising costs of petrochemical feedstocks and partially due to an enhanced public desire for environmentally friendly green products. One of the most vocal supporters of these polyurethanes made using natural oil polyols is the Ford Motor Company.

Chemistry

generalized polyurethane reaction



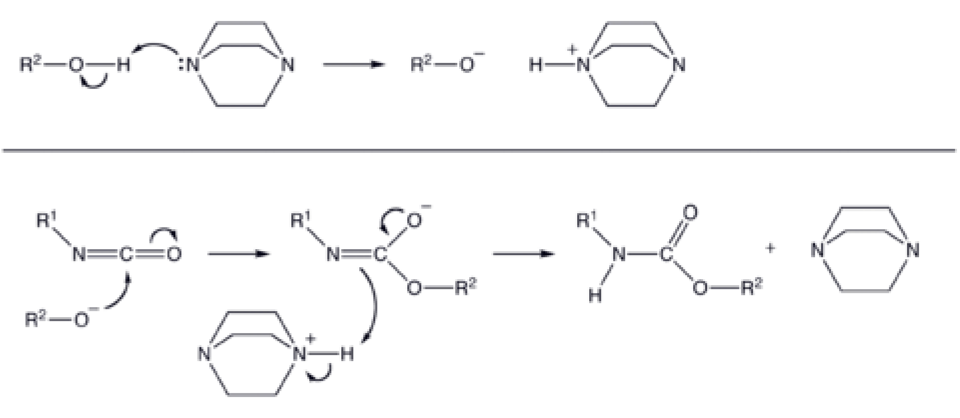
$$R^1\text{-}N{=}C{=}O + R^2\text{-}O\text{-}H \longrightarrow R^1\text{-}\overset{H}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R^2$$

Polyurethanes are in the class of compounds called **reaction polymers**, which include epoxies, unsaturated polyesters, and phenolics. A urethane linkage is produced by reacting an isocyanate group, -N=C=O with a hydroxyl (alcohol) group, -OH. Polyurethanes are produced by the polyaddition reaction of a polyisocyanate with a polyalcohol (polyol) in the presence of a catalyst and other additives. In this case, a polyisocyanate is a molecule with two or more isocyanate functional groups, $R\text{-}(N{=}C{=}O)_{n \geq 2}$ and a polyol is a molecule with two or more hydroxyl functional groups, $R'\text{-}(OH)_{n \geq 2}$. The reaction product is a polymer containing the urethane linkage, -RNHCOOR'-. Isocyanates will react with any molecule that contains an active hydrogen. Importantly, isocyanates react with water to form a urea linkage and carbon dioxide gas; they also react with polyetheramines to form polyureas. Commercially, polyurethanes are produced by reacting a liquid isocyanate with a liquid blend of polyols, catalyst, and other additives. These two components are referred to as a polyurethane system, or simply a system. The isocyanate is commonly referred to in North America as the 'A-side' or just the 'iso'. The blend of polyols and other additives is commonly referred to as the 'B-side' or as the 'poly'. This mixture might also be called a 'resin' or 'resin blend'. In Europe the meanings for 'A-side' and 'B-side' are reversed. Resin blend additives may include chain extenders, cross linkers, surfactants, flame retardants, blowing agents, pigments, and fillers.

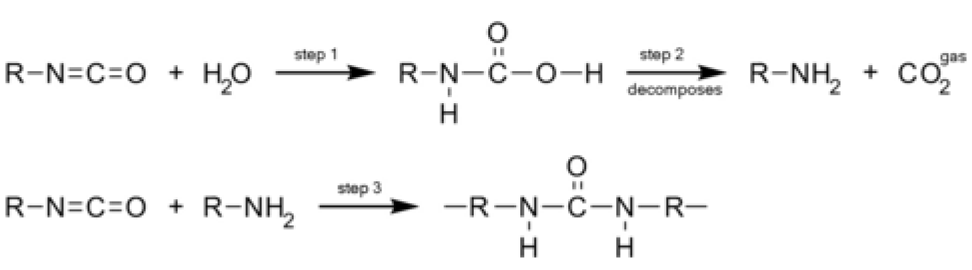
The first essential component of a polyurethane polymer is the isocyanate. Molecules that contain two isocyanate groups are called diisocyanates. These molecules are also referred to as monomers or monomer units, since they themselves are used to produce polymeric isocyanates that contain three or more isocyanate functional groups. Isocyanates can be classed as aromatic, such as diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI); or aliphatic, such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI). An example of a polymeric isocyanate is polymeric diphenylmethane diisocyanate, which is a blend of molecules with two-, three-, and four- or more isocyanate groups, with an average functionality of 2.7. Isocyanates can be further modified by partially reacting them with a polyol to form a prepolymer. A quasi-prepolymer is formed when the stoichiometric ratio of isocyanate to hydroxyl groups is greater than 2:1. A true prepolymer is formed when the stoichiometric ratio is equal to 2:1. Important characteristics of isocyanates are their molecular backbone, % NCO content, functionality, and viscosity.

The second essential component of a polyurethane polymer is the polyol. Molecules that contain two hydroxyl groups are called diols, those with three hydroxyl groups are called triols, et cetera. In practice, polyols are distinguished from short chain or low-molecular weight glycol chain extenders and cross linkers such as ethylene glycol (EG), 1,4-butanediol (BDO), diethylene glycol (DEG), glycerine, and trimethylolpropane (TMP). Polyols are polymers in their own right. They are formed by base-catalyzed addition of propylene oxide (PO), ethylene oxide (EO) onto a hydroxyl or amine containing initiator, or by polyesterification of a di-acid, such as adipic acid, with glycols, such as ethylene glycol or dipropylene glycol (DPG). Polyols extended with PO or EO are polyether polyols. Polyols formed by polyesterification are polyester polyols. The choice of initiator, extender, and molecular weight of the polyol greatly affect its physical state, and the physical properties of the polyurethane polymer. Important characteristics of polyols are their molecular backbone, initiator, molecular weight, % primary hydroxyl groups, functionality, and viscosity.

PU reaction mechanism catalyzed by a tertiary amine



carbon dioxide gas formed by reacting water and isocyanate


$$R{-}N{=}C{=}O + H_2O \xrightarrow{\text{step 1}} R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H \xrightarrow[\text{decomposes}]{\text{step 2}} R{-}NH_2 + CO_2^{\text{gas}}$$

$$R{-}N{=}C{=}O + R{-}NH_2 \xrightarrow{\text{step 3}} {-}R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}R{-}$$

The polymerization reaction is catalyzed by tertiary amines, such as dimethylcyclohexylamine, and organometallic compounds, such as dibutyltin dilaurate or bismuth octanoate. Furthermore, catalysts can be chosen based on whether they favor the urethane (gel) reaction, such as 1,4-diazabicyclo[2.2.2]octane (also called DABCO or TEDA), or the urea (blow) reaction, such as bis-(2-dimethylaminoethyl)ether, or specifically drive the isocyanate trimerization reaction, such as potassium octoate.

One of the most desirable attributes of polyurethanes is their ability to be turned into foam. Blowing agents such as water, certain halocarbons such as HFC-245fa (1,1,1,3,3-pentafluoropropane) and HFC-134a (1,1,1,2-tetrafluoroethane), and hydrocarbons such as n-pentane, can be incorporated into the poly side or added as an auxiliary stream. Water reacts with the isocyanate to create carbon dioxide gas, which fills and expands cells created during the mixing process. The reaction is a three step process. A water molecule reacts with an isocyanate group to form a carbamic acid. Carbamic acids are unstable, and decompose forming carbon dioxide and an amine. The amine reacts with more isocyanate to give a substituted urea. Water has a very low molecular weight, so even though the weight percent of water may be small, the molar proportion of water may be high and considerable amounts of urea produced. The urea is not very soluble in the reaction mixture and tends to form separate "hard segment" phases consisting mostly of polyurea. The concentration and organization of these polyurea phases can have a significant impact on the properties of the polyurethane foam. Halocarbons and hydrocarbons are chosen such that they have boiling points at or near room temperature. Since the polymerization reaction is exothermic, these blowing agents volatilize into a gas during the reaction process. They fill and expand the cellular polymer matrix, creating a foam. It is important to know that the blowing gas does not create the cells of a foam. Rather, foam cells are a result of blowing gas diffusing into bubbles that are nucleated or stirred into the system at the time of mixing. In fact, high-density microcellular foams can be formed without the addition of blowing agents by mechanically frothing or nucleating the polyol component prior to use.

Surfactants are used to modify the characteristics of the polymer during the foaming process. They are used to emulsify the liquid components, regulate cell size, and stabilize the cell structure to prevent collapse and surface defects. Rigid foam surfactants are designed to produce very fine cells and a very high closed cell content. Flexible foam surfactants are designed to stabilize the reaction mass while at the same time maximizing open cell content to prevent the foam from shrinking. The need for surfactant can be affected by choice of isocyanate, polyol, component compatibility, system reactivity, process conditions and equipment, tooling, part shape, and shot weight.

Though the properties of the polyurethane are determined mainly by the choice of polyol, the diisocyanate exerts some influence, and must be suited to the application. The cure rate is influenced by the functional group reactivity and the number of functional isocyanate groups. The mechanical properties are influenced by the functionality and the molecular shape. The choice of diisocyanate also affects the stability of the polyurethane upon exposure to light. Polyurethanes made with aromatic diisocyanates yellow with exposure to light, whereas those made with aliphatic diisocyanates are stable.

Softer, elastic, and more flexible polyurethanes result when linear difunctional polyethylene glycol segments, commonly called polyether polyols, are used to create the urethane links. This strategy is used to make spandex elastomeric fibers and soft rubber parts, as well as foam rubber. More rigid products result if polyfunctional polyols are used, as these create a three-dimensional cross-linked structure which, again, can be in the form of a low-density foam.

An even more rigid foam can be made with the use of specialty trimerization catalysts which create cyclic structures within the foam matrix, giving a harder, more thermally stable structure, designated as polyisocyanurate foams. Such properties are desired in rigid foam products used in the construction sector.

Careful control of viscoelastic properties — by modifying the catalysts and polyols used —can lead to memory foam, which is much softer at skin temperature than at room temperature.

There are then two main foam variants: one in which most of the foam bubbles (cells) remain closed, and the gas(es) remains trapped, the other being systems which have mostly open cells, resulting after a critical stage in the foam-making process (if cells did not form, or became open too soon, foam would not be created). This is a vitally important process: if the flexible foams have closed cells, their softness is severely compromised, they become pneumatic in feel, rather than soft; so, generally speaking, flexible foams are required to be open-celled.

The opposite is the case with most rigid foams. Here, retention of the cell gas is desired since this gas (especially the fluorocarbons referred to above) gives the foams their key characteristic: high thermal insulation performance.

A third foam variant, called microcellular foam, yields the tough elastomeric materials typically experienced in the coverings of car steering wheels and other interior automotive components.

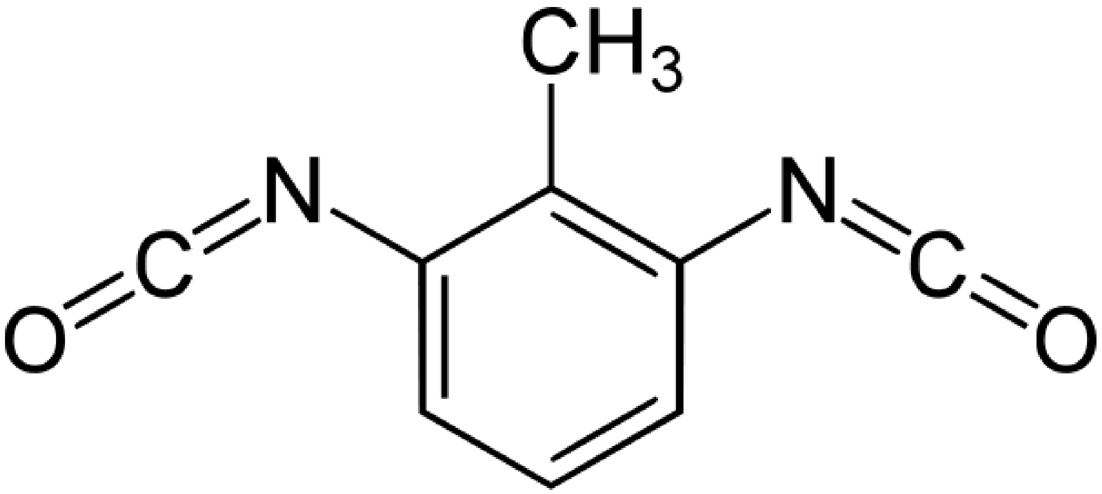
Raw materials

For the manufacture of polyurethane polymers, two groups of at least bifunctional substances are needed as reactants; compounds with isocyanate groups, and compounds with active hydrogen atoms. The physical and chemical character, structure, and molecular size of these compounds influence the polymerization reaction, as well as ease of processing and final physical properties of the finished polyurethane. In addition, additive such as catalysts, surfactants, blowing agents, cross linkers, flame retardants, light stabilizers, and fillers are used to control and modify the reaction process and performance characteristics of the polymer.

Isocyanates

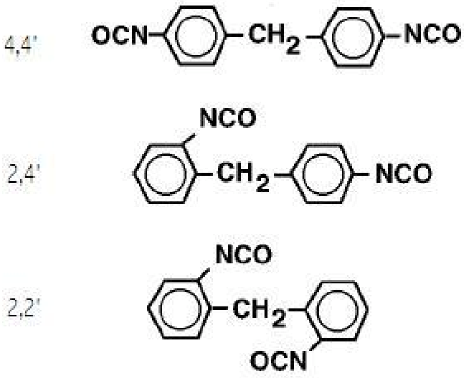
Isocyanates with two or more functional groups are required for the formation of polyurethane polymers. Volume wise, aromatic isocyanates account for the vast majority of global diisocyanate production. Aliphatic and cycloaliphatic isocyanates are also important building blocks for polyurethane materials, but in much smaller volumes. There are a number of reasons for this. First, the aromatically linked isocyanate group is much more reactive than the aliphatic one. Second, aromatic isocyanates are more economical to use. Aliphatic isocyanates are used only if special properties are required for the final product. For example, light stable coatings and elastomers can only be obtained with aliphatic isocyanates. Even within the same class of isocyanates, there is a significant difference in reactivity of the functional groups based on steric hindrance. In the case of 2,4-toluene diisocyanate, the isocyanate group in the para position to the methyl group is much more reactive than the isocyanate group in the ortho position.

Phosgenation of corresponding amines is the main technical process for the manufacture of isocyanates. The amine raw materials are generally manufactured by the hydrogenation of corresponding nitro compounds. For example, toluenediamine (TDA) is manufactured from dinitrotoluene, which then converted to toluene diisocyanate (TDI). Diamino diphenylmethane or methylenedianiline (MDA) is manufactured from nitrobenzene via aniline, which is then converted to diphenylmethane diisocyanate (MDI).

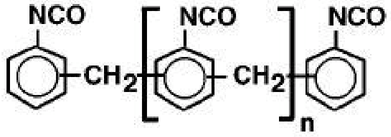


2,6-Diisocyanatotoluene

The two most important commercial, aromatic isocyanates are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). TDI consists of a mixture of the 2,4- and 2,6-diisocyanatotoluene isomers. The most important product is TDI-80 (TD-80), consisting of 80% of the 2,4-isomer and 20% of the 2,6-isomer. This blend is used extensively in the manufacture of polyurethane flexible slabstock and molded foam. TDI, and especially crude TDI and TDI/MDI blends can be used in rigid foam applications, but have been supplanted by polymeric MDI. TDI-polyether and TDI-polyester prepolymers are used in high performance coating and elastomer applications. Prepolymers are available that have been vacuum stripped of TDI monomer, which greatly reduces their toxicity. Diphenylmethane diisocyanate (MDI) has three isomers, 4,4'-MDI, 2,4'-MDI, and 2,2'-MDI, and is also polymerized to provide oligomers of functionality three and higher.



Pure MDI's



Polymeric MDI's

Only the 4,4'-MDI monomer is sold commercially as a single isomer. It is provided either as a frozen solid or flake, or in molten form, and is used to manufacture high performance prepolymers. Monomer blends, consisting of approximately 50% of the 4,4'-isomer and 50% of the 2,4'-isomer, are liquid at room temperature and are used to manufacture prepolymers for polyurea spray elastomer applications. 4,4'-MDI blends containing MDI uretonimine, carbodiimide, and allophonate moieties are also liquid at room temperature, and are used in the manufacture of integral skin and microcellular foams. 4,4'-MDI-glycol prepolymers offer increased mechanical properties in the same applications, but are prone to freezing at temperatures below 20 °C. Polymeric MDI (PMDI) is used in rigid pour-in-place, spray foam, and molded foam applications. Polymeric MDI that contains a very high portion of high-functionality oligomers is used to manufacture polyurethane and polyisocyanurate rigid insulation boardstock. Modified PMDI, which contains high levels of MDI monomer, is used in the production of polyurethane flexible molded and microcellular foams. The relative percentage of the 4,4'- and 2,4'- isomers is adjusted to change the reactivity and storage stability of the isocyanate blend, as well as the firmness and other physical properties of the finished goods. Other aromatic isocyanate include p-phenylene diisocyanate (PPDI), naphthalene diisocyanate (NDI), and o-tolidine diisocyanate (TODI).

The most important aliphatic and cycloaliphatic isocyanates are 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate, IPDI), and 4,4'-diisocyanato dicyclohexylmethane (H_{12}MDI or hydrogenated MDI). They are used to produce light stable, non-yellowing polyurethane coatings and elastomers. Because of their volatility and toxicity, aliphatic isocyanate monomers are converted into prepolymers, biurets, dimers, and trimers for commercial use. HDI adducts are used extensively for weather and abrasion resistant coatings and lacquers. IPDI is used in the manufacture of coatings, elastomeric adhesives and sealants. H_{12}MDI prepolymers are used to produce high performance coatings and elastomers with optical clarity and hydrolysis resistance. Other aliphatic isocyanates include cyclohexane diisocyanate (CHDI), tetramethylxylene diisocyanate (TMXDI), and 1,3-bis(isocyanatomethyl)cyclohexane (H_6XDI).

Polyols

Polyols are higher molecular weight materials manufactured from an initiator and monomeric building blocks. They are most easily classified as polyether polyols, which are made by the reaction of epoxides (oxiranes) with an active hydrogen containing starter compounds, or polyester polyols, which are made by the polycondensation of multifunctional carboxylic acids and hydroxyl compounds. They can be further classified according to their end use as flexible or rigid polyols, depending on the functionality of the initiator and their molecular weight. Taking into account functionality, flexible polyols have molecular weights from 2,000 to 10,000 (OH# from 18 to 56). Rigid polyols have molecular weights from 250 to 700 (OH# from 300 to 700). Polyols with molecular weights from 700 to 2,000 (OH# 60 to 280) are used to add stiffness or flexibility to base systems, as well as increase solubility of low molecular weight glycols in high molecular weight polyols.

Polyether polyols come in a wide variety of grades based on their end use, but are all constructed in a similar manner. Polyols for flexible applications use low functionality initiators such as dipropylene glycol (f=2), glycerine (f=3) or a sorbitol/water solution (f=2.75). Polyols for rigid applications use high functionality initiators such sucrose (f=8), sorbitol (f=6), toluenediamine (f=4), and Mannich bases (f=4). Propylene oxide is then added to the initiators until the desired molecular weight is achieved. Polyols extended with propylene oxide are terminated with secondary hydroxyl groups. In order to change the compatibility, rheological properties, and reactivity of a polyol, ethylene oxide is used as a co-reactant to create random or mixed block heteropolymers. Polyols capped with ethylene oxide contain a high percentage of primary hydroxyl groups, which are more reactive than secondary hydroxyl groups. Because of their high viscosity (470 OH# sucrose polyol, 33 Pa·s at 25 °C), carbohydrate initiated polyols often use glycerine or diethylene glycol as a co-initiate in order to lower the viscosity to ease handling and processing (490 OH# sucrose-glycerine polyol, 5.5 Pa·s at 25 °C). Graft polyols (also called filled polyols or polymer polyols) contain finely dispersed styrene-acrylonitrile, acrylonitrile, or polyurea (PHD) polymer solids chemically grafted to a high molecular weight polyether backbone. They are used to increase the load bearing properties of low-density high-resiliency (HR) foam, as well as add toughness to microcellular foams and cast elastomers. PHD polyols are also used to modify the combustion properties of HR flexible foam. Solids content ranges from 14% to 50%, with 22% and 43% being typical. Initiators such as ethylenediamine and triethanolamine are used to make low molecular weight rigid foam polyols that have built-in catalytic activity due to the presence of nitrogen atoms in the backbone. They are used to increase system reactivity and physical property build, and to reduce the friability of rigid foam molded parts. A special class of polyether polyols, poly(tetramethylene ether) glycols are made by polymerizing tetrahydrofuran. They are used in high performance coating and elastomer applications.

Polyester polyols fall into two distinct categories according to composition and application. Conventional polyester polyols are based on virgin raw materials and are manufactured by the direct polyesterification of high-purity diacids and glycols, such as adipic acid and 1,4-butanediol. They are distinguished by the choice of monomers, molecular weight, and degree of branching. While costly and difficult to handle because of their high viscosity, they offer physical properties not obtainable with polyether polyols, including superior solvent, abrasion, and cut resistance. Other polyester polyols are based on reclaimed raw materials. They are manufactured by transesterification (glycolysis) of recycled poly(ethyleneterephthalate) (PET) or dimethylterephthalate (DMT) distillation bottoms with glycols such as diethylene glycol. These low molecular weight, aromatic polyester polyols are used in the manufacture of rigid foam, and bring low cost and excellent flammability characteristics to polyisocyanurate (PIR) boardstock and polyurethane spray foam insulation.

Many polyols are polydispersive materials, being blends of two or more polyols each of specific molecular weights, to give intermediate molecular weight materials. It is not unusual to find blends of polyether and polyester polyols, to give specific compromises in properties.

Specialty polyols include polycarbonate polyols, polycaprolactone polyols, polybutadiene polyols, and polysulfide polyols. The materials are used in elastomer, sealant, and adhesive applications that require superior weatherability, and resistance to chemical and environmental attack. Natural oil polyols derived from castor oil and other vegetable oils are used to make elastomers, flexible bunstock, and flexible molded foam. Copolymerizing chlorotrifluoroethylene or tetrafluoroethylene with vinyl ethers containing hydroxyalkyl vinyl ether produces fluorinated (FEVE) polyols. Two component fluorinated polyurethane prepared by reacting FEVE fluorinated polyols with polyisocyanate have been applied for make ambient cure paint/coating. Since fluorinated polyurethanes contain high percentage of fluorine-carbon bond which is the strongest bond among all chemical bonds. Fluorinated polyurethanes have excellent resistance to UV, acids, alkali, salts, chemicals, solvents, weathering, corrosion, fugi and microbial attack. These have become the first choice for high performance coating/paints.

Chain extenders and cross linkers

Chain extenders (f=2) and cross linkers (f=3 or greater) are low molecular weight hydroxyl and amine terminated compounds that play an important role in the polymer morphology of polyurethane fibers, elastomers, adhesives, and certain integral skin and microcellular foams. The elastomeric properties of these materials are derived from the phase separation of the hard and soft copolymer segments of the polymer, such that the urethane hard segment domains serve as cross-links between the amorphous polyether (or polyester) soft segment domains. This phase separation occurs because the mainly non-polar, low melting soft segments are incompatible with the polar, high melting hard segments. The soft segments, which are formed from high molecular weight polyols, are mobile and are normally present in coiled formation, while the hard segments, which are formed from the isocyanate and chain extenders, are stiff and immobile. Because the hard segments are covalently coupled to the soft segments, they inhibit plastic flow of the polymer chains, thus creating elastomeric resiliency. Upon mechanical deformation, a portion of the soft segments are stressed by uncoiling, and the hard segments become aligned in the stress direction. This reorientation of the hard segments and consequent powerful hydrogen bonding contributes to high tensile strength, elongation, and tear resistance values. The choice of chain extender also determines flexural, heat, and chemical resistance properties. The most important chain extenders are ethylene glycol, 1,4-butanediol (1,4-BDO or BDO), 1,6-hexanediol, cyclohexane dimethanol and hydroquinone bis(2-hydroxyethyl) ether (HQEE). All of these glycols form polyurethanes that phase separate well and form well defined hard segment domains, and are melt processable. They are all suitable for thermoplastic polyurethanes with the exception of ethylene glycol, since its derived bis-phenyl urethane undergoes unfavorable degradation at high hard segment levels. Diethanolamine and triethanolamine are used in flex molded foams to build firmness and add catalytic activity. Diethyltoluenediamine is used extensively in RIM, and in polyurethane and polyurea elastomer formulations.

table of chain extenders and cross linkers				
hydroxyl compounds – difunctional molecules				
	MW	**s.g.**	**m.p. °C**	**b.p. °C**
ethylene glycol	62.1	1.110	-13.4	197.4
diethylene glycol	106.1	1.111	-8.7	245.5
triethylene glycol	150.2	1.120	-7.2	287.8
tetraethylene glycol	194.2	1.123	-9.4	325.6
propylene glycol	76.1	1.032	supercools	187.4
dipropylene glycol	134.2	1.022	supercools	232.2
tripropylene glycol	192.3	1.110	supercools	265.1
1,3-propanediol	76.1	1.060	-28	210
1,3-butanediol	92.1	1.005	-	207.5
1,4-butanediol	92.1	1.017	20.1	235
neopentyl glycol	104.2	-	130	206
1,6-hexanediol	118.2	1.017	43	250
1,4-cyclohexanedimethanol	-	-	-	-
HQEE	-	-	-	-
ethanolamine	61.1	1.018	10.3	170
diethanolamine	105.1	1.097	28	271
methyldiethanolamine	119.1	1.043	-21	242
phenyldiethanolamine	181.2	-	58	228
hydroxyl compounds – trifunctional molecules				
	MW	**s.g.**	**f.p. °C**	**b.p. °C**

glycerol	92.1	1.261	18.0	290
trimethylolpropane	-	-	-	-
1,2,6-hexanetriol	-	-	-	-
triethanolamine	149.2	1.124	21	-
hydroxyl compounds – tetrafunctional molecules				
	MW	**s.g.**	**m.p. °C**	**b.p. °C**
pentaerythritol	136.2	-	260.5	-
N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine	-	-	-	-
amine compounds – difunctional molecules				
	MW	**s.g.**	**m.p. °C**	**b.p. °C**
diethyltoluenediamine	178.3	1.022	-	308
dimethylthiotoluenediamine	214.0	1.208	-	-

Catalysts

Polyurethane catalysts can be classified into two broad categories, amine compounds and organometallic complexes. They can be further classified as to their specificity, balance, and relative power or efficiency. Traditional amine catalysts have been tertiary amines such as triethylenediamine (TEDA, also known as 1,4-diazabicyclo[2.2.2]octane or DABCO, an Air Products's trade mark), dimethylcyclohexylamine (DMCHA), and dimethylethanolamine (DMEA). Tertiary amine catalysts are selected based on whether they drive the urethane (polyol+isocyanate, or gel) reaction, the urea (water+isocyanate, or blow) reaction, or the isocyanate trimerization reaction (e.g. using potassium acetate, to form isocyanurate ring structure). Since most tertiary amine catalysts will drive all three reactions to some extent, they are also selected based on how much they favor one reaction over another. For example, tetramethylbutanediamine (TMBDA) preferentially drives the gel reaction over the blow reaction. On the other hand, both pentamethyldipropylenetriamine and N-(3-dimethylaminopropyl)-N,N-diisopropanolamine balance the blow and gel reactions, although the former is more potent than the later on a weight basis. 1,3,5-(tris(3-dimethylamino)propyl)-hexahydro-s-triazine is a trimerization catalyst that also strongly drives the blow reaction. Molecular structure gives some clue to the strength and selectivity of the catalyst. Blow catalysts generally have an ether linkage two carbons away from a tertiary nitrogen. Examples include bis-(2-dimethylaminoethyl)ether (also known as A-99, formerly a Union Carbide product), and N-ethylmorpholine. Strong gel catalysts contain alkyl-substituted nitrogens, such as triethylamine (TEA), 1,8-diazabicyclo[5.4.0]undecene-7 (DBU), and pentamethyldiethylenetriamine (PMDETA). Weaker gel catalysts contain ring-substituted nitrogens, such as benzyldimethylamine (BDMA). Trimerization catalysts contain the triazine structure, or are quaternary ammonium salts. Two trends have emerged since the late 1980s. The requirement to fill large, complex tooling with increasing production rates has led to the use of blocked catalysts to delay front end reactivity while maintaining back end cure. In the United States, acid- and quaternary ammonium salt-blocked TEDA and bis-(2-dimethylaminoethyl)ether are common blocked catalysts used in molded flexible foam and microcellular integral skin foam applications. Increasing aesthetic and environmental awareness has led to the use of non-fugitive catalysts for vehicle interior and furnishing applications in order to reduce odor, fogging, and the staining of vinyl coverings. Catalysts that contain a hydroxyl group or an active amino hydrogen, such as N,N,N'-trimethyl-N'-hydroxyethyl-bis(aminoethyl)ether and N'-(3-(dimethylamino)propyl)-N,N-dimethyl-1,3-propanediamine that react into the polymer matrix can replace traditional catalysts in these applications.

Organometallic compounds based on mercury, lead, tin (dibutyltin dilaurate), bismuth (bismuth octanoate), and zinc are used as polyurethane catalysts. Mercury carboxylates, such as phenylmercuric neodeconate, are particularly effective catalysts for polyurethane elastomer, coating and sealant applications, since they are very highly selective towards the polyol+isocyanate reaction. Mercury catalysts can be used at low levels to give systems a long pot life while still giving excellent back-end cure. Lead catalysts are used in highly reactive rigid spray foam insulation applications, since they maintain their potency in low temperature and high humidity conditions. Due to their toxicity and the necessity to dispose of mercury and lead catalysts and catalyzed material as hazardous waste in the United States, formulators have been searching for suitable replacements. Since the 1990s, bismuth and zinc carboxylates have been used as alternatives but have short comings of their own. In elastomer applications, long pot life systems do not build green strength as fast as mercury catalyzed systems. In spray foam applications, bismuth and zinc do not drive the front end fast enough in cold weather conditions and must be otherwise augmented to replace lead. Alkyl tin carboxylates, oxides and mercaptides oxides are used in all types of polyurethane applications. For example, dibutyltin dilaurate is a standard catalyst for polyurethane adhesives and sealants, dioctyltin mercaptide is used in microcellular elastomer applications, and dibutyltin oxide is used in polyurethane paint and coating applications. Tin mercaptides are used in formulations that contain water, as tin carboxylates are susceptible to degradation from hydrolysis.

Surfactants

Surfactants are used to modify the characteristics of both foam and non-foam polyurethane polymers. They take the form of polydimethylsiloxane-polyoxyalkylene block copolymers, silicone oils, nonylphenol ethoxylates, and other organic compounds. In foams, they are used to emulsify the liquid components, regulate cell size, and stabilize the cell structure to prevent collapse and sub-surface voids. In non-foam applications they are used as air release and anti-foaming agents, as wetting agents, and are used to eliminate surface defects such as pin holes, orange peel, and sink marks.

Production

The main polyurethane producing reaction is between a diisocyanate (aromatic and aliphatic types are available) and a polyol, typically a polypropylene glycol or polyester polyol, in the presence of catalysts and materials for controlling the cell structure, (surfactants) in the case of foams. Polyurethane can be made in a variety of densities and hardnesses by varying the type of monomer(s) used and adding other substances to modify their characteristics, notably density, or enhance their performance. Other additives can be used to improve the fire performance, stability in difficult chemical environments and other properties of the polyurethane products.

Health and safety

Fully reacted polyurethane polymer, CAS # 9009-54-5 (CAS registry number), is chemically inert. No exposure limits have been established by OSHA (Occupational Safety and Health Administration) or ACGIH (American Conference of Governmental Industrial Hygienists). It is not regulated by OSHA for carcinogenicity. Polyurethane polymer is a combustible solid and will ignite if exposed to an open flame. It begins to break down at about 240 °C (464 °F). Decomposition can produce isocyanates, carbon monoxide, nitrogen oxides, and hydrogen cyanide. Firefighters should wear self-contained breathing apparatus in enclosed areas. Polyurethane polymer dust can cause irritation to the eyes and lungs. Proper hygiene controls and personal protective equipment (PPE), such as gloves, dust masks, respirators, mechanical ventilation, and protective clothing and eye wear should be used.

Liquid resin blends and isocyanates may contain hazardous or regulated components. They should be handled in accordance with manufacturer recommendations found on product labels, and in MSDS (Material Safety Data Sheet) and product technical literature. Isocyanates are known skin and respiratory sensitizers, and proper engineering controls should be in place to prevent exposure to isocyanate liquid and vapor.

In the United States, additional health and safety information can be found through organizations such as the Polyurethane Manufacturers Association (PMA) and the Center for the Polyurethanes Industry (CPI), as well as from polyurethane system and raw material manufacturers. In Europe, health and safety information is available from ISOPA, the European Diisocyanate and Polyol Producers Association. Regulatory information can be found in the Code of Federal Regulations Title 21 (Food and Drugs) and Title 40 (Protection of the Environment).

Manufacturing

The methods of manufacturing polyurethane finished goods range from small, hand pour piece-part operations to large, high-volume bunstock and boardstock production lines. Regardless of the end-product, the manufacturing principle is the same: to meter the liquid isocyanate and resin blend at a specified stoichiometric ratio, mix them together until a homogeneous blend is obtained, dispense the reacting liquid into a mold or on to a surface, wait until it cures, then demold the finished part.

Dispensing equipment

Although the capital outlay can be high, it is desirable to use a meter-mix or dispense unit for even low-volume production operations that require a steady output of finished parts. Dispense equipment consists of material holding (day) tanks, metering pumps, a mix head, and a control unit. Often, a conditioning or heater-chiller unit is added to control material temperature in order to improve mix efficiency, cure rate, and to reduce process variability. Choice of dispense equipment components depends on shot size, throughput, material characteristics such as viscosity and filler content, and process control. Material day tanks may be single to hundreds of gallons in size, and may be supplied directly from drums, IBCs (intermediate bulk containers, such as totes), or bulk storage tanks. They may incorporate level sensors, conditioning jackets, and mixers. Pumps can be sized to meter in single grams per second up to hundreds of pounds per minute. They can be rotary, gear, or piston pumps, or can be specially hardened lance pumps to meter liquids containing highly abrasive fillers such as wollastonite, chopped or hammer milled glass fibres.

A high pressure polyurethane dispense unit, showing control panel, high pressure pump, integral day tanks, and hydraulic drive unit.

A high pressure mix head, showing simple controls. Front view

A high pressure mix head, showing material supply and hydraulic actuator lines. Rear view.

The pumps can drive low-pressure (10 to 30 bar, ~1 to 3 MPa) or high-pressure (125 to 250 bar, ~12.5 to 25.0 MPa) dispense systems. Mix heads can be simple static mix tubes, rotary element mixers, low-pressure dynamic mixers, or high-pressure hydraulically actuated direct impingement mixers. Control units may have basic on/off – dispense/stop switches, and analogue pressure and temperature gages, or may be computer controlled with flow meters to electronically calibrate mix ratio, digital temperature and level sensors, and a full suite of statistical process control software. Add-ons to dispense equipment include nucleation or gas injection units, and third or fourth stream capability for adding pigments or metering in supplemental additive packages.

A low pressure mix head with calibration chamber installed, showing material supply and air actuator lines.

Low pressure mix head components, including mix chambers, conical mixers, and mounting plates

5-gallon (20-liter) material day tanks for supplying a low pressure dispense unit

Tooling

Distinct from pour-in-place, bun and boardstock, and coating applications, the production of piece parts requires some type of tooling to contain and form the reacting liquid. The choice of mold-making material is dependent on the expected number of uses to end-of-life (EOL), molding pressure, flexibility, and heat transfer characteristics. RTV silicone is used for tooling that has an EOL in the thousands of parts. It is typically used for molding rigid foam parts, where the ability to stretch and peel the mold around undercuts is needed. The heat transfer characteristic of RTV silicone tooling is poor. High-performance, flexible polyurethane elastomers are also used in this way.

Epoxy, metal-filled epoxy, and metal-coated epoxy is used for tooling that has an EOL in the tens-of-thousands of parts. It is typically used for molding flexible foam cushions and seating, integral skin and microcellular foam padding, and shallow-draft RIM bezels and fascia.

The heat transfer characteristic of epoxy tooling is fair; the heat transfer characteristic of metal-filled and metal-coated epoxy is good. Copper tubing can be incorporated into the body of the tool, allowing hot water to circulate and heat the mold surface. Aluminum is used for tooling that has an EOL in the hundreds-of-thousands of parts. It is typically used for molding microcellular foam gasketing and cast elastomer parts, and is milled or extruded into shape. Mirror-finish stainless steel is used for tooling that imparts a glossy appearance to the finished part. The heat transfer characteristic of metal tooling is excellent. Finally, molded or milled polypropylene is used to create low-volume tooling for molded gasket applications. Instead of many expensive metal molds, low-cost plastic tooling can be formed from a single metal master, which also allows greater design flexibility. The heat transfer characteristic of polypropylene tooling is poor, which must be taken into consideration during the formulation process.

Applications

In 2007, the global consumption of polyurethane raw materials was above 12 million metric tons, the average annual growth rate is about 5%.

Testing

Effects of visible light

Polyurethanes, especially those made using aromatic isocyanates, contain chromophores which interact with light. This is of particular interest in the area of polyurethane coatings, where light stability is a critical factor and is the main reason that aliphatic isocyanates are used in making polyurethane coatings. When PU foam, which is made using aromatic isocyanates, is exposed to visible light it discolors, turning from off-white to yellow to reddish brown. It has been generally accepted that apart from yellowing, visible light has little effect on foam properties. This is especially the case if the yellowing happens on the outer portions of a large foam, as the deterioration of properties in the outer portion has little effect on the overall bulk properties of the foam itself.

It has been reported that exposure to visible light can affect the variability of some physical property test results. Increasing exposure time and/or light intensity during the storage of foam samples under ambient laboratory conditions increased the amount of permanent set induced in some compression set tests (the samples did not fully return to their original size and/or shape). Variability resulted from uncontrolled light exposure of cut samples prior to being compressed. Other foam properties were not substantively affected. It was recommended that specimen preparation and testing be done rapidly to minimize variation in results or if specimens are prepared but not tested for a week or more, that the samples should be protected from light exposure.

Higher-energy UV radiation promotes chemical reactions in foam, some of which are detrimental to the foam structure.