Fundamentals of Epoxy Formulation

Brahmadeo Dewprashad
Halliburton Services, P. O. Drawer 1431, Duncan, OK 73536

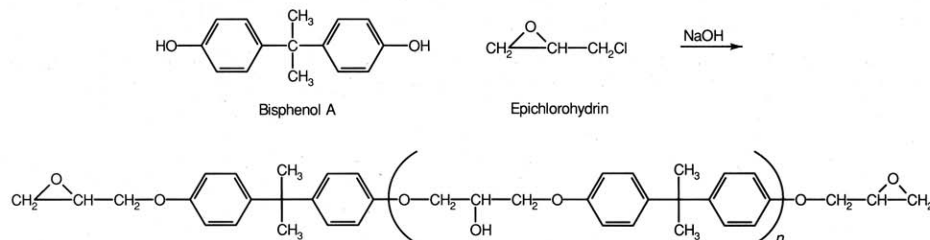
E. J. Eisenbraun
Oklahoma State University, Stillwater, OK 74078

Epoxy resins, first offered commercially in 1946, are used extensively now as protective coatings, adhesives, electrical laminates, reinforced plastics, and commercial flooring. An understanding of the chemistry of epoxy formulation is usually a goal in polymer chemistry courses. This article is intended as background for lectures on this topic.

Epoxy resins are characterized by the presence of one or more three-membered rings, variously known as the epoxy, epoxide, oxirane, or ethoxyline group and an aliphatic, cycloaliphatic or aromatic backbone. Reaction of this functional group with a curing agent or hardener results in a thermoset polymer. This is known as curing, and heat may be required for completion. Other constituents, e.g., diluents and fillers, may be included to facilitate processing and to modify properties of the thermoset. There are numerous oxirane starting materials and a great variety of coreactants are available; as such, epoxides are extremely versatile. The term *epoxy resin* is applied to the starting oxirane materials and the coreacted thermoset products. The second-order transition temperature or glass transition temperature (T_g) is one of the more useful properties for characterizing a resin and determining its useful temperature range. This temperature establishes the upper useful limit of the cured resin. The pot life or working time of an epoxy formulation is the time that it remains suitable for application as the mixture becomes progressively viscous.

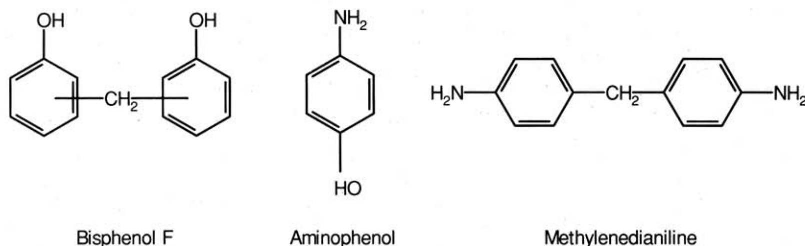
Resins

The first commercial, and still most widely used, epoxy resins were the diglycidyl ether of bisphenol A and higher molecular weight species. They usually are produced by reacting bisphenol A and excess epichlorohydrin in the presence of NaOH as shown below. The degree of polymerization is regulated by the ratio of reactants; as such, a range of commercial resins is available with n up to 25. The low molecular-



weight liquid products have an n value about 1 or below. Above this value, the resins are brittle solids.

There are many other epoxy resins on the market including glycidyl ethers based on bisphenol F, aminophenols and diamines, e.g. methylenedianiline (MDA).



The latter two form tri- and tetrafunctional resins, respectively. In these cases, the built-in tertiary amines in the backbone accelerate cure but are responsible for shortening the shelf-life. Generally, multi-functional resins, when cured with a suitable hardener at high temperatures, provide outstanding heat resistance due to the large number of crosslinkages in the network.

Novolac resins are produced by the intereaction of phenol or its alkyl substituted derivatives, e.g., cresol, and formaldehyde, in the presence of acid. This provides random ortho- and para-methylene bridges as shown (Fig. 1). Epoxy novolac resins are solids at room temperature, have

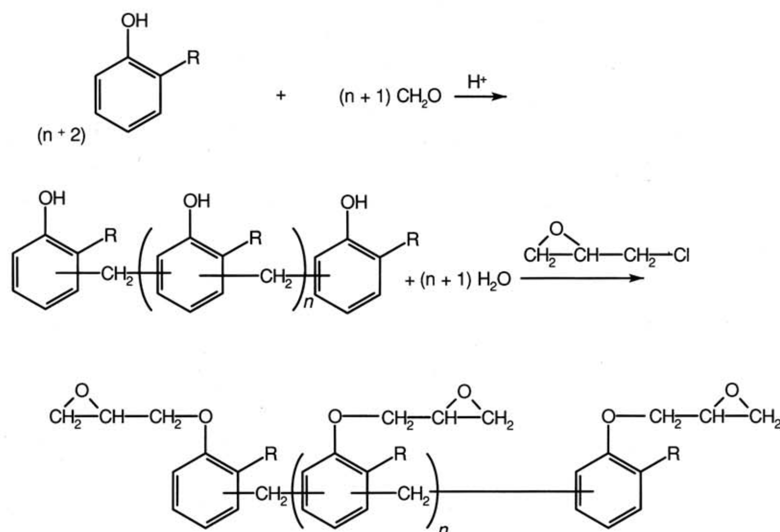


Figure 1. Synthetic route to Novolac resins.

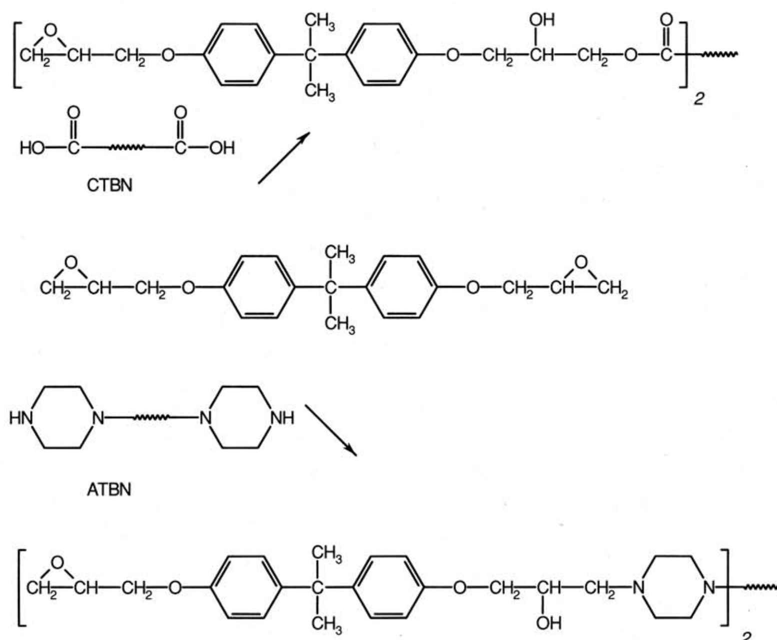


Figure 2. CTBN and ATBN toughening or epoxy resin.

higher functionality than resin-based on bisphenol A and are used in applications where high-temperature performance and resistance to chemical attack are important.

Since epoxy resins are mutually soluble, blends of solid and liquid resins can be used to obtain specific properties. A consideration of the features of the epoxy molecule that make it uniquely suited for multiple applications should help in determining the resin/resin mix to be used. For example, the polymer obtained from bisphenol A is chemically resistant because of the ether linkage and tough because of the methyl groups. The hydroxyl groups are good sites for adhesion and can be used as additional reactive sites. In addition, aromatic groups add rigidity to the structure, thereby improving the high temperature performance of the resin.

A number of higher molecular weight and multifunctional resins have been borne in organic cosolvents to reduce their viscosity and facilitate application. More recently, stricter environmental regulations have resulted in lower permissible levels of solvent release during cure. However, there are now available water-borne epoxy-dispersed resins (*1*). A judicious choice of surfactants results in a stable dispersion and chemically stable epoxy resin. These dispersions have many of the advantages of conventional epoxies and can be cured with agents used with traditional epoxies.

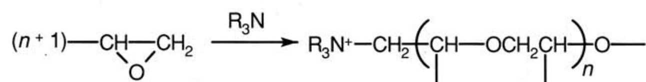
Commercial resins do not have only epoxy terminal groups since other end groups may result from the manufacturing process and for a given type of resin, more than one range of molecular weights may be offered. Some are composed of mixtures of two or more resins and may contain modifiers and diluents.

Epoxy networks may become brittle and display low fracture toughness. To overcome this, a small proportion of a low glass transition polymer or elastomer is added. During cure a finely dispersed elastomer phase is formed. This inhibits crack propagation without substantial sacrifice of other performance characteristics such as shear strength, modulus, and glass transition temperature. Carboxyl-terminated poly(butadiene-co-acrylonitrile) (CTBN) and amine-terminated poly (butadiene-co-acrylonitrile) (ATBN) usually are used as tougheners via esterification or aminoalkylation, respectively, of one of the epoxy groups (Fig. 2) (*2*, *3*). Several such toughened resins are commercially available. Usually, second-phase toughening of these materials becomes more effective when an excess curing agent is used. The butadiene component of the elastomer contains unsaturation and is believed to be the site for premature thermal and/or oxidative degradation. Incorporation of elastomeric polysiloxane modifiers is an active area of research (*4*). The stability, hydrophobic character, and low surface energies are expected to enhance these properties in the resin and make them useful as epoxy modifers.

Epoxy resins usually are characterized by their color, viscosity, and epoxide equivalent weight (EEW). The latter is defined as the weight of resin (in grams) which contains one gram equivalent of epoxy. For example, the EEW of a diepoxy resin is one-half the average molecular weight. The term "epoxy value" also is employed and is obtained by dividing the EEW by 100.

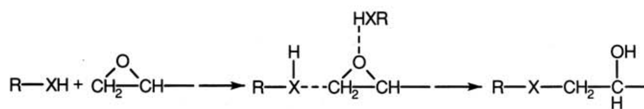
Curing Agents

An epoxy resin is reactive either with itself or with curing agents (hardeners). During curing, resin and curing-agent react and eventually form networks. Curing agents are either catalytic or coreactive. The former functions as an initiator for epoxy resin homopolymerization resulting in a network with ether linkages as shown below. Tertiary amines or Lewis acids such as BF_3 usually are used as catalyst.



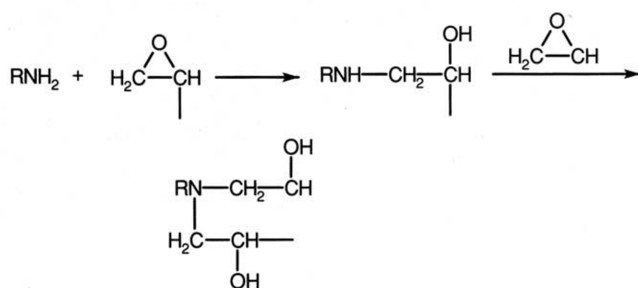
The coreactive curing agent acts as a co-monomer in the polymerization process. The epoxide ring is susceptible to

attack from a wide variety of substances. The most important group of coreactive curing agents are those with active hydrogen atoms, e.g., phenols, alcohols, thiols, primary and secondary amines, and carboxylic acids. Accelerators often are used to enhance the curing rate under ambient conditions and their effect can be ascribed to their capability to hydrogen bond or coordinate the epoxide ring to facilitate nucleophilic ring opening.



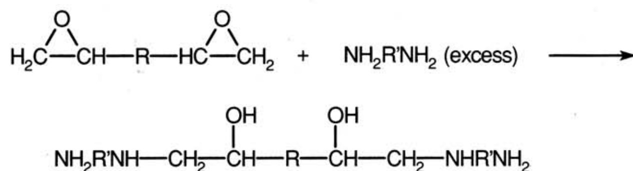
The groups adjacent to the epoxide ring influence the curing rate. Electron-withdrawing groups often enhance the reactivity of the epoxy resin to nucleophilic reagents while retarding its reactivity toward electrophilic reagents.

Primary and secondary amines are used widely as curing agents, and their reaction is shownbelow.



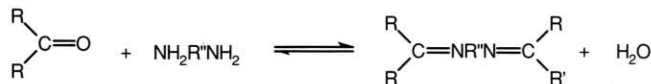
There is no evidence of etherification in the reaction between the epoxide and the derived hydroxyl, provided a stoichiometric equivalent or excess of an amine is maintained (*5*, *6*). The cure is accelerated by alcohols. Aliphatic amines, being more basic, cure epoxy resins at room temperature without accelerators but are seldom used unmodified as they are volatile, toxic, and skin irritants. In addition, they are hygroscopic, have a low pot life and show a tendency to form carbamate with CO_2 from air. Their performance usually is enhanced via the following three routes.

Liquid epoxy resin adducts (containing free amine) are formed by reacting excess diamine with epoxy resin.

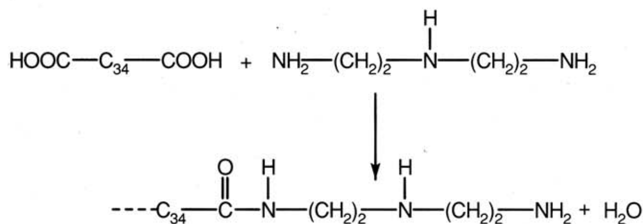


Cyanethylation of the free amine also is used, resulting in a product that has the advantage of improved wetting/adhesion. The resulting nitrile group provides additional sites for surface interaction of both the electrophilic and nucleophilic functionalities.

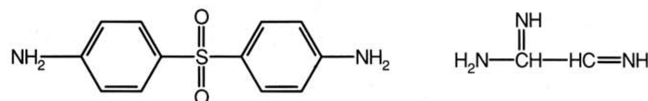
Primary aliphatic amines are reacted with ketones to give ketimines. These are latent hardeners, readily hydrolyzed by moisture to regenerate the curing agent.



Polyamides are used widely in coating and adhesive formulations. They are reaction products of polyamines and dimerized or trimerized vegetable-oil fatty acids. By varying stoichiometry and choice of amine and fatty acid, polyamides of different reactivities and viscosities can be prepared.



Dicyandiamine (cyanoguanidine), when milled with sufficient thoroughness into a resin, provides a one-package system stable for at least six months. The system remains two-phase at ambient conditions but at higher temperatures there is cure. This hardener cures through all three nitrogen-containing functional groups and consumes both epoxy and hydroxyl groups in the resin.



Diaminodiphenylsulfone   Dicyandiamine

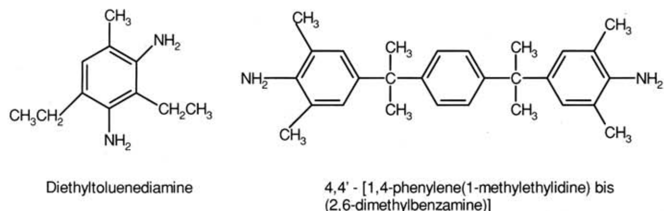
Aromatic diamines, due to their low basicity, require an elevated cure temperature. The resulting products have excellent temperature and chemical resistance. Of these, methylenedianiline (MDA) containing systems have been very popular. However, the EPA has determined MDA to be an animal carcinogen and established very low level workplace exposure limits for its use. Diaminodiphenylsulfone (DDS), which has been in use for some time, is nontoxic and gives superior high temperature properties. The electron-withdrawing effect of the sulfone group decreases the nucleophilic character of the amino group and necessitates an increase in temperature during curing. Most aromatic amines are solids and, therefore, difficult to incorporate into epoxy resin systems. However, a diaminodiphenyl sulfone epoxy adduct containing 20–30% of the hardener has been used to improve the solubility of the curing agent in the resin (*7*).

The adduct functions as a solubilizing agent for the free amine. In addition, liquid eutectic blends of several solid aromatic amines are offered commercially.

Some of the more recently developed liquid curing agents with alkylated aromatic nuclei are toxicologically safer. However, they are less reactive and require longer and/or hotter curing conditions with some loss of performance at high temperature (*8*).

Two such curing agents are diethyltoluenediamine and 4,4'-[1,4-phenylene(1-methylethylidene) bis (2,6-dimethylbenzenamine)]. Decreased reactivity can be ascribed to steric hindrance by alkyl groups adjacent to the amino group.

Anhydrides, particularly cyclic ones such as phthalic anhydride, are used commonly and their reactions are shown



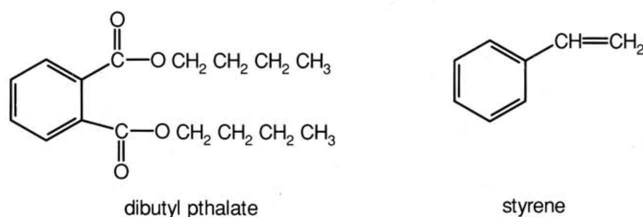
in Figure 3. Their use requires that they be cured at elevated temperatures but offers the advantages of longer pot lives and good electrical properties. Anhydride-cured formulations exhibit better thermal stabilities than similar amine-cured systems. The uncatalyzed reaction of acid anhydrides with epoxides is slow, even at 200 °C. However, the curing reaction proceeds rapidly with either acidic or basic catalyst. The reaction of acid anhydrides with commercial resins is believed to be initiated by water or hydroxy group to generate the half ester that then reacts with an epoxy group to form another hydroxy group, which can continue the polymerization (*9*). A competing reaction results in the formation of a β-hydroxy ether. Etherification, due to homopolymerization, does not consume anhydride. When no catalyst is used, the major reaction is esterification with some etherification and the recommended anhydride to epoxy ratio is 0.85:1. With an acid catalyst, etherification increases and a ratio of 0.55:1 anhydride to epoxy is recommended. Equivalent amounts are required if a tertitary amine catalyst is used (*10*).

Curing agents are characterized by color, viscosity, gel time, and weight per active hydrogen (HEW). The latter is obtained by dividing the molecular weight by the number of active hydrogens. In the case of the anhydrides, the molecular weight is divided by the number of anhydride groups. In many formulations, curing agent quantities are described by "hpr" and this is the weight needed to cure 100 parts by weight of the specified resin, most commonly, a bisphenol A-based material of EEW around 188.

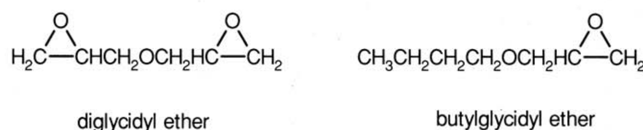
Diluents, Fillers, and Additives

An adhesive or coating must have a viscosity appropriate to the applications. Diluents are low viscosity liquids added to an epoxy resin system to reduce the viscosity and they generally provide a plasticizing effect on the cured resin. However, they may be lost during cure, resulting in shrinkage and loss of adhesion.

Dibutyl phthalate, styrene, and phenolic resins are common diluents.



Epoxy-containing reactive diluents may be either monoepoxy such as butyl glycidyl ether or epoxy resins (di- or polyepoxy) such as diglycidyl ether. The former give somewhat reduced cured properties but generally provide significant viscosity reduction at relatively low concentrations. The latter may be used at high concentrations with little effect upon cured properties, sometimes even leading to selective improvements. Diluents that are not reactive to epoxy also are used. These either react with the curing agent or other functional groups present in the epoxy resin. They will affect properties as they influence cross-linking density and system functionality.



Fillers are inert particulate materials and often are used with epoxy resin systems to reduce cost. They have the added advantage of reducing shrinkage during cure and maintaining the integrity of the adhesive bond. The heat liberated during cure tends to disrupt the adhesive bond as unmodified epoxy resins have a high coefficient of thermal expansion. However, the amount of filler that can be used is limited by the maximum permissible viscosity for a given application. Some of the commonly used fillers are Aluminum, Silica, Mica, and Kaolin. Other types of additives can be used to modify particular attributes of the formulation (*11*); for example, silicones are used for flow control and air release.

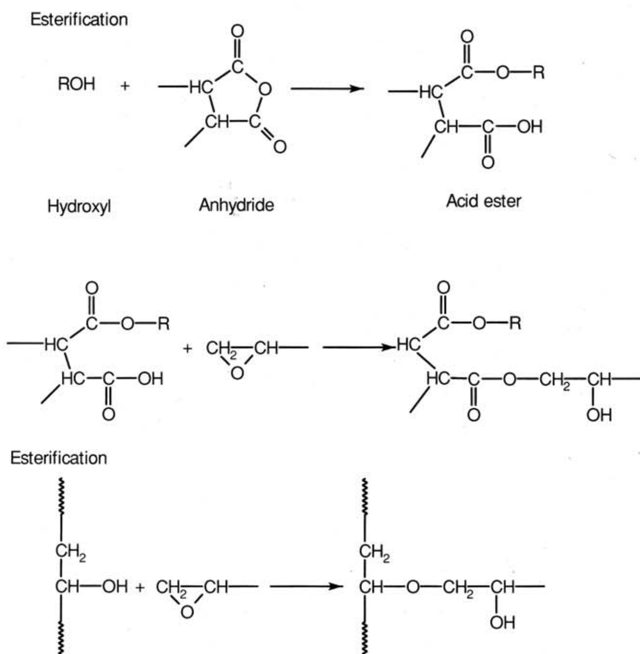


Figure 3. Reactions of anhydride with epoxy resin.

Stoichiometry and Cure

The optimum quantities of resin and curing agent may be calculated from the EEW and HEW of the resin and hardener, respectively. For example, a resin with EEW of 187 and a hardener with HEW of 62 requires 18.7 g and 6.2 g, respectively, for the stoichiometric ratios. This assumes that networks result exclusively from complete reaction of epoxide and curing agents. This is an approximation since steric and diffusion restrictions and epoxide homopolymerization also occur. In fact, it has been demonstrated that various cyclic structures are present in networks formed with a primary amine curing agent (*12*). Consequently, the quantities of reactants usually are determined empirically by varying their proportions, curing as completely as possible, and determining the T_g or the heat-deflection temperature (HDT). At their T_g, polymers change from rigid, glass-like to soft, elastomeric materials. The HDT is the temperature at which the thermoset distorts upon heating under load and also is known as the deflec-

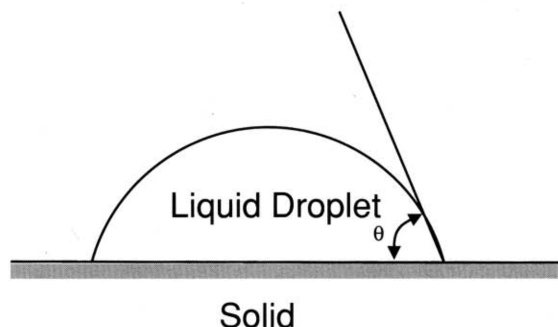


Figure 4. Contact angle of a liquid droplet on a planar syrface.

tion temperature. These values will be at their maximum at optimum reaction ratios.

Reaction ratios depend on the end use requirements of the cured resin. Higher room temperature compressive strengths are obtained at the expense of high temperature stability when an excess of the curing agent is used. Generally, to raise the T_g and thereby the upper temperature limit of the cured resin, the number of crosslinks per unit volume must be increased. This consequently reduces the flexibility. Alternatively, to increase flexibility, the crosslink density and T_g must be reduced. This can be achieved by adding flexible resins, low functionality epoxy resins, polyurethane modifiers, or by switching to low functionality curing agents. Generally, adhesive formulations with low glass transition temperatures give higher room temperature bond strengths than those with higher glass transition temperatures.

The temperature of the resin usually increases above that of the equipment during cure. The exotherm becomes more significant when larger amounts are used or the mix is heated to elevated temperatures. Amine curing agents usually give high exotherms; anhydrides liberate heat slowly and generally give low exotherms even with elevated-temperature cures. The exotherm is an important consideration when temperature-sensitive surfaces are coated. The cure conditions contribute to the amount of crosslinkage and thus the final properties of the thermoset. For maximum crosslinkage, the system usually is cured above its ultimate glass transition temperature since the polymer chains can be expected to have low mobility and thus low reactivity below the glass transition temperature.

Several analytical techniques are available to study cure. Infrared spectroscopy provides a fast and accurate means for determining the extent of cure by following the disappearance of the epoxide absorption peak at 910 cm^{-1} and appearance of the hydroxyl peak at 3,450 cm^{-1} (*13*). Absorptions of functionalities on the backbone of the resin usually are used as internal standards. Also, high resolution, solid-state ^{13}C NMR spectroscopy has been used to determine the chemical structure of the crosslinked network (*14*). The spin-lattice relaxation time has been shown to be related to the extent of cure of epoxy resins (*15*). Dynamic mechanical analysis is a popular research technique.

Wetting and Setting

An adhesive or coating must spread freely and make intimate contact with the surface to which it is applied, i.e., it must be capable of wetting the surfaces. The resin is applied in the liquid state and with sufficient pressure that it will flow into the small crevices of the solid surface.

The degree to which a liquid wets a solid is measured by the contact angle θ (Fig. 4). This angle is defined as that between a substrate plane and the free surface of a liquid droplet at the line of contact with the substrate. When $\theta = 0$, the liquid spreads freely over the surface and is said to completely wet it. The larger the contact angle, the less likely the liquid will flow over the surface and fill completely every crevice and pore in the surface. Where there are accessible pores, crevices, and capillaries in the surface, the liquid resin will penetrate to some extent and so increase adhesion.

The surface free energies of all liquids (excluding the liquid metals) are less than 100 erg cm^{-2}, at RT. Hard surfaces have surface free energies ranging from around 500 to 5000 erg cm^{-2}; the values increase with hardness and melting point. Soft organic solids have surface energies generally under 100 erg cm^{-2}. Organic and most inorganic liquids have comparatively low surface energies and would be expected to spread freely on solids of high surface energies since this results in a large decrease in the surface energy of the system (*16*). However, a film adsorbed by the solid converts it into a low-energy surface having a critical surface tension less than the surface tension of the liquid. The interface of each adherent must be kept as smooth and free as possible of low-energy surface films and dust to prevent gas pocket formation and occlusions. Optimal adhesion is obtained only when the maximum surface area and surface reactivity are made available. Surface areas can be increased by physical roughening, or by chemical or plasma etching, flame treatment, and/or abrasion to remove outer oxidation layers.

Although attempts to form chemical bonds between the surface and resin are common, the nature and extent of chemical coupling are not known. However, to make adhesive joints between polymers and metal or glass able to withstand severe conditions of high temperature and high humidity, coupling agents or adhesion promoters are widely employed. Silanes are the most commonly used ones and are believed to be capable of interlinking the two adherents by reacting with the surface molecules of both surfaces (*17*).

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