The Chemistry of Structural Adhesives: Epoxy, Urethane, and Acrylic Adhesives

14

Kirk J. Abbey and Dennis J. Zalucha

Introduction

Adhesives have been used successfully in a variety of applications for centuries. Today, adhesives are more important than ever in our daily lives, and their usefulness is increasing rapidly. In the past few decades there have been significant advances in materials and in bonding technology. People now routinely trust their fortunes and their lives to adhesively bonded structures and rarely think about it.

At the same time, the subject of adhesives and adhesion continues to receive much attention by both industrial and academic researchers as evidenced by many measures including the continued growth of membership and attendance at the annual meeting of The Adhesion Society [1]. The scientific literature continues to grow at a rapid pace. New books devoted to general and specialized aspects of adhesion and adhesives continue to appear [2–23]. New patents on adhesive compositions and processes are granted almost daily. Figure 14.1 shows U.S. Patent activity for the past 10 years as discerned by specifically claimed text. There are more patents that mention the use of one of these types of structural adhesives elsewhere in the patent for assembly of some type of article or use other wording with equivalent meaning. Figure 14.2 shows a sample of the most active world patenting organizations irrespective of adhesive chemistry. There are scientific journals devoted to the science and technology of adhesives and their use (Table 14.1). Specialized Internet sites have also appeared in recent years (Table 14.2). A significant portion of the publications dealing with adhesives is concerned with epoxy, urethane, and acrylic structural adhesives as they are used in a wide variety of commercially important applications. This chapter reviews some of the chemistry of these adhesive types as it applies to structural applications, that is, to those applications where the adhesive bond must carry a load while being resistant to dimensional changes, also known as creep.

Adhesion

Materials are generally defined as adhesives by what they do. Almost any organic polymer and even many inorganic materials can function as adhesives in some situations. However, whether they are organic polymers or inorganic, or perhaps even solders or brazing alloys, all adhesives share common traits in performing their functions.

1. An adhesive, by surface attachment only, transfers and distributes mechanical loads among the components of an assembly.
2. At some time in the course of the bond formation, the adhesive must be liquid or behave as a liquid in order to wet the adherends.
3. An adhesive carries some continuous, and often variable, load throughout its life.
4. An adhesive must work with the other components of the assembly to provide a durable product that is resistant to degradation by elements of the environment in which it will be used.

The expectations of the user are extremely important in determining whether an adhesive is “good” or “bad.” Adhesives are judged on the ability of the whole assembly to meet the user’s expectations, which will, in turn, depend on the way the assembly is loaded and tested and on what and where the weakest points of the assembly are located [8]. Adhesion is not an intrinsic property of any polymer but is rather a property of the whole assembly. Structural adhesives are distinguished from nonstructural adhesives by the magnitude of the load that they carry.

K.J. Abbey (✉)
Thomas Lord Research Center, 110 Lord Drive,
Cary, NC 27511, USA
e-mail: kirk_abbey@lord.com

D.J. Zalucha
Midland, MI, USA

J.A. Kent (ed.), *Handbook of Industrial Chemistry and Biotechnology*,
DOI 10.1007/978-1-4614-4259-2_14, © Springer Science+Business Media New York 2012

Fig. 14.1 U. S. patents issued from 1999 to 2009. Search terms used in claims were "acrylic adhesive," "epoxy adhesive," and "urethane adhesive" summed with "polyurethane adhesive"

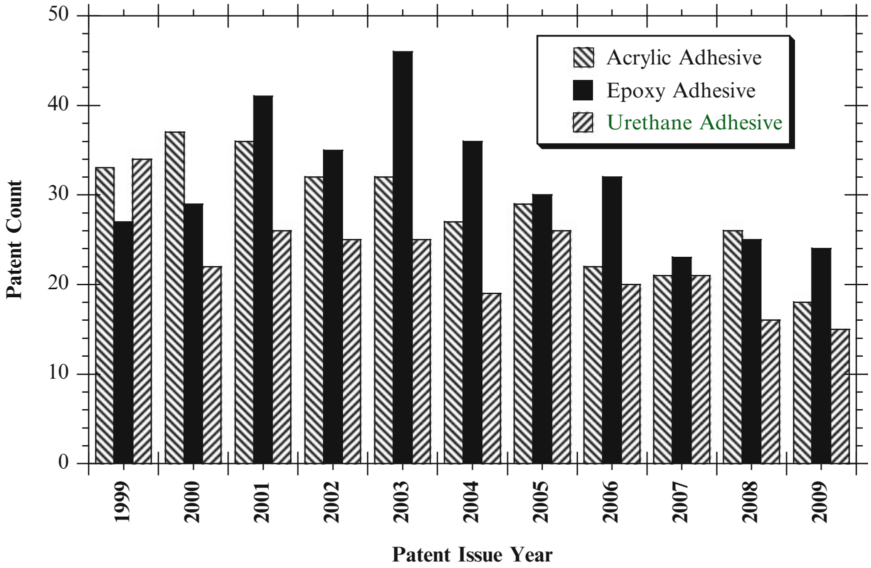


Fig. 14.2 Sampling of citations based on *CA Selects Plus: Adhesives*, for July–August 2010 [24]

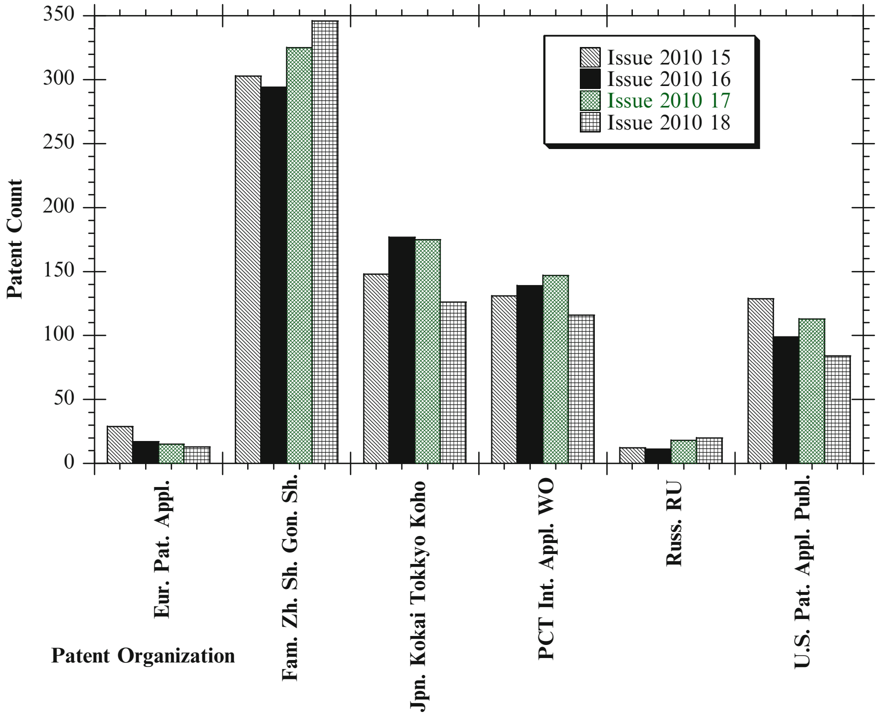


Table 14.1 Journals devoted to adhesion and adhesives

Title	Publisher
The Journal of Adhesion	Taylor & Francis, Inc.
Journal of Adhesion Science and Technology	Brill Academic Publishers
International Journal of Adhesion and Adhesives	Elsevier
CA Selects Plus: Adhesives	American Chemical Society
Adhesives & Sealants Industry	Business News Publishing Co.

Curing

The chemistry of a structural adhesive is designed to do at least two important things. First, the adhesive must at some time pass through a fluid state in order to wet the adherends. Second, the adhesive in its final state in the bond line must be a solid, high-molecular-weight polymer that is able to carry and transfer mechanical forces. In almost all cases, the polymer matrix of a structural adhesive will be cross-linked. The chemistry must make possible some manufacturing process for the assembly that allows for the liquid state,

Table 14.2 Internet web sites focused on adhesives

Web address	Publisher
http://www.adhesivesandsealants.com	VertMarkets, Inc.
http://www.adhesiveshq.com	Verdex Group, Thomas Publishing
http://www.specialchem4adhesives.com	SpecialChem, S. A.
http://www.adhesionsociety.org	The Adhesion Society

and there must be some mechanism for passing from the liquid to the solid, load-bearing state. The process of going from the liquid to the solid state is usually termed "curing."

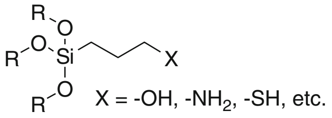
There are three general ways in which adhesives are cured. In the first "hot-melt" method, the adhesive can be applied in a molten state and allowed to cool and solidify in the bond line. In the second method, the adhesive can be applied as a solution or dispersion and the carrier liquid allowed to evaporate, leaving behind the high-molecular-weight polymer. In the third method the adhesive consists of a low-viscosity fluid containing reactive groups that undergo polymerization in the bond line to build the molecular weight sufficiently to carry a load, entailing in most cases forming a cross-linked network. This method is the one most commonly used with epoxy, urethane, and acrylic structural adhesives. The chemistry, methods, and mechanisms for accomplishing this polymerization will be covered in more detail in the following sections.

Adhesion Mechanisms

Focusing on the third cure method, once the liquid adhesive has been applied to the adherends and intimate contact and wetting have been established, the liquid mass is cured by polymerizing it to a solid, high-molecular-weight, load-bearing state. It now transfers load among the components of the assembly. The mechanisms of adhesion can be grouped into three or four categories. Kinloch identifies four categories and devotes an entire chapter to elaborate these in detail [7]. In this review, three mechanisms will be invoked to explain the adhesion of one material to another: (1) mechanical interlocking, (2) electrostatic attraction, and (3) the formation of chemical bonds across the interface. All three mechanisms may play some role in any given bonding situation although often one contributes much more than the others.

Mechanical interlocking is usually invoked when describing the adhesion of ice to glass. Silver amalgam dental fillings are held in place largely by mechanical interlocking. Although there probably are some exceptions, mechanical interlocking usually is not a major factor in bond formation with structural adhesives because, unlike water freezing, most materials contract on cooling or curing. Interdiffusion of polymer chains (i.e., entanglements) may also be considered to be mechanical interlocking at the atomic scale, but it requires mutually compatible and essentially uncross-linked compositions to occur. This is likely to be most important in the welding of plastics.

The other extreme in bonding is the formation of direct covalent chemical links across the interface. These bonds would be expected to be quite strong and durable, but they require special attention not only to the chemistry of the adhesive, but also to that of the substrate. It is necessary that there be mutually reactive chemical groups tightly bound on the adherend surface and in the adhesive. There is evidence that such bonds can be formed under controlled conditions. Silane coupling agents are one example of using specific reactive groups to promote the formation of direct chemical bonds.



By far the dominant adhesion mechanism, particularly in the absence of covalent linkages, is the electrostatic attraction of the polar groups of the adhesive to polar groups of the adherends. These are mainly forces arising from the interaction of permanent dipoles, including the special cases of hydrogen bonding (10–25 kJ/mol) and Lewis acid–base interactions (<80 kJ/mol) [25, 26]. These forces provide much of the attraction between the adhesive and the adherend and also provide a significant portion of the cohesive strength of the adhesive polymer. These interactions are generally classified as attractive long-range forces that drop off inversely to the sixth power of the distance, $1/r^6$, when r is very large compared to the dipole charge separation distance; that is, $r > 1.5$ nm. However, at shorter distances attractive interactions rise more rapidly especially when dipoles are aligned.

In two articles on the cohesive and adhesive strengths of polymers, Mark [27, 28] derives some estimates of what adhesive bond strengths might be achievable with covalent bonds or polar forces across an interface. He concludes that the bonds actually achieved in real life are only a small fraction of what he estimates for the situation in which covalent chemical bonds are the main contributors to adhesion. He further proposes that even if there are a significant number of covalent chemical bonds across the interface, the failing strength of the bond still will depend on the strength of the polar bonds. The polar bonds will fail at a lower strength than the covalent bonds, and the applied load then will be concentrated on the covalent bonds. The measurable mechanical strength of a partially covalent adhesive bond still will be dominated by the polar forces. The implication is that although increasing the proportion of covalent bonds across the interface can enhance durability, the ultimate load-carrying capacity probably will not be significantly affected.

Surfaces

Adhesives must function solely through surface attachment. Therefore, the nature and the condition of the adherend surface are crucial to the formation of strong and durable bonds. By "surface" we usually mean that region of a material which interacts with its surroundings. There is some region of a bonded assembly where the adhesive and the adherend interact, but only rarely is this a sharp boundary. Usually it is a very diffuse, somewhat ill-defined region of interaction that has become known as an interphase rather than an interface. For example, the interaction with a freshly cleaved single crystal of zinc might occur over only a few atomic layers or a few nanometers. Rough or porous surfaces present more surface area than smooth ones of the same dimensions, and the adhesive might reach a depth of several hundred nanometers on a porous adherend such as wood or paper.

One very important aspect of surfaces is that they rarely have the same chemical composition as the bulk material and often seem to be entirely unrelated to the bulk. The surface usually consists of several regions having no clear boundaries. A metal alloy might have a well-defined bulk composition, but at the surface there probably will be a region that is still metallic but is of different chemical composition because of alloying elements or impurities that have segregated at the surface. On top of this region there probably will be a layer of oxides and hydroxides formed by reaction with the atmosphere. There also will be many other contaminants such as nitrogen, sulfur, and halogen compounds formed by interaction with the pollutants in the atmosphere. Finally there will be several layers of adsorbed water. The surface of a metal also might be contaminated with rolling oils, cutting lubricants, drawing compounds, or corrosion inhibitors. Mechanical working of the metal might even mix these contaminants with the other surface materials to create something like an inhomogeneous "frosting" on the surface.

Engineering plastics display some of the same surface phenomena as metals, in that the surface is very different from the bulk. The manufacturing process often introduces anisotropy so that the mechanical properties of the material are different in different directions. In addition, it is common to find that components of the plastic have accumulated at the surface. Low-molecular-weight polymers or oligomers, plasticizers, pigments, mold release agents, shrink control agents, and other processing aids as well as adsorbed contaminants often are present.

The nature of the surface of an engineering plastic can change rapidly in response to its surroundings. The bulk of the material might be in the glassy state, but because of the concentration of low-molecular-weight material and contaminants, the surface region can be quite mobile. Exposure of the surface to a polar environment, such as by wiping with a polar solvent, can cause polar groups in the plastic surface to preferentially orient themselves outward. Exposure to a nonpolar medium can bring out the nonpolar nature of the surface.

The cured adhesive itself can be expected to be inhomogeneous particularly when arising from a formulated composition containing fillers, rubber-toughening agents, and other additives. Low-molecular-weight materials can be drawn into the surface of a porous adherend, leaving higher-weight polymer and fillers behind. The polar or nonpolar nature of the adherend influences the orientation and morphology of adhesive polymers in the interphase. Compounds at the adherend surface can catalyze or inhibit polymerization. Solvents in the adhesive can swell the adherend or dissolve portions of the adherend surface.

The interphase region is complex, and its composition is usually unknown. Primers or surface treatments often are used to improve control of the interphase and provide increased adhesion, durability, and resistance to aggressive environments. The chemistry of primers and surface treatments is as varied as the chemistry of the adhesives, but they will not be considered further in this chapter.

Any bonded construction consists of at least two adherends and one adhesive and contains at least two interphase regions. It is important to remember that the performance of the construction, its durability, its mechanical properties, and its response to tests and challenges, are all properties of the entire assembly. The successful use of adhesives depends on taking account of all parts of the construction and the process. Whereas the adhesive is just one part of the assembly, its chemistry plays an important role in the bonding process.

The following sections discuss the chemistry of some major classes of thermosetting, structural adhesives.

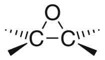
Epoxy Structural Adhesives

Introduction

Epoxy adhesives command a large portion of the structural adhesives market. Many people are probably familiar with epoxy structural adhesives, as these are the typical two-part adhesives found in hardware stores and supermarkets. Epoxy adhesives owe their popularity with both the general public and industry to their ease of use, their relative safety, and their compatibility with many adherends (Fig. 14.3). The various chemical reactions involving the epoxy ring provide a fertile field for the development of a wide range of properties [29]. Even a half century after the first epoxy patents were issued [30], new patents on epoxy adhesive technology continue to appear every month (Fig. 14.1).

Fig. 14.3 Construction of a bicycle frame from carbon fiber composite tubing using an Araldite™ epoxy adhesive (Courtesy of Huntsman Advanced Materials)

Epoxy adhesives get their name from the portion of the adhesive containing 1,2-epoxy, epoxide, or oxirane ring. This three-member ring consists of two carbon atoms joined to an oxygen atom. The highly strained geometry of this moiety with a strain energy of 114 kJ/mol accounts for its reactivity with many nucleophilic or electrophilic compounds.

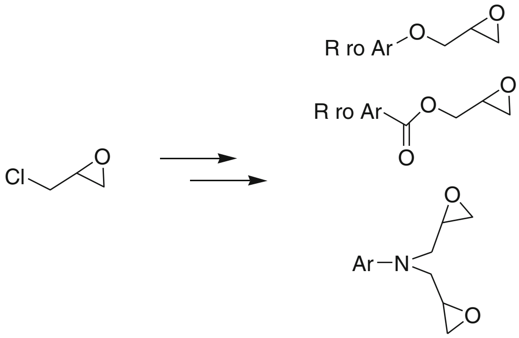


Epoxy Ring

Typical epoxy resins used to formulate epoxy adhesives have at least two epoxy rings, usually at the ends of a relatively short-chain prepolymer. The epoxy groups then are reacted with other epoxy groups in a chain-growth polymerization or with another curative in a step-growth polymerization to produce a polymer network, which can be either thermoplastic or thermoset. The polymer linkages created by reaction of the epoxy ring are polar and provide adhesion to a variety of polar surfaces. With the proper backbone polymers and curing agents, cured epoxy adhesives can be very tough and resistant to chemical degradation. Bonded assemblies can have a high degree of durability and environmental resistance. Epoxy adhesives are widely used in the transportation industry where they can greatly reduce the amount of welding required.

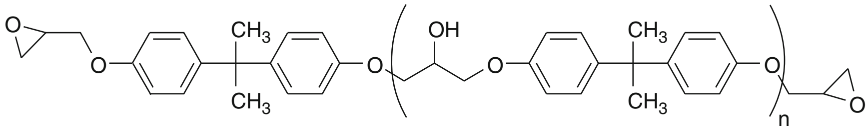
Commercial Epoxy Resins

Epichlorohydrin, or 1-chloro-2,3-epoxypropane, is the key raw material in the manufacture of the most widely used epoxy resins known as glycidyl ethers, amines, and esters. The most commercially important epoxy resins for structural application, for coatings, or for adhesives are the diglycidyl ether of bisphenol A (DGEBA, also referred to as bisphenol A diglycidyl ether, BADGE) and its higher homologues. Pure DGEBA crystallizes after a short time in storage, melting point 42 °C. Because of this, most liquid grades used in epoxy adhesives contain 10–15% higher oligomers, average $n \approx 0.15$–0.20 as well as some side products. Typical commercial resins have molecular weights of about 370 and epoxide equivalent weights in the range of about 180–190, and will have some small percentage of material that is less than difunctional. Various grades of liquid DGEBA resins are manufactured by several companies including Dow Chemical (D.E.R.™) [31], Momentive Specialty Chemicals (formerly, Hexion Specialty Chemicals, Resolution Performance Products, and Shell Chemical, EPON™) [32], Reichhold (Epotuf™) [33], Polystar (ChemRes™) [34], and Huntsman (Araldite™) [35].



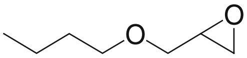
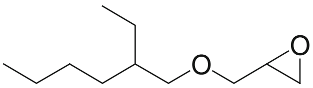
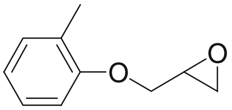
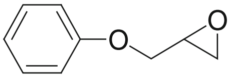
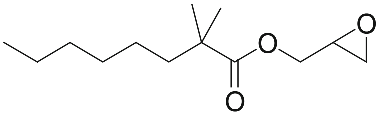
Epichlorohydrin derived epoxy resins

The higher-molecular-weight epoxy resins can be produced commercially either through the direct reaction of bisphenol A, NaOH, and epichlorohydrin or by chain extension of the DGEBA with bisphenol A. For resins with $n > 2$, the number of secondary hydroxyls exceeds the number of oxirane groups. They are often used as the reactive site for coatings. The value of n can be as high as 90 [36]. The higher-weight polymers give greater toughness but with a greater tendency for swelling by solvents. Their high T_g's and higher melt viscosity make them less suitable for most adhesive applications.



Bisphenol A resin

Table 14.3 Select examples of monofunctional epoxy diluents

Composition	Nominal structures	Trade name
n-Butyl glycidyl ether		Heloxy Modifier 61[a] 6741[b]
2-Ethylhexyl glycidyl ether		Heloxy Modifier 116[a] 6746[b]
o-Cresyl glycidyl ether		Heloxy Modifier 62[a] 6742[b] Araldite® DY-K[c]
Phenyl glycidyl ether		Heloxy Modifier 63[a] 6740[b]
Glycidyl ester of neodecanoic acid		Cardura™ Glycidyl Ester[a] 6770[b] Glydexx™ N 10[d]

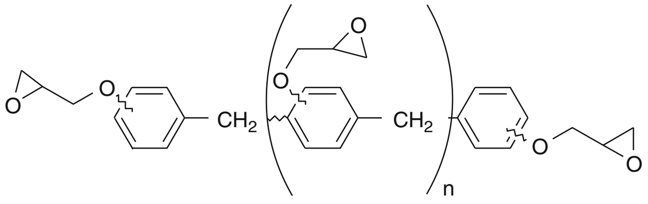
[a] Momentive Specialty Chemicals (formerly Hexion Specialty Chemicals/Resolution Performance Chemicals/Shell Chemicals)

[b] Pacific Epoxy Polymers, Inc.

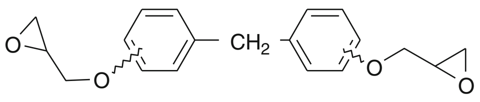
[c] Huntsman

[d] ExxonMobil Chemical

Another important class of aromatic epoxy resins is the epoxy novolac resins. Novolacs are polymers made by condensing phenol or cresol with formaldehyde in the presence of an acid catalyst. The result is a chain of phenol or cresol groups held together by methylene bridges in a mixture of *ortho* and *para* isomers. The hydroxyl groups then can be reacted with epichlorohydrin and dehydrohalogenated with base to produce an epoxy functional novolac. The simplest, containing only two rings, is the diglycidyl ether of bisphenol F. It is a liquid resin having an epoxy equivalent weight (EEW) of about 165.



Epoxy phenol novalac



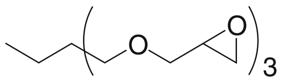
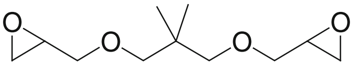
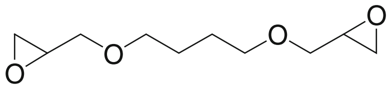
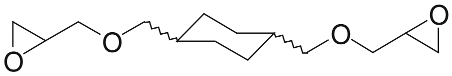
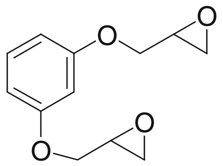
Diglycidyl ether of bisphenol F

Unlike that of the higher molecular weight bisphenol A resins, the EEW of the epoxy novolac resins remains relatively constant with increasing molecular weight because all of the aromatic rings contain hydroxyl groups that can be epoxidized. Higher-molecular-weight epoxy novolac resins can produce adhesives with higher cross-link densities. The value of *n* for epoxy novolac resins used in adhesives is usually in the range of about 0.2–3.5.

Various aliphatic and aromatic monoglycidyl ethers are available that can be used as reactive diluents of many formulated epoxy structural adhesives. They are used to lower the viscosity of the composition without introducing low-molecular-weight unreactive species that might migrate out of the adhesive after it is cured. These compounds are made in much the same way that the polyfunctional epoxy resins are made. Some of the common reactive diluents are given in Table 14.3.

Butyl glycidyl ether has the lowest viscosity and gives the greatest viscosity reduction for the same weight concentration. However, it has a higher vapor pressure than either cresyl glycidyl ether or the higher alkyl glycidyl ethers, and is more likely to cause problems with skin sensitivity and toxicity. The cresyl glycidyl ether is particularly effective at reducing the tendency of liquid epoxy resins to crystallize on storage. For safety reasons the higher-molecular-weight,

Table 14.4 Select polyfunctional diluent resins

Composition	Nominal structures	Trade name
Trimethylolpropane triglycidyl ether		6752[a] Heloxy™ Modifier 48[b]
Neopentylglycol diglycidyl ether		Araldite DY-T[c] 6749[a] Heloxy™ Modifier 68[b]
1,4-Butanediol diglycidyl ether		6749[a] Heloxy™ Modifier 67[b] Araldite® RD-2[c]
Cyclohexane dimethanol diglycidyl ether		6757[a] Heloxy™ Modifier 107[b]
Resorcinol diglycidyl ether		6769[a]

[a] Pacific Epoxy Polymers, Inc.
[b] Momentive Specialty Chemicals (formerly Hexion Specialty Chemicals/Resolution Performance Chemicals/Shell Chemicals)
[c] Huntsman

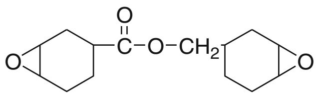
lower-vapor-pressure materials find more use even though they might be less efficient than those with a higher vapor pressure.

Aliphatic and other specialty aromatic polyfunctional glycidyl ethers are also widely used either for viscosity reduction or improving one or more particular properties. Table 14.4 lists examples of some of these.

The diglycidyl ether of 1,4-butanediol is a low-viscosity difunctional epoxy that is a somewhat less efficient diluent than the monoepoxides but does offer the advantage of having two reactive sites. Neopentylglycol diglycidyl ether and cyclohexane dimethanol diglycidyl ether impart greater rigidity than the 1,4-butanediol diglycidyl ether. Resorcinol diglycidyl ether is a very reactive material useful for reducing viscosity and gives higher cross-link densities than bisphenol A resins themselves.

Epoxidized oils such as soybean oil or linseed oil, which are made by oxidizing the internal unsaturation in the fatty acid chain, find much use as plasticizers, particularly in vinyl resins. An internal epoxy ring is much less reactive than a terminal epoxy ring and usually does not take part in typical epoxy curing reactions under mild conditions. These materials can be used as plasticizers in epoxy adhesives but cannot really be considered reactive diluents.

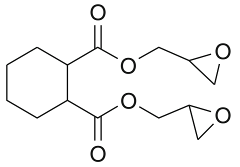
The cycloaliphatic compounds such as 3′,4′-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (TGY-6110 from Tyger Scientific, Inc. or Uvacure 1500 from Cytec) are made by direct epoxidation of the corresponding cyclohexene with peracetic acid. They produce high T_g polymers too brittle for use as the sole epoxy compound in adhesives. They are marketed towards the ultraviolet cationic cure coatings applications.



3’,4’ Epoxycyclohexylmethy

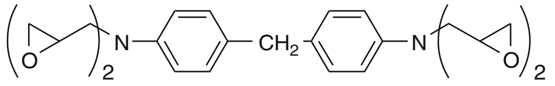
3,4-epoxycyclohexane carboxylate

Tougher polymers of somewhat lower T_g are obtained from glycidyl esters such as the diglycidyl ester of hexahydrophthalic acid (Epalloy* 5200, Emerald Performance Materials Co.). The glycidyl esters are prepared by reacting the corresponding cycloaliphatic carboxylic acid with epichlorohydrin and dehydrohalogenating with NaOH.



Diglycidyl ester of hexahydrophthalic acid

There is also a variety of other specialty epoxy resins used in limited quantity for applications demanding some specific performance property. Tri- and tetra-functional materials such as triglycidyl-*p*-aminophenol, triglycidyl isocyanurate, or *N*,*N*,*N*′,*N*′ tetraglycidyl-4,4′-diaminophenyl methane (tetraglycidyl methylene dianiline, Huntsman MY 720) have been used in adhesives requiring high heat resistance and good chemical resistance.



Tetrglycidyl methanedianiline

A typical sales specification for an epoxy resin used in adhesives will include the epoxy equivalent weight (EEW), also sometimes called the weight per epoxy (WPE), viscosity, and density at some specified temperature and the average functionality or number of epoxy groups per molecule. Sometimes a specification on total chlorine is included, which gives some indication of bound chlorine not removed by the NaOH in the dehydrohalogenation process. This bound chlorine is the result of epichlorohydrin side reactions during the epoxy synthesis. A high chlorine content indicates that there will be a large number of molecules of low functionality because each chlorine remaining represents one epoxy ring not formed in the dehydrohalogenation step.

Epoxy Cure Chemistry

Epoxy structural adhesives rely on the chemical reactions of the epoxy group with other reactants to pass from a liquid, wetting state to a solid, load-bearing state. There are a number of ways in which this is done, but all fall under one, or some combination, of three general schemes: step-growth polymerizations through reaction with curing agent, chain-growth polymerizations initiated by Lewis acids, or chain-growth polymerizations initiated by Lewis bases.[1] Often the cure times of the slower step-growth curing adhesives are shortened by including Lewis acid or Lewis base catalysts.

It would be tempting to consider the step-growth and chain-growth polymerization reactions as if they were independent and one could have the choice of either in any particular situation. The truth is that there are aspects of both types of polymerization in the cure of almost every epoxy structural adhesive. Such multiple-cure reactions often make it difficult to calculate the stoichiometry of an epoxy adhesive formulation. One type might predominate, depending on the formulation and cure conditions, but the effects of the other could not be completely discounted. The significance of this statement can be seen by looking at the two generalized reactions.

A typical step-growth reaction is one in which a single epoxy ring reacts with the active hydrogen of the curing agent. The general reaction is:

Model epoxy reaction

In order to form a high-molecular-weight polymer, both the epoxy-containing material and the curative must be at least difunctional. If both behave as difunctional materials, the resulting polymer is linear, and then it is necessary to drive the reaction nearly to completion to obtain a high-enough molecular weight to be useful. Neither of the reactants can contain a significant amount of monofunctional material. Monofunctional impurities or reactive diluents will act as chain terminators and limit the ultimate molecular weight obtainable.

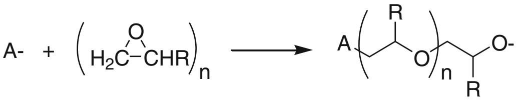
Chain-growth polymerizations occur through the reaction of epoxy rings with the active site on a growing chain and not with each other or with a second curing agent. After being initiated by a Lewis acid or a Lewis base, the growing chain will continue to consume epoxy groups and can reach a high molecular weight very rapidly. Because the epoxy groups are reacting with the growing chain, even a monofunctional epoxy compound can be polymerized. If A* is the initiator and M the monomer unit, the general reaction is:

$$A^* + nM \rightarrow A - M_{n-1}M^*$$

Chain-growth reaction

where the asterisk indicates the active site of the growing chain.

Lewis bases initiate anionic chain-growth polymerizations, the generalized reaction being that of a propagating alkoxide anion.

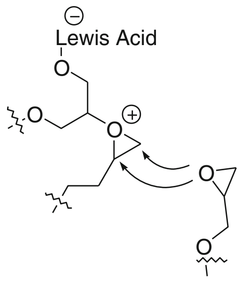


Anionic chain growth

---

[1] Lewis acids and Lewis bases are discussed in “Chain-Growth Polymerizations.”

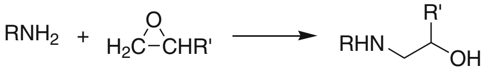
Lewis acids initiate cationic chain-growth polymerizations. There are several possible chain propagation reactions, and the mechanism of cationic chain growth is still open to some debate. However, the propagating species is likely to be an alkylated epoxy cation, or oxonium ion.



In chain-growth polymerizations, epoxy reactants containing more than one epoxy ring per molecule can form tightly cross-linked, three-dimensional networks, as each epoxy group acts as a difunctional reactant.

Step-Growth Polymerization. Only a relative few of the dozens of active hydrogen compounds that undergo reactions with the epoxy ring find widespread use in epoxy structural adhesives. The most common are amines, acid anhydrides, phenols, thiols, and carboxylic acids.

Primary and secondary amines react with epoxy groups to form secondary or tertiary amine linkages. The uncatalyzed reactions proceed at room temperature with the glycidyl ethers and glycidyl esters over many hours with handling strength of >50 psi being achieved in about 2–3 h. The resulting polymer depends on the structure of the reactants and the degree of cure, and thus a variety of final adhesive properties can be had. The reaction is susceptible to general acid catalysis, that is, by hydrogen bonding. Indeed, the reaction is autocatalytic as secondary alcohols are generated during the ring opening reaction. Better hydrogen-bond donors, such as phenols, are commonly used [37–39]. The reaction of the secondary amine with the epoxy group produces a tertiary amine, which can in turn be the Lewis base that initiates an anionic chain-growth polymerization of the remaining epoxy groups, depending on cure conditions.



Epoxy amine reaction

The simple linear aliphatic diamines, $H_2N(CH_2)_nNH_2$, can be used as curatives in adhesives. For small values of n, the short distance between the amine groups can hinder the reaction of the second amine and slow the cure process. Also, the resulting products tend to be brittle for values of n less than about 6.

More flexible, tougher products can be obtained by using liquid diamines or polyamines having more flexible backbones. For example, Jeffamine T-403 (Huntsman) is a low-viscosity liquid (70 mPa/s) having a molecular weight of about 440 and an amine hydrogen equivalent weight of about 81. It is a poly(propylene oxide) triamine made from the polyether initiated by trimethylol propane, and is promoted as a flexible cross-linker for epoxy systems. Their lower reactivity relative to other aliphatic amine may be a consideration in their usage.

Various polyamines also are useful as curatives for epoxy adhesives. An example of a simple polyamine is diethylenetriamine (DETA).

$$H_2NC_2H_4NHC_2H_4NH_2$$

Diethylenetriamine (DETA)

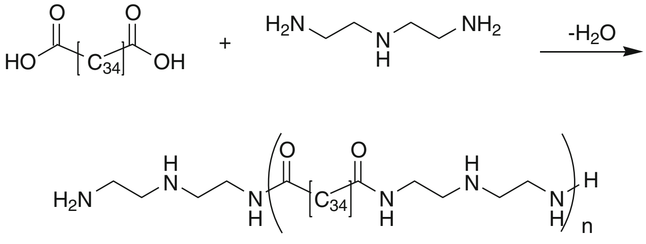
Its higher-weight homologues also are quite useful and are made by adding (CH_2CH_2NH) groups, leading to a homologous series of the form.

$$H_2N-(C_2H_4NH)_n-C_2H_4NH_2$$

where n is two, the material is triethylenetetraamine (TETA), and for $n = 3$ it is tetraethylenepentamine (TEPA), and so on. These three are the most important members of this series for adhesive applications, and are used more often than the simple aliphatic diamines. They often are used in combination with some other curative. Calculating stoichiometry can be difficult with these polyamines. All the active hydrogens might not be available because of steric factors introduced by the first reactions, or because once the first one or two active hydrogens are reacted with epoxy rings, the molecule is anchored into the chain and cannot readily diffuse to other epoxy groups. Therefore, a modest excess of polyfunctional amine is often added to the adhesive formulation. If the amine is used in too much excess, as with any other imbalanced stoichiometry, the final composition may have too many dangling chain ends, that is, be soft and cheesy, or even have unreacted amine that can leach from the product.

Other series of polyamines can be made too. For example, propyl groups can replace some or all of the ethyl groups, or the compound might be modified by reaction with an excess of a monoepoxide to give a hydroxy functional amine. Such modifications are made to improve adhesive properties and sometimes to lower toxicity of the curing agent or make it easier to handle.

Among the most important amine functional epoxy curing agents are the polyamidoamine resins. These are made from dimerized unsaturated fatty acids by reaction of the dimer acid with a polyamine such as DETA.



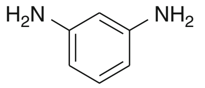
Polyamide Polyamine synthesis

These polyamidoamines are available from several suppliers worldwide (Cognis (Veramide®), Arizona Chemical (Uni-Rez®), Air Products (Ancamide™), and others) and are among the most common curatives in the general-purpose, "do-it-yourself" two-package epoxy adhesives. They have a distinctive odor somewhat like popcorn and are easily recognized in adhesive formulations. The polyamide backbone does contribute to the overall good mechanical properties of the polyamide amine cured adhesives.

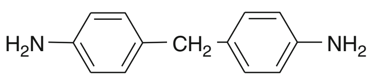
The polyamidoamines are very high-viscosity liquids, some having viscosities over 50,000 mPa/s. Typical amine equivalent weights are 100–150. The polyamidoamines react with bisphenol A epoxy resins at room temperature although the adhesives usually require several hours to reach sufficient molecular weight to carry a load. Cure times can be shortened to a few minutes at about 150 °C.

Epoxy adhesives cured with polyamidoamines are flexible, tough, durable adhesives useful on a wide variety of adherends. They probably have contributed heavily to making the words "epoxy" and "adhesive" equivalent for many people.

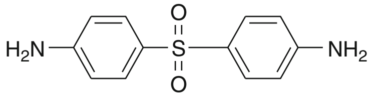
A variety of aromatic polyfunctional amines is also used in curing epoxy adhesives. They generally are slower to react than the aliphatic amines and require a heat cure to be practical. They do provide generally better high-temperature properties than the aliphatic amines. The most commonly used aromatic amine curatives are *m*-phenylenediamine (MPDA, DuPont), methylenedianiline (MDA, Bayer), and diaminodiphenyl sulfone (DDS, Aceto). Albemarle Corporation's Ethacure® 100 is claimed to be a more user-friendly curative that can be used in place of MPDA or MDA.



m-Phenylenediamine



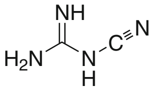
Methylenedianiline



Diaminodiphenyl sulfone

All of the curatives described so far are used to make two-package adhesives in which the curing agent is packaged separately from the epoxy resin. Once they are mixed, they have a limited pot life, usually less than a few hours.

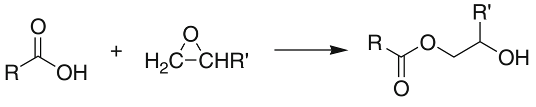
It is possible to make one-package epoxy adhesives that can have very long shelf lives at room temperature but cure rapidly when heated. One amine curative widely used to make single-package heat-cured epoxy adhesives is dicyandiamide (cyanoguanadine), commonly known as dicy.



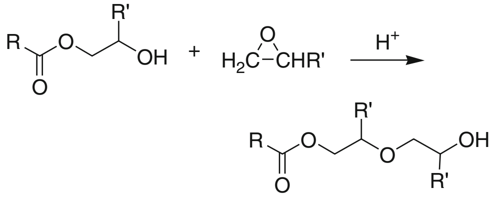
Dicyandiamide

It is made by dimerizing cyanamide in basic aqueous solution, and is a colorless solid melting at 208 °C. Dicyandiamide is soluble in polar solvents, but at room temperature is insoluble in bisphenol A epoxy resins. It can be made into a very fine powder and milled into epoxy resins to form stable dispersions. Because the dicy is insoluble in the epoxy, the only possible reaction sites are at the particle surfaces. Although some reaction certainly occurs over a short time, the adhesives easily can have a useful shelf life of 6 months. On heating to about 150 °C, the dicyandiamide becomes soluble in the epoxy resin, and the adhesive polymerizes rapidly. Cure can be accelerated by incorporation of tertiary aromatic amines or substituted ureas.

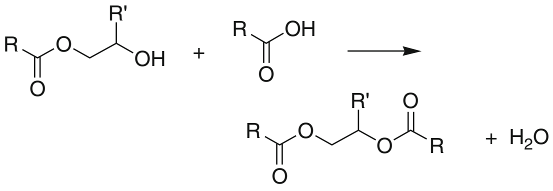
Carboxylic acids can be used to cure epoxy adhesives or otherwise modify epoxy adhesives. The reactions can be complex. If no hydroxyl groups are present initially, the first reaction will be that of the active hydrogen with the epoxy ring to form an ester. This will produce a hydroxyl group on the backbone and allows for competing reactions. The organic acid can catalyze the etherification reaction with the hydroxyl group or undergo a condensation esterification reaction directly with the hydroxyl group.



Epoxy acid reaction



Etherification reaction

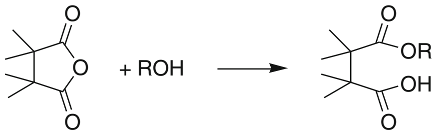


Condensation reaction

These reactions usually are slow at room temperature, and the adhesives must be cured with heat. Tertiary amines or amidines can be used to catalyze the reaction whereby the carboxylate anion is the nucleophile and the ammonium or amidinium ion act as hydrogen-bond donors. Dusek et al. have shown that transesterification only occurs after essentially complete consumption of the carboxylic acid in compositions initially having equivalent amounts of acid and epoxy groups [40, 41]. The transesterification leads to an equilibrium sol–gel composition.

Acid anhydrides also can be used to cure epoxy adhesives although they usually are used only where good service at high temperatures is required. Most of the anhydride-cured epoxy adhesives are cured at high temperature. Because most of the anhydrides are relatively small molecules, the products tend to be tightly cross-linked and can be somewhat brittle.

The first step in the anhydride cure in the absence of a tertiary amine catalyst is ring opening of the anhydride by active hydrogen, perhaps from water or hydroxyl groups already present on the epoxy resin. The resulting acid then reacts as a typical organic acid. In the presence of a tertiary amine, the initial formation of a zwitterionic acylammonium carboxylate salt is possible. The carboxylate anion then reacts with the epoxide as a nucleophile.

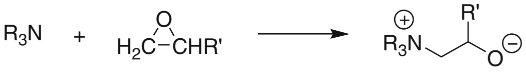


Anhydride ring opening by hydroxyl

An interesting class of curatives, but with more limited usage, is that of thiols (also known as mercaptans). Thiols react with terminal epoxide groups quite rapidly when a tertiary amine catalyst is present even at temperatures below 0 °C. The reaction is similar to that found with hydroxyl groups and produces a polythioether product. These are the familiar "five-minute" epoxy adhesives and have the characteristic odor of thiols. The rapid cure can be controlled so as to give very good open, or handling, time by the incorporation of very minor amounts of weakly acidic components such as chlorophenol, paraben esters, or carboxylic acids [42]. One limitation on wider application is the commercial availability of suitable polythiols. CapCure™ (Cognis) or GPM™ (Gabriel Performance Products) trifunctional thiols are widely used, but give cured products with low T_g's unsuitable for many structural applications.

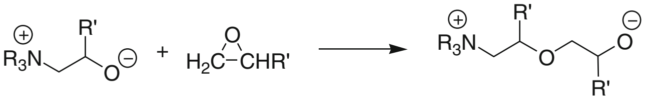
Chain-Growth Polymerizations. Chain-growth polymerizations are very important to many commercially successful epoxy structural adhesives. They can be extremely rapid and contribute to the fast cure times needed for high productivity in many manufacturing operations.

A Lewis base is a compound that contains an unshared pair of electrons capable of undergoing chemical reactions. Tertiary amines are examples of Lewis bases, and often are used in epoxy curing agents. In an anionic epoxy polymerization the propagating species is the alkoxide anion generated by the reaction of the Lewis base with an epoxy ring.



Formation of anionic chain initiator

This anion can continue to react with epoxy rings, adding them to the chain until the anion is destroyed in some side reaction.



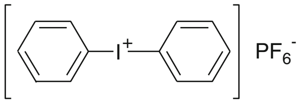
Anionic chain propagation

The product is a polyether, which can be tightly cross-linked when polyfunctional epoxides are used, as each epoxy ring can become part of a different chain.

Lewis acids, compounds with empty orbitals capable of accepting electron pairs, initiate cationic polymerization of epoxy resins. In this case the propagating species is a positive ion. The most commonly used Lewis acids are the boron trihalides, particularly BF_3 and BCl_3. They usually are used in the form of complexes because both are gases at room temperature and are so reactive with epoxy resins that they can be difficult to control. Lewis base complexes with the boron trihalides have much lower reactivity at room temperature but can react quickly on relatively mild heating, depending on the particular complex. Boron trifluoride readily forms complexes with ethers, alcohols, and amines, and several of these complexes are commercially available.

A boron trifluoride ethanolamine complex can be included in the curative portion of a two-package epoxy adhesive. When the two packages are mixed at the time of use, the mixture can have a pot life of hours at room temperature but polymerize in minutes at temperatures of 100–150 °C.

One very interesting new application of Lewis acids in curing epoxy adhesives has appeared within the last 30 years. The Lewis acid initiator for the cationic polymerization is formed by the heat or ultraviolet light-induced decomposition of Lewis acid:Lewis base salts. Several patents by Crivello and coworkers [43–47] describe compounds containing aromatic onium salts such as iodonium or sulfonium, in which the cation is stabilized by the aromatic rings. The field is covered in more detail in a recent review [48].



Diphenyl iodonium salt

The counterion generally is a large stable anion such a $[SbF_6]^-$, $[AsF_6]^-$, $[PF_6]^-$, or, $[BF_4]^-$. The more stable anions are less likely to terminate the growing cationic chains than are typical anions. The salts can be dissociated with heat to release the cation, which appears capable of initiating cationic polymerization of many materials in addition to epoxy rings. If the proper dye sensitizers are added, the cation can be liberated by ultraviolet light to initiate the polymerization. The cations persist for quite some time after the light source is removed. Acids of the form $H^+SbF_5X^-$, where X is a halogen, also have been used to catalyze epoxy reactions [49].

Evolution

The main advances being made on the chemical structure and manufacture of epoxy resins is being driven by microelectronic applications, which are not typically thought of as "structural." For these applications where failure is often induced by mismatched thermal expansion coefficient and fatigue on cycling in temperature, extremely low halide content is essential. The epichlorohydrin route to epoxy resins generally imparts too much residual chlorine content that is not easily removed by subsequent purification steps. A number of alternative routes using hydrogen peroxide have been proposed with various catalysts or coreactants. The patent by Khan et al. [50] proposes one improvement and the patent's background section provides a good review of related processes. The direct oxidation of olefins by molecular oxygen, while limited in scope, can be done to prepare monofunctional epoxies used as reactive diluents [51].

Formulations continue to investigate methods to improve toughness. Several studies of nano-fillers have recently appeared showing improvements with different curing agents and temperatures [52–55]. Nano-dispersed triblock copolymers were also obtained under certain cure temperatures that yielded toughening [56]. Hyperbranched resins terminated with epoxy groups show improvements over linear liquid rubber including lower viscosity at similar toughness [57–60].

Summary

Epoxy structural adhesives have proven to be versatile and reliable compositions. Their widespread use and acceptance is in part due to the varied chemistry of the epoxy ring and the skill of scientists and adhesive formulators in developing high-quality compositions that can produce reliable, reproducible structural joints even when applied by relatively unskilled users. New compositions and chemical reactions continue to be disclosed, and it is certain that the knowledge of epoxy chemistry will continue to grow. Many of the new discoveries will find their way into new epoxy structural adhesives.

Urethane Structural Adhesives

Introduction

The term "urethane adhesive" as it is generally used encompasses a lot of chemistry that is not necessarily urethane chemistry. "Urethane" is the common name for the compound ethyl carbamate. In common usage, "urethane adhesive" generally means an adhesive polymer derived from isocyanate chemistry and reactions of isocyanates with active hydrogen compounds. However, isocyanate reactions do not always lead to urethane linkages, and there are ways of arriving at urethane linkages without involving isocyanates. In this section the common approach is taken; that is, an adhesive that uses reactions of the isocyanate group to bring about polymerization in the bond line is considered a urethane adhesive.

The study of industrial applications of isocyanate chemistry and polymers derived from isocyanates received much attention in Europe, particularly Germany, in the 1930s and during World War II. Patents on aspects of urethane chemistry appeared as early as 1937 [61]. The effort going into understanding isocyanate chemistry and commercializing urethane products continues [62–66].

The isocyanate group consists of a linear arrangement of nitrogen, carbon, and oxygen atoms.

$$-N{=}C{=}O$$

Several possible electronic configurations can be drawn, most of which involve a positive charge on the central carbon atom. This partial positive charge on the carbon atom accounts for much of the reactivity of the isocyanate group with nucleophilic groups. Not only does the isocyanate group react with a variety of potential curing agents, but also it is very reactive with many of the adherend surfaces on which urethane adhesives are used.

The same high reactivity that makes the isocyanate a desirable reactant for structural adhesives also renders the unreacted isocyanate more acutely toxic than, for instance, epoxy adhesives. Only a few isocyanates are safe enough and easy enough to handle that they find widespread use in urethane structural adhesives.

Isocyanate Preparation

Organic isocyanates are the major building blocks of urethane structural adhesives. They can be synthesized by a variety of routes, but most of the commercially available isocyanate compounds used in adhesives are made by the reaction of a precursor primary amine or amine salt with phosgene, followed by dehydrohalogenation. The reaction with phosgene usually is carried out at a relatively low temperature of less than 60 °C. The temperature then is raised to 100–200 °C to remove the HCl.

$$RNH_2 + COCl_2 \longrightarrow$$

$$RNHCOCl + HCl \xrightarrow{\text{heat}} RNCO + 2\,HCl$$

Isocyanate synthesis by phosgenation

There are many possible side reactions, and the yield depends on the reaction conditions, which usually are specific to the starting materials and desired product. Much work has gone into determining the reaction conditions for manufacturing as clean a product as possible.

The amount of isocyanate in a commercial isocyanate or isocyanate-containing formulation usually will be specified as weight percent isocyanate (as NCO) or as an amine equivalent weight, which is the weight of material containing sufficient isocyanate to react with 1 mol of amine hydrogen.

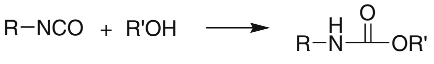
Isocyanate Reactions

Organic isocyanates can undergo a large number of reactions with active hydrogen compounds. One test commonly used to determine the presence of active hydrogen atoms and the number of active hydrogens per molecule is the Tschugaeff–Zerewitinoff analysis or, more commonly, the Zerewitinoff test. An excess of a Grignard reagent, methyl magnesium iodide, is added to the sample to be tested, and the amount of methane evolved in measured.

$$CH_3MgI + RH \rightarrow CH_4 + RMgI$$

Zerewitinoff reaction

Urethane adhesives take their name from the product of the most common step-growth polymerization reaction used to generate the adhesive polymers. Isocyanates react with hydroxyl groups to create urethane (or carbamate) linkages:



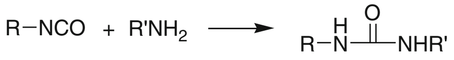
$$R{-}NCO + R'OH \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OR'$$

Urethane formation

If both the isocyanate and the hydroxyl-containing material are difunctional, if the mixture is made up to have one isocyanate per hydroxyl, if there are no side reactions, and if the reaction can be driven to completion, a single linear thermoplastic polymer should result. If one or more of the reactants is more than difunctional, it is possible to create an infinite three-dimensional network.

In general, primary hydroxyl groups are faster to react than secondary hydroxyls, which are in turn faster than tertiary hydroxyls, absent catalysts. When reacted with hydroxyl-containing compounds, aliphatic isocyanates tend to be more sluggish than their aromatic counterparts. Urethane linkages made with tertiary hydroxyls tend to be less stable and at high temperature can dissociate into an olefin and an amine with loss of carbon dioxide. Metal compounds, particularly tin compounds such as dibutyl tin dilaurate, and various amines catalyze the isocyanate–hydroxyl reaction.

Isocyanates will react with amines to produce substituted ureas, primary amines being faster than secondary amines.



$$R{-}NCO + R'NH_2 \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}NHR'$$

Urea formation from 1° amine

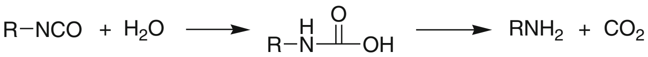
$$R{-}NCO + R'R''NH \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}NR'R''$$

Urea formation from 2° amine

The ureas are more rigid linkages than the urethane structure, but they also are generally more resistant to heat and chemical degradation. The reaction of isocyanates with amines is generally so rapid that it is nearly impossible to control the reaction well enough to make it useful in formulating urethane adhesives. What usually happens is that the reaction takes place faster than it is possible to mix the adhesive. If it is necessary to include urea linkages in the final production, it can be done by making a prepolymer that has the urea linkages in it already or by taking advantage of the slower reaction of isocyanates with water.

Small (much less than stoichiometric) amounts of diamines sometimes are added to the hydroxyl portion of the adhesive to provide a rapid but limited molecular weight increase as soon as the components are mixed [67, 68]. In this way a two-package adhesive can be made that will flow easily before mixing but will not readily flow after mixing. Such adhesives can be applied to vertical surfaces or overhead, and will remain in place until the bonds are closed and cured.

The reactions of amines and isocyanates are important in adhesives because of the possible reaction of isocyanates with water. Because isocyanates react readily with water, raw materials used in formulating adhesives must be dry, and the compositions must be protected from moisture, including atmospheric humidity, during storage. The first reaction with water is the formation of a carbamic acid, which rapidly loses carbon dioxide to form a primary amine.

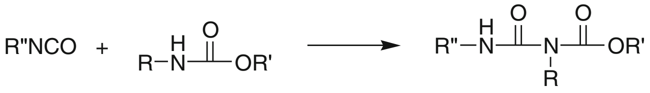


$$R{-}NCO + H_2O \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OH \longrightarrow RNH_2 + CO_2$$

Water NCO reaction

The primary amine then can react with another isocyanate to produce a urea. Thus 1 mol of water consumes at least two equivalents of isocyanate, builds molecular weight, and liberates carbon dioxide in the process. If this happens in a closed container such as a drum of adhesive, the result can be explosive, particularly as the reaction mass rises in temperature because of the exothermic reactions. On the other hand, these reactions can be useful in a bond line because under the proper conditions desirable urea linkages can be introduced into the curing adhesive through the reactions of small amounts of water normally present on the adherend surfaces.

The hydrogen atom attached to the nitrogen atom of the urethane group is active enough that it can react with another isocyanate group to produce an allophanate. This is an additional cross-linking mechanism for urethane polymers and can disturb the stoichiometry of the system by consuming an additional isocyanate group for each allophanate formed. Elevated temperatures usually are needed to produce allophanates in uncatalyzed systems; allophanation reactions can be catalyzed by tertiary amines.



$$R''NCO + R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OR' \longrightarrow R''{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\underset{R}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OR'$$

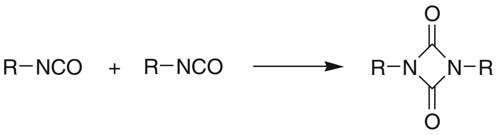
Allophanate formation

In a similar fashion, a urea hydrogen atom can react with an additional isocyanate group to produce a biuret.

$$R''NCO + R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R' \longrightarrow R''{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\underset{R}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R'$$

Biuret formation

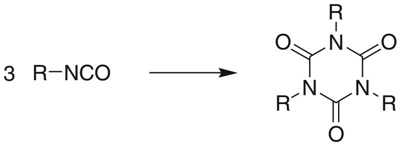
Isocyanate groups also will react with themselves to form a variety of compounds. Two isocyanate groups can react to form a dimer or uretidinedione.



Isocyanate dimerization

These dimers can be dissociated to regenerate the original isocyanates with heat, and some of the dimers, such as the dimer of toluene diisocyanate (TDI), have become commercially important.

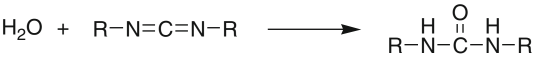
Three isocyanate groups can react to form a trimer or substituted isocyanurate ring. Phosphines or bases such as sodium acetate or sodium formate can catalyze this reaction. The isocyanurate ring is thermally stable, has good chemical resistance, and can enhance the resistance of a urethane adhesive to aggressive environments.



Isocyanates also can react with each other to produce carbodiimides with the loss of carbon dioxide. This reaction requires high temperatures unless catalyzed by specific phosphorus compounds. Formation of carbodiimides normally is not an important cross-linking mechanism in polyurethane adhesives. However, carbodiimides are sold by Angus Chemicals, a division of Dow Chemical (ZOLDINE™ XL-29SE), Nisshinbo Industries (Carbodilite™), and Picassain Polymers, a division of Stahl USA (XL-701). They have been recommended as water scavengers, cross-linkers, and stabilizers for carboxyl functional polyurethanes. The carbodiimide can react with water to give a urea, which still can react with additional isocyanate to produce a biuret.

$$R{-}NCO + R{-}NCO \xrightarrow{\text{catalyst}} R{-}N{=}C{=}N{-}R + CO_2$$

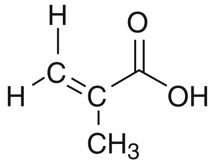
Carbodiimide formation



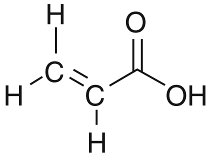
$$H_2O + R{-}N{=}C{=}N{-}R \longrightarrow R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R$$

Carbodiimide reaction with water

Carbodiimides can react with additional isocyanate groups to form uretone imines, which sometimes are used to modify polyisocyanates used in urethane structural adhesives.



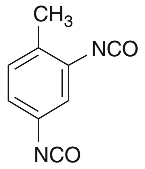
Methacrylic acid



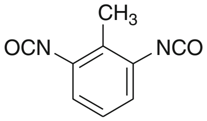
Acrylic acid

Important Isocyanates

Dozens of isocyanate functional compounds have been synthesized, but only a few find much use in urethane structural adhesives. The choices are largely dictated by a combination of performance, price, and safety considerations. Most of the materials used in adhesives are derived from the aromatic isocyanates, toluene diisocyanate (TDI) and 4,4′-diphenylmethane diisocyanate (MDI).

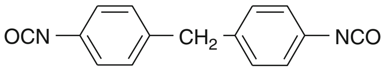


2,4-Toluene diisocyanate



2,6-Toluene diisocyanate

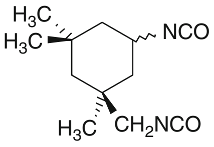
(TDI)



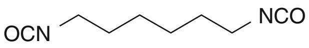
4,4’-Diphenylmethane diisocyanate

4,4-Methylene bis(phenyl isocyanate) (MDI)

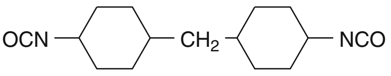
Where color and light stability of the adhesive are important, and cure speed or cost is less important, aliphatic isocyanates are frequently used. Adhesives derived from isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), or 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI) are available.



Isophorone diisocyanate (IPDI)



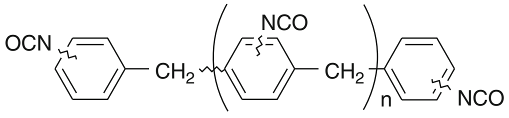
Hexamethylene diisocyanate (HDI)



4,4-Dicyclohexylmethane diisocyanate (H12MDI)

The common commercial TDI is an 80/20 mixture of the 2,4- and 2,6-isomers. The pure 2,6-isomer is available also and is sometimes called TDS. To make TDI, toluene first is nitrated to produce a mixture of the 2,4- and 2,6-dinitro isomers. The dinitrate is reduced to the diamine and reacted with phosgene, which is followed by dehydrohalogenation to give the diisocyanate. Because of its relatively high vapor pressure and toxicity, adhesives rarely contain TDI monomer. Typically, excess TDI is reacted with another material such as trimethylolpropane or a polyester diol or polyether diol to produce a higher-molecular-weight isocyanate functional compound, which is safer and easier to handle than the free TDI. Still, there will be some free TDI present in the adduct, and much work has gone into finding synthesis schemes to minimize the free TDI in prepolymers and adducts [69, 70].

MDI can be considered the first member of a series of polyisocyanates of the general form:

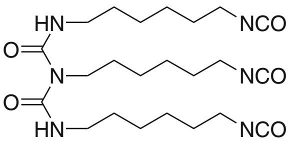


Aromatic polyisocyanates

MDI is the most important member of the series although materials with *n* of 1 or more also are available. The precurser amine is made by condensation of aniline hydrochloride with formaldehyde, followed by reaction with phosgene and dehydrohalogenation. When the aniline is present in excess, the diamine and consequently the diisocyanate are produced in greatest yield, with nearly all of this being the 4,4′-isomer.

MDI is a solid at room temperature with a melting point of about 38°C, which usually is stored and shipped in the molten state for convenience. However, on standing in the liquid state, the MDI slowly dimerizes, and the liquid MDI becomes saturated with dimer at about 1% dimer by weight. The dimer then begins to precipitate. The isocyanate content of the remaining liquid will then remain constant.

HDI can be used as an aliphatic cross-linker in urethane adhesives but presents significant health risks because of its toxicity and high vapor pressure. HDI is more commonly used in the form of its biuret, which is much safer and easier to handle than HDI.



Biuret of hexamethylene diisocyanate

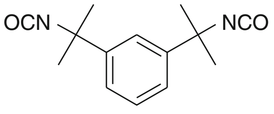
IPDI is another low-viscosity aliphatic diisocyanate that is useful in formulating light-stable polyurethane adhesives, and is somewhat lower in cost than HDI. IPDI has a low vapor pressure at room temperature but, like most low-weight isocyanates, still can present a health hazard. Higher-molecular-weight adducts of IPDI, such as its isocyanurate trimer, are available. The trimer is a high-melting solid (100–115 °C), and one loses the advantage of the low-viscosity liquid in using it but gains in safety and easy handling.

In IPDI, the two isocyanate groups are not equivalent. One is attached directly to the aliphatic ring, and a methylene group separates the other from the ring. Because their environments are different, the reactivity of the two groups are different; and the reactivity can depend on the choice of catalyst. For instance, Ono et al. [71] have shown that when IPDI is reacted with a primary hydroxyl group, the primary NCO is most reactive when the catalyst is 1,4-diazabicyclo [2.2.2]octane. The secondary NCO attached to the ring is the most reactive when dibutyl tin dilaurate is the catalyst.

The saturated analogue of MDI, $H_{12}MDI$, has found limited use as an aliphatic isocyanate in adhesives. This material is known by a variety of names including Desmodur W™ (Bayer), hydrogenated MDI (or HMDI or $H_{12}MDI$), reduced MDI (RMDI), and saturated MDI (SMDI). It is a low-viscosity liquid with a fairly high vapor pressure, so it too must be handled with care. In adhesive compositions, the diisocyanate usually is used to make an isocyanate functional prepolymer by reacting excess diisocyanate with a hydroxyl or amine functional polymer such as a polyester diol.

Because it contains two saturated six-member rings, $H_{12}MDI$ can exist in three isomeric forms, in which the orientations of the NCO groups with respect to the rings and each other are different. The *trans–trans* isomer is a solid at room temperature so that over time this isomer can precipitate from the remaining liquid isomers. Samples of $H_{12}MDI$ that have been stored at cool temperatures for a while often have a solid layer of *trans–trans* precipitate in the bottom.

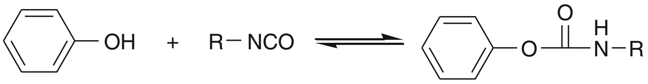
An offering by Cytec Specialty Chemicals, the *meta* isomer of tetramethyl xylene diisocyanate (TMXDI), is interesting because it contains an aromatic ring, but the NCO groups themselves are aliphatic isocyanates and have reaction characteristics typical of aliphatic diisocyanates. It reacts even more sluggishly than the more standard aliphatic isocyanates because of steric interactions, making the reactions easier to control. Compounds such as dimethyl tin dilaurate, lead octoate, or tetrabutyl diacetyl distannoxane have been shown to be effective catalysts for the isocyanate–hydroxyl reaction. The manufacturer claims that it is less toxic than many other isocyanates.



m-TMXDI

Blocked Isocyanates

Blocked isocyanates are compounds formed by the reaction of an organic isocyanate with an active hydrogen compound where the reaction is reversible with moderate heat. The blocked isocyanate can be used in formulating adhesives or other reactive compositions even in the presence of materials that normally would react rapidly with the isocyanate. Phenol is one example of a blocking agent used with isocyanates. There are many other blocking agents in use, including lactams, oximes, and malonates. Even isocyanate dimers such as TDI dimer could be considered blocked isocyanates because they will dissociate with heat to regenerate the isocyanates.



Phenol blocking reaction

There are two major limiting factors to the use of blocked isocyanates in urethane structural adhesives. First, the adherends must be sufficiently heat resistant to withstand the temperatures needed to cause rapid dissociation of the blocked isocyanate. Second, the blocking agent is present to continue competition with the intended curing agent for reaction with the isocyanate. After the adhesive is cured, the blocking agent remains trapped in the bond line and could contribute to poor mechanical properties in the bond, poor resistance to harsh environments, or exude or extract into the environment. Applications on porous substrate, such as wood, or where de-blocking occurs before closure of the bond, such as laminating, are compatible with some of these limitations.

Evolution

Urethane adhesives have also received much attention. New processes are being developed for the phosgene-free

Fig. 14.4 Assembly of an aircraft headliner using an Araldite™ two-part urethane adhesive (Courtesy of Huntsman Advanced Materials)

production of isocyanate-containing raw materials from formamides through reaction with organic carbonates [72, 73]. Methods of stabilizing isocyanate compositions continue to be developed [74, 75]. Formulators continue to produce new mixtures and intermediates from standard materials (Fig. 14.4) [76–78]. New blocking agents for isocyanates are being developed to facilitate the formulation of stable urethane adhesives compositions rapidly curable when heated [79, 80].

Summary

Urethane structural adhesives have proved quite successful in bonding applications that take advantage of their toughness, particularly when the adhesive must function at low temperatures. The reactivity of the isocyanate group may require some extra care in handling and storing the adhesives but the same reactivity provides many opportunities for the polymer chemist and adhesive formulator. The principal reaction used in curing urethane structural adhesives is the reaction of the isocyanate group with primary and secondary hydroxyl groups. Both the isocyanate groups and the hydroxyl groups can be carried on a wide variety of low-molecular-weight oligomers such as polyesters, polyethers, polybutadienes, polyurethanes, and polymer blends so that many of the desired properties of the final adhesive can be built into the polymer before the adhesive is cured.

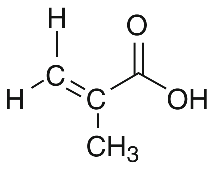
Acrylic Structural Adhesives

Introduction

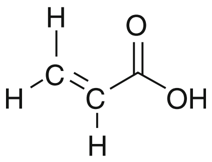
Acrylic structural adhesives are more recently developed products compared to epoxy or urethane adhesives. They first appeared in Europe in the mid-1960s and were commercialized in the United States a few years later [81]. They share many similarities to anaerobic adhesives that preceded them by a few years.[2] The first offerings were rather brittle products of use in limited applications where toughness and flexibility were not critical. However, because these new acrylic structural adhesives polymerized in the bond line through a free-radical chain-growth polymerization mechanism, they did have the big advantage of curing rapidly at room temperature. This polymerization mechanism offered a variety of potential advantages in manufacturing. Bonded structures could be assembled relatively rapidly without the need of curing ovens. Assemblies did not need to be stored for long periods while room-temperature cures were completed. The adhesives could be made at very low viscosities for easy handling and dispensing. In the past 40 years there has been much creative work done with the chemistry of acrylic adhesives so that now they are available in many forms with a wide range of properties.

Acrylic Monomers

All acrylic structural adhesives consist basically of a solution or a mixture of polymers and unsaturated, low-molecular-weight, free-radical-polymerizable monomers with other materials added as needed for the particular intended use. In addition, some precursor of the polymerization initiator will be present. The most common monomers used are methacrylic acid (2-methyl propenoic acid) and its esters or, less commonly, acrylic acid (propenoic acid) and its esters.



Methacrylic acid



Acrylic acid

Several processes for making acrylic acid have been developed [82]. Since the 1980s manufacturers have almost exclusively used a two-step, vapor-phase oxidation of propylene that proceeds through acrolein. The acrylic acid then

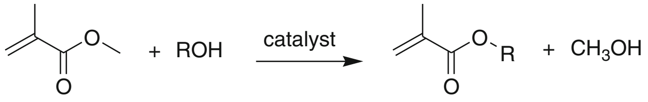
---

[2] See the discussion in [6], pp. 217.

can be esterified with the appropriate alcohols. If current shifts in petroleum prices continue, one of the alternative routes to acrylic acid may become economically preferable.

Unlike acrylic acid, methacrylic acid continues to be produced by a variety of processes including oxidation of ethylene, propylene, or isobutylene [83]. The older commercial process for making methacrylic acid based on propylene proceeded through acetone cyanohydrin. This process is steadily declining in usage because of high waste costs. Rapid development of specialty catalysts in the 1980s by several Japanese companies has moved isobutylene-based production to the forefront. Also, for companies with internal synthesis gas (syngas) production, routes based on ethylene are economically viable.

Direct esterification of methacrylic acid with alcohols using sulfuric acid or other catalysts can be used to prepare methyl methacrylate (MMA) and other esters. Commercial routes for the direct preparation of MMA and some lower alkyl esters also exist. In the 1990s, researchers at Shell developed a direct route to MMA from propyne (methylacetylene), carbon monoxide, and methanol using a Pd(II) catalyst. The limited availability of propyne may slow the expansion of this highly efficient route to high purity MMA. Transesterification of MMA is often the preferred route for the preparation of other esters.



Transesterification of MMA to other methacrylate esters

The choice of monomers that are useful in acrylic structural adhesives is rather limited. Cost always is an important factor, and because acrylic structural adhesives consume only a very small portion of the world's output of acrylic monomer, the formulator usually must rely on acrylic monomers that are made in large quantity for other uses. In addition, the monomers must polymerize readily at room temperature. If a mixture of monomers is to be used, the monomers must copolymerize easily. Finally, the monomers must be good solvents or dispersants for the polymers used in formulating the adhesive. The acrylic monomers finding most use in acrylic structural adhesives are methyl methacrylate and tetrahydrofurfuryl methacrylate. The later, albeit more expensive, has a much higher flashpoint and a generally perceived low odor, yet maintains good solvency.

Curing

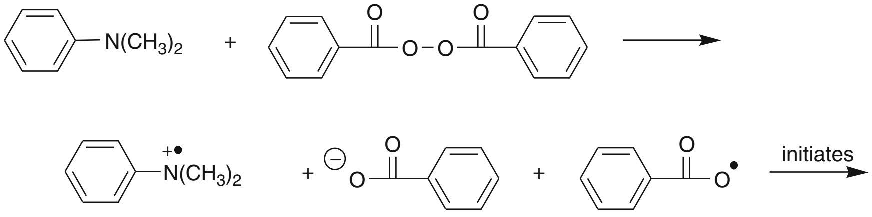
The curing reaction of an acrylic structural adhesive is the chain-growth polymerization of the acrylic monomer. The monomer units are not reactive with each other but react only with a growing chain having an active site on one end. In order to begin a chain, one must generate an initiator in the monomer solution. In the case of acrylic structural adhesives, this initiator nearly always is a free radical, a species having an unpaired, reactive electron. After chains have been initiated, there are three general types of reaction that can occur: propagation, chain transfer, and chain termination. If "*" represents the active site, "A*" represents the initiator, and M is a monomer unit, then the four reaction types are:

Initiation	$A^* + M \rightarrow AM^*$
Propagation	$AM^* + nM \rightarrow AMnM^*$
Chain transfer	$AMnM^* + M \rightarrow AMnM + M^*$
Termination	$RM^* + R'M^* \rightarrow$ RMMR' (combination)
	$RM^* + R'M^* \rightarrow RMC = CH_2 + RMCHCH_3$ (disproportionation)

In addition, a growing chain might undergo chain transfer or be terminated by reaction with a variety of unknown impurities invariably present in any mixture.

The initiating radical is usually created in a redox reaction. Common reactions involve the reduction of an organic peroxide by some reducing agent such as an amine or an ion capable of undergoing a one-electron transfer reaction. Anaerobic adhesives generally rely on metal ions derived from the surface to be bonded as part of the redox system. Acrylic adhesives generally embody the reducing agent in the monomer mixture and place the oxidizer in a monomer free package.

One example of an efficient free-radical initiator generating reaction is the reduction of diacyl peroxides such as benzoyl peroxide (BPO) by tertiary aromatic amines such as *N*,*N*-dimethyl aniline (DMA).



Benzoyl peroxide reaction with N,N-dimethyl aniline

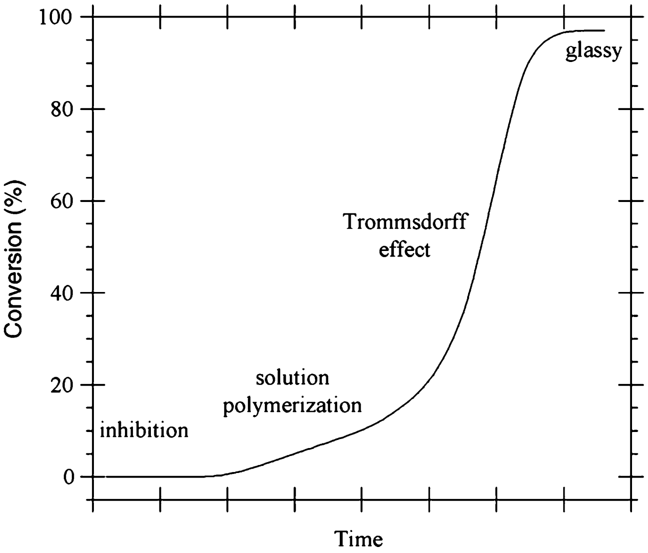
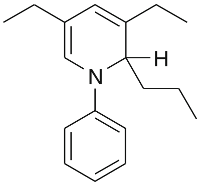


Fig. 14.5 Four stages of free-radical polymerization in bulk

The condensation products of amines and aldehydes have often been used as the reductant. The most common commercial example is that arising from aniline and butyraldehyde for which the active ingredient has been identified as 3,5-diethyl-1,2-dihydro-1-phenyl-2-propylpyridine (DHP). A high purity grade, >85% active, has become available in recent years (Vertellus Specialties Inc., formerly Reilly Industries, Reilly PDHP™ Adhesive Accelerator; R. T. Vanderbilt Company, Vanax™ 808 HP).



DHP

The free-radical polymerization of methacrylate adhesives may show four stages, Fig. 14.5: inhibition, solution polymerization, “gel” polymerization, and glassy polymerization. All commercial monomers have inhibitors added to help prevent premature polymerization during storage. During the inhibition stage, the redox system generates radicals and some minor addition to monomer may occur, but the inhibitors and any dissolved oxygen, a very potent inhibitor of free-radical polymerization, will prevent the formation of polymer and any significant consumption of monomer. Once the oxygen and inhibitors are consumed, very high-molecular-weight polymer will form, $0.1–1 \times 10^6$, if no efficient chain transfer agents are present. As the reaction progresses, the polymer–monomer solution becomes increasingly viscous and the termination process is retarded. At about 25–30% monomer consumption, the polymer entanglements (gel) become so profound that a rapid rise in observed rate of polymerization is noted as the rate of termination reactions plummets. This rapid acceleration is referred to as the Trommsdorff effect. Because the diffusion of monomer molecules is not appreciably retarded by the “gel,” there is no significant reduction in the propagation rate. Eventually, the polymer–monomer solution will approach the glassy state and even small molecules such as monomer and the redox components cannot move easily. For all practical purposes, the reaction comes to a halt soon thereafter as the smaller, more rapidly diffusing oxygen molecules reenter the bondline and quench the remaining polymer radicals.

Another consequence of oxygen inhibition of free-radical reactions is that the adhesive surface exposed to air will contain a higher concentration of lower-molecular-weight species than the bulk of the adhesive. This can result in the surface being soft, tacky, or even remaining fluid.

Formulation

Although the free-radical chain-growth polymerization brings processing advantages, it also brings limitations. The product of the polymerization of the monofunctional acrylic monomers is a linear thermoplastic polymer. In the case of a copolymer that is largely MMA, the glass transition temperature of the polymer will be well above room temperature if the polymer has been driven to a high-enough molecular weight. The resulting adhesive is brittle, and although its shear strength might be quite high, its ability to withstand peeling forces or impacts will be low. One could use monomer mixtures yielding copolymers having lower glass transition temperatures and expect that the adhesive might be somewhat tougher. However, this parameter is difficult to control because when curing the acrylic adhesive in the bond line, one really is doing a bulk polymerization under uncontrolled conditions and trying to produce a specific polymer with a specific set of material and performance properties. The approach taken by most adhesive manufacturers or formulators is to use “prepolymers,” high-molecular-weight oligomers that can be made under controlled conditions and then dissolved or dispersed in the acrylic monomer. By forming key elements of the polymer chains under controlled conditions, many of the desired properties of the final product can be built into the adhesive when it is formulated and before the material is cured. The prepolymer can cause the solution polymerization stage of polymerization to be skipped, thereby decreasing the cure time substantially.

The simplest approach to improving toughness is to dissolve or disperse a nonreactive rubbery polymer in the monomer mixture that is to be polymerized. Examples of such materials are nitrile rubbers, polyethers, and acrylic rubbers. The choice will depend on cost, desired properties, and the solubility of the polymer in the monomer. As the monomer polymerizes, it will lose its solvating ability for the dissolved polymer. Eventually, when enough of the monomer has been consumed, it can no longer hold the polymer in solution, and the polymer precipitates. The polymer then can segregate as a totally separate phase or as distinct domains heterogeneously dispersed throughout the acrylic polymer matrix, or it can be homogeneously trapped in the acrylic matrix, depending on the rates of reaction, the compatibility with the acrylic polymer, and the relative mobility of the dissolved polymer.

One way of influencing the way in which the added oligomer is distributed in the final cured produce is to provide reactive sites on the oligomer so that it can be incorporated into the acrylic matrix as it forms. For instance, if the added oligomer contains terminal, active, acrylic, or methacrylic unsaturation, it can be easily incorporated into the growing acrylic polymer chains as the adhesive cures. Then it is unable to precipitate as a separate phase and must remain more or less uniformly distributed throughout the matrix. On the other hand, incompatible polymers can be added to deliberately encourage the formation of reinforcing domains. If the oligomer has two or more functional groups capable of participating in the polymerization, there is at least the possibility of forming cross-links in the polyacrylate matrix. Particular advantage has been claimed for combinations of reactive and nonreactive rubbers with attention to their molecular weights [84].

A technology developed at du Pont [85] combines the use of reactive sites on the oligomers with the initiation reaction. The resulting family of acrylic structural adhesives has become popularly known as “second generation acrylics.” They consist essentially of solutions of chlorosulfonated polyethylene (formerly made by du Pont as Hypalon, but discontinued in 2010; available from Tosoh Chemical as Toso-CSM™) in acrylic or methacrylic monomers. The chlorosulfonyl groups present on the polymer will react with amine aldehyde condensation products, DHP above, to generate free-radical initiators, at least some of which are claimed to be on the oligomer backbone. The speculation is that the adhesive polymer chains then grow by graft polymerization from various sites on the rubber oligomer. Peroxides and metal ions can be added to accelerate the initiation and polymerization. One of the significant advantages of this type of acrylic structural adhesive is the ability to bond oily or dirty metals with only minimal surface preparation, although some surface preparation usually is necessary to improve bond durability (Fig. 14.6).

Other acrylic structural adhesives can be used on poorly prepared metal surfaces. Inclusion of reactive monomers having phosphate groups can lead to significant improvements in primary bonds to many unprepared metals [86]. Kowa American supplies one such monomer, 2-hydroxyethylmethacrylate acid phosphate.

Fig. 14.6 Applying Fusor™ adhesive for repair of a steel automobile hood (Courtesy of Lord Corporation)

Many other modifications to acrylic adhesives are useful. Improved heat resistance of acrylic adhesives can be achieved by incorporating small amounts of epoxy resin into the formulations [87], or by including cyanate esters and organometallic compounds to provide an additional cross-linking mechanism [88]. Lower sensitivity of oxygen can be achieved by incorporation of a wax that migrates to the monomer–air interface providing a diffusion barrier or by using more efficient initiators [86, 89]. Innovations in acrylic adhesive have led to new initiator reactions that provide rapid initiation and cure while at the same time allowing for improved shelf life [90]. Acrylic adhesives cured by ultraviolet light have been made from mixtures of acrylic functional urethane prepolymers mixed with free radically polymerizable monomers and photo initiators [91–93]. Refined formulations with significantly improved peel strength have recently been introduced [94].

Organoborane initiators for acrylic adhesives have received much attention arising from the observation that they give exceptional adhesion to low energy surfaces, such as polyethylene and polypropylene without surface preparation [95]. Earlier use of tributylborane–amine complexes in MMA and activated with isocyanates, acid chlorides, or sulfonyl chlorides for a dental resin was reported in 1969 [96]. In the mid-1990s, 3M became active in the area of amine-blocked organoboranes with a focus on polyolefin bonding [97]. A commercial product appeared in the mid-1990s that was later twice improved, Scotch-Weld™ DP-8010 [98]. By 2005, more than 30 patents had since appeared covering particular blocking groups, de-blocking agents, and additives to improve adhesive performance. Later Dow Chemical made a push into this field with more than 16 patents on adhesive composition as well as others in specific automotive applications [99]. It has been commercialized under the LESA trademark [100]. The amine-blocked organoborane adhesives generally require refrigeration for good shelf live. A family of more robust, internally coordinated organoboranes has been disclosed [101, 102].

Summary

Acrylic structural adhesives have the advantage of easy handling and processing and rapid cure at room temperature. The ability of some compositions to adhere to unprepared metal surfaces or low surface energy substrates can allow substantial cost savings in manufacturing processes. The brittleness of the polymers made from the monomers often can be overcome by formulating to include tough, reactive oligomers in the liquid adhesive. The variety of possible initiators and mechanisms for generating them has brought many innovative compositions to market.

Hybrid Adhesives

Adhesives usually are classified as epoxy, urethane, or acrylic, based upon the chemistry used to bring about the polymerization of the liquid adhesive. However, the distinction among the various types of adhesives is not always clear, and many hybrid adhesives have been developed and marketed. The objective usually is to take advantage of the desirable mechanical properties or chemical resistance of one polymer while retaining the processing attributes of a different cure system [103].

It is common in acrylic structural adhesives to use oligomers that have a desirable backbone and are terminated with free-radical-polymerizable bonds. A variety of isocyanate-terminated polyurethanes can be adapted for use in acrylic structural adhesives by reacting the terminal isocyanates with a hydroxy functional acrylic monomer such as 2-hydroxyethyl methacrylate [86, 104, 105]. A recent acrylic/siloxane hybrid adhesive using a trialkylborane initiator has recently been described [106].

Sometimes the system is formulated so that multiple-cure mechanisms are possible and can occur sequentially or simultaneously. Compositions that rely on both epoxy and urethane chemistry are examples [68, 107, 108]. These are compositions containing the DGEBA, an isocyanate or isocyanate-terminated prepolymer, amines or other reactants for either epoxy or isocyanates, and catalysts.

Some of the more interesting and innovative work has occurred in areas combining aspects of more than one chemistry type. For instance, moisture-curable thermoplastic adhesives have received much attention. Hot-melt adhesives have been developed that contain active, moisture-curable isocyanate groups. The compositions provide rapid processing on assembly lines because a reasonable bond is formed as soon as the thermoplastic adhesive cools from the melt. However, bond strength and performance improve with time as the composition is slowly cross-linked to a thermoset by reaction of the isocyanates with atmospheric moisture [109, 110].

Evolution

The fundamental chemistry of the structural adhesives described here can change very little. Vinyl and acrylic monomers polymerize by chain-growth polymerization initiated by free radicals or ions. Isocyanate and epoxy compounds react with compounds containing active hydrogen in step-growth polymerizations. Epoxy-containing compounds undergo chain-growth polymerization initiated by certain Lewis acids and Lewis bases. These reactions will remain the most important ones for the polymerization of these raw materials.

Most of the raw materials used in large quantities in structural adhesives are used because they are widely available, relatively safe, and inexpensive. Quite often they are made in large quantities for uses other than adhesives and the adhesive manufacturers have taken advantage of supply and price. Few new basic raw materials are being developed specifically for the adhesive industry although the traditional raw materials are being combined in new ways to enhance desired adhesive properties. New initiators, adhesion promoters, primers, and specialty chemicals are being developed for use in small quantities to provide wider application latitude and improved performance.

The evolution of structural adhesives will certainly continue. Each increment in strength, durability, processing speed and ease, safety, reliability and reproducibility opens new commercial markets, not only to displace older joining methods but also to allow for the manufacture of new structures not possible without adhesives. One area receiving much academic as well as patent activity is “self-healing” systems. One such epoxy system is described by Wu et al. where the healing chemistry can be the same or different such as olefin methathesis [111].

Conclusion

Epoxy, urethane, and acrylic structural adhesives have been commercially successful because each can be used, under the proper conditions, to make reliable, durable, and useful adhesively joined assemblies. The adhesives are classified according to the polymerization reactions used to bring the liquid adhesive to a high-molecular-weight load-bearing state. The reactive sites on the uncured adhesive and the overall polarity of the cured adhesive are important in the adhesion of the polymer to any specific material. The polymerization reactions determine the processing requirements and are important to the mechanical properties and environmental resistance of the cured adhesive. Through the use of specific reactive oligomers it is possible to build certain molecular structures into the composition that will remain in the cured adhesive to provide desired mechanical or chemical properties.

The successful use of adhesive joining in producing any assembly depends on viewing the assembly as a whole from the very beginning of its design. The key is remembering that the adhesive is only one component of the assembly. Adhesion is a property of the whole assembly.

References

1. The Adhesion Society. http://www.adhesionsociety.org, 2 Davidson Hall—0201, Blacksburg, VA 24061, phone: 540-231-7257, fax: 540-231-3971, e-mail: adhesoc@vt.edu
2. Wake WC (1982) Adhesion and the formulation of adhesives, 2nd edn. Applied Science, New York
3. Lee L-H (1984) Adhesive chemistry, developments and trends. Plenum, New York
4. Panek JR, Cook JP (1984) Construction sealants and adhesives, 2nd edn. Wiley-Interscience, New York
5. Adams RD, Wake WC (1984) Structural adhesive joints in engineering. Elsevier, New York
6. Hartshorn SR (ed) (1986) Structural adhesives chemistry and technology. Plenum, New York
7. Kinloch AJ (1987) Adhesion and adhesives science and technology. Chapman and Hall, London
8. Tong L, Steven GP (1999) Analysis and design of structural bonded joints. Kluwer Academic, Boston
9. Ward N, Young T (2001) The complete guide to glues and adhesives. Krause, Iola
10. Gierenz G (ed) (2001) Adhesives and adhesive tapes. Wiley, New York
11. Moore DR (ed) (2001) Fracture mechanics testing methods for polymers, adhesives and composites. Elsevier, Amsterdam
12. Veselovskii RA, Kestelman VN, Veselovsky RA (2001) Adhesion of polymers. McGraw-Hill, New York
13. Pocius AV (2002) Adhesion and adhesives technology. Hanser Gardner, Munchen
14. Pocius AV, Dillard D, Chaudhury M (2002) Surfaces, chemistry and applications: adhesion science and engineering. Elsevier Science & Technology, Amsterdam
15. Pizzi A (ed) (2003) Handbook of adhesive technology. Marcel Dekker, New York
16. Swanson DW (2005) Adhesive materials for electronic applications: polymers, bonding, and reliability. William Andrew, Norwich
17. Fisher LW (2005) Selection of engineering materials and adhesives. CRC, Boca Raton
18. Packham DE (2005) Handbook of adhesion. Wiley, Hoboken
19. Dillard D (2010) Advances in structural adhesive bonding. Woodhead Publishing, Cambridge
20. Adams RD (2005) Adhesive bonding, science, technology, and applications. CRC, Boca Raton
21. Petrie EM (2006) Epoxy adhesive formulations. McGraw-Hill, New York
22. Pizzi A, Mittal KL (2003) Handbook of adhesive technology. Marcel Dekker, New York
23. Yacobi BG, Hubert M (2003) Adhesive bonding in photonics assembly and packaging. American Scientific, Stevenson Ranch
24. Chemical Abstracts Service (2005) American Chemical Society
25. Fowkes FM, Mostafa MA (1978) Acid-base interactions in polymer adhesion. Ind Eng Chem Prod Res Dev 17(1):3–7
26. Fowkes FM (1983) Acid-base interactions: relevance to adhesion science and technology. In: Mittal KL (ed) Physicochemical aspects of polymer surfaces, vol 2. Plenum, New York, p 583
27. Mark HF (1979) Future improvements in the cohesive and adhesive strength of polymers—part I. Adhes Age 22(7):35–40
28. Mark HF (1979) Future improvements in the cohesive and adhesive strength of polymers—part II. Adhes Age 22(9):45–50
29. May CA (ed) (1988) Epoxy resins: chemistry and technology, 2nd edn. Marcel Dekker, New York
30. Castan P (1943) Process of preparing synthetic resins. US Patent 2,324,483
31. Dow Chemical (1999) Dow Liquid Epoxy Resins, Form No. 296-00224-0199 WC_M. http://epoxy.dow.com/index.htm
32. Hexion Specialty Chemical (a Momentive company). http://www.hexion.com/Products/TechnicalDataSheets.aspx?id=2273
33. Reichhold, Inc. http://www.reichhold.com/en/coatings-products.aspx?cat=Brands&pid=24
34. Polystar, LLC. http://www.polystarusa.com/products.php?c=Epoxy+Resins&cid=10
35. Huntsman Corp., EPON Product Overview 2009-08. http://www.huntsman.com/advanced_materials/eng/Home/Coatings/Publications/Coatings/index.cfm?PageID=5898
36. Hexion Specialty Chemical (a Momentive company), Eponol™ Resin 53-BH-35
37. Partansky AM (1968) A study of accelerators for epoxy-amine condensation reaction. Am Chem Soc Div Org Coat Plast Chem 28(1):366
38. Partansky AM (1970) A study of accelerators for epoxy-amine condensation reaction. In: Lee H (ed) Epoxy resins. Am Chem Soc Adv Chem Ser 92:29–47. doi:10.1021/ba-1970-0092.ch004
39. Hine J, Linden S-M, Kanagasabapathy VM (1985) Double-hydrogen-bonding catalysis of the reaction of phenyl glycidyl ether with diethylamine by 1,8-biphenylenediol. J Org Chem 50(25):5096–5099. doi:10.1021/jo00225a021
40. Matejka L, Pokomy S, Dusek K (1982) Network formation involving epoxide and carboxyl groups. Polym Bull (Berlin) 7(2–3):123–128
41. Dusek K, Matejka L (1984) Transesterification and gelation of polyhydroxy esters formed from diepoxides and dicarboxylic acids. In: Riew CK, Gillham JK (eds) Rubber modified thermoset resins. Am Chem Soc Adv Chem Ser 208:15–26. doi:10.1021/ba-1984-0208.ch002
42. Abbey KJ, Pressley MW, Durso SR (1999) Controlled cure of thiol-epoxy systems. In: Speth DR (ed) Proceedings of the 22nd

annual meeting of The Adhesion Society, Panama City Beach, FL, 21–24 Feb 1999
43. Crivello JV (1979) Heat curable compositions. US Patent 4,173,551
44. Crivello JV (1980) Heat curable cationically polymerizable compositions and method of curing same with onium salts and reducing agents. US Patent 4,216,288
45. Crivello JV (1982) UV curable compositions and substrates treated therewith. US Patent 4,319,974
46. Crivello JV, Ashby BA (1982) Methods of adhesive bonding using visible light cured epoxies. US Patent 4,356,050
47. Crivello JV, Lee JL (1984) Photocurable compositions. US Patent 4,442,197
48. Yagci Y, Reetz I (1998) Externally stimulated initiator systems for cationic polymerization. Prog Polym Sci 23(8):1485–1538
49. Tarbutton KS, Robins J (1989) Acid catalyzed, toughened epoxy adhesives. US Patent 4,846,905
50. Khan NH, Razi Abdi SH, Kureshy RI, Singh S, Ahmad I, Jasra RV, Ghosh PK (2007) Catalytic process for the preparation of epoxides from alkenes. US Patent 7,235,676
51. Mikawa M, Uchida S-I (2003) Catalyst for production of epoxides and methods for production thereof and epoxides. US Patent 6,600,056
52. Kinloch AJ, Lee JH, Taylor AC, Sprenger S, Eger C, Egan D (2003) Toughening structural adhesives via nano- and micro-phase inclusions. J Adhes 79:867–873. doi:10.1080/00218460390242234
53. Kinloch AJ, Mohammed RD, Taylor AC, Eger C, Sprenger S, Egan D (2005) The effect of silica nano particles and rubber particles on the toughness of multiphase thermosetting epoxy polymers. J Mater Sci 40:5083–5086. doi:10.1007/s10853-005-1716-2
54. Liang YL, Oldak RK, Pearson RA (2007) Particle size effect in rubber-glass sphere toughened epoxies. In: Jagota A (ed) Proceedings 30th annual meeting of The Adhesion Society, Inc., The Adhesion Society, Blacksburg, VA, pp 343–345, 2007
55. Ragosta G, Abbate M, Musto P, Scarinzi G, Mascia L (2005) Epoxy-silica particulate nanocomposites: chemical interactions, reinforcement and fracture toughness. Polymer 46 (23):10506–10516. doi:10.1016/j.polymer.2005.08.028
56. Oldak RK, Hydro RM, Pearson RA (2007) On the use of triblock copolymers as toughening agents for epoxies. In: Jagota A (ed) Proceedings 30th annual meeting of The Adhesion Society, Inc., The Adhesion Society, Blacksburg, VA, pp 153–156, 2007
57. Boogh L, Pettersson B, Månson J-AE (1999) Dendritic hyperbranched polymers as tougheners for epoxy resins. Polymer 40:2249–2261. doi:10.1016/S0032-3861(98)00464-9
58. Mezzenga R, Boogh L, Petterson B (2000) Chemically induced phase separated morphologies in epoxy resin-hyperbranched polymer blends. Macromol Symp 149:17–22. doi:10.1002/1521-3900(200001)149:1<17::AID-MASY17>3.0.CO;2-O
59. Mezzenga R, Månson JAE (2001) Thermo-mechanical properties of hyperbranched polymer modified epoxies. J Mater Sci 36:4883–4891. doi:10.1023/A:1011880019156
60. Mezzenga R, Plummer CJG, Boogh L, Månson JAE (2001) Morphology build-up in dendritic hyperbranched polymer modified epoxy resins: modeling and characterization. Polymer 42:305–317. doi:10.1016/S0032-3861(00)00307-4
61. Bayer O (1937) Verfahren zur Herstellung von Polyurethanen bzw. Polyharnstoffen. German Patent 728.981
62. Saunders JH, Frisch KC (1962, 1964) Polyurethanes, chemistry and technology, vols 1 and 2. Interscience, New York
63. Oertel G (ed) (1994) Polyurethane handbook, 2nd edn. Hanser, Munich
64. Randall D, Lee S (eds) (2003) The polyurethane book. Wiley, New York
65. Dunn DJ (2004) Engineering and structural adhesives (Rapra Review Reports, 15(1), Report 169). Rapra Technology Ltd., Shropshire
66. Rapra Technology Ltd (2004) Polyurethane adhesives (Rapra Published Search Number 114). Rapra Technology Ltd, Shropshire
67. Fabris HJ, Maxey EM, Uelzmann H (1973) Urethane adhesive having improved sag resistance. US Patent 3,714,127
68. Goel AB (1988) Sag resistant urethane adhesives with improved antifoaming property. US Patent 4,728,710
69. Baueriedel H (1986) Adhesives based on polyurethane prepolymers having a low residual monomer content. US Patent 4,623,709
70. Bolte G, Henke G, Kruedenscheidt M, Omoruyi A (2003) Low monomer polyurethane prepolymer and process therefore. US Patent 6,515,164
71. Ono H-K, Jones FN, Pappas SP (1985) Relative reactivity of isocyanate groups of isophorone diisocyanate. Unexpected high reactivity of the secondary isocyanate group. J Polym Sci Polym Lett Ed 23:509–515. doi:10.1002/pol.1985.130231003
72. Okawa T (1992) Process for producing isocyanate compound. US Patent 5,166,414
73. Mason RW (2004) Non-phosgene route to the manufacture of organic isocyanates. US Patent 6,781,010
74. Nagata T, Yamashita H, Kusumoto M, Okazaki K (1994) Stabilizing method of isocyanate compounds and isocyanate compositions stabilized thereby. US Patent 5,302,749
75. Rosen R, Bernard J-M, Duffy CS (2007) Color stability of isocyanates. US Patent 7,297,746
76. Ohashi Y, Matsuda H, Nishi E, Nishida T (1997) Moisture curing urethane adhesive composition. US Patent 5,698,656
77. Fukatsu S, Hattori Y (1998) Moisture curable polymer composition and process for production thereof. US Patent 5,767,197
78. Suen W (2010) Two component polyurethane adhesive. US Patent 7,834,123
79. Schoener TE, Housenick JB (2002) Polyurethane reaction system having a blocked catalyst combination. US Patent 6,348,121
80. Ambrose R, Retsch WR Jr, Chasser A (2001) Blocked isocyanate-based compounds and compositions containing the same. US Patent 6,288,199
81. Bader E (1967) Polychloroprene adhesives. US Patent 3,333,025
82. Bauer W Jr (2004) Acrylic acid and derivatives. In: Kirk-Othmer encyclopedia of chemical technology, 5(1):342–369. Seidel A, Ed. Wiley, New York. doi:10.1002/0471238961.010318250201210
83. Wilczynski R, Juliette JJ (2006) Methacrylic acid and derivatives. In: Kirk-Othmer encyclopedia of chemical technology, 16 (5):227–270. Seidel A, ED. Wiley, New York. doi:10.1002/14356007.a16_441
84. Huang J-P, Righettini RF, Dennis FG (2001) Adhesive formulations. US Patent 6,225,408
85. Briggs PC, Muschiatti LC (1975) Novel adhesive compositions. US Patent 3,890,407
86. Zalucha DJ, Sexsmith FH, Hornaman EC, Dawdy TH (1981) Structural adhesive formulations. US Patent 4,223,115
87. Dawdy TH (1984) Epoxy modified structural adhesives having improved heat resistance. US Patent 4,467,071
88. McCormick FB, Drath DJ, Gorodisher I, Kropp MA, Palazzotto MC, Sahyun MRV (2000) Energy-curable cyanate/ethylenically unsaturated compositions. US Patent 6,069,219
89. Righettini RR, Dawdy TH (1999) Free radical polymerizable compositions including para-halogenated aniline derivatives. US Patent 5,932,638
90. Edelman R, Catena W (1999) Rapid curing structural acrylic adhesive. US Patent 5,865,936
91. Usifer DA, Broderick IC (1995) Urethane adhesive compositions. US Patent 5,426,166

92. Usifer DA, Broderick IC (1996) Urethane adhesive compositions. US Patent 5,484,864
93. Hu S (2006) Radiation-curable compositions for optical fiber coating materials. US Patent 7,105,583
94. Maxlok™ acrylic adhesives. http://lordmaxlok.com
95. Imai Y, Fujisawa S, Matsui H, Yamazaki H, Masuhuara E (1973) Japanese Kokai 48-100477
96. Fujisawa S, Imai Y, Masuhara E (1969) Studies on dental self-curing resins: 2. Characterization of the various complexes of Tri-n-butyl borane as an initiator, Iyo Kizai Kenkyujo hokoku. Reports of the Institute for Medical and Dental Engineering, Tokyo Medical and Dental University 3:64–71
97. Zharov JV, Krasnov JN (1996) Polymerizable compositions made with polymerization initiator systems based on organoborane amine complexes. US Patent 5,539,070
98. 3M Technical Literature for DP-8010, Jan 2002
99. Sonnenschein MF, Webb SP, Rondan NG (2004) Amine organoborane complex polymerization initiators and polymerizable compositions. US Patent 6,706,831; and 15 more recent patents by the lead inventor
100. Leaversuch RD, Long-glass PP (2002) makes inroads in automotive front ends. Plast Technol. http://www.plasticstechnology.com/articles/200207cu1.html, Gardner
101. Kendall JL, Abbey KJ. (2004) Internally coordinated organoboranes. US Patent Application
102. Abbey KJ, Kendall JL (2004) Internally coordinated organoboranes: stability and activation in polyolefin adhesives. Polym Mater Sci Eng 91(2):175–176
103. Pohl E, Osterholz FD (1987) Novel vulcanizable silane-terminated polyurethane polymers. US Patent 4,645,816
104. Brownstein AM (1969) Anaerobic adhesive. US Patent 3,428,614
105. Su W-FA (1986) UV curable high tensile strength resin composition. US Patent 4,618,632
106. Sonnenschein MF, Webb SP, Wendt BL (2008) Poly(acrylate/siloxane) hybrid adhesives for polymers with low surface energy. Int. J. Adhesion and Adhesives 28(3):126–134. doi:10.1016/j.ijadhadh.2007.07.001
107. Hawkins JM (1972) Epoxy resin adhesive compositions containing an isocyanate terminated polyurethane prepolymer and a chain extender. US Patent 3,636,133
108. Trieves R, Pratley KGM (1986) Two-component adhesive or sealing composition. US Patent 4,623,702
109. Anderson GJ, Zimmel JM (1999) Thermally stable hot melt moisture-cure polyurethane adhesive composition. US Patent 5,939,499
110. McInnis EL, Santosusso TM, Quay JR (2001) Hot melt adhesives comprising low free monomer, low oligomer isocyanate prepolymers. US Patent 6,280,561
111. Wu DY, Meure S, Solomon D (2008) Self-healing polymeric materials: a review of recent developments. Prog Polym Sci 33:479–522. doi:10.1016/j.progpolymsci.2008.02.001