# ADHESIVES

## 1. Adhesive Compositions

An adhesive is a material that is used to join two objects through nonmechanical means. It is placed between the objects, which usually are called *adherends*, when it is part of a test piece or *substrate* that is part of an assembly, to create an adhesive joint. Although some adhesives form joints that almost immediately are as strong as they will be in actual use, other adhesives require further operations for the adhesive joint to reach its full strength. Adhesives can be made in several different physical forms, and the form of a given adhesive will define the possible methods of its application to the substrate.

An adhesive is comprised of a base chemical or a combination of chemicals that define its general chemical class. Most adhesives contain a curing agent or catalyst that will cause an increase in the molecular weight of the system and frequently the formation of a polymeric network. Nearly all adhesives also contain additives or modifiers that fine tune the adhesive and may significantly influence its behavior before and after formation of the adhesive joint. These additives include solvents, plasticizers, tackifiers, fillers, pigments, toughening agents, coupling agents, stabilizers, etc. Additives or modifiers increasingly are chosen for their ability to provide more than one benefit, eg, a pigment may not only color but also may reinforce an adhesive. In some cases, the process used to combine these diverse ingredients will strongly influence the properties of an adhesive. Although inorganic adhesives do exist, this article will be restricted to organic polymeric adhesives.

Consumers, designers, and engineers generally choose between adhesive bonding and mechanical or thermal methods when deciding how to join one object to another. Mechanical methods utilize bolts, screws, and rivets. Thermal methods include welding, soldering, and brazing. Adhesive bonding is the obvious choice for joining in cases in which the substrate is thin and relatively weak, eg, paper, or strong but relatively brittle, eg, glass. Use of adhesives in these situations avoids formation of stress concentration points and possible damage to the substrates. Even where the substrates will bear mechanical fastening, the geometry of certain parts sometimes makes welding or bolting more costly if not entirely impossible, as in the case of the aluminum honeycombs used in aerospace structures or tube-to-tube joining used in motor vehicle frame construction. Because they are usually applied so as to cover the entire joined surface in a continuous rather than point-by-point fashion, adhesives can provide a measure of environmental protection and mechanical reinforcement or stiffening well beyond the capabilities of mechanical fasteners. Stresses in adhesive joints are distributed over a relatively large area, which generally increases the mechanical and cosmetic integrity of joined parts. The energy damping capability of many polymeric adhesives contributes a mechanical damping component to joints that can increase their toughness and impact resistance. Adhesives are a great help in reducing the weight of structures because they add little weight and can facilitate the use of thinner substrates. Joining of dissimilar materials for reasons of economics, weight, or performance is frequently accomplished using adhesive bonding, providing properties already mentioned as well as electrical and thermal insulation, protection against galvanic corrosion, and acoustic damping. In some cases, adhesives are used in conjunction with joining methods such as welding and riveting, via weldbonding and rivet bonding, respectively, in order to maximize stiffness, strength, and fatigue resistance of joints.

Where an adhesive is the obvious choice, it is often the least expensive choice as well. In industrial situations, where the performance expected of the adhesive is high and broad and its cost is that of a specialty rather than a commodity material, it is common to see users take a systems approach to make the best choice of joining method or the best choice of adhesive, if adhesive bonding is seen to be the best joining method. The systems approach to choosing adhesives goes well beyond comparing the cost per gallon of adhesives. It considers the number of parts to be joined, the time and cost constraints of assembly, spatial limitations, the need for substrate surface cleaning or preparation, the cost of all application, fixturing, and curing equipment, environmental and safety requirements, disposal costs, and, finally, part performance, and lifetime.

## 2. Market Economics

In 1996, the global adhesive and sealant industry was estimated to have a size of ~7.5 million metric tons or 16.5 billion lb. The monetary value of this volume was considered to be ~US$20.0 billion (1). The value of the market was estimated to be $28.0 billion in 1998 led by North America with a 33% share followed by Europe (30%), the Far East (19%), and the rest of the world (18%) (2). By 2002, the same marketplace is expected to grow to 16.7 million metric tons or 36.8 billion lb (3). Adhesives make up >80% of the adhesives and sealants market. It has been estimated that the global use of adhesives will continue to grow annually 3–4% from 2000 through 2005, but for some types of adhesives and for some markets, the growth could be much larger.

In the United States, the adhesive and sealants business was producing ~US$1 billion from sales in 1972. By 1999, the U.S. adhesive business was estimated to be nearly 15.2 billion lb in size with an approximate value of US$9.5 billion. The size of the U.S. adhesive market is anticipated to grow to 17.4 billion lb by 2004 (4). The largest markets for adhesives in the United States are construction, primary wood-bonding, textiles, and packaging. Markets that command some of the highest prices for adhesives include dental, aerospace, and microelectronics.

The late 1990s were marked by significant numbers of consolidations and partnerships in the adhesive industry that are expected to continue into the 21st century. In 1999, only seven companies produced 49% of the adhesives sold in the world (5). The remainder of the adhesive industry is highly fragmented; in the United States alone there are ~500 adhesive companies. North American and European adhesive companies have partnered to serve the global operations of automotive OEMs expecting worldwide service. Several companies have formed joint ventures in the People's Republic of China (6) in anticipation of large market growth in that country. Such arrangements are expected to increase in number as makers of adhesives accelerate their pursuit of greater market share and opportunities in the most lucrative markets. Concurrently with these changes, many large resin suppliers have spun off their adhesive resin operations into new companies or sold off their adhesive raw materials divisions to established companies. An active adhesive formulator must keep track of raw materials sources and be prepared to trace older materials to their new sources.

The adhesives industry has been affected by environmental and regulatory concerns regarding health and safety issues of adhesive ingredients, use of solvents, and other issues. Less than 5% of the adhesives used in the United States in 1999 contained organic solvents. The use of adhesives with solvents is decreasing by ~2% annually. All other adhesives are waterborne or contain no carrier solvent. Recycling of adhesives has become more important as paper recycling has become very common, and the quality of recycled paper depends in part on the nature of adhesive residues present in recycle feedstock (7). Historically, certain adhesives have been based on natural products such as starch, natural rubber, and animal glue, and many adhesives still use as modifiers various tree-based rosins and terpenes, but there has been a strong shift away from naturally derived adhesives. Between 1972 and projected out to 2003, the value of U.S. adhesives made of synthetic resin and rubbers will have increased almost eight times while the value of U.S. adhesives made from natural bases will have increased only about five times (8). In the 1920s, nearly all primary wood bonding was done with adhesives produced from natural products (9). By the 1970s, that need was filled almost entirely by synthetic adhesives. As the price of crude oil rises and oil reserves dwindle, there is increasing interest in making more adhesives from renewable resources (10).

## 3. Classification of Adhesives

There are many ways to classify adhesives. These include chemical class, joint strength, bulk modulus, physical form, ultimate use, general market, method of application, and price. Another classification scheme involves considering the activation of an adhesive and the driving force for its change from a liquid-like system to a solid-like system. Each of these methods of classification provides a framework within which to understand adhesives.

The primary chemical classes from which adhesives are made include epoxies, acrylics, phenolics, urethanes, natural and synthetic elastomers, amino resins, silicones, polyesters, polyamides, aromatic polyheterocyclics, and the various natural products such as carbohydrates and their derivatives as well as plant- and animal-based proteins. Chemical class was once a relatively clean differentiator of adhesives, but so many adhesives now are hybrids, designed to take advantage of specific attributes of more than one chemical class or type of material. Hybridization can be accomplished by incorporating into an adhesive a nonreactive resin of a different chemical class; adding another type of reactive monomer, oligomer, or polymer; or chemically modifying an oligomer or polymer prior to adhesive compounding.

The measured overlap shear strength or peel strength of an adhesive joint is sometimes used to classify adhesives. The choice of substrate is a key element of such a comparison, certain aluminums or steels being most commonly chosen as standards, but glass, polyolefins, and other substrates are also used. Pressure-sensitive adhesives will be found at the low end of the bond strength spectrum, and structural adhesives will be found at the high end. In the middle will be found materials that are strong but not necessarily structural in nature; these are often called semistructural adhesives. Many sealants are strongly adherent, and some of these are referred to as adhesive sealants.

Market is a useful adhesive category for those interested in the buying and selling of adhesives, but market-based category can be very broad. Construction adhesives, eg, include joint compound, carpet glues, ceramic and vinyl tile adhesives, a variety of wood-bonding adhesives, and double-sided foam tapes for hanging architectural glass. Although the adhesives used in some of these product categories are relatively standardized, there are many choices in other product categories. Similar breadth and depth would be encountered among adhesives used in the automotive, medical, and electronics industries. Within each of these market areas and most other market areas there will be found both commodity and specialty adhesives.

Most of those who develop adhesive compositions consider the form and ultimate use of an adhesive to be the most useful categories because these guide and direct adhesive development. The ability of the adhesive formulator to satisfy an end use will be very much related to the completeness of the information available concerning performance attributes required or expected. Price is a category of immense interest to the adhesive developer as it helps to define the raw materials from which the formulator may choose. The adhesive development team often must work closely with the customer to learn what is really needed from an adhesive.

## 4. Forms and Types of Adhesives

As supplied, adhesives can be found in the form of low-viscosity liquids, viscous pastes, thin or thick films, semisolids, or solids. Before application to a substrate, an adhesive need not be sticky or otherwise particularly adherent. A distinct exception is the pressure-sensitive adhesive (PSA), which is inherently tacky when first made. Such an adhesive is applied as a thin film with or without a backing, the combination of the adhesive and the backing defining an adhesive tape. The PSA remains throughout its useful lifetime essentially the same material it was when first made. All other forms and types of adhesives undergo a transformation that is central to their function as an adhesive. This transformation is usually carried out through imposition of time, heat, or radiation, either actively or passively.

An adhesive applied as a true solution or a dispersion of solids will dry through loss of water or another solvent, leaving behind a film of adhesive. A reactive adhesive system will form internal chemical bonds through the processes of cross-linking, chemical reaction that joins dissimilar long-chain molecules, or polymerization, chemical reaction that joins similar monomer units. Solid adhesives are heated in order to be applied and then on cooling become functional adhesives. The transformation from a liquid, paste, or semisolid to a functional adhesive is loosely termed *curing*. Additional general terms that refer to this transformation include *setting up* and *hardening*. Adhesives may also cure in stages. The first stage of curing is sometimes referred to as the B stage, and adhesives that have undergone some level of precure in their manufacture are often said to have been *B-staged*. For many adhesive applications, the ability of an adhesive to gel, precure, or develop green strength or handling strength is a key characteristic, being most important for parts that will be bonded and then transported to the next step in their processing. *Adhesives* are referred to as such before and after cure.

## 5. Pressure-Sensitive Adhesives

PSAs are inherently and permanently soft, sticky materials that exhibit instant adhesion or tack with very little pressure to surfaces to which they are applied. The level of adhesion may build with time and be surprisingly high. PSAs generally have a high cohesive strength and often can be removed from substrates without leaving a residue. Some applications take advantage of a PSAs ability to quickly form a strong bond and under stress force failure elsewhere in a system, an attribute used to advantage in tamper-proof packaging and price stickers. At the other end of the spectrum lie PSAs that can be repeatedly repositioned. The primary characteristics used to describe the performance of PSAs are tack, adhesion strength in peel, and resistance to shear forces.

PSAs can be sold in bulk or solution for later coating by product manufacturers. Most PSAs, however, are sold as components of tapes or labels. PSAs are also used to make protective or masking films, some of which also function as conventional tape products, and others are sold in the form of aerosol sprays for graphic arts work. Tape products join one object to another, as when one wraps a gift, seals a box, or puts up a notice. They consist of a film or web carrier coated on one or both sides with a PSA. The carrier is usually a paper or synthetic polymer made in the form of a solid or a foamed film. The carrier is a key component of the tape. Such a construction is usually slit and wrapped on itself to form rolls of adhesive tape from which sections of the desired length can be removed. A release coating is sometimes added to the backside of the tape backing so that the tape can be removed from the roll cleanly, easily, and quietly without splitting the adhesive from the backing. Double-sided tapes that have no release liner effect release through opposite pairing of chemically different adhesives that are chemically incompatible or use of adhesives of different levels of cross-linking that are physically incompatible. There also may be a primer on one or both sides of the tape carrier to ensure better adhesion of the PSA or the release coating. Some tapes are sold with release liners that must be removed after the tape is taken off its roll. Tapes can be applied manually or via mechanized tape dispensers for packaging, splicing, and other applications. Labels are sold with the PSA already present for their attachment to a variety of surfaces. Transfer tapes are PSAs that are provided on a liner from which the adhesive film can be transferred to another surface. PSAs that are effectively sticky hot-melt adhesives can be applied in discrete lines, dots, or other shapes using manual and automated equipment. The convenience and adaptability of PSAs has gained them wide use in diverse applications in virtually every market served by adhesives.

Many PSA compositions contain a base elastomeric resin and a tackifier, which enhances the ability of the adhesive to instantly bond as well as its bond strength. The elastomer may be useful without cross-linking but will often require either chemical or physical cross-linking for establishment of sufficient cohesive strength. Heat, ultraviolet (uv), or radiation are usually the activators of the cross-linking, and suitable catalysts are used, with their choice depending on the base resin. Small amounts of epoxy or hydroxy functionality are sometimes added to allow uv cures if the base resins are not themselves uv-curable. Electron beam curing has received attention but tends to be more costly than uv curing. Elastomers used as the primary or base resin in tackified multicomponent PSAs include natural rubber, polybutadiene, polyorganosiloxanes, styrene–butadiene rubber, carboxylated styrene–butadiene rubber, polyisobutylene, butyl rubber, halogenated butyl rubber, and block polymers based on styrene with isoprene, butadiene, ethylene–propylene, or ethylene–butylene. Any of these resins may be blended with each other to alter or optimize properties. Polychloroprene, *cis*-polyisoprene, and some waxes are rarely used as the main components in PSAs but have found some use as modifiers. Natural rubber grafted with methyl methacrylate, styrene–acrylonitrile copolymers, and other elastomers have been found useful as components of primers for PSA products. Polymers that can be useful as PSAs without tackification but may be modified beneficially with their addition include poly(alkyl acrylate) homopolymers and copolymers, polyvinylethers, and amorphous polyolefins. Comonomers useful for acrylate PSAs include acrylic acid, methacrylic acid, lauryl acrylate, and itaconic acid.

Much of the art of making PSAs rests in the choice of tackifier and the balance between base resins and tackifiers, of which there are numerous choices (11). Tackifiers commonly used with natural rubber, butyl rubber, and polyacrylates include rosins and rosin derivatives manufactured from pine tree gums. The styrenic block polymer base resins respond well to tackification with aliphatic and partially aromatic materials miscible with their continuous nonstyrenic phase or phases. Materials useful as PSA tackifiers have a lower molecular weight than the base resin. They are useful because they lower the modulus of the bulk adhesive in the rubbery region of the modulus-temperature spectrum, that is, above the glass transition temperature. Tackifiers also tend to raise the glass-transition temperature of the system. Tackifiers that react with PSA resins have been introduced to counteract tendencies of tackifiers to migrate, bloom, or volatilize; these kinds of tackifiers are based on isocyanato-reactive or vinyl functional groups (12). Plasticizers are mentioned somewhat synonymously with tackifiers as modifiers for PSAs, but their use is recommended cautiously as any improvements they provide in tack can be quickly offset by losses in strength if the glass transition temperature of the material is lowered too much.

Silicone pressure-sensitive adhesives are blends or reaction products of the combination of a polyorganosiloxane, such as poly(dimethyl siloxane) or its copolymers with diphenylsiloxane or methylphenyl siloxane, with a polysiloxane resin, which is largely inorganic. Pendant vinyl groups may also be incorporated into silicone PSAs, making cross-linking possible with peroxide and other kinds of cures. These kinds of PSAs are most often tackified with additional silicone gums and siloxane resins of varying molecular weight. The silicone PSAs are unique in their resistance of temperatures up to 400°C; performance at elevated temperatures can be optimized using the siloxane resins and rare earth or transition metal esters (13).

The large bulk of PSAs are coated onto continuous webs or films to make pressure-sensitive tapes, labels, etc. While many PSAs continue to be coated out of organic solvents, many have been converted to water-based formulations or are extruded as hot-melt adhesives that upon cooling retain their tack. Aqueous emulsions of carboxylated styrene–butadiene and various acrylate copolymers are among the most useful as bases for water-based PSAs. The complexity of latex chemistry introduces additives such as chain-transfer agents and defoamers (14) into some emulsion-based PSAs. Proper coating of these kinds of PSAs can require addition of thickening agents based on water-soluble polymers. Other additives that may be found in PSAs include cross-linking agents, catalysts, heat stabilizers, antioxidants, photoinitiators, depolymerizers (or peptizers), and various fillers. Reinforcing agents such as phenolics and higher molecular weight relatives of the tackifiers are sometimes added to improve cohesive strength. As made, PSAs are generally colorless or off-white in appearance but are sometimes pigmented for color adjustment or become pigmented through addition of a colored filler such as titanium dioxide, talc, or silver.

## 6. Hot-Melt Adhesives

Hot-melt adhesives are solid adhesives that are heated to a molten liquid state for application to substrates, applied hot, and then cooled, quickly setting up a bond. The largest uses of hot-melt adhesives are in packaging, bookbinding, disposable paper products, wood-bonding, shoemaking, and textile binding. The advantages of hot-melt adhesives include their easy handling in solid form, almost indefinite shelf life, generally nonvolatile nature, and, most importantly, ability to form bonds quickly without supplementary processing. They are considered friendly to the environment and are expected to see expanded use on a worldwide basis as the market continues to move away from solvent-based adhesives. The disadvantages of hot-melts lie in their tendency to damage substrates that cannot withstand their application temperatures, limited high temperature properties, and only moderate strength.

Application temperatures typically used for hot-melts range from ∼65–220°C. Although the industry still refers to most temperature-sensitive adhesives as hot-melts, one will see references to warm-melt adhesives that soften at ∼121°C and cool-melt adhesives that soften below ∼100°C, but these terms are somewhat arbitrarily applied. Decreases in the application temperatures for hot-melts have lessened safety concerns associated with this type of adhesive. While most hot-melts are supplied as sticks or pellets, they are also produced as flat films or sheets, rolls, fibrous nonwovens, powders, strings, bulk masses, or dots or lines on liners.

Hot-melts generally are based on one or more thermoplastic resin. The largest portion of commercial hot-melt adhesives has for many years been based on ethylene–vinyl acetate copolymers having a vinyl acetate content of ∼20–40%. The styrenic block polymers that are thermoplastic elastomers also make up a large portion of hot-melts. Other resins that have been found useful as bases for hot-melts are synthetic elastomers, ethylene–ethyl acrylate copolymers, amorphous polyolefins, branched polyethylenes, polypropylene, polybutene-1, phenoxy resins, polyamides, polyesters, and polyurethanes. Combinations of these resins allows for property and cost adjustments. Tackifiers and plasticizers are commonly added to hot-melts to improve their flow and adhesion to substrates. Examples include synthetic hydrocarbons, natural terpenes, rosins, and various phthalates. Polybutene is occasionally used as the base resin for hot-melts having good cold flow and high wet-out characteristics, but it may also be used as a flexibilizer or plasticizer. Waxes are important hot-melt ingredients, lowering melt viscosity and improving wet out of the substrate. Reactive tackifiers exist to address migration. The polyamide, polyester, and polyurethane hot-melts are often classed separately from the other resins on which hot-melts are based. All are the result of condensation reactions. They are frequently used with few additives and their properties are instead adjusted by changing the starting ingredients of the polymers. They may, however, contain additives that make them better suited to specific uses. Adhesives based on these polymers are considered to deliver higher performance by virtue of better high-temperature resistance and higher strength and may provide better adhesion to polar substrates than the other largely hydrocarbon hot-melt adhesives (15).

Conventional hot-melt adhesives cool to set and do not chemically cross-link. Such systems have an open time of a few seconds to a few minutes. The need for more heat-stable adhesives and stronger bond strengths has driven the development of reactive hot-melts that undergo cross-linking. These are primarily based on polyurethane hot-melts with residual isocyanate groups that react with water after application to form a thermoset adhesive material. Water is provided by the surrounding air and substrate. Cure of these hot-melts is nearly complete within 24 h, but time for full cure will depend on temperature and ambient and substrate moisture content. An extension of the water-activated isocyanate cross-linking reaction is found in the use of polyurethanes that have been silylated to provide active hydrogens for reaction with residual isocyanates in polyurethanes (16). The acceptance of reactive polyurethane hot melts has led to development of reactive block polymer and acrylate hot-melts that rely on radiation cure through activation of epoxy or vinyl groups (17); these are used primarily as PSAs.

Hot-melt adhesives are usually clear, off-white, white, or amber. Colored versions are available for nonbonding decorative use, eg, arts and crafts. Good color retention with heat aging is an important feature of a heat-stable hot-melt system, and antioxidants and heat stabilizers are common ingredients in hot-melt adhesives. Photoinitiators are frequently present when uv or other radiation curing will be used. Other useful additives include fillers and reinforcing agents. When there is some lack of cohesiveness in blends of base resins, compatibilizers may be used to improve the apparent miscibility of these resins (18). Hot-melts can be based on either amorphous or semicrystalline resins. Particularly in the case of semicrystalline resins, the rate of cooling can dramatically affect adhesion to a substrate (19). To control the development of crystallinity, nucleating agents may be added to formulations based on crystallizable polymers such as polyesters.

## 7. Solution Adhesives

Adhesives delivered out of solutions are typically used for joining large areas destined for nonstructural or semistructural service. The solution may be made with an organic solvent or with water or may be an aqueous dispersion. It is important that the liquid carrier have some means of escaping from the bondline in order for the proper bond strength to develop. It should be appreciated that many PSAs are made by casting out of liquids, but when put into use as components of tapes or labels, these adhesives are soft solids containing virtually no liquid.

**7.1. Solvent-Based Solution Adhesives.** Contact adhesives, activatable dry film adhesives, and solvent-weld adhesives make up the solvent-based adhesives. Contact adhesives are solutions of high polymers that are applied to all surfaces to be joined via spray or brush, allowed to dry partially, and then given time under pressure to allow the adhesive layers to fuse. Heat is sometimes used to increase tack or accelerate drying. These adhesives are commonly used to join wood veneers to wood bases, synthetic laminates to particleboard countertops, and paper products to other materials. The major dry film adhesive is solvent-applied natural rubber, which is unique in its ability to adhere to itself without tackification and useful for self-sealing envelopes and similar employment. After being coated on to paper or another substrate, activatable dry film adhesives must be wiped or sprayed with a liquid to regain their adhesiveness; the activating liquid now is nearly always water. Solvent-weld adhesives are used to join plastic parts such as poly(vinyl chloride) (PVC) piping. The adhesive is usually a solution of PVC or chlorinated PVC that is applied to the outer surface of the pipe and the inner surface of a connector piece that are joined firmly together before the solvent has evaporated.

The most widely used contact adhesive is a solution of polychloroprene or modified polychloroprene in solvent blends of aromatic hydrocarbons, aliphatic hydrocarbons, esters, or ketones, eg, toluene–hexane–acetone. Viscosity, dry time needed before bonding, bond strength, and price are affected by the solvent. Using various combinations of the isomeric forms of polymerized 2-chlorobutadiene permits a fine-tuning of the crystallization rates of the dissolved polymer as the solvent evaporates. The polychloroprene may also be modified by the incorporation of methacrylic acid or mercaptans. Metal oxides (MgO and ZnO) that scavenge acids are often part of polychloroprene adhesives and also may act as cross-linking agents. Oxygen scavengers such as butylated hydroxytoluene (BHT) [128-37-0] or naphthylamines [25168-10-9] are added to prevent dehydrochlorination. To build initial handling strength, the solvent-based polychloroprene contact adhesives may be modified with alkyl phenolics, terpene phenolics, or phenolic-modified rosin esters, the first of these being the most effective and least deleterious (20). Chlorinated rubbers are sometimes added to these adhesives to improve their adhesion to plasticized PVC and other plastics. Added just before adhesive application, isocyanates are useful in modification of polychloroprene contact adhesives, reacting perhaps through hydrolysis of the pendant allylic groups present from the small number of 1,2 isomeric segments (21). The remainder of the solvent-based contact adhesives are comprised of polyurethane, SBR, styrene–butadiene–styrene block polymers, butadiene–acrylonitrile rubber, natural rubber, or various acrylic or vinyl resins in suitable solvents.

**7.2. Water-Based Solution Adhesives.** Solution adhesives based on water dispersions and aqueous emulsions are steadily gaining in use largely at the expense of solvent-based adhesives. These are rarely true solutions, with the exception of the viscosity modifiers often used to adjust flow characteristics. Dispersions of polyurethanes in water find use in bonding of plastic sheets and films, cloth, shoe parts, foams, PVC veneers, and carpets. Other water-dispersible resins can be added to the polyurethane dispersion to lower costs and modify performance characteristics. The largest group of water-dispersed or water-dissolved adhesives are made of natural products, which are covered separately. At one time, vegetable gums were used widely as water-activatable adhesives, but poly(vinyl alcohol) (PVA) has replaced them in envelope sealing and similar areas.

Poly(vinyl acetate) (PVAC) emulsions, the basis of the ubiquitous household white glues, are among the most familiar water-based adhesives. These are widely used for paper and wood bonding. They contain a substantial percentage of vinyl alcohol content, formed via partial hydrolysis from the vinyl acetate homopolymer as vinyl alcohol itself is not a stable molecule. Such latexes are stabilized through the use of surfactants, one choice being well-hydrolyzed PVAC. After application to the substrate, latex adhesives cure by the evaporation of water accompanied by the coalescence of the latex particles. On the porous substrates with which these are most frequently used, the water exits the bondline through the substrate as well as the adhesive, preventing voiding or foaming that might weaken the bond. Subtle changes in properties can be engineered through the use of other comonomers or the use of liquid plasticizers. Glyoxal [107-22-2] or other cross-linking agents can be added to PVAC latex adhesives to combat creep (22).

Polychloroprene latex adhesives have been available for many years. They are stable at pH values between ~10 and 12. The latex particles are usually lightly cross-linked. Except for the substitution of water for the organic solvent, the ingredients in these kinds of adhesives are similar to those found in their solvent-based counterparts. Terpene-phenolics are particularly effective as tackifiers for contact adhesives based on polychoroprene latexes, but rosin acids, rosin esters, hydrocarbons, and coumarone-indenes are also useful, particularly where heat-assisted bonding is not possible. Dehydrochlorination leading to acid generation is particularly possible with the water-based polychloroprene adhesives. Like other water-based adhesives, these may require addition of biocides or preservatives to prevent the breeding of microorganisms (23).

## 8. Structural Adhesives

Structural adhesives are designed to bond structural materials. Most any adhesive giving shear strengths in excess of ~7 MPa (~1000 psi) may be called a structural adhesive. Structural adhesives are generally the first choice when bonding metal, wood, and high-strength composites to construct a load-bearing structure. Bonds formed with structural adhesives cannot be reversed without damaging one or the other substrate. They are the only kind of adhesive that might be expected to be able to sustain a significant percentage of its initial failure load in a hot and humid or hot and dry environment. Any one of these descriptors names structural adhesives the strongest and most permanent type of adhesive. For good reason, they are sometimes referred to as engineering adhesives. The strength and permanence of structural adhesives is largely achieved using reactive adhesives, a term that has become something of a synonym for structural adhesives. Epoxies are the most widely used class of structural adhesive chemistry, but acrylates, urethanes, phenolics, and other classes have been used to great advantage, and the combination of these different chemical classes to create hybrid adhesives propagates the best virtues of each. Reactive adhesive systems that are arguably not always considered structural adhesives but are conveniently grouped here are also reviewed in this section.

### 8.1. Epoxy Resins.

Epoxy resins have a long and distinguished record as structural adhesives. Their use dates to 1950 or earlier, and their utility for adhesives was recognized upon their development. Most epoxy adhesives are resins based on what is commonly known as the diglycidyl ether of bisphenol A (DGEBPA). These resins are based on the reaction of 4,4′-isopropylidene diphenol (bisphenol A) ($C_{15}H_{16}O_2$) [80-05-7] and epichlorohydrin ($C_3H_5ClO$) [106-89-8]. The molecular weight of the commercial difunctional resins formed by this reaction will vary with the molar ratio of the reactants. At a molecular weight of ~400 or less, these resins are viscous liquids that are immensely useful in epoxy adhesives. Commercially viable solid resins based on DGEBPA have molecular weights ranging up to ~4000. Many epoxy adhesives will also contain a small amount of an epoxy diluent having low viscosity and a more flexible structure; this resin adjusts the flow of the system and also helps to wet out the fillers that are usually present.

A wide variety of epoxy resins are commercially available: monofunctional or polyfunctional, aliphatic, cyclic, or aromatic. Brominated epoxies may be useful where flammability is a concern. An oxirane functionality is all that is needed to make an epoxy resin, and structural adhesives are only one of over a dozen different uses for epoxy resins. Many epoxy resins on the market will not necessarily be suitable for adhesives, but their availability does expand the choices available for adhesive formulators. The specialty epoxy resins developed specifically for adhesive use sometimes will be more costly than the DGEBPA resins but may provide the basis for a specialty adhesive that can meet a unique need and therefore command a proportionally higher price. Examples of these are epoxy-functional dimer acids, urethanes, and various elastomers.

Epoxy resins based on DGEBPA usually are quite stable at temperatures up to 200°C. Curing agents, sometimes called hardeners, must be added to the epoxy to cause cross-linking and chain extension to occur and a bond to form. Certain types of curing agents will be favored over others for each of the three types of epoxy structural adhesives: one-part (1K) epoxy paste adhesives, 2K epoxy paste adhesives, and 1K epoxy film adhesives. The strained oxirane ring is reactive with functional groups having either nucleophilic (basic) or electrophilic (acidic) character. Acid anhydrides, carboxylic groups, and hydroxyl groups react very slowly with the oxirane ring and are usually used with catalysts that accelerate their reaction with epoxies. Those groups that readily react without catalysts but often benefit from their use include amines and mercaptans. Both the epoxy resin and the curative package (curing agent plus catalyst) will influence final cure speed.

One-part (1K) paste adhesives usually consist of a DGEBPA resin, a reactive diluent, and latent curing agents that are insoluble with the resin at room temperature but dissolve at elevated temperatures to trigger cure. These kinds of adhesives are in use in the aerospace, automotive, and electronics industries. Dicyanodiamide or dicyandiamide ($C_2H_4N_4$), [461-58-5], is the most frequently mentioned latent curing agent for cures occurring in the range 170–180°C; practitioners refer to this material as *dicy*. Also useful in this range are metal-complexed imidazoles, complexes of Lewis acids (eg, boron trifluoride with amines), and diaminodiphenylsulfone. Cure temperature can be lowered by using micronized dicyanodiamide ground to a particle size of 5–15 μm. Cure can be accelerated by use of aromatic tertiary amines, imidazole derivatives, and epoxy resin adducts with tertiary and other amines. Substituted ureas such as Monuron ($C_9H_{11}ClN_2O$), [150-68-5], and nonchlorinated substituted ureas such as 3-phenyl-1,1-dimethylurea ($C_9H_{12}N_2O$), [101-42-8], have also found use as accelerators in 1K epoxy adhesives. Dihydrazides offer a range of melting points depending on structure, their cure temperatures with epoxies beginning as low as 100–110°C. Adducts of dicyanodiamide that melt at temperatures in the 115–120°C range are available. Accelerated 1K epoxies show faster cures once heated but suffer from decreased shelf lives; after manufacture, they are usually stored in refrigerators or preferably freezers although this is usually impractical for drum quantities. For these same reasons, their manufacture is carried out at temperatures well below their activation temperatures and at low shear rates to avoid viscous heating.

The low viscosity two-part (2K) epoxy adhesives sold in hardware stores as 5-min epoxies are based on cure with polymercaptans regulated with amines to control worklife. The human nose can sense some mercaptans in air at the parts per billion (ppb) level, making them valuable as gas odorants, but they are tremendously useful as curing agents, particularly when used in thin films as for adhesives. Their low toxicity is also an advantage. Capcure 3-800 [101359-87-9] is a commonly found polymercaptan. Low odor polymercaptans have been developed that combine strategies of odor masking, odor counteracting, and absorbency to stabilize polymercaptans, reducing the level of odor by ~75% (24). Higher molecular weight versions of the polymercaptans are useful as the base resins of polysulfide sealants, which are sometimes categorized as adhesives. In full formulation, the polysulfide base resins are blended with curing agents such as manganese dioxide or sodium perborate, accelerators or retarders, fillers, plasticizers, thixotropes, adhesion promoters, and pigments (25). These materials are used primarily in the construction and aerospace industries.

Many 2K epoxies utilize curing agents that are the reaction products of amines of low molecular weight with fatty acids. These are variously known as polyamidoamines, polyamides, and amidoamines and sold in a range of molecular weights under trade names such as Versamid and Ancamide. The fatty acid portion of these amines gives them larger bulk than the lower molecular weight amine curing agents, which facilitates formulation of adhesives having mix ratios closer to 1:1 by volume. This volume ratio is of benefit for both packaging and off-ratio tolerance. Curing with polyamidoamines generally produces relatively flexible adhesives having good chemical resistance. Because they typically cure slowly, they are frequently used in combination with other amines such as diethylenetriamine (DETA), triethylenetriamine (TETA), tetraethylenepentamine, aminoethylpiperazine, modified imidazolines, and oligomeric amine-terminated polyethers. Some of the amines in this group are used as sole curing agents, and others, such as DETA and TETA, are used as epoxy adducts to reduce toxicity and increase stability. Aromatic amines, although useful for epoxy resin composite matrices, find little use in epoxy adhesives.

Another family of curing agents is based on substituted phenols such as tris(dimethylamino)phenol ($C_{12}H_{21}N_3O$), [31194-38-4], and tris[(dimethylamino)methyl]phenol ($C_{15}H_{27}N_3O$), [90-72-2]. These tertiary amines can produce rather brittle adhesives if used as sole curing agents, but are valuable as accelerators for other amines. They act as catalysts for dicarboxylic acid anhydride cures. Amines are also useful as accelerators for the oxirane-alcohol reaction, which is sluggish at room temperature but with catalysis will proceed above 120°C. Imidazoles are also generally useful as catalysts or cocuring accelerators for epoxy reactions with amines, hydroxyls, and thiols. Organic and inorganic salts sometimes find use in epoxy adhesives, coatings, and encapsulating compounds. Acid catalysts such as boron trifluoride–amine complexes find some use in epoxy adhesives but tend to require long cures, even at elevated temperatures, which normally works against their use in adhesives. Epoxy resins react slowly with acid anhydride curing agents but can be accelerated with acids or bases, imidazoles being used most often, however, anhydrides are not often used as curing agents in epoxy adhesives.

Epoxy film adhesives are 1K adhesives in film form. They are formulated much like 1K paste adhesives but often contain solid epoxy resins and additional resins that provide binding properties. These may be partially cured (B-staged) to provide a more dimensionally stable film. Epoxy film adhesives have been widely used in the aerospace industry where their relative stability accommodates the long build times needed for aircraft manufacture. Their cured properties can be outstanding in terms of strength, toughness, and durability. They can be supplied in film form and cut to size or provided as tapes in convenient slit widths. They may be made to be tacky using rubber resins and other mild tackifiers or they may be dry. Film adhesives of a more aggressive pressure-sensitive character have been developed by coating or laminating with pressure-sensitive formulations or formulating such that the bulk adhesive (26) is a pressure-sensitive adhesive in its own right but can be cured to a semistructural or structural strength. Epoxy film adhesives based on thermoplastic polyamide resins are very tough when cured but can be susceptible to moisture absorption.

In addition to resins and curing agents, epoxy adhesives will contain many functional additives and modifiers. Flexibilizers and tougheners such as polysulfides, epoxidized fatty acids, epoxidized polybutadiene, and amine- and carboxy-terminated acrylonitrile butadiene polymers react with the epoxy network. Flexibilizers remain in phase with the epoxy while tougheners typically phase separate to form domains, the result producing a tougher adhesive with more or less strength reduction relative to an unmodified system. Particulate tougheners may also be added to epoxy adhesives. These include core-shell resins, functionalized elastomeric particles, and ground reclaimed rubber. Positive aspects of structural adhesives based on epoxy resins include good adhesion to many substrates, no emission of volatiles upon cure, low shrinkage, and a broad formulating range based on a history of use dating to the 1940s. The lack of outgassing allows most curing to be done at ambient pressure although clamping till cure is standard protocol for any adhesive bonding operation. Shrinkage can be further decreased with use of appropriate fillers, with harder fillers by some reports providing the lowest shrinkage.

### 8.2. Acrylics.

Historically, acrylics offer several useful characteristics as structural adhesives. Most well known is their relatively high speed of reaction via free radical polymerization. The details of their reaction provide a useful division of the different classes of acrylic structural adhesives into redox-activated adhesives, encompassing both anaerobic acrylics and nonaerobic structural acrylics, and cyanoacrylates. These will be considered in turn.

Oxygen inhibits the polymerization of acrylic monomers to a useful extent, and its exclusion kicks off polymerization of monomeric acrylates. Early versions of anaerobic acrylics relied solely on this mode of initiation and polymerization, containing little besides acrylate monomers and diacrylic esters (27). Later it was found that if hydroperoxides were incorporated into the acrylic monomer, small amounts of free metal ions from metal substrates could help to create free radicals that initiated polymerization of the acrylate monomers. Only small amounts of metal ions are needed, iron, nickel, zinc, and copper being some of those of major industrial interest. Even though a major alloying element, such as aluminum, eg, may not be capable of helping to generate free radicals via the redox reaction, minor alloying elements, such as copper, may be available that can act in this capacity. The speed of reaction is limited by the ability of the metal ion to reduce the peroxide. Free radical initiators used in anaerobic acrylics have included cumene hydroperoxide, *tert*-butyl hydroperoxide, and potassium persulfate ($K_2S_2O_8$), [7727-21-1]. Other useful initiators for this cure are combinations of saccharin [81-07-2] with aromatic amines such as *N*,*N*′-diisopropyl-*p*-toluidine [24544-09-0] or 1-acetyl-2-phenylhydrazine [114-83-0]; such combinations were originally thought to be accelerators useful only with peroxide initiators until it was found that they were themselves initiators (28). Various accelerators can be used with initiators to hasten cure of these adhesives; classes of compounds useful as accelerators include cyclic peroxides, amine oxides, sulfonamides, and triazines (29).

A key ingredient in anaerobic acrylic adhesives is the acrylate monomer or monomers. These include primarily acrylic acid and methacrylic acid and their many and various esters such as lauryl acrylate, cyclohexyl methacrylate, methyl methacrylate, hydroxyalkyl methacrylates, and tetrahydrofurfuryl methacrylate. These monomers vary in their volatility, reactivity, and cost, the less volatile monomers forming the basis of low odor acrylic adhesives. In addition to the monomer acrylates, there generally is also present a diacrylate that acts as a cross-linker, the alkyl glycol dimethacrylates being widely used in this function. Other ingredients used in these adhesives include stabilizers or polymerization inhibitors such as phenols or quinones; chelating agents that snatch up trace metals to prolong shelf life; and various modifiers such as inert fillers, inorganic and polymeric thickeners, elastomers to improve toughness, and bismaleimides that improve high temperature performance (30).

The low viscosities and good wetting properties of these adhesives allow them to penetrate and flow in tight spaces, which is taken advantage of in many of their uses. Threadlocking and sealing are primary applications. When applied to the threads of bolts or pipes, to flanges, and to other tight-fitting machine parts that are later screwed into or pressed against a mating surface, the adhesive cures due to the exclusion of air and the formation of free radicals via the reaction of metal ions with the initiator. Other applications include bonding of optical fibers, impregnation of porous parts, crimp-bonding of electrical parts, and fastening of press-fit parts. Anaerobic adhesives are one-part adhesives, usually packaged in small oxygen-permeable plastic containers that have not been entirely filled, this arrangement providing a sufficient supply of polymerization-inhibiting oxygen to ensure good shelf life.

The nonaerobic structural acrylic adhesives are two-part adhesive systems. They are generally less oxygen inhibited than the anaerobic acrylics and do not rely on metal surface activation in the same way as the anaerobics. These adhesives are very similar in formulation to the anaerobics, each borrowing technology from the other as it has developed. Lower oxygen sensitivity is accomplished through higher concentrations of accelerators and initiators. The accelerators and initiators are usually redox couples such as the commonly used hydroperoxide/amine–aldehyde condensates (oxidant–reductant), which react to form alkoxy radicals. The most widely used condensate is that resulting from reaction of *n*-butyraldehyde [123-72-8] with aniline [62-53-3] in the form of a polymeric resin that is available commercially [9003-37-6]. This material has a complex structure, the major component and active ingredient apparently being dihydropyridine [27790-75-6] (31). Another common redox couple is based on hydroperoxide coupled with an alkyl aromatic amine such as *N*,*N*-dimethylaniline [121-69-7]. A number of 2K acrylic formulations include metals, metal oxides, or metal salts (32).

The 2K nonaerobic acrylic adhesives can be used in any of three ways. The first is as a no-mix two-part, the use of which involves applying a thin layer of accelerator (in dilute solution) to one mating surface, flashing off the solvent, applying the adhesive to the second mating surface, and joining the two surfaces. It is perhaps a poor choice of terms, but the accelerator contains the initiator (eg, peroxide) or may contain a redox couple. As long as the bondline thickness is no more than ~500 μm (0.020 in.) for one-side activation or ~1000 μm for two-side activation, cure is expected to be adequate. The 2K acrylics that are meant to be mixed utilize a different kind of accelerator that contains the catalyst system in a carrier resin such as an epoxy and perhaps a diluent. These can be used in a fashion similar to the no-mix adhesives, but this approach may not produce optimal properties. Typically, the 2K acrylics are made by mixing the accelerator into the one-part acrylics and immediately applying this mixture to the substrate. Volume mix ratios will range from ~2:1 to ~20:1. Additional ingredients commonly found in these compositions include various elastomeric polymeric tougheners such as chlorosulfonated polyethylene, butadiene–acrylonitrile elastomers, and polyurethane acrylates. These tougheners are usually incorporated into the adhesives by dissolution in the acrylic monomers, creating adhesives sometimes referred to as second-generation acrylics. Their development by DuPont (33) and others marked the entry of acrylic structural adhesives into a large number of new applications.

Due to their high reactivity, these 2K acrylic adhesives are used in many situations where fast ambient cure is important. Since the incorporation of the redox couple catalysts, acrylic adhesives have advanced their use on metals as well as plastics, woods, and ceramic substrates. As a class, they tend to be fairly accommodating of oily metal and unprepared plastics and composites. Offensive odors often accompany the common forms that use the less expensive lower alkyl acrylates. Colors of these materials are clear, off-white, white, and amber. They are not often intentionally pigmented although they may be tinted with functional metal additives or aluminum powders.

A very important class of acrylic adhesives, the cyanoacrylates, are distinguished by their relative simplicity of formulation and their nearly instant bonding properties. The name recognition of “super glue” surpasses that of nearly any commercial adhesive though it is now known by a variety of other ungenericized trademarks. First discovered in the 1940s during World War II, cyanoacrylates were rediscovered and first truly appreciated in the 1950s and brought to the market in 1958. Then as now they are largely based on ethyl and methyl cyanoacrylate. Other monomers of interest have been the isopropyl, butyl, allyl, ethoxyethyl, methoxyethyl, methoxypropyl, and fluoroalkyl esters.

Cyanoacrylate adhesives cure by polymerizing anionically. They are catalyzed by mild nucleophiles (bases), such as an $OH^-$ ion, which can readily be found in small quantities on many surfaces. Strong acids, found in many woods and acid-treated metals, can inhibit polymerization. As long as the adhesive film thickness is as low as possible, that is, practically zero, sufficient catalyst provided by the substrate will be available, hence the usual directive to apply the adhesive sparingly and to avoid using it as a void filler or to bond porous surfaces. Bond thicknesses higher than ~13 μm (0.005 in.) are not recommended unless appropriate surface activators are used. As the conversion to a cured adhesive is a polymerization, it passes through and is subject to the same stages as any addition polymerization: initiation, propagation, chain transfer, and chain termination. Like the anaerobic adhesives, these adhesives are conveniently initiated by coating onto surfaces suitable initiators such as alcohols, epoxides, various amines, caffeine, and other heterocyclic compounds (34). Compositions may also incorporate accelerators as well as inhibitors, the latter usually being either phenolics designed to inhibit premature polymerization due to heat or light or anionic polymerization inhibitors consisting of sulfur dioxide, other acid gases, or complexes of sulfur dioxide with organic or inorganic compounds. Normally quite brittle, cyanoacrylate adhesives can be flexibilized using monomers having longer alkyl side chains (2-octyl cyanoacrylate) or by incorporating plasticizers such as acetyl tri-butyl citrate (35). Various approaches have been taken to toughening the cyanoacrylates (36). As uncross-linked thermoplastic adhesives, the cyanoacrylates begin to soften and flow at $\sim 80^\circ C$ and will also depolymerize. Their durability in hot moist environments is considered to be poor, especially on metals. This problem has been addressed through introduction of difunctional or bifunctional cross-linkers, addition of heat-resistant adhesion promoters, and various other strategies aimed at improving moisture resistance. The last important component of the cyanoacrylate adhesive is the thickener, which is usually polymeric in nature.

Cyanoacrylates have long been known to be effective adhesives for human skin and other soft human tissues. They are effective when used for sutureless wound closures and hemorrhage prevention, the butyl cyanoacrylate being most widely used (37) based on a good balance between biodegradability and inflammatory response. Flexibilizers as well as aids to biodegradation are added to make these more suitable for tissue bonding. In everyday use, the outstanding capability of cyanoacrylate adhesives to instantly bond human skin is seen as a negative feature. Skin-adhesion inhibitors that have been found useful include alkanols, carboxylic acid esters (38), and copolymers of maleic acid, vinyl chloride, and vinyl acetate (39). These slow the adhesive's reaction rates against human skin or at least lower adhesion to it.

**8.3. Urethanes.** The core of a urethane adhesive is an isocyanate compound. Isocyanates react with a variety of functional groups having active hydrogens to generate a variety of linkages that give the resulting polymers their names. These include reaction with alcohols to form urethanes [$R{-}NH{-}CO{-}O{-}R'$], with amines to form ureas [$R{-}NH{-}CO{-}NH{-}R'$], with thiols to form thiocarbamates [$R{-}NH{-}CO{-}S{-}R'$], with amides to form acylureas [$R{-}NH{-}CO{-}N(R'){-}CO{-}R''$], with urethanes to form allophanates [$R{-}NH{-}CO{-}N(R'){-}CO{-}O{-}R''$], and with ureas to form biurets [$R{-}NH{-}CO{-}N(R'){-}CO{-}NH{-}R''$]. Isocyanates can also react with water, generating carbon dioxide through the degradation of the unstable carbamic acid [R-NH-COOH]. This last reaction is the basis for the making of polyurethane (PU) foams. To a great extent, what is classified as urethane chemistry encompasses the entire chemistry available to isocyanates.

Most polyurethane structural adhesives are two-part systems based on the reactions of isocyanates and polyisocyanates with oligomers or polymers having at least two hydroxyl groups, which are generically referred to as diols or polyols. Although part of many earlier adhesive formulations, toluene diisocyanate (TDI) is now decreasing in use while use of diphenylmethane diisocyanate (MDI) is growing. Other common diisocyanates include 1,6-hexamethylene diisocyanate (HMDI or HDI) and isophorone diisocyanate (IPDI). Also available are the modified MDIs, multifunctional isocyanates often termed polyisocyanates, polymeric polyisocyanates, and isocyanate-capped oligomers that are often referred to as urethane prepolymers (40). Materials now available that have very low monomeric isocyanate content are expected to bring about increased use of urethanes in adhesives (41). Hydroxyl-functional materials useful in urethane adhesives have molecular weights between ~500 and 3000 and functionalities between 2 and 3. The base oligomer is usually a polyester, polyether, polycarbonate, or polydiene such as polybutadiene. Cross-linked polyurethanes can be made with the use of trifunctional isocyanates and triols or through reactions of urethanes with urethanes, ureas, or isocyanates to yield the trimer isocyanurate.

In many cases, as polyurethanes are formed, long- and short-chain diols alternate along the chain to form segments that are either "soft" or "hard". On a microscope scale, the soft and hard segments coexist in a domain morphology characteristic of what are known as segmented polyurethanes. The very good impact and fatigue resistance of PUs is attributed to this phase-separated microstructure. Because it is the integral component of the soft segment, the particular diol or polyol chosen will greatly influence the rubbery and impact-resistance properties of the PU. Likewise, the isocyanate chosen will strongly influence the strength, modulus, and hardness of the PU. The domain morphology of segmented PUs is most pronounced for systems containing no chemical cross-linking. In contrast to most adhesive systems, low levels of cross-linking tend to degrade the properties of PU adhesives because of disruption of the domain morphology.

Because isocyanates react with so many different organic functional groups and can also react with water, which is found nearly everywhere, catalysts are very important for the control of isocyanate reactions. Many of the catalysts used may push one reaction over another, but they do not necessarily entirely block unwanted reactions. Tertiary amines, principally bis(dimethylaminoethyl)ether, are frequently used to promote the isocyanate–water reaction, producing a blowing or foaming that generally would not be desirable for adhesives. Compounds that drive the isocyanate–hydroxyl action without substantially encouraging the isocyanate–water reaction include organometallic complexes such as dibutyltin dilaurate and stannous octoate. At temperatures $>100^\circ$C, urethanes and ureas will react with isocyanates to form the allophanates and biurets described previously, but above 130°C, these groups will decompose. Dimerization of isocyanates to form uretidiones is catalyzed by bases such as trialkylphosphines, pyridines, and tertiary amines. Formation of the trimer of isocyanates, isocyanurate, is favored through use of phosphines, amines, and various metal salts such as potassium acetate.

One-part urethane adhesives have been used for many years as high-performance sealants. In this capacity, they provide a useful combination of strength, flexibility, and elastic recovery. As adhesives, these systems have limited use unless formulated to overcome their inherent disadvantages. One-part polyurethane adhesives are typically moisture cured and rely on a multistep reaction sequence as follows: isocyanate reacts with water to form carbamic acid, the unstable carbamic acid loses carbon dioxide and generates an amine, the amine reacts with additional isocyanate to form a urea, and the urea reacts with additional isocyanate to form a biuret, which includes a cross-link. Unless it diffuses out of the system, the $CO_2$ can cause foaming. Formulators learn to minimize the isocyanate content (%NCO) of a system in order to balance cure speed with foam control. Cure speeds—and foaming rates—of these systems decrease from the outside in and vary with the amount of atmospheric moisture in the air, which changes hourly and seasonally.

A different kind of moisture-activated 1K urethane adhesive utilizes a moisture-activated curing agent such as oxazolidine (42). Oxazolidines are formed by dehydration and subsequent ring closure of aminoalcohols by aldehydes or ketones. When the presence of water causes that reaction to reverse, hydroxyl and amine groups are formed. These react readily and directly with isocyanates. Monooxazolidines are useful primarily as water scavengers, but bis (oxazolidines) can participate in the curing reactions of urethane adhesives.

More sophisticated 1K urethane adhesives use blocked isocyanates along with polyol curing agents. Useful blocking compounds include phenols, malonates, methylethylketoxime, and caprolactam. These react with isocyanates, but at high temperatures or in the presence of strong nucleophiles, the reaction reverses, freeing the isocyanate. Such systems do not rely on water for reaction, nor do they suffer from the detriments of $CO_2$ generation, but they do require heat for cure. Another approach to a stable 1K urethane is to use a solid polyol, such as pentaerythritol, that melts at elevated temperatures and then reacts with the isocyanate (43). Other schemes for 1K urethanes are described by Edwards (44).

As a class, urethane adhesives have somewhat poorer thermooxidative and moisture resistance than acrylic and epoxy structural adhesives. This finding has historically limited their expansion into certain areas of use. A 2K adhesive having the ability to survive automotive paint oven temperatures, which run as high as 205°C, uses polyols with high percentages of hydroxyl groups, an acrylonitrile-grafted triol, a phosphorus adhesion promoter, and a DABCO trimerization catalyst (45). The 1K adhesives made with blocked isocyanates tend to be unable to withstand high temperatures due to volatility of the blocking agents, and other approaches are also unsatisfactory for high-temperature stability. Use of micronized dicyanodiamide as a latent catalyst and curing agent for isocyanates has produced 1K urethane adhesives showing some capability to tolerate heating to well over 250°C while bonding well to FRP (46). Sensitivity to hydrolysis has been another of the historic disadvantages of traditional urethane structural adhesives.

Two-part polyurethane adhesives will usually contain fillers and may contain pigments that facilitate visual qualitative off-ratio mixing detection. To increase cure speed, polyamines are sometimes added to the polyol curative, which also contains the catalysts. In addition to their primary ingredients, one-part moisture-curing urethane adhesives will typically contain fillers and perhaps pigments. Arguably the largest user of urethane structural adhesives is the transportation industry, which uses urethane structural adhesives for bonding of automotive parts made of SMC, FRP, and RRIM composites and plastics. One-part urethanes are widely used for bonding of windshields to automotive vehicle frames. Though 1K urethanes are not conventionally considered to be structural in nature, automotive engineers hold that the windshield is part of the primary structure of the vehicle, conferring on these one-part urethanes the status of a structural adhesive. Wood bonding is another significant market for polyurethane structural adhesives.

As a group, polyurethane structural adhesives produce bond strengths on the lower end of the strength scale for structural adhesives, but their high flexibility, usually strong peel strength, and generally good impact and fatigue resistance recommend their use when these characteristics are important. A variety of adhesives have been developed that incorporate polyurethanes into acrylic or epoxy structural adhesives (47). Inclusion is done through use of isocyanate-functional ingredients or polyurethanes end-capped with a non-isocyanato functional group. The broad reactivity of isocyanates offers many other options for hybridization.

**8.4. Phenolics.** Phenolic resins were the basis of the first synthetic structural adhesives. They are formed by the reaction of phenol, ($C_6H_6O$) [108-95-2], and formaldehyde, ($CH_2O$) [50-00-0]. There are two types of phenolic resins, resoles and novolaks (or novolacs), the former being comprised of methylol-terminated resins and the latter, of phenol-terminated resins. Resoles result from use of basic reaction conditions and an excess of formaldehyde and will cure via self-condensation at 100–200°C with loss of water. Novolaks are produced using acidic reaction conditions and formaldehyde/phenol molar ratios of 0.5–0.8. They require addition of a curing agent for cure. Hexamethylenetetramine ($C_6H_{12}N_4$), [100-97-0], is a widely used novolak curing agent. Resoles and novolaks are sometimes referred to as one- and two-step resins, respectively.

Formulators can choose from a variety of commercially available phenolic compounds, including, in addition to phenol itself, the isomers of cresol, the isomers of xylenol, resorcinol, catechol, hydroquinone, bisphenol A, and various alkylphenols. Formaldeyhde is usually used as the second major component, but acetaldehyde, furfuraldehyde, and paraformaldehyde (the polymer of formaldehyde) have been used sometimes alone and sometimes along with formaldehyde. The reactions of these various components are complex but have been elucidated by painstaking research described by Robins (48) and others.

Like epoxies, the phenolics are very brittle unless modified by tougheners. The first successful tougheners were poly(vinyl formal) resins that were added as a powder sprinkled over a layer of resole phenolic applied out of solution. These Redux adhesives were the first toughened thermoset adhesives and were the basis of the first durable adhesive bonding technology for aerospace aluminum in the 1940s and 1950s. These were superseded in the 1960s by film adhesives formed from liquid phenolics filled with poly(vinyl formal) powders. Other tougheners followed: poly(vinyl butyral), nitrile rubbers, polyamides, acrylics, neoprenes, and urethanes. Epoxy–phenolics are important hybrid adhesives and offer an immensely useful combination of strength, toughness, durability, and heat resistance. Phenolic structural adhesives as a class of materials are highly resistant to most chemicals.

Phenolic adhesives are found as powders, liquids, pastes, and supported and unsupported films. Among the pastes, both 1K and 2K systems are available. Fillers are commonly used in paste adhesives. Support of film adhesives is provided by glass, cotton fabric, nylon, or polyester scrims. The novolaks are almost exclusively powders in pure form, but the resoles often are found as liquids. The resole systems are usually cured at temperatures exceeding 170°C. The condensation cure of the resole phenolics systems requires that they be cured under high pressures to minimize evolution of bubbles from water vapor, which is usually done in autoclaves or hot presses at pressures of ~200 to nearly 1400 kPa (29–203 psi) (49). Cure times range from 1 to 4 h depending on temperature. The cure conditions required for the resole phenolic adhesives have limited their use, and to a great extent they as well as the relatively brittle novolak phenolics have been displaced by epoxies for aerospace aluminum bonding applications for which they were once the first choice. Nitrile–phenolic adhesives have a long history of use not only in aerospace applications but also in automotive applications such as the bonding of brake linings and the friction materials used in transmissions. Resole phenolic resin adhesives are widely used in the making of plywood and particle-board as both binders and for laminating of veneers; resorcinol is frequently used along with phenol or as the sole hydroxyl compound. In wood bonding, the porosity of the wood allows escape of the water vapor generated during curing of the adhesive and is believed to facilitate mechanical anchoring of the adhesive in the wood. Phenolics are also widely used as foundry resins for making sand-shell molds.

**8.5. Urea–Formaldehyde and Related Adhesives.** Urea–formaldehydes (UF) are the most significant members of the class of materials known as the amino resins or aminopolymers. These are the polymeric condensation products of the reaction of aldehydes with amines or amides. A molar excess of formaldehyde is used, and this along with the temperature and the pH dictate the properties of the final product. The initial reactions of urea and formaldehyde to form mono- and dimethylolureas can be catalyzed by either acids or bases, but the final condensation reactions will proceed only under acid conditions. These adhesives are widely used to make plywood and particleboard in processes utilizing heated hydraulic presses with multiple outlets for water vapor release. Temperatures up to 200°C may be used. The UF adhesives in the first use contain hardeners composed of ammonium chloride or ammonium sulfate solutions or mixtures of urea and ammonium chloride plus fillers such as grain and wood flours. Particleboard adhesives, which are really binders, contain similar hardening agents, a worklife extender (ammonia solution), insecticides, wax emulsions, and fire-retarders. The slow hydrolysis of the methylenebisurea ($NH_2CONHCH_2NHCONH_2$), [13547-17-6], has been linked to the slow release of formaldehyde from UF adhesives (50). The wood industry has been under increasing pressure to reduce and eliminate unreacted and evolved formaldehyde from these products and has made great efforts to do so. Melamine–formaldehyde (MF) and the less expensive melamine–urea–formaldehyde (MUF) resins are the bases of high performing wood-bonding adhesives. Their resistance to water is superior to that of the UF resins, but their higher cost has limited their use. The urea in the MUF resins decreases the cost of the MF resins. Uses of these are similar to those for the UF resins with the addition of paper-laminates for wood panels. Melamine reacts more easily with formaldehyde than does urea, making possible full methylolation of melamine (51). Condensation of methylolated melamine with formaldehyde does occur under both acidic and slightly alkaline conditions, but acid catalysts or compounds generating acids are usually used in MF adhesives. Compounds such as acetoguanamine, ϵ-caprolactame, and *p*-toluenesulfonamide are often added to combat inherent brittleness and decrease stiffness. Ammonium salts are useful in making bulk wood products, but laminates can be adversely affected by these compounds; a complex of morpholine and *p*-toluenesulfonic acid is one hardener employed for this particular kind of MUF or MF adhesive. Defoamers and judicious amounts of release or wetting agents may also be used.

**8.6. High Performance Adhesives.** A number of adhesive needs exist that require resistance to very high temperatures and other environmental stressors such as certain gases, solvents, radiation, and mechanical loads. The upper temperature limits of the most durable epoxy and phenolic adhesives lie between ∼200 and 250°C. The aerospace industry requires adhesives that are resistant to temperatures of nearly 400°C for hundreds of hours or ∼150°C for much longer times. Heterocyclic polymers such as polyimides and polyquinoxalines have been the basis of most heat-resistant adhesives. Microelectronics adhesives sometimes also must deal with high heat, but they must also conduct heat away from heat-sensitive parts. This has been the inevitable result of increasing miniaturization. Epoxies continue to be the basis of many microelectronics adhesives, but adhesives based on stiff-chained thermoplastic resins such as polyethersulfone and polyetheretherketone have made some inroads. Electrical conductivity is most commonly enhanced with silver flake or powder, but nickel, copper, and metal-coated metals are also being used in this function (52). Thermal conductivity is usually adjusted through incorporation of aluminum, aluminum nitride, or other metals or ceramics (53).

## 9. Adhesives Made from Natural Products

The first adhesives developed by humans were based on naturally available materials such as bone, blood, milk, minerals, and vegetable matter. Beginning with the commercial development of Baekeland's phenolic resin adhesives by the General Bakelite Co. around 1910, synthetic adhesives began to replace natural product adhesives for existing applications. The use of adhesives by industry began to grow and diversify over the ensuing decades. In certain industries, among them furniture, food, bookbinding, and textiles, adhesives based on natural products continue to be used to a significant extent. These adhesives can be divided into those based on proteins, carbohydrates, and natural rubbers or oils. Historically, glue is a term used to refer to adhesives made from animal matter or vegetable-based protein.

**9.1. Protein-Based Adhesives.** The protein sources for these adhesives include mammals, fish, milk, soybeans, and blood. Animal and fish parts that yield useful proteins include hides, skins, bones, and collagen from cartilage and connective tissues. Most animal proteins are extracted using water and vary considerably in molecular weight, amino acid sequence, and inorganic impurities. For those proteins that are not already soluble in water, such as collagen, solubilization is accomplished by imposition of heat, pressure, or, most commonly, addition of acids or alkalis. Final molecular weights are in the range of

10,000–250,000 (54). Following solubilization, the protein solution is boiled down and dried to a final moisture content of 10–15%. Milk and cheese yield the relatively simple mixture of proteins called casein [9000-71-9]. Proteins are extracted from milk through direct acidification following decreaming and may also be generated through fermentation of lactose by bacteria to create lactic acid. Blood is almost entirely made up of proteins and after spray drying to remove water can be stored for an extended period of time. Soybeans are important sources of both proteins and triglyceride oils. Proteins for adhesives are obtained from harvested soybeans by extracting or pressing out oils and then heating the remaining matter no higher than 70°C lest its alkaline solubility be compromised. Soybean meal is ~45–55% protein, the balance consisting of carbohydrates (~30%) and ash (55).

Proteins are highly susceptible to changes in their structure through changes in pH, and the process of denaturation used when necessary to unfold protein molecules and break down their molecular weight to effect solubilization must only go far enough to obtain those effects but not deteriorate their adhesive qualities. Additional acids and bases are used in preparation of working adhesives made from proteins. Formulations of protein-based adhesives, in general, include the dried protein, water, an alkali compound that helps dispersion, and a hydrocarbon oil defoamer. Hydrated lime and sodium silicate solutions are usually added to modulate viscosity and to improve water resistance. Plasticizers are sometimes added as are fillers, biocides, preservatives, and fungicides. Protein-based adhesives are widely used for bonding of porous substrates such as wood, and as water is removed from the adhesive by absorption, air drying, and the optional application of heat, the proteins become fully denatured and the adhesive is set. A variety of denaturing and curing agents or cross-linkers can be used with protein-based adhesives, including hexamethylenetetramine, carbon disulfide [75-15-0], thiourea [62-56-6], dimethylolurea, and various metal salts. Blood glues may contain aldehydes and alkaline phenol–formaldehydes as cross-linkers. Although very strong, protein-based adhesives have been largely restricted to nonstructural interior wood bonding applications and other uses where their susceptibility to water and moisture do not jeopardize their stability, and the use of the various cross-linkers is targeted primarily at improving their water resistance. The most water-resistant protein-based adhesives are the blood or blood–soybean blends, but even they are not fully weatherproof. Casein or casein–soybean blends are next in line, and soybean and animal hide glues exhibit the least water resistance. The use of blood and casein adhesives is limited by the low yield of adhesive-grade dried blood from drying processes and the lack of appreciable suppliers of casein in the United States alongside a large number of diverse global sources. There has been a strong push from the soybean industry to have soy products more widely accepted in various industrial uses, but considerable work remains to be done in this area. Protein-based fibrin sealants have been the subject of considerable interest as medical adhesives and are considered by some to have many advantages when compared to cyanoacrylates and other types of adhesives (56), but their development has been limited due to human blood contamination issues.

**9.2. Carbohydrate-Based Adhesives.** Carbohydrates are available from a wide variety of plants, the shells of marine crustaceans, and bacteria.

The raw adhesive materials obtained from these sources include cellulose, starch, and gum. Cellulose [9004-34-6] is a semicrystalline polymeric form of glucose having a molecular weight of $<1000$ to nearly 30,000. It is present in plant matter at a level between $\sim 30$ and 90%. Like some of the naturally occurring proteins, cellulose must be chemically treated in order to be used as an adhesive. Reaction of its hydroxyl groups is used to convert cellulose to cellulose esters and ethers. Important cellulose esters include cellulose nitrate, cellulose propionate, cellulose butyrate, cellulose acetate propionate, and cellulose acetate butyrate (57). The most important cellulose ethers include carboxymethylcellulose (CMC), ethylcellulose, methylcellulose, and hydroxyethylcellulose. The cellulose adhesives are film formers having a thermoplastic nature. A typical adhesive formulation includes a few percent of the cellulose, less than a percent each of a plasticizer and a natural protein, and the great balance of water or another solvent. Methylcellulose is the basis of a common nonstaining waterbased wallpaper adhesive. Celluloses are very effective aqueous solution thickeners and are sometimes used in that capacity, so their solubility is limited by viscosity increases. Starches are the most significant class of carbohydrate adhesives. The source of the basic materials is broad and includes corn, wheat, rice, and potatoes as well as seeds, fruits, and roots from which starch is isolated by hot water leaching. Starch is a naturally occurring polymer of glucose. It occurs for the most part in either of two forms or something intermediate between the forms: amylose [9005-82-7], which is highly linear and has a degree of polymerization of 500–700, and amylopectin [9037-22-3], which is branched and has a degree of polymerization of $\sim 1500$–2000. Starch is also semicrystalline in nature. Its tightly packed granules must be opened to make it suitable for adhesive use, which is accomplished through heating, oxidation, or alkali or acid treatment. Colloidal suspensions of starches can be made by heating in water, but these have a tendency to solidify on cooling. Treatment with an alkali such as sodium hydroxide can lower the gelation temperature. Treatment with a mineral acid plus heat followed by neutralization with a base degrades the amorphous regions of the starch granule but does not disturb the crystalline regions, allowing a higher percentage of solids to be used in making an aqueous solution called a thin-boiling starch. Oxidation with alkaline hypochlorite produces a material similar to acid-treated starch but having better tack and adhesive properties. Dry roasting of starch in the presence of an acid catalyst produces dextrin [9004-53-9], which ranges in color from white to yellow to dark brown and shows different tendencies to repolymerize depending on the temperatures, times, and catalyst concentrations used. Additives used in dextrin adhesives include tackifiers such as borax [1303-96-4], viscosity stabilizers, fillers, plasticizers, defoamers, and preservatives. Formaldehyde precondensates and other compounds are added to improve water resistance. Starch-based adhesives are used in corrugated cardboard, paper bags, paper or paperboard laminates, carton sealing, tube winding, and remoistenable adhesives. Gums are naturally occurring polysaccharides obtained from various plants or microorganisms and usually prepared as adhesives by dispersion in either hot or cold water. Although they find use in applications similar to those mentioned for starches, they are more often found as additives in synthetic adhesives in which they act as rheology modifiers.

**9.3. Other Nature-Based Adhesives.** The use of natural rubber, an important adhesive component obtained from the rubber tree, is discussed in the section on Pressure-Sensitive Adhesives. Tannins are polymeric polyphenols isolated as one of two products from the bark of conifers and deciduous trees. Lignin is widely available as a waste material from pulp mills and has a complex structure. Tannin-based adhesives have attained some level of success in the marketplace. Despite considerable interest in and work toward more commercial use of lignins in adhesives for wood bonding, they have not yet succeeded in capturing market share. A vinyl-functionalized sugar has been developed for use in products including, most prominently, adhesives (58). Modification of sugars to make liquid epoxy resins has also been accomplished (59). Use of whey and whey by-products as adhesive components has been investigated (60). Modification of natural materials to make polyols and diisocyanates has been pursued in both the United States and the United Kingdom (61). It can be expected that additional plant-based monomers and polymers will be developed as the chemical industry comes to terms with the limited supply and rising costs of petrochemicals, making “green adhesives” a not-uncommon reality in the not-too-distant future (62).

## 10. Direct Bonding

Strictly speaking, direct bonding does not include the use of conventional adhesives or seemingly any adhesive at all. However, the joining of two extremely smooth solid surfaces into a spontaneous bond requires careful preparation and surface treatment that reflect the sophisticated use of chemistry, physics, and engineering. Practitioners of direct bonding consider its gluelessness to be a considerable benefit within its primary areas of applications, optics, electronics, and semiconductors, which benefit from minimal or no contamination (63). Such bonds are also considered jointless due to the atomic distances between the joined surfaces. The most prominent use of direct bonding may be wafer bonding, a key part of the silicon-on-insulator technology behind the making of integrated circuits, that is, computer chips (64). Direct bonding also is used in construction of waveguides for optical devices.

The inclusion of direct bonding among a list of adhesive types reflects the supposition that conventional adhesives of any composition are useful because they compensate for the shortcomings of most surfaces one might wish to join. Indeed, if smooth enough, even polytetrafluoroethylene will adhere to itself. In the case of what is called stiction, direct bonding is not seen as desirable, and steps are taken to prevent it from occurring (65). Redesign can be used to avoid material contact altogether. Surfaces can be roughened on a fine scale using chemical treatments.

## 11. Adhesive Formulation and Design

A 1999 compilation of chemicals used in adhesives listed 6300 materials (66), but the total number of compounds available for adhesive formulating is well in excess of this figure. Formulators of adhesives are in constant search of unique adhesive ingredients and their unusual combinations in order to satisfy the ever-increasing needs of their customers. In the interests of competition, many vendors of adhesive raw materials continue to protect the proprietary nature of their products by providing coded product names, a practice that though entirely understandable runs contrary to the need for the educated formulator to know the chemistry and structure of raw materials rather than relying on vague descriptions of the effects of a raw material in some standard formulation on some standard substrate.

Formulating adhesives is both a skill and an art. The novice formulator will find it invaluable to seek out other formulators in the same organization and learn from them as much as possible or at least whatever their time and patience allow. Maintaining such relationships over time can provide great benefit to the beginner as well as the veteran formulator, who will soon start learning from the former novice. The written and electronic literature of many vendors of adhesive raw materials includes information on formulating, including starting formulations. To the extent possible, one can also consult with vendor technical staff. The open technical literature, encompassing technical and trade journals, conference proceedings, and patents, provides considerable information on formulations, and its age should not discourage one from reading it as there is much to be learned from the older literature. The literature on nonadhesive polymer-based products, such as coatings, molding plastics, and composite matrix materials, may prove helpful in describing interesting raw materials not commonly used in adhesives. Likewise, components commonly used in one class of adhesives may be found to be useful in modifying adhesives of another class. The best teacher of formulating is experience, that is, trial and error.

There is more to adhesive formulation than the combining of various raw materials. The formulator must be a multidimensional technical professional able to juggle several different fields of science and engineering, legal issues, environmental considerations, computer hardware and software, and business concerns. It is not unusual to create a remarkable adhesive only to find that a key ingredient is unstable or too expensive for the intended market or poses unacceptable health and safety risks. Some customers have lists of ingredients that will not be allowed in items sold to them. Government entities require increasingly stricter labeling of adhesives and other chemical products, the requirements varying from country to country.

Better tools for adhesive formulation have been developed with the onset of the personal computer and computer workstations. These include software for design of experiments, databases used to track endless variations in adhesive recipes, mixtures design software for faster product optimization, and simple and complex spreadsheets used to determine cost at the front end of development. On-line searching of and access to the scientific and patent literature as well as the information on business trends and supplier's products available on the Internet have made information gathering easier. Adhesive development accelerates more each year, and the savvy formulator must keep pace.

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