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History of Adhesives

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ABSTRACT

Adhesives are the diplomats of the polymer world. They exist for the purpose of bringing other materials together; their success is measured by the production cost, properties, and permanence of the assembly. Historically, the starches, protein glues, and natural rubber were supplemented or replaced by phenolics and amino resins for plywood and particleboard; synthetic rubbers for construction, textile bonding, and pressure-sensitives; polyvinyl acetate for packaging, gypsum board, and the home handyperson's "white glue"; hot melts for bookbinding. Three of the newer families of adhesives are outstanding in performance: the epoxies; the isocyanates and polyurethanes; and the versatile acrylics, including the spectacularly growing cyanoacrylates and anaerobics. They are especially useful for the bonding of metals, synthetic fibers, plastic film, and other "difficult" substrates in product assembly, aerospace, textiles, construction, furniture, film laminates, and pressure-sensitives. Synergism and hybrid functionality are hallmarks of many of the new adhesives. Controlled cross-linking, improved adhesion, and other characteristics are attained through adroit blending of functional groups: vinyl unsaturation, carboxyl, glycidyl, hydroxyl, isocyanate, and methylol amide.

Adhesives are the most social of polymer products. They exist for the purpose of bringing other materials together. Not only do they bond wood to wood and steel to steel, they also combine pairs of materials as disparate as glass and paper, fibers and rubber, aluminum foil, and plastic film.

In the course of their matchmaking, the adhesives themselves undergo a metamorphosis. When applied to substrates, they must be sufficiently fluid to spread rapidly, achieving molecular contact. Once the two substrates have been brought together, however, the adhesives must harden and develop strength so that the composite resists disruption. A huge rheologic change is thus required [1, 2]. Flow times may be of the order of 1 s during application, but must eventually exceed 10^8 s if the composite structure is to be deemed creep resistant.

The change can be accomplished in various ways:

1. By cooling a molten thermoplastic
2. By evaporating water or organic solvent from a latex or solution
3. By cross-linking or irreversible setting

Each of these has a long history, encompassing inorganics as well as organic materials. Indeed, if we reach back into the Precambrian era, we can designate molten rock and mortar as the first thermoplastic adhesives. (And as polymer protagonists, we must temper our hubris with the realization that the leading adhesive that sets irreversibly is an inorganic, namely the Portland cement in concrete.)

Be that as it may, it is the organic adhesives that interest us here. In nature, organic thermoplastics applied as hot melts are represented by rosin and other resins, waxes, and bitumens. Among natural organic adhesives applied from water or solvent are starches, animal glue, casein, and rubber.

Even cross-linking has ancient beginnings—the drying of blood, the coagulation of egg albumin by heat or light, the treatment of casein with lime. The air oxidation of drying oils was practiced by painters in the Renaissance.

Perhaps the earliest adhesive material used on a large-scale by Homo sapiens was the proteinaceous gluten that enabled the seeds of grain to agglomerate into a baking dough. But the industrial manufacture of glues goes back only 300 years, and the important synthetic adhesives are products of the 20th century.

Holland was the site of the first animal glue plant, set up in 1690. It was not until 1808 that the first animal glue factory was set up in the United States. Rubber cements, cellulose nitrate dopes, laminating veneers, fish glue, and waterproof adhesives were other 19th century developments.

THE FORMALDEHYDE CONDENSATION RESINS

The grandfather of synthetic resin adhesives is phenol formaldehyde. The resin was obtained, either inadvertently or intentionally, by Baeyer and several others, but it was the work of Baekeland et al. in the early 1900s that directly established the phenolic resins as molding materials [3].

It occurred to both Baekeland (1912) and earlier French investigators (1901) that phenolic resin might be useful for bonding wood veneers. An important improvement was the introduction by Alysworth in 1911 of hexamethylenetetramine ("hexa") as a curing agent for novolacs (methylol-terminated soluble phenolics). Hexa permits cure with less evolution of volatiles; consequently less pressure is required to produce plywood and other laminates having good properties. Today, the bonding of plywood by phenol formaldehyde remains the largest single end use for an adhesive material. The phenolic resin is inexpensive, and the plywood does not warp or delaminate in the hot dampness of August.

Urea formaldehyde resins [4] were known for a decade before they came into significant use as adhesives, around 1930. Their most important application is as the binder for particleboard, utilized in furniture and flooring. They are among the least expensive of all synthetic adhesives.

STARCH AND DEXTRIN

Cornstarch and dextrins are cheaper still, and consequently are preferred for the manufacture of corrugated board and other package and paper products. They gained a tremendous boost with the Stein-Hall process patented by J. V. Bauer in 1936 [5]. This technique takes advantage of starch's ability to gelatinize very quickly when heated to the right temperature. The Stein-Hall process made possible such high production rates for corrugated cartons that it superseded the sodium silicate process, even though silicate was half the cost.

ELASTOMERS

Natural rubber, in the form of solutions in organic solvents, has been utilized for waterproofing and textile laminations for some 200 years [6].

In 1930, R. G. Drew of Minnesota Mining and Manufacturing Co. [7] patented a development of major significance: pressure-sensitive tapes whose masscoats are blends of rubber with low molecular weight resins such as the rosin esters. In half a century, pressure-sensitive tapes and labels have become ubiquitous for holding, bonding, masking, sealing, protecting, reinforcing, splicing, stenciling, identifying, packaging, and insulating [8]. SBR, thermoplastic elastomers, and acrylics have come in to supplement or replace natural rubber.

One theme keeps recurring in the history of adhesives: the blending of an elastomeric material, whose T_g is below room temperature, with a hard, strong, high melting or cross-linkable resin. The resin supplies the strength, while the elastomer provides resilience and toughness. Best results are achieved when resin and rubber are on the border of compatibility, so that there is excellent adhesion between the two phases.

Styrene-butadiene rubber, SBR, polymerized in emulsion was developed in the United States in the early 1940s as a replacement for natural rubber, which became unavailable because of World War II. Technical difficulties had to be overcome in the 1950s before SBR could be utilized on a large scale as an adhesive. The cold SBR process results in a narrow molecular weight distribution which leads to better tires. The hot SBR process, on the other hand, yields better adhesives because of its mix of low molecular weight fractions (for tack or quick stick) plus high molecular weight fractions (for shear strength).

SBR and other styrene-butadiene polymers have become the largest volume polymers going into adhesive compositions, with applications in carpet backing, construction, tire cord, and packaging as well as pressure-sensitive adhesives.

Intriguing variants of these polymers are the styrene-isoprene and styrene-butadiene block copolymers prepared by anionic copolymerization. These, like other elastomeric adhesive compositions, are two-phase structures. The resin phase, which provides the strength, consists of discrete domains of polystyrene, while the diene makes up the continuous elastomeric phase. Unlike the other elastomer/resin combinations, however, the copolymer molecules run through the two phases instead of stopping at the interface. These thermoplastic elastomers are the creation of research at Shell and Phillips. They were first marketed commercially in 1965 [9].

While SBR is the most consequential, it was not the first of the synthetic elastomers to attain significance as adhesives during the 1930s and 1940s. That honor belongs to neoprene (chloroprene) [10]. First made by DuPont in 1930, neoprene gained appreciation quickly as a contact cement for construction, panels, furniture, automotive assembly, and shoe manufacture. Special grades were developed for adhesives. A significant advance was the discovery that strength could be greatly increased by blending with suitable terpene or phenolic resin [11, 12].

Nitrile rubber, developed a few years later, proved to be a high performance material, especially when blended with phenolic resins [13]. The capabilities of nitrile rubbers, and indeed many other polymers for adhesives, have been enhanced by the incorporation of carboxyl groups.

Carboxyl-containing elastomers [14] were described as early as 1939, but gained their greatest impetus through the work of Brown, Anderson and associates at B. F. Goodrich Chemical Co. An excellent example of these is Hycar CTBN (carboxyl-terminated butadiene-nitrile), a liquid polymer. Carboxyl elastomers are formulated with phenolic resins for greatest strength. The carboxyl group in these and other polymers improves their adhesion to metals and other surfaces.

Polysulfide rubbers, patented by Patrick in 1940 [15], were commercialized by Thiokol Chemical Corp. As sealants for the construction of high rise buildings, they provided long-term stability as well as resilience. Consequently they superseded caulks and sealants based on unsaturated oils. Polysulfides are yielding in turn to butyls and acrylics.

Butyl rubber, a popular base for elastomeric caulks, was the invention of Thomas and Sparks [16] who, in the 1930s, copolymerized isobutylene with small proportions of diene to provide cross-linking sites.

In blends of elastomer with high melting resin, the elastomer can be either the major or minor component, depending upon the balance between heat resistance and toughness that is required. Table 1 lists several commercially important blends which are mainly elastomers.

Silicones, patented in 1945 [17], are the fastest growing architectural sealants, despite their high price. They offer an outstanding combination of properties; adhesion, elasticity, transparency or light color, and resistance to aging.

Silicone sealants are characteristically branched poly(dimethyl siloxanes) capped with acetate groups. When the polymer is squeezed

TABLE 1. Resin-Modified Elastomeric Adhesives

Rubber	Resin	Typical end use
Natural rubber	Rosin esters	Pressure-sensitive tapes
SBR	Rosin esters	Pressure-sensitive tapes
SBR	Thermoplastic phenolics	Construction mastics
Neoprene	Terpene phenolics	Contact cements, construction
Nitrile	Phenolics	Contact adhesives, automotive
Butyl	Phenolics	Hot melt sealant
Butadiene-styrene-vinyl pyridine	Resorcinol-formaldehyde	Bonding tire cord to rubber

out of the tube or cartridge, it is hydrolyzed by the moisture of the air, giving off acetic acid. The resultant silanols yield cross-linked elastomers.

THERMOPLASTIC RESINS

The first thermoplastic which was even partially man-made was cellulose nitrate (celluloid), developed in the United States in 1870 by the Hyatt brothers and in England by Parkes at about the same time [18].

Nitrocellulose was already familiar as an explosive, suitable for gun powder. The Hyatts tamed it by reducing the nitrogen content and plasticizing it with camphor. Half a century later, tricresylphosphate and other synthetic plasticizers were found to be effective. Celluloid "dopes"—solutions in acetone and other oxygenated solvents—were significant adhesives and binders for plastics, leather, and paper until superseded by less flammable materials.

Polyvinyl acetate, the first important completely synthetic thermoplastic adhesive, was discovered in 1912, but did not become commercial until some 20 years later [19]. Growth in the United States accelerated in the 1940s when polyvinyl acetate dispersions were introduced. The adhesives industry has become the most important outlet for polyvinyl acetate. Sold in hardware stores and supermarkets, it is known to the public as "white glue" (e.g., Elmer's Glue). In addition to consumer adhesives, polyvinyl acetate goes into packaging, paper coating, furniture, textile bonding, construction, and many other applications.

Vinyl acetate has been copolymerized with dozens of other monomers. For adhesives, three types of comonomers have become particularly important:

Esters of unsaturated acids, especially acrylates
Unsaturated acids, especially acrylic acid
Ethylene

The acrylate esters and ethylene reduce T_g, acting as internal and nonvolatile plasticizers. The carboxyl monomers are aids to adhesion.

These vinyl acetate-ethylene emulsion copolymers, containing perhaps 15% ethylene in the polymers, were introduced in 1965 by Air Reduction Co. and rapidly gained acceptance for difficult bonding applications.

Near the other end of the composition spectrum from the VAE emulsion polymers are the EVA hot melts [20]. Ethylene vinyl acetate copolymers contain 18, 28, or up to 45% vinyl acetate. They are more readily compounded with tackifier resins and waxes than polyethylene itself. Since their commercial introduction only two decades ago, the EVA hot melts have become a huge industry, pouring 200 million pounds per year into packaging, bookbinding, textile bonding, etc.

While EVA was developed expressly for hot melts, several other polymers have diversified in the 1960s from plastics and fibers into hot melt adhesives, namely polyethylene, polypropylene, polyamides, and polyesters.

Polyethylene and polypropylene go into packaging. Polyethylene goes into carpet backing as well. Polyamides and unsaturated polyesters are utilized in shoes and other product assembly where high performance is required.

The acrylics, both thermoplastic and thermosetting, are among the oldest of synthetic polymers, yet the newest of adhesives and sealants.

Acrylic esters were known in the 1890s and reported in 1901 [21].

Commercial production of acrylate ester polymers in emulsion form was begun in 1929.

Although superior in properties to polyvinyl acetate, the acrylic emulsions are more expensive and consequently have had slow growth. Their main applications today are in textile bonding and pressure-sensitive adhesives. With methyl methacrylate as a comonomer, they age well. Cross-linked, they withstand laundering and dry cleaning.

Anaerobic adhesives compositions are blends of dimethacrylates or diacrylates with hydroperoxides and other ingredients. They are stable in the presence of air but polymerize when oxygen is excluded. This characteristic has made them popular for the locking of nuts and bolts in automotive and other product assembly despite prices of $25/lb and higher. Originally developed at General Electric Co. [22], they were commercialized by Loctite Corp. [23] in one of the great success stories of the past 20 years.

Another variety of acrylics is even higher priced: the cyanoacrylates, sold in bulk at $60/lb. The alkyl cyanoacrylates were first prepared by Ardis and patented in 1949 [24]. One method involves the condensation of an alkyl cyanoacetate with formaldehyde to give a polymer which is depolymerized at high temperature to yield the cyanoacrylate ester. Various improvements were made by researchers at Eastman Kodak, which became the principal supplier of the monomer [25].

The chief virtue of the cyanoacrylates for adhesives is that they polymerize in seconds in the presence of moisture from the air. As a result, they are useful for mechanical and electronic assembly and repair, and have become popular for home repair tasks under such trade names as Super Glue or Krazy Glue.

OTHER THERMOSETTING ADDITION POLYMERS

The thermosetting condensation polymers already discussed, phenol formaldehyde and urea formaldehyde, liberate water as a by-product. Consequently, the condensation polymerization must be carried out under high pressure if the plywood, particleboard, or other composite is to have integrity and strength. These resins are usually prepared as solid powders which become viscous melts when heated, flowing in response to the high pressure.

In the 1940s and 1950s, three classes of thermosetting resin adhesives were welcomed precisely because they could be cross-linked without formation of volatile by-products: unsaturated polyesters, epoxies, and polyurethanes. When used as adhesives, they are liquids whose viscosity is moderate even at room temperature; consequently they flow readily to make contact with the substrate.

Unsaturated polyesters are the main binders for the 2 billion pound reinforced plastics industry, of importance in automobile bodies, boat hulls, building panels, chemical piping, etc. Indeed, if binders for reinforced plastics were classified as adhesives, the unsaturated polyesters would top the list. The general purpose polyesters are usually liquid oligomers of phthalic anhydride, maleic anhydride, and a molar excess of propylene glycol, cross-linked by copolymerization with styrene. Glycol maleates were prepared as early as 1894 [26], but the commercial development of unsaturated polyesters and fiberglass reinforced composites was carried out at Pittsburgh Plate Glass and United States Rubber Co., beginning in the mid-1930s. The impetus for large-scale production came from the military and marine needs of World War II [27].

Epoxy resins [28] were first patented in 1943 by P. Castan, who disclosed both acidic and alkaline curing agents [29, 30]. The development of epoxy coatings from oligomers containing hydroxyl as well as epoxide groups was the accomplishment of Greenlee and associates at Devoe and Reynolds in the late 1940s and early 1950s [31]. Meanwhile, researchers at Shell Development Co. were learning to utilize propylene as the starting material for epichlorohydrin, which is reacted with bisphenol A to make the liquid diglycidyl ether needed for adhesives as well as casting and potting. New acidic and basic catalysts were also discovered [32].

The commercial development of epoxide resins and their products was greatly facilitated by a patent cross-licensing agreement between Shell, Bakelite, Ciba, Devoe and Reynolds, Reichhold, and Dow.

The epoxy adhesives are usually two-component formulations in which one part is a liquid epoxy resin while the other contains a hardener. Primary/secondary amines and polyamide-amines are reactive hardeners, while tertiary amines are catalysts. One or both components usually contain fillers also. Main applications for the epoxy adhesives are in construction (including binders and grouts), electrical/electronic, furniture, aircraft, aerospace, automotive, and other product assembly.

Isocyanates and polyurethanes were developed by Otto Bayer and associates in the 1930s [33]. It became apparent about 1940 that these materials would have useful adhesives properties. When hydroxylated buna rubber was vulcanized with diisocyanates instead of sulfur, the stocks adhered strongly to the metal parts of the vulcanization press.

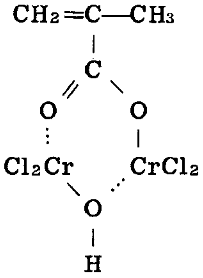
Thus serendipity led to the first really good adhesives for bonding rubber to metal, provided the rubber contains hydroxyl groups.

Later it was found that the hydroxyl need not be in the rubber if it is present in the adhesives. Two-part adhesives were developed in which the isocyanate reacted with a hydroxyl-bearing polyester, giving exceptional adhesion to rubber, metal, textiles, vinyl film, and other substrates.

Today, isocyanate and polyurethane systems are utilized as foundry binders, in textile laminates, to rebond polyurethane foam scrap, in packaging, in footwear, in vinyl laminates, and to bond reinforced plastics parts in automobiles.

COUPLING AGENTS

Shortly after the advent of fiberglass reinforced polyesters in the 1940s, it was found that the flexural strength and other properties of these reinforced plastics could be greatly enhanced with the aid of coupling agents [34]. A coupling agent is a hybrid molecule, one part of which has affinity for glass fiber while the other part reacts with (or is at least compatible with) the resin binder. The first of these was methacrylato chromic chloride, sold by DuPont as Volan:



Methacrylato chromic
chloride (Volan)

In this bifunctional molecule, the chromic chloride portion forms a good bond with the glass fiber while the vinylidene group reacts with the styrene and fumarate unsaturations of the polyesters. The green color of this material became a hallmark of quality, signifying that reinforced plastic laminates containing it would resist delamination in the presence of water.

The success of Volan spurred the search for other coupling agents, and these were found among the organosilanes. The first of these was vinyl triethoxysilane [35].

In the United States, production of organofunctional silane coupling agents is largely in the hands of Union Carbide Corp. and Dow Corning Corp. For blends of polyester with styrene, as well as other unsaturated resins, the coupling agents are likely to be either methacrylato chromic chloride or unsaturated silanes such as vinyl trimethoxysilane:

$CH_2{=}CHSi(OCH_3)_3$

On the other hand, to achieve a better bond between epoxy resin and glass fiber, it is necessary to use either amino silanes to react with the epoxy resin, or glycidyl silanes to react with the amine curing agent. The most popular of these is the γ-aminopropyltriethoxysilane:

$NH_2CH_2CH_2CH_2Si(OC_2H_5)_3$

Cured epoxy resins, with their secondary hydroxyls, amine groups, and phenylene linkages, have inherently better adhesion to glass fiber than do the unsaturated polyesters. At the same time, the epoxies are utilized in reinforced plastics for high performance products such as chemical piping and aerospace structures. Consequently, the slight improvement in properties that is gained through coupling agents is most welcome.

Titanates date back to 1937 as potential coupling agents. However, production did not begin in earnest until 1975 with Kenrich Petrochemicals' TTS. Titanates, like organosilanes, are being used to improve the properties of thermoplastic compositions heavily compounded with fillers such as calcium carbonate.

HYBRIDS

The coupling agents are among the adhesives materials pointing the way to the future: a hybrid molecule. The heterofunctional adhesive is capable of bonding two disparate substrates. It can also provide a combination of properties such as tensile strength and toughness which are seemingly incompatible. Table 2 shows some examples.

THE FUTURE

The development of adhesives is now emphasizing the four e's:

Energy
Environment
Economics
Excellence

TABLE 2. Hybrid Adhesives

Adhesives	Purpose
Silane coupling agent	Bond glass fiber to polyester or epoxy resin
Resorcinol-formaldehyde resin plus butadiene/styrene/vinyl pyridine latex	Bond tire cord to rubber
Epoxy/nitrile film	Aircraft and aerospace bonding
Modified phenolic resins	Bonded abrasives; friction materials
Vinyl acetate/acrylate esters/acrylic acid terpolymers	Binder for nonwoven fabric
Epoxy/polyamide-amine	Consumer adhesives
Isocyanate-containing phenolics and alkyds	Foundry binders

Organic solvent-based adhesives are on the decline. They are wasteful and their cost is escalating almost as rapidly as that of the petroleum from which most of them are derived. Regulations of the Environmental Protection Agency (EPA), the California Air Resources Board (CARB), and other government agencies restrict the emission of solvents which may pollute the air.

Water-based adhesives are nonpolluting and economical to formulate, but do sometimes require energy for evaporation. Water-based acrylic and neoprene formulations are gradually replacing flammable solvent cements.

Most of all, the solvent-free, anhydrous adhesives are favored in their several varieties.

High strength hot melts, based on polyamides and polyesters, are being examined as automobile body solders, along with epoxy systems. Hot melt pressure-sensitives based on acrylics are being designed so that they can be postcross-linked to give them the heat resistance that is needed for automobile masking tape that must go through the paint cycle.

For structural adhesives the epoxy resins continue to be the favored thermosetting materials, either alone or toughened with nylon or nitrile rubber.

The epoxies function well at elevated temperatures. At more moderate temperatures the two-part polyurethane systems are increasing in popularity along with the cyanoacrylates and the anaerobic dimethacrylate compositions.

In a world of ominous disruption, the adhesives continue to go about their business of combining and uniting.

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