

HANDBOOK OF ADHESIVES
Third Edition

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Third Edition

Edited by

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Whippany, New Jersey*



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Preface

Adhesives are indispensable. They are required in myriad products—aircraft and abrasives, cars and cartons, shoes and safety glass, tape and tires. This Third Edition of *Handbook of Adhesives*, like the 1962 and 1977 editions, seeks to provide the knowledge needed for optimum selection, preparation, and utilization of adhesives and sealants. The information is detailed and explicit, with several hundred illustrative formulations.

Expert information has been supplied in 47 chapters written by 70 industry specialists, professors, and consultants. Five chapters on fundamentals provide the theoretical and economic underpinnings—why adhesives work, how they are selected, how the surface is prepared, how they are applied, how they are set, how the cured joint is tested. The economic importance of the adhesive-using industries is spelled out, with specifics on the role of adhesives in construction, packaging, autos, aircraft/aerospace, textiles, footwear, abrasives, electronics, and in the home. The next 28 chapters cover the adhesive materials—thermosetting, thermoplastic, elastomeric, natural polymers, cou-

pling agents, and other key ingredients. Special attention is given to such flourishing categories as acrylics, anaerobics, cyanoacrylates, polyurethanes, epoxy resins, polyvinyl acetate, high temperature adhesives, hot melts, silicones, and silanes.

The last 14 chapters, on adherends and bonding technology, involve the auto industry, aircraft, electronics, the bonding of wood, textiles, rubber and plastics, construction, abrasives, pressure-sensitives, nonwovens, and sealants. Mechanical handling of two-component systems is examined. The concluding chapter highlights the exciting progress that is being made in the use of robotics to apply adhesives, techniques already far advanced in automotive assembly.

To Jerry Miron and Arnold Brief of Skeist Incorporated, my long time consulting associates, I express my gratitude and appreciation for their invaluable support.

IRVING SKEIST
Whippany, New Jersey

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Section A

Fundamentals

Introduction to Adhesives

IRVING SKEIST AND JERRY MIRON

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Adhesives are social substances. They unite materials, creating a whole that is greater than the sum of its parts. They are small in volume compared to the metals, glass, wood, paper, fibers, rubber, and plastics that they join together; but just as enzymes, hormones, and vitamins are required for individual well-being, the adhesives are recognized as essential to the health of our industrial society.

ADVANTAGES OF ADHESIVE BONDING

The rapid growth of the adhesives industry has resulted from its many advantages over other methods of joining materials:

1. Thin films, fibers and small particles, that could not be combined as well, or at all, by other techniques, are readily bonded with adhesives. Typical of such uses are:

- (a) Laminates of plastic films, aluminum foil, fabrics, and paper.
- (b) Glass wool insulation and fiber glass mat composites.
- (c) Abrasive wheels, sandpaper, emery cloth, and brake linings.
- (d) Tires reinforced with rayon, nylon, polyester, glass fiber, and steel.

- (e) Corrugated board, paper bags, labels, tapes, stamps, and envelopes.
- (f) Safety glass.
- (g) Nonwoven fabrics, flocked fabrics, and tufted carpets.
- (h) Clay-coated paper for printing.
- (i) Particle board.
- (j) Veneer furniture.

2. Stresses are distributed over wider areas, making possible lighter and stronger assemblies than could be achieved with mechanical fastening. For example, airplane wings, tails, and fuselages may be constructed of sandwich panels comprising a honeycomb core bonded to thin faces of aluminum or magnesium; consequently the possibility of fatigue failure is decreased. Glued floors, wood framing and entire room modules, factory-prebuilt for economy, have the tensile, flexural, and impact strength to resist the rigors of transportation and hoisting into place. In reinforced plastics and advanced composites, glass fiber is adhered to the unsaturated polyester matrix, or graphite fiber to epoxy matrix, with the aid of functional silanes and other coupling agents.

3. The strength-to-weight ratios and dimensional stability of anisotropic materials can be improved by cross-bonding. Thus wood, inherently nonuniform and water-sensitive, is

converted into warp-resistant, water-resistant plywoods. Nonwoven fabric having the same properties in all directions is made by lightly bonding a random web of fiber.

4. The glue line provides electrical insulation in capacitors, printed circuits, motors, potted resistors, etc.

5. The glue line can be a moisture barrier, sealing window panels in curtain wall construction. In laminates for packaging, the glue line adds greatly to the moisture-vapor resistance.

6. Dissimilar materials can be joined, e.g., aluminum-to-paper, iron-to-copper. When two metals are bonded, the adhesive separates them and prevents corrosion. When the two adherends are markedly different in coefficient of thermal expansion, a flexible adhesive lessens the stress due to temperature change. Laminates of dissimilar materials can give combinations superior to either adhered alone; for example, a polyethylene-cellophane composite has the heat-sealability and water-resistance of the former plus the grease-resistance and printability of the latter.

7. Finally, what is often the key consideration: adhesive bonding may be faster and cheaper than the weaving of cloth; soldering, brazing or welding of metals; or mechanical fastening of rivets, bolts, or nails.

HISTORY

Adhesives were utilized in a sophisticated manner even in ancient times. Carvings in Thebes dating back 3300 years depict the gluing of a thin piece of veneer to what appears to be a plank of sycamore. The glue pot and brush are shown.¹ Still earlier, in the palace of Knossos in Crete, wet lime was the binder for chalk, iron ocher, and copper blue frit pigments with which the walls were painted.² The Egyptians utilized gum Arabic from the acacia tree, egg, glue, semiliquid balsams, and resins from trees. Wooden coffins were decorated with pigments bonded with "gesso," a mixture of chalk and glue.

Papyrus was an early nonwoven fabric. Reeds 12 to 20 ft high and 3 in. in diameter were cut in thin slices, laid side by side, and beaten with a mallet. After these were brushed over with flour paste, fresh slices of reed were

laid at right angles, and the beating was repeated. The finished papyrus was a luminous brown.²

We read in Genesis that slime (bitumen) was the preferred mortar of the builders of the Tower of Babel—the first adhesives technologists to have problems of semantics. Bitumen and tree pitches were the sealants for the vessels that plied the Mediterranean. In the days of the prophets, as now, the adhesive had to be specific for the adherend. "He that teacheth a fool is like one that glueth potsherds together," we are advised in the Apocrypha (Jesus ben Sirach, Ecclesiasticus, Chapter 22). Educators are still struggling with the first problem, but the latter has been solved with epoxy adhesives.

According to Pliny, the Romans caulked their ships with pine wood tar and beeswax. Anticipating the laminate and the printed circuit, Pliny described the application of gold leaf to paper with egg white. We learn also that the Romans, like the ancient Chinese, made bird lime, an adhesive from the juice of the mistletoe, with which they smeared twigs to catch small birds.

Glues from fish, stag horns, and cheese were known in the days of Theophilus for fixing together wooden objects. Here is his ninth century recipe for *glutine casei*:

"Soft cheese is cut very small, and is washed with warm water in a small mortar with a pestle, until, being frequently poured in, the water comes away pure. Then this cheese, compressed by the hand, is put into cold water until it hardens. After this it is very finely ground, with another piece of wood, upon a smooth wooden table, and in this state it is again placed in the mortar, and is carefully ground with the pestle, water mixed with quick lime being added, until it is made as thick as lees. The tablets of altars fastened together with this glue, after they are dry, so adhere together, that neither heat nor humidity are able to disjoin them."

Except for the introduction of rubber and pyroxylin cements a hundred years ago, there was little advance in adhesives technology until well into the twentieth century. In these last few decades, the natural adhesives have been im-

proved, and a spate of synthetics has poured from the laboratories.

INFORMATION SOURCES

The second edition (1977) showed some 40 books on adhesives and adhesion since 1947. Another score of more recent volumes are listed in the References to this chapter,³⁻²¹ along with eight periodicals from six countries,²²⁻²⁹ of which *Adhesives Age*²⁴ is the most widely known.

The Gordon Research Conferences, the American Chemical Society, and many universities are among the organizations which sponsor symposia on adhesion and adhesives.

Techno-economic studies of the adhesives industry are prepared by various consulting firms, including ours.

TYPES OF ADHESIVES

Adhesives may be classified in many ways, e.g., by mode of application and setting, chemical composition, cost, and suitability for various adherends and end products.

Application and Setting

The adhesive must be applied to the substrate in a fluid form to wet the surface completely and leave no voids, even if the surface is rough. Consequently, the adhesive must be low in viscosity at the time of application.

To develop high cohesive strength, however, the adhesive must set. In a completed joint with an organic adhesive, the latter layer is either a *soluble*, usually *thermoplastic* and *fusible* material of extremely high viscosity, or a *cross-linked*, *infusible* thermoset resin or rubber.

The transition from fluid to solid may be accomplished in several ways:

1. *Cooling of α Thermoplastic.* Thermoplastics soften and melt when heated, becoming hard again when cooled. The heating must result in sufficiently high fluidity to achieve successful wetting. The thermoplastic may be coated on one substrate by various techniques:

- from hot-melt,
- as a powder,
- by extruder,

from solvent or latex followed by drying and cooling.

By convention, "hot-melt" often denotes a lower molecular weight, less viscous material than "thermoplastic."

If the cooled coating is not tacky, the coated substrates can be piled and stored for future use, when they will have to be heated to reactivate the adhesive. Alternatively, the bond is often made immediately after application of the hot-melt, powder, or extruded coating. This procedure offers best production rates, since the cooling of a hot-melt is faster than evaporation of solvent or chemical setting.

Paper, paperboard, and cellophane for food packaging present examples of the various modes of applying thermoplastic adhesives. The substrate can be protected with a heat-sealable moisture barrier by kiss-coating the web with molten wax, for bread wraps; by extruder-coating with polyethylene, for milk cartons and multiwall bags; or by applying a saran solution or latex and evaporating the solvent or water. Where resistance to moisture is not needed, as in the sealing of cartons containing cans, a reduction in cost is achieved by applying the heat-sealable adhesive as a powder rather than a continuous film. Acrylic and vinyl copolymer powdered resins have speeded production of some types of nonwovens.

Two important determinants of strength in hot-melts are molecular weight and polarity. Thus paraffin wax and polyethylene are both aliphatic hydrocarbon polymers; but the far greater molecular weight of the polyethylene results in much higher tensile strength, tear strength, and heat resistance.

Several families of hot-melts now offer still greater strength. The EVA's are ethylene-vinyl acetate copolymers which are compounded with waxes and tackifiers to make adhesives for packaging, bookbinding, and furniture edge-banding. Polyamides and polyesters are employed for the soles of shoes, the edge-banding of furniture, and the side-seaming of cans.

While the rapid setting of hot-melts is usually desirable, there is at least one exception. Labels for bottles and cans are sometimes coated with a "delayed tack" adhesive, e.g., polyvinyl acetate formulated with a plasticizer

that is solid at room temperature, so that when activated by heat, the label remains sticky for as long as a minute, facilitating the operation of a high-speed packaging line.

Safety glass for automobiles is a sandwich of highly plasticized polyvinyl butyral, a thermoplastic, between two sheets of plate glass. The compounded PVB must be optically clear, stable to light, and free from volatiles; but above all, it must be tough and a good adhesive, holding glass fragments tenaciously in case of accident which cracks the glass.

Perhaps the largest volume hot-melt of all is the asphalt which binds aggregate on our road surfaces.

2. Release of Solvent or Carrier. Solutions and latexes contain the adhesive composition in admixture with water or organic solvents. These liquids lower the viscosity sufficiently to permit wetting of the substrate. Once this has been accomplished, however, they must be removed. Porous substrates such as paper permit the liquid to be drawn away from the glue layer. If both adherends are impermeable, however, it is necessary to evaporate the water or solvent before mating the two surfaces, thus slowing down production. This is the great disadvantage of solutions and latexes in adhesive applications. In addition, organic solvents may be undesirable because of cost, shortages, flammability, toxicity, or tendency to pollute. In recent years, regulations such as Los Angeles County's Rule 66 have established upper limits on the amounts of various solvents that are permitted as effluents from industrial applications.

Thus the three E's—Economy, Energy, and Environment—are in opposition to solvent-based adhesives. Nevertheless, their excellent wetting characteristics, plus applicability at low temperatures and high coverage, will enable them to retain an important role.

In a *solution*, the concentration of "solids"—i.e., material which will remain in the final adhesive layer—is usually under 30% for organic solvents but may be higher with water as the solvent, and especially in latexes. For a solution, too great a solids content results in such high viscosity that the dope has poor wetting characteristics. The higher the molecular weight of the dissolved polymer, the lower is the maximum permissible concentration.

Therefore, in the manufacture of solvent cements, one employs resins having far lower molecular weights than those preferred for plastics and elastomers. The "half second" cellulose esters and nitrocellulose are examples of short-chain polymers which are adequate as adhesives, but might be too weak as plastics.

Water is not only the carrier for latexes but is also the most important of the solvents. Starches and dextrans, protein glues, and polyvinyl alcohol are the more significant water-soluble organic adhesives. Sodium silicates, comprising the most important family of inorganic adhesives, are water soluble.

To achieve concentrations above 50% it is necessary that at least a portion of the polymer be present in agglomerates of greater than colloidal size. In a *latex*, the polymer is present in the form of globules existing as a discrete phase in an aqueous matrix. Natural and synthetic rubbers, vinyl resins, and acrylics are the most important of the adhesive latexes. The polymer is not limited in molecular weight since the viscosity does not depend on what is contained within the discrete particles. The viscosity of the latex depends primarily on solids content and the composition of the aqueous phase. Latexes are commonly available in concentrations of 35 to 55%; but it is possible, in some cases, to go considerably higher before reaching an excessive consistency.

In many operations, for example the coating of paper on the machine at high speeds, the elimination of water becomes a bottleneck. In choosing a binder for clay and pigment, there is an increasing tendency to abandon starch solutions in favor of combinations of casein or soy protein with synthetic latexes.

Organosols are akin to latexes in being two-phase compositions, but with a continuous organic phase instead of water. Organosols are dispersions of vinyl chloride resin in plasticizers and volatile organic solvents. Once again, they are sufficiently fluid to promote good wetting of the substrate, which may be paper, cloth, or metal. After application to the substrate, the coating is heated to flash off the solvent and fuse the resin.

3. Polymerization in situ. This is the group of bonding agents making the most rapid technological progress. All the thermosetting resins

come under this heading, including those which are first applied to the substrate in solution form. This category also includes elastomers that are vulcanized to develop higher cohesive strength. In addition, some vinyl-type monomers, especially methyl methacrylate, cyanoacrylate esters, and the dimethacrylates, are polymerized readily *in situ*.

The main advantage of these materials over solvent-based adhesives is that strength can be developed in the glue line after the two adherends have been brought together. Faster production, lower cost, and stronger bonds may result from the elimination of solvents.

The reaction-sensitive adhesives fall into two groups:

1. Those formed by *condensation*, usually with water as a by-product. This group includes the phenolic and amino resins, which are the oldest of the all-synthetic adhesives.
2. Those formed by *addition polymerization* without by-product formation. Among this group are several of the most interesting of the new adhesives, including polyesters, epoxies, urethanes, cyanoacrylates, anaerobics, and radiation-curable polymers. Conventional acrylics and vulcanizing rubbers are also in this category.

When a composite is made with an adhesive from group (1), it is necessary to apply pressure to overcome the deleterious influence of the water or other volatile by-product. On the other hand, adhesives of group (2) may be cured with only contact pressure. This is especially advantageous in the preparation of large objects which cannot be conveniently placed in a press.

Some of the curing adhesives require heat, whereas others react at room temperature with the help of catalysts, and in some instances with activation by light. Again, it is an advantage to make a bond without the aid of an oven. Among the adhesives which can be processed in the cold, with proper formulation, are resorcinol formaldehyde, unsaturated polyesters, methyl methacrylate, cyanoacrylate esters, epoxies, and urethanes. The polymerization reaction is usually exothermic, so that the glue line may become somewhat warmer than the ambient

temperature, especially if the adherends are poor conductors of heat.

For some decades, dentists have filled cavities with pastes of polymethyl methacrylate in monomeric MMA. Now, adhesives companies are offering similar formulations for industrial applications.

The *anaerobic* adhesives, a development of recent years, are dimethacrylates which, when properly compounded, remain liquid so long as oxygen is present, but cure rapidly when air is excluded. They have rapidly achieved wide usage in metal assembly. They are covered in a separate chapter in this volume.

The term *aerobic* adhesives is being advanced for a series of two-component structural acrylic adhesives which have reduced sensitivity to oxygen inhibition. In contrast to the anaerobic adhesives, they can be applied to porous surfaces and to fill wider gaps, e.g., up to 60 mils.⁶⁰

The *radiation-curable* adhesives are most commonly either polymers with acrylate side chains or unsaturated polyesters. They can be cured by ultraviolet light or by electron beam radiation, which has greater penetration but is more costly. Acrylate-type U.V.-curable coatings have achieved an important place in the coil-coating of steel and aluminum. For adhesives, the technique is less useful; but it has been employed for the sealing of electric light bulbs. Also, an ingenious method for making nonwoven webs involves the cryogenic polymerization of frozen monomer with the aid of U.V. radiation.

4. *Pressure-Sensitive Adhesives*.¹⁶ These adhesives, unlike the other classes, do not undergo a progressive increase in viscosity. Instead, they are permanently in the intermediate *tacky* stage. One of their chief merits for some applications, in fact, is that they wet so inadequately that they can be removed from the adherend surface without "mark off," i.e., without leaving a residue of adhesive on that surface. One of the important early advances in pressure-sensitive tape technology was the discovery that a slightly gelled adhesive layer would fulfill this requirement.

While this deficiency in adhesive strength is deliberate, the low cohesive strength of pressure-sensitive materials is undesirable. Low

bond strength precludes the pressure-sensitive tapes from heavy-duty applications. It is inevitable that a permanently tacky material will be easily deformed and ruptured.

Most pressure-sensitive masscoats contain a blend of elastomers—natural rubber, reclaim and SBR—with tackifiers of low or medium molecular weight, antioxidants, etc. These are applied to the web-tape or label backing from solutions; but the newer “thermoplastic elastomers”—block copolymers of styrene with isoprene or butadiene—can be applied from melt. Where excellent color and resistance to light and oxidation are needed, the higher priced acrylic ester copolymers are preferred. Polyisobutylene, also resistant to ultraviolet degradation, is utilized for removable labels.

Two sided pressure-sensitive tapes, as well as most PS labels, are interlined with release paper to prevent them from sticking together prior to use. The adhesive or antistick property requires that the release web have a surface energy significantly lower than the surface tension of the masscoat. Silicone coatings meet this criterion.

Origin

The organic and semiorganic adhesives may be classified according to origin as:

1. Natural: starch, dextrans, asphalt, animal and vegetable proteins, natural rubber, and shellac.
2. Semisynthetic: cellulose nitrate and the other cellulose, polyamides derived from dimer acids, and castor-oil based polyurethanes.
3. Synthetics:
 - (a) Vinyl-type addition polymers, both resins and elastomers: polyvinyl acetate, polyvinyl alcohol, acrylics, unsaturated polyesters, butadiene-acrylonitrile, butadiene-styrene, neoprene, butyl rubber, and polyisobutylene.
 - (b) Polymers formed by condensation and other step-wise mechanisms: epoxies, polyurethanes, polysulfide rubbers, and the reaction products of formaldehyde with phenol, resorcinol, urea, and melamine.

Cure; Solubility; Crosslinking

Alternatively, adhesives may be categorized according to the solubility and fusibility of the final glue line:

1. *Soluble*, including *thermoplastic* (soluble and fusible): starch and derivatives, asphalts, some proteins, cellulose, vinyls, and some acrylics.
2. *Crosslinked* (insoluble and infusible): phenol- and resorcinol-formaldehyde, urea- and melamine-formaldehyde, epoxies, polyurethanes, natural and synthetic rubbers if vulcanized, anaerobics, and unsaturated polyesters.

The term “*thermosetting*” has been used traditionally for crosslinking compositions, even when they do not require elevated temperature to initiate the chemical reaction.

Crosslinking may involve the reaction of two chemically different intermediates, e.g.:

- (a) formaldehyde condensed with phenol, resorcinol;
- (b) formaldehyde condensed with urea, melamine;
- (c) isocyanate reacted with polyol to give polyurethane;
- (d) epoxide reacted with primary amine or polyamide-amine;
- (e) unsaturated polyester copolymerized with styrene;
- (f) sulfur-vulcanized diene rubbers.

Crosslinking may also take place among molecules of a single species, for example:

- (a) epoxide catalyzed by tertiary amine;
- (b) dimethacrylate compounded anaerobically so that it will polymerize when air is excluded;
- (c) peroxide-vulcanized rubbers.

Most adhesives which crosslink at room temperature are packaged in two containers, mixed just before use. The *moisture-curable* adhesives and sealants, however, are single-component compositions which have long shelf life as long as they are in closed containers, but react when dispensed and thus exposed to water vapor in the air. Among the growing roster of moisture-curable systems are three types of

sealants, as well as various adhesives:

- (a) *Isocyanate prepolymers*, made, e.g., by reaction of polyether polyol with an excess of aromatic diisocyanate, react with moisture to yield polyurethane-ureas. The concomitant formation of carbon dioxide gas is a drawback.
- (b) *Silicones* are made moisture-curable by blocking the end hydroxyls with easily hydrolyzable acetate groups. Consumer sealants of this type are recognizable by the acetic acid odor, when first applied.
- (c) *Polysulfide sealants* can be compounded with calcium peroxide or barium peroxide, which reacts with moisture to release hydrogen peroxide, which cures the polysulfide. Cure is slower than with the lead dioxide cure of two-component systems.
- (d) *Unsaturated polyesters* likewise utilize barium peroxide, plus a cobalt salt, as a latent catalyst system activated by moisture.
- (e) *Cyanoacrylates* polymerize spontaneously in the presence of basic catalysts, even with very weak bases such as water. Setting takes place within a few seconds after exposure to atmospheric moisture.
- (f) *Epoxy resins* can be compounded with ketimines which, on exposure to moisture, release amine curing agents. This technology, already used in coatings, may be applicable also to the adhesive bonding of porous substrates.

Hybrids and Coupling Agents

Many adhesive-bonded compositions are hybrids, combining two types of groups. An important benefit of many types of hybrids is a non-Hookeian (nonlinear) stress-strain curve, with increased area under the curve (work to break), hence higher toughness, impact strength, and peel strength. Typically they have at least two T_g 's (glass transition temperatures), one below room temperature for the elastomeric component (providing good elongation), the other well above room temperature for the rigid component (providing good tensile

and compressive strength). The size range of hybrids is broad:

	Å
Composites	10^4 – 10^5 and larger
Intermolecular	10^2 – 10^3
Polymer blends	
Intramolecular	10 – 10^2
Random copolymers	
Graft and block copolymers	
Other hybrids	

Among the more significant adhesive hybrids are:

1. *Neoprene (polychloroprene)-phenolics*: good "green" strength, adjustable open times, and high cured strength.
2. *Nitrile-phenolics*: excellent strength at high temperatures (but requires pressure because of evolution of water vapor).
3. *RFL (resorcinol formaldehyde resin plus latex)*: bonding of tire cord to rubber.
4. *Epoxy-nitrile*: metal bonds with high peel strength.
5. *EVA-wax-low molecular weight resin*: hot-melts for packaging, bookbinding, furniture edge-banding, etc.

Coupling agents are bifunctional hybrids designed to improve the adhesion between phases in composites and blends. Usually the disperse phase is inorganic, and the coupling agents accordingly consist of an organic functional group and an inorganic residue. The organic active site is utilized either to form a true chemical bond with the organic matrix, or at least to assure strong affinity to it, while the inorganic part reacts with or is absorbed by the reinforcement. Currently, the most popular types of coupling agents are of the silane type, $X-R-Si(R')_3$. The $R'-Si$ bond is hydrolyzable. R' may be alkoxy, chloro, or acetoxy. The organic functional sites "X" are designed to match the polymer. Among these are amino and epoxide for bonding to epoxy resins as well as other polymers, and vinyl for bonding to unsaturated polyester.

One of the important adhesion problems which has received much attention but still remains not completely solved is the coupling of

some reinforcing fibers to thermosetting and thermoplastic matrix in *advanced composites*. While silanes work well on glass, bonding of graphite and aramid fibers could still be improved. Titanate coupling agents seem to work better on aramid than do silanes,⁵⁸ and graphite fibers are often sized with uncatalyzed epoxy resins when epoxy is used as composite matrix as well. However, new trends in advanced composites are toward heat-resistant thermoplastic matrices which could be even more difficult to couple with fibers.

Adhesive Films

Both thermosetting and thermoplastic adhesives are available in film form. Films offer many advantages. They are uniform in both composition and thickness, convenient to handle, free from volatiles. But they are difficult to make, hence expensive; also, they require heat and pressure to achieve satisfactory bonds.

The largest volume film adhesive, polyvinyl butyral for safety glass, has been discussed above under the heading "thermoplastics." Another thermoplastic pressure-sensitive acrylic, is the film material that is growing most rapidly. It is used to bond nameplates and trim on appliances, metal office furniture, machinery, etc.

The thermosetting films are employed for metal-to-metal bonding in aircraft, as well as less demanding appliance, electrical, and automotive requirements. These adhesives are hybrids designed to provide an optimum combination of shear strength, elongation, and heat resistance. Nitrile-phenolic and epoxy-nitrile are the leaders, followed by vinyl butyral-phenolic, epoxy-nylon, and epoxy-phenolic. The nitrile rubber in the epoxy-nitrile is a carboxyl-terminated butadiene-nitrile polymer which reacts with the epoxy at the elevated cure temperature.

High Temperature Resistance; Flame Retardance

Resistance to prolonged exposure to high temperatures is required of some adhesives for the aircraft, aerospace, and electrical industries. Many less glamorous end uses—foundry molds and cores, coated and bonded abrasives, brake linings and other friction materials, and other

mal insulation—also demand binders with good heat resistance.

Phenolics, the oldest completely synthetic adhesives, perform well at elevated temperature, and are available at the low cost that is a necessity in the more mundane applications. The aromatic rings, the high crosslink density, and the resonance-intensifying hydroxyl groups all contribute to heat resistance as well as high shear strength. But cured phenolics still contain methylene linkages which provide sites for thermal degradation.

Where still more heat resistance is needed, we now have the *polyimides*, *polybenzimidazole*, *polyquinoxalines*⁵³ and other linear polymers in which the methylene content is reduced or eliminated. Conjugated unsaturation increases the thermal stability of these materials. Unfortunately, as the extent of condensation approaches that of the "ladder polymer" pyrones which might provide optimum heat resistance, the polymers become more intractable.

The type of polymer produced by condensing aromatic polyacids and polyamines depends on the functionality of the reactants:

Amine Functionality	Acid Functionality	Polymer
2	2	Polyamide (nylon)
2	3	Polyamide-imide
2	4	Polyimide
4	2	Polybenzimidazole
4	4	Pyrrone

Flame retardancy is a characteristic now required by the U.S. Government, under the Flammable Fabrics Act, of an increasing number of products including carpets, mattresses, automotive upholstery, and children's sleepwear. The lowest cost flame-retardant organic adhesives are *vinyl chloride polymers* plasticized with phosphate esters, and these are indeed being utilized for carpet backing and in the bonding of automotive fabrics. Ironically, some of the copolymers which were hailed in the early 1970's as answers to the Government's flame retardance regulations have later been withdrawn because they fail to meet the requirements of another Government agency, OSHA, for low content of vinyl chloride monomer, polybranched a condensation

Other flame-retardant adhesives contain vinylidene chloride latexes, halogenated epoxies, or additives such as diammonium phosphate or ammonium sulfamate. The epoxy resin derived from tetrabromo- or tetrachlorobisphenol A is used in special aircraft adhesives.

MATCHING ADHESIVE TO ADHEREND

The adhesive and adherend must be compatible, if their union is to last.

When two materials are bonded, the resultant composite has at least five elements: adherent No. 1 / interface / adhesive / interface / adherend No. 2.

The strength of the adhesive joint will be the strength of its weakest member. If one of the adherends is paper, excessive stress will usually result in a "paper tear." With stronger substrates, however, the failure will be either *adhesive* at an interface or *cohesive* within the glue. Failure will not be at an interface if the adherend surface has been properly prepared and the adhesive wets the adherend and is otherwise appropriate. In other words, the adhesion between glue and substrate should be greater than the cohesion within the glue line. This will occur provided the combining of adhesive and adherend has caused a decrease in free energy, and provided also that excessive strains are not built up when the adhesive sets.

Let us consider the latter requirement first. Adhesives usually shrink as they harden. (Inorganic cements are exceptions.) Polymerization, the loss of solvent, even the cooling of a hot-melt may cause the glue line to contract. Strains are set up which induce the adhesive to pull away from the substrate. In addition, strains are produced when the adhesive joint is flexed. Various remedies may lessen the danger of failure from these causes:

1. Choose low-shrinking resins, e.g., epoxies rather than unsaturated polyesters.
2. Choose adhesives that are less rigid than the adherends; otherwise flexing will cause a concentration of stress in the glue line. (However, excessive flexibility in the adhesive may be accompanied by low cohesive strength.)
3. Keep the glue line as thin as possible, consistent with the smoothness of the adherends, if the stresses are chiefly tensile.

But porous adherends require the application of sufficient adhesive to avoid a "starved glue line." If the joint is to be exposed to considerable shear stress, the glue line should be somewhat thicker.

4. Incorporate inert and preferably inorganic fillers.
5. After applying the adhesive to an impervious substrate, evaporate water or solvents thoroughly before mating with a second impervious adherend.

In Chapter 3 of this Handbook, Gent and Hamed provide a comprehensive presentation of adhesion theory. Surface preparation is discussed by Mahoney in Chapter 4, and adhesives evaluation is examined in Rice's Chapter 5.

In this introductory chapter, we focus on two factors relating choice of adhesive to the substrate: *critical surface tension* and *solubility parameter*.

Let us examine the types of bonds that may exist between adhesive and adherend. These chemical bonds may be either primary or secondary.

Primary bonds include electrovalent, covalent, and metallic bonds. *Electrovalent* or *heteropolar* bonds may be a factor in protein adhesives. *Covalent* or *homopolar* bonds play a part in some finishing treatments for fiber glass. The *metallic* bond is formed by welding, soldering, and brazing. The metals and alloys involved are essentially high temperature thermoplastic adhesives, but are outside the scope of this volume.

By far the most important of the adhesive bonds are the *secondary* or *Van der Waals'* bonds that give rise to attraction between molecules. Most significant of these are the *London* or *dispersion forces*. They are responsible for virtually all the molar cohesion of nonpolar polymers such as polyethylene, natural rubber, SBR, and butyl rubber. These forces act at a distance of approximately 4 Å, and fall off rapidly, as the sixth power of the distance between atoms. Consequently, molecules must be in close proximity for London forces to be effective. This helps to explain why a very flexible molecule such as natural rubber is a better adhesive than a moderately flexible molecule such as polystyrene. Low modulus, indicating free-