

Adhesives

Adhesives unite materials, creating a whole that is greater than the sum of its parts . Their volume is small compared to the metals, glass, wood, paper, fibers, rubber, and plastics they bond.

The “adhesive” bonds “adherends,” which are substrates such as glass, metal, plastics, and wood . In a typical adhesive bond, the basic components are:

(SUBSTRATE/INTERFACE/**ADHESIVE**/INTERFACE/SUBSTRATE)

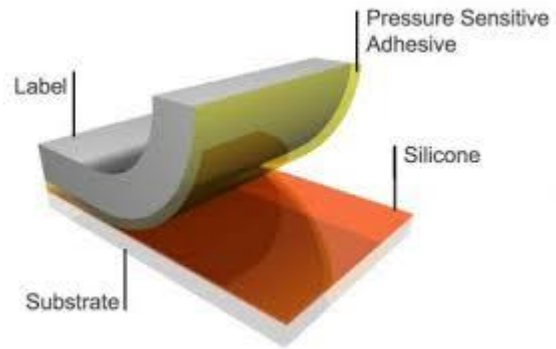
Adhesives may be classified in many ways including mode of application and setting, chemical composition, cost, suitability for various adherends, and end products.



Applications

Adhesives must be applied to substrates in a fluid form to wet the surfaces, which requires low viscosity to flow onto the surfaces while eliminating voids. After application to surfaces (adherends), the adhesive must solidify to develop bonding strength. The transition from fluid to solid may be accomplished in the following ways:

1. Cooling of a thermoplastic. Thermoplastics soften and melt when heated, becoming hard again when cooled. Methods of applying adhesives in this way include hot-melt applicators; dry powders that are heated after application ;and extruders.
2. Release of solvent or carrier. Solutions and latices contain the adhesive composition in admixture with water or organic solvents. These liquids lower the viscosity to permit wetting of the substrate. After wetting has been accomplished, they must be removed.
3. Polymerization. The fluid adhesive is applied to the substrate followed by rapid polymerization to bond the substrates. The reaction-sensitive adhesives fall into two main groups: condensation and addition polymerizations.
4. Pressure-sensitive adhesives. These adhesives are fluid applied and do not undergo a chemical reaction. After wetting the substrates, they remain in the gel state which is a tackiness capable of being removed rather than a permanent bond.



Origin

1. Natural. Starch, dextrans, asphalt, animal and vegetable proteins, natural rubber, and shellac.
2. Semisynthetic. Cellulose nitrate and other cellulose derivatives, polyamides derived from dimer acids, and castor oil-based polyurethanes.
3. Synthetic. Vinyl-type addition polymers: polyvinyl acetate, polyvinyl alcohol, acrylics, unsaturated polyesters, butadiene-acrylonitrile, butadiene-styrene, neoprene, butyl rubber, and polyisobutylene. Polymers formed by condensation and other stepwise mechanisms: epoxies, polyurethanes, polysulfide rubbers, and the reaction of formaldehyde with phenol, resorcinol, urea, and melamine.

Solubility

Adhesives can be categorized by solubility or fusibility of the final adhesive (glue) line.

1. Soluble. Thermoplastics, starch derivatives, asphalts, some proteins, cellulose derivatives, vinyls, and some acrylics.
2. Insoluble. Thermosets, phenol- and resorcinol-formaldehyde, urea- and melamine-formaldehyde, epoxies, polyurethanes, natural and synthetic rubbers if vulcanized, anaerobics, and unsaturated polyesters.

Hardening of the adhesive

To formation of intrinsic adhesion forces across the adhesive/substrate interface it is a necessary, though sometimes insufficient, requirement that intimate interfacial contact occurs between the adhesive and substrate. This means that at some time in the bonding operation the adhesive must be in a liquid form, ideally with a relatively low viscosity. However, in service most adhesive joints carry some mechanical loads, even if only those resulting from the weight of the substrates, and to be able to transfer mechanical loads efficiently from one substrate to the other requires that the adhesive is a solid with an adequate stiffness and strength. These conflicting requirements mean that once the adhesive has established interfacial contact, i.e. completely wet the substrate, it must then 'harden' or 'set'.

HARDENING BY SOLVENT OR DISPERSING MEDIUM REMOVAL

Solutions and latices usually contain the already polymerized adhesive dissolved or dispersed in organic solvents or water. In the case of a solution the adhesive is dissolved in the liquid which therefore acts as a solvent, whilst latex consists of a dispersion or emulsion of the adhesive in a liquid medium, normally water. 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 up to 35-55% with water as the carrier, especially with latices.

The presence of these liquids lowers the viscosity sufficiently to enable the adhesive to wet the substrate readily but once this has been achieved the solvent or dispersing medium must be removed. With porous substrates such as paper or wood they may be drawn away from the adhesive layer by capillary action. However, if both substrates are non-porous it is necessary to evaporate the water or organic liquid before bringing the two adhesively coated substrate surfaces into contact to form the joint.

The need to use and then remove a liquid carrier for the adhesive introduces several disadvantages:

1. The liquid may attack the substrate, e.g. water may corrode metallic substrates and organic solvents may dissolve or craze plastic substrates.
2. When the substrates are both non-porous the need to evaporate the liquid prior to forming the joint greatly slows down the production rate and this is one of the main disadvantages of solutions and latices in adhesive applications.
3. In such bonding operations the mechanism of adhesion which operates when the dried adhesively coated substrate surfaces are brought together is interdiffusion and this limits the type of adhesive that may be used to a rubber. However, a thermoplastic adhesive may be used but an additional thermalwelding step is then required.
4. The use of organic solvents often pose major problems because of cost and possible toxicity or flammability.

Obviously water-based adhesives overcome these problems but drying times are longer for such adhesives and the performance of the bonded joints is often inferior. This poorer performance is often attributable to the lack of 'cleaning action' of water in removing contaminants on the substrate surface, compared to that of organic solvents, again emphasizing the interaction between the choice of substrate surface pretreatment and that of the adhesive .

The main polymers used as solutions and latices are shown in Table 1, but it should be recalled that any commercial adhesive will be a complex formulation.

<i>Water-based</i>	<i>Water- or solvent-based</i>
Starch	Natural rubber
Gums	Styrene–butadiene rubbers
Albumen	Butyl rubber
Sodium silicate	Poly(chloroprene) rubbers
Casein	Nitrile rubbers
Sodium carboxymethylcellulose	Reclaim rubbers
Lignin	Polyurethane rubbers
Poly(vinyl alcohol)	Poly(vinyl acetate) and copolymers
<i>Solvent-based</i>	Poly(vinyl ether)
Nitrocellulose	Poly(vinyl chloride) and copolymers
Cellulose acetate butyrate	Polyacrylate and poly(methacrylate)
Cyclized rubber	Polyamides (nylons)
Polyisobutylene	Asphalt
	Urea formaldehyde
	Phenol formaldehyde
	Resorcinol formaldehyde
	Rosin esters

Table 1 Main types of polymers used in adhesive formulations based upon hardening via removal of a solvent or dispersing medium

HARDENING BY COOLING

The basic concept with the adhesives that harden by cooling is that a thermoplastic polymer will soften and melt when heated and, if its viscosity falls to a sufficiently low value, the molten polymer may successfully wet the substrate materials to be bonded. Upon cooling, the thermoplastic polymeric adhesive will resolidify, and possibly recrystallize, and therefore develop high cohesive strength. For obvious reasons, these adhesives which harden by cooling are referred to as 'hot-melt' adhesives. Therefore, as usually supplied they contain no water or volatile solvents, i.e. they possess a 100% solids level.

Hot-melt' adhesives provide a most rapid method of obtaining an adequate joint strength so that assemblies can be bonded without complex jigs being necessary to keep the substrates in place whilst the adhesive slowly hardens. Nevertheless, pressure must still usually be applied to the contacting surfaces immediately the adhesive is applied, and must be maintained until the adhesive has cooled and hardened sufficiently; although this is often only a matter of a few seconds at most. If, however, the cooling of the molten adhesive is too rapid then inadequate wetting may occur. This situation is encountered if the substrate has a high thermal conductivity since the adhesive in immediate contact with the substrate surface may be prematurely chilled before it has completely wetted the substrate.

HARDENING BY CHEMICAL REACTION

The adhesives which harden primarily by chemical reaction are usually applied to the substrates as monomers or oligomers (sometimes referred to as 'resins') and are then polymerized in situ in the joint between the substrates. The starting products may already be in the form of liquids which have a low viscosity at room temperature. Alternatively, in order to achieve the requirement of a low viscosity they may be applied from a solution or latex, where the liquid is removed prior to chemical reaction (and in the case of non-porous

substrates prior to joint formation) or heat may be applied. Thus, this class of adhesives has a very wide range of forms at room temperature: low-viscosity liquids (either with a solvent present or as 100% solids), thixotropic pastes, powders, rods and tacky or tack-free films. The polymerization reaction may lead to a crosslinked rubber, a thermoplastic or a thermosetting polymeric adhesive.

It is convenient to divide the chemical reactions by which this class of adhesives harden into two groups:

1. Those which harden by a step-growth polymerization where reactions take place between multifunctional monomer molecules. Functionality is the number of sites at which a monomer molecule is able to react. In order to form linear macromolecules it is necessary that the monomers are bifunctional. If the monomers have a functionality of greater than two it is sometimes possible to form crosslinked polymers, i.e. rubbers or thermosetting plastics, rather than linear molecules, i.e. thermoplastics.
2. Those which harden by an addition polymerization where the monomer molecules add onto the growing chain one at a time and which does not involve the formation of small molecules such as water.

NON-HARDENING ADHESIVES

Unlike all the other classes described above these adhesives do not typically undergo hardening after they have been applied to the substrate surfaces and the joint formed. They are generally in the form of an already polymerized adhesive which is coated onto one or both sides of a backing material such as cellulose, polyester, foamed polyurethane, poly(vinyl chloride), aluminium or lead. The adhesive is usually permanently tacky and based upon natural rubber, styrene-butadiene rubber (random and, more recently, block copolymers), polyisobutylene or an acrylic polymer, but as usual is a complex formulation containing many additives. The adhesive is formulated so that it flows sufficiently, when hand pressure is applied to the joint for a short period of time, to wet the substrate adequately in order to attain a certain, albeit minimal, level of joint strength. Thus, the term 'pressure-sensitive' is often applied to this class of adhesives.

It is interesting to note that pressure-sensitive tapes and labels are usually interlined with a release-coated backing to prevent them from sticking together prior to use. This adhesive requirement leads to the selection of a release coating with a significantly lower surface free energy than the pressuresensitive adhesive (see Section 2.3.1). Silicone coatings meet this criterion and are commonly employed for this purpose.

Reference

1. **Jan W. Gooch** , Analysis and deformation of Polymeric Materials, Print ©1997 Kluwer Academic / Plenum Publishers New York.
2. **A. J. Kinloch**, Adhesion and Adhesives, **SCIENCE AND TECHNOLOGY**, Originally published by Chapman & Hall in 1987