

ADHESIVES

An adhesive is a material used for holding two surfaces together. An adhesive must wet the surfaces, adhere to the surfaces, develop strength after it has been applied, and remain stable.

Adhesion is a specific interfacial phenomenon. There are three main theories of adhesion: adsorption, electrical and diffusion. All probably apply to most adhesives.

Surface preparation before applying the adhesive is of prime importance.

The raw materials for adhesives are mainly polymeric materials, both naturally occurring and synthetic.

A useful way to classify adhesives is by the way they react chemically after they have been applied to the surfaces to be joined. There is a huge range of adhesives, and one appropriate for the materials being joined must be chosen.

INTRODUCTION

For a material to perform as an adhesive it must have four main requirements:

- It must "wet" the surfaces - that is it must flow out over the surfaces that are being bonded, displacing all air and other contaminants that are present.
- It must adhere to the surfaces - That is after flowing over the whole surface area it must start to adhere and stay in position and become "tacky".
- It must develop strength - The material must now change its structure to become strong or non-tacky but still adherent.
- It must remain stable - The material must remain unaffected by age, environmental conditions and other factors as long as the bond is required.

The basic definition of an adhesive as used by the Adhesive Sealant Council in America is *A material used for bonding that exhibits flow at the time of application.*

There is no simple theory of adhesion, and the truth for any one system is probably a combination of adsorption, electrostatic attraction and diffusion. The three main theories are discussed below.

There are many methods of classifying adhesives. Some use a system of end use, e.g. adhesives for metals, adhesives for textiles etc. However a system based on the chemical properties and performance is more appropriate and will be used in this article. Before discussing these classifications the different raw materials will be described.

From a practical viewpoint the most important aspect of adhesion technology is preparation of the surfaces of the materials to be bonded together, and this is discussed.

ADHESION THEORY

Several theories of adhesion exist which are based on surface-chemical phenomena. It is generally considered that there is no generalised, unified theory of adhesion since the phenomenon is known to exist between a great diversity of material types. In some special cases, either pure adsorption, or electrical or diffusion attractive forces are found at an adhesive-bound interface. More frequently, one finds adhesion to be a synergistic combination of all of these driving, attractive forces. This is especially true in the case of practically all adhesive bonding situations.

Adsorption theory

In adsorption theory the attractive forces between materials is interpreted in terms of the chemisorbed and physisorbed atomic and molecular species that exist at an interface.

Essentially this theory regards adhesion as one particular property of a phase interface wherein polar molecules or groupings will be orientated in an ordered way. The forces are initially involved in this mechanism are the van de Waals' forces - the orientation, induction and dispersion effects. If a molecule, which is large enough to contain a polar group and a non-polar part as separate and distinct entities, approaches an interface at which the dielectric constant changes it will orientate itself. It will move so that its non-polar part will be in the medium of lower dielectric constant and its polar part in the medium of high dielectric constant. This is the process that takes place in adsorption and must really take place if an adsorption theory is valid.

Electrical theory

This theory explains adhesive attraction forces in terms of electrostatic effects at an interface.

This is based on the phenomenon of a electrical double layer formed at the junction of two materials. At any boundary an electrical double layer is produced and the consequent coulombic attraction might account for the adhesion and resistance to separation.

Diffusion theory

In this theory adhesion is attributed to intermolecular entanglements at the interface.

This is applied to the union of high polymers. The fundamental concept is that adhesion arises through the interdiffusion of the adherend and the adhesive. It is based upon the chain nature of the structure with the consequent flexibility and the ability of the chains to undergo Brownian movements on a sub-molecular scale. When the adhesive is applied in solution (most probably) and if the adherend is sensibly soluble in the solvent the substrate molecules will also diffuse to an appreciable extent into the adhesive layer. Overall the clean-cut boundary between the adherend and the adhesive disappears and is replaced by a layer representing a gradual transition from one polymer to the other. A major difference in this theory is that it implies a three dimensional volume process rather than a two dimensional surface process.

Practical view-point

From these preliminary remarks it can be seen that adhesives are scientifically and technologically diverse subjects encompassing the fields of polymeric materials, rheology, surface chemistry, engineering mechanics and process technology. Adhesion on the other

hand is a specific interfacial phenomenon pertaining to the degree to which the surface of two different materials are attracted to each other. The molecular basis of adhesion is rarely studied in practice; one resorts to secondary means of determining the forces of adhesion (contact angle, contact potential, adhesive joint strength). In particular, one must make a clear distinction between the forces of adhesion and adhesive joint strength. The latter is in the realm of engineering mechanics and is required for engineering design purposes, adhesive joint strength is therefore the most important engineering property of an adhesive material.

ADHESIVE RAW MATERIAL TYPES

Natural

Starch and dextrin

These materials are derived from cereals or roots such as corn, wheat, tapioca, sago, etc. The basic constituent is polysaccharide which on hydrolysis yields long chain glucose units. Variations can occur with the use of different food materials and with changes in hydrolysis methods.

The main use for these adhesives is the paper industry where they are used in multiwall bags, corrugated paper etc. Dextrin which is dry roasted starch is used in remoistenable adhesives.

Gelatine (animal, fish, vegetable glues)

There is a wide range of products included in this overall category. Generally they are all proteins which are derived from the hydrolysis of either collagen or soya flour, or by separating casein from skim milk.

- Animal glues from bones and hides are used in gummed tape, textiles and the paper industry such as book-binding and case making.
- Fish glues manufactured from skins have been used in rubber gasket to steel bonding, paper to steel etc.
- Caseins from skim milk are used mainly in wood to wood bonds.
- Soya bean glues are used in paper backs.
- Blood glues are mainly used in veneering and plywood.

Asphalt and Bitumin

These high fractions of crude oil are more used as sealers rather than adhesives except in the bonding of coarse grade papers to produce waterproof building papers.

Natural rubber

Rubber is derived as a latex from the rubber tree (*Hevea brasiliensis*). The raw latex is collected and concentrated and either sold as a latex or coagulated and sold as solid for solvent dissolution. Adhesives made from natural rubber, which is essentially polyisoprene, are very tacky and are used in pressure sensitive applications or where long bond times and tack are required such as tapes, ceramic tile adhesives, flooring adhesives etc.

Resins, Shellac

Natural resins have been used as adhesives. Shellac is used in bonding mica splittings to form micaboard and used to be used in abrasives. Gum arabic is used in remoistenable adhesives. Copal gums are used in spirit soluble lino cements.

Semi-synthetic

Cellulosic

Cellulose is in the structural elements of plants and is a polymer made up of glucosidic rings joined by oxygen. The glucosidic ring contains three hydroxyl groups which are reacted to form the various derivatives. Ethers and esters can be formed to give either water soluble or solvent soluble polymers.

- Cellulose nitrate - mainly as a clear general purpose home handyman adhesive.
- Cellulose acetate butyrate - paper to paper and plastic adhesives.
- Methyl cellulose - leather paste to prevent shrinkage as drying and wallpaper pastes.
- Ethyl cellulose - low temperature adhesives.

Synthetic

Vinyls

The vinyl ester family is one of the more polymers not only for the coating industry but also the adhesive industry. The number of vinyl derivatives is very large and all have some specific properties. Some members are produced either as an emulsion or as a solvent soluble type.

- Polyvinyl acetate - paper converting, packaging, wood, leather, tile and home handyman adhesives.
- Polyvinyl alcohol - paper applications, textiles.
- Polyvinyl butyral - laminated safety glass.
- Polyvinyl formal - adhesives wire enamel.
- Polyvinyl chloride - pipe adhesives.
- Polyvinyl ether - pressure sensitive tapes.

Acrylics

Structurally similar to the vinyls but have very different properties. They can be produced either as an emulsion or solvent soluble form. They are used as pressure sensitive adhesives, and for flooring, paper lamination, textiles, flocking adhesives etc.

Reactive acrylic bases

These adhesives differ from the standard acrylics which are final polymers in that they are mixtures of acrylic monomers usually with a synthetic rubber. They are catalysed during the bond formation by means of a peroxide or amine using a free radical mechanism.

Advantages are very fast bond time, accurate metering of the catalyst is unnecessary, and their ability to bond a wide variety of substances.

- Second generation acrylics - two component adhesives with part A being a rubber dissolved in acrylic monomers and part B the peroxide catalyst. Used for metal to metal, metal to plastic etc.
- Anaerobic - single component type that remains stable in the presence of oxygen and only crosslinks in its absence. Used in thread locking applications.
- Cyanoacrylate - single component that polymerises very rapidly at room temperature. Used where fast bonds are required.

Synthetic rubbers

Numerous polymers have been developed to match and improve upon natural rubber. Natural rubber is polyisoprene and has good tack properties but normally not very high strength. With all rubber adhesives it is usual to add various resins and other compounding ingredients to give specific properties. These include:

- Polychloroprene - most important type used for contact adhesives. Bonds a wide variety of substances such as wood, laminates, leather etc.
- Styrene-butadiene - pressure sensitive tapes, tile adhesives, floor adhesives etc.
- Styrene-butadiene-styrene - pressure sensitive tapes, hot melt adhesives
- Polyisobutylene - electrical tapes, sealing tapes.
- Acrylonitrile-butadiene - leather, rubber, vinyl adhesives.
- Polyurethane - often cross linked with an isocyanate, used in vinyl laminations.
- Polysulfide - mainly as sealants but also with epoxy resins for concrete adhesives.
- Silicone - used as an adhesive-sealant in glass to glass, glass to metal bonds.

Aldehyde condensation resins

These are condensation polymers of aldehydes with amino compounds and phenolics forming methylol derivatives. Some of these resins are the earliest synthetics developed.

- Phenolic - abrasive discs, brake linings, foundry industry, fibre bonding, plywood.
- Resorcinol - plywood manufacture
- Urea - particleboard, plywood
- Melamine - particle board.

Epoxy Resins

The reaction between epichlorohydrin and bisphenol A yields a large class of resins known as epoxy. These resins can be cross linked to hard strong adhesives.

- Epoxy - This is the main group and is characterised by having the epoxide group ideally at each end of the molecule. The group can be cross linked with amines and amides. The resultant adhesive is used in bonding metal, concrete, ceramics etc.
- Phenoxy - These are high molecular polyethers also derived from epichlorohydrin and bisphenol A (in an equimolar ratio). They differ from epoxy resins in that they are deficient in epoxide groups but have a high hydroxyl which allows cross linking with iso-cyanates, amines etc. They are used in ceramic and metal bonding.

Amine Base Resins

There are many amine derived polymers that show good adhesive properties. Most are condensation reactions and show good adhesion to metals particularly at high temperatures.

- Polyamide - most polyamide resins are used with epoxy adhesives; however those resins similar to nylon, (i.e. based on dimer acids) are used as the thermoplastic adhesives in shoe and electronic industries.
- Polyimide - the product of an aromatic dianhydride and an aromatic diprimary amine. Used as aluminium to aluminium adhesive at elevated temperatures.
- Polybenzimidazole - aromatic bis(*o*-diamine) with a di-phthalate eg. 3,3'-diaminobenzidine and di-phenylisophthalate. Used for stainless steel bonding.
- Polyquinoxaline - an aromatic bis(*o*-diamine) with an aromatic bisglyoxal. Also used for stainless steel bonding at high temperatures.
- Polyethylenimine - a highly branched polyamine. Particular interest is that it is water soluble and used for priming cellophane aluminium foil etc.

Polyester resin

Reaction product of dipolyalcohol and a polybasic acid.

- Unsaturated - uses a cobalt salt together with a peroxide. Used for bonding glass fibres and metal to metal.
- Saturated - thermoplastic type mainly used in shoe lasting operations.

Polyolefin Polymers

Polyethylene and other olefins can also be used in adhesives particularly as the base for thermoplastic types. Normally some modification with other resins is carried out.

- Polyethylene - used as the base for hot melt adhesives in packaging.
- Polypropylene - also used in packaging hot melts.
- Ethylene-vinyl acetate - here the polyethylene chain has vinyl acetate groups attached. Commonly between 25 and 30% vinyl acetate is used. Main use is in hot melt adhesives for packaging, labelling, bookbinding.
- Ethylene-ethyl acrylate - an ethyl acrylate group is substituted for the vinyl acetate. Have better adhesion to polyolefin.
- Ionomers - These polymers contain carboxyl groups on the polyethylene chain partially neutralised with zinc or sodium. Used for bonding polyolefins.

Inorganics

Soluble silicates

Manufactured by melting silica sand with sodium carbonate and then dissolving in water. Used in bonding paper, corrugated board and some applications of metal to plywood bonds. Some versions can be used in refractory cements.

Phosphate cements

Either silicate-phosphoric acid or zinc phosphate etc. Used as dental cements.

Hydraulic cements

These products set by hydration and include calcium silicate (Portland cement), lime cements, gypsum cements etc. Used for bonding stone chips as concrete, grains to form mortar for bricks etc.

Miscellaneous cements

Such materials as glycerine, liquid sulfur and aggregate, and oxides and nitrides are used speciality aspects.

ADHESIVE TYPES

Adhesives can be classified into three main types given below. There are of course several products that are combinations of these three types but essentially all adhesives can be grouped into these categories.

Chemical reactive types

Basically an adhesive of this type is supplied in a low molecular weight form and after application a polymerisation reaction is allowed to take place. This polymerisation can be achieved by:

Two component pack

Supply the produce as a two component pack, i.e. base plus hardener. Examples of this type are:

- Epoxy adhesives based on epichlorhydrin bisphenol. Cured with amines or polyamide.
- Phenolics adhesives i.e. a novalac type with hexamethylene tetramine.
- Unsaturated polyesters using an organic peroxide, i.e. M.E.K. peroxide and cobalt naphthenate.
- Polysulfide with lead dioxide or an isocyanate.
- Polyurethanes with isocyanate.
- Silicone polymers utilising a metal salt of an organic acid, e.g. lead octoate.
- Reactive acrylics - rely on peroxides or amines.

Moisture

Polymerisation can be achieved by relying on moisture either on the surface of the adherend or in the atmosphere to effect a cross-linking mechanism on some other "natural" component.

In this case the adhesive is supplied as a single component. Examples are:

- Polyurethane containing an isocyanate group.
- Cyanoacrylates. These are the instant bond adhesives.
- Silicones containing an acetylene group. These are the common R.T.V. silicones which with moisture releases acetic acid causing a cross-linking of the paste to an elastomer.
- Anaerobic which rely on absence of oxygen.

Heat

The final method of curing a chemical reactive type is by utilising heat to polymerise the adhesive components. Examples are:

- Epoxies with the catalyst incorporated in the adhesive in a latent form, e.g. dicyandiamide which will require a temperature of 175° C to effect a cure.
- Phenolics of the resole type.
- Polyvinyl acetates which are based on polyvinyl alcohol reacted with an aldehyde. The conversion is normally about 80% and on heating after application the cross-linking is completed.
- Urethanes incorporating a blocked isocyanate. The free isocyanate groups are all reacted with a temporary blocking agent such as phenol which is stable up to 150°C.

The problems associated with the above three types of adhesives are:

- Two components types - difficult to ensure correct and adequate mixing of the two components (often by unskilled personnel or in adverse conditions).
- Moisture curing types - poor shelf life even when stored in sealed containers. Once container is opened the life will drop rapidly.
- Heat curing types - again poor shelf life plus the problem of heating the adhesive or adherend.

Thermoplastic type

Basically the adhesives in this class are thermoplastic in nature which means they are heated to a sufficient temperature where they will flow and wet the substrates and then set and develop the bulk strength on cooling. The ideal Hot Melt adhesive is a solid up to a temperature of 80° C (as a minimum) but will then melt sharply to give a low viscosity fluid that is easily applied and capable of wetting the adherend followed by rapid setting upon

cooling. They normally contain a base high molecular weight polymer together with tackifying resins and viscosity depressants.

Examples of polymers that are used as the base for Hot Melt adhesives are:

- Ethylene vinyl acetate - a polyethylene chain containing the highly polar acetate group.
- Ethylene-ethyl acrylate which has an ethyl acrylic grouping.
- Ionomers - derived from ethylene acrylic acid copolymers but including a metal cation or some of the pendant carboxyl groups. The metal cation is free to cross-link with the anionic side groups similar to a thermosetting resin but the reaction is thermally reversible.
- Phenoxies - similar chemical structure to epoxides.
- Polyamides of low to intermediate molecular weight based on the unsaturated dibasic acids of vegetable origin.
- Polyesters (saturated).
- Vinyl resins such as polyvinyl acetate, polyvinyl butyral and polyvinyl ethers - used in various special areas.

Evaporation or diffusion types

In adhesives of this class the adhesive polymers is essentially in its final form however, wetting of the adherend is achieved by dissolving or dispersing the polymers in a suitable solvent.

Solvent Based Systems

- Rubber adhesives - usually based on an elastomer which is either natural or synthetic. The synthetic rubbers that are used in adhesives are polychloroprene nitrile (a copolymer of butadiene and acrylonitrile) butyl (a copolymer of isobutylene and isoprene) and styrene butadiene rubber. Natural rubber is essential isoprene. Normally resins, usually phenol-formaldehyde based, are incorporated.
- Phenolic or resorcinced formaldehyde resins dissolved in a solvent.
- Vinyl resins such as polyvinyl acetate, polyvinyl chloride, polyvinyl ether etc.
- Acrylic resins based on methyl methacrylate, ethyl acrylate, acrylic acid etc.
- Miscellaneous resins such as cellulose acetate and polyamides.

Water Based Systems

There are very few polymers of sufficient molecular weight to be attractive as adhesives that will dissolve in water. However, dispersions or emulsions are very important. Examples are:

- Rubber latices - again either natural or synthetic such as polychloroprene, nitrile or styrobutadiene rubber.
- Vinyl resins, where polyvinyl acetate emulsions are very widely used.
- Acrylic resins which offer some advantages over PVA types such as water and solvent resistance.

The problems associated with evaporation type adhesives are fairly straightforward.

- Elimination of the dispersing medium which could be toxic or inflammable or slow to leave the adherend.
- A large percentage of the adhesive is basically waste and non-recoverable.
- Possible damage to the adherend by the dispersing medium.

The disadvantages of Hot Melt adhesives are of course the heating associated with their application and possible thermal degradation if held at a high temperature for a long time and the thermoplastic nature of the polymer. Also the stress concentrations built up by the actual covering and shrinking process.

SURFACE PREPARATION

For effective bonding, the adhesive must intimately wet the surface of each substrate being joined together. In addition, a chemical bond must form between the surface of the adhesive and the substrate. To satisfy these conditions, the surface of the substrate must be clean, reasonably smooth, and chemically receptive to the chosen adhesive. Surface preparation is the process whereby the adherend surface is cleaned and/or chemically treated to promote better adhesion.

To a large extent, surface preparation determines how well and for how long a bond will hold. In fact, if the chosen adhesive can withstand the service conditions to which the bond will be subjected, life and service expectancy of that bond will be directly proportional to the degree of surface preparation. It is no exaggeration to say that, so critical is surface preparation, that the finest adhesive will produce a poor bond unless the adherend surface has been properly prepared.

Surface preparation promotes adhesion by making it possible for the adhesive to wet the actual surface of the substrate, rather than its apparent surface. In many cases, what appears to be the surface is, in reality, a layer of grease, dirt, oil, or some other contaminant. The way to clean such surfaces for adequate wettability will depend on the type of contaminant and whether the adherend is metal, wood, or some non-metal material.

Metal surfaces

Contaminants that create bonding problems on metal surfaces include grease, dust, dirt, oil, and oxide caused by air corrosion. Grease and oil not only interfere with bonding, but also make certain types of cleaning operations, such as chemical surface alteration, ineffective.

Of course, whether a metal adherend requires chemical surface alteration, solvent cleaning, abrasive blasting, or a combination of cleaning methods, depends upon how strong the bond must be. Bond strength is determined by such factors as wettability of the metal, its coefficient of thermal expansion (and that of the material it is being bonded to), and various other considerations

Wood surfaces

Wood is a type of non-metallic material that requires separate consideration. Common wood contaminants include resin, wax, and various products of oxidation. Special properties of this material make it popular in many applications that call for adhesive bonding. At the same time its physical properties require special procedures in surface preparation to assure effective bonding.

To begin with, wood should be dried to the level of moisture content appropriate to its service use when bonded. Surface contamination should be sanded, planed, or machined away. Debris from such mechanical cleaning operations can be removed by air pressure, vacuuming or brushing, or it can be wiped away with a solvent-moistened cloth. Once the surface is cleaned, it should be handled as little as possible prior to bonding.

Other non-metal surfaces

Other non-metal surfaces are subject to many of the same sorts of contamination as wood and metal. The basic methods of surface preparation for non-metals are solvent, chemical, and abrasive cleaning. Whichever method is used, the objective is the same: to physically remove material from the substrate in order to provide a clean adherend surface. Generally the order of cleaning follows a regular pattern. The adherend surface receives an initial solvent cleaning, followed by chemical surface alteration or abrasion. Then it is recleaned with solvent. For effective adhesion, bonding should take place as soon as possible after surface preparation has been completed.

How much surface preparation is enough?

The answer to this question depends in large measure on the degree of bonding strength required. Let us suppose, for example, that we wish to bond two pieces of aluminium together with a two-component epoxy that cures at room temperature. The following table shows how lap-shear strength varies with the amount of surface preparation the metal receives. For some uses, the 31 kg/cm² obtained by simply bonding the aluminium as is, without any surface preparation, may suffice. But a simple vapour degreasing can make that bond almost twice as strong. If maximum strength is required, it may be necessary to go through all surface/preparation steps.

GROUP TREATMENT	kg/cm ²
1. As received	31.2
2. Vapour degrease	58.8
3. Vapour degrease, (alkaline clean) 15% NaOH	117.5
4. Solvent wipe, sand (not wet and dry), 120 grit	93.4
5. Vapour degrease, wet and dry sand, wipe off with sandpaper	121.4
6. Unsealed anodised	136.0
7. Vapour degrease. Na ₂ Cr ₂ O ₇ - H ₂ SO ₄ tap water rinse	193.8
8. Vapour degrease, alkaline clean, Na ₂ Cr ₂ O ₇ -H ₂ SO ₄ tap water rinse	198.7
9. Vapour degrease, grit blast, 90-mesh grit, alkaline clean, Na ₂ Cr ₂ O ₇ -H ₂ SO ₄ distilled water rinse	217.3

Often the most suitable solution is to do some surface preparation but omit those latter steps that would provide more bonding strength than needed at an unnecessary extra cost in time, effort, chemicals and equipment. If the maximum strength the bond could possibly need is 170kg/cm² then going beyond step 7 would represent wasted effort.

It is important, too, to identify the contaminant to be removed.

A contaminant such as fingerprints may be so insignificant that it need not be removed at all. Hot soap and water may be all that is needed to remove a layer of dirt. Identifying the contaminant by testing to see which detergent, solvent, alkaline or acid it response to can save much time and effort.

Once surface preparation has been completed, further handling should be minimised, and the adhesive should be applied as soon as possible. If immediate bonding is not possible, measures must be taken to protect the freshly cleaned substrate against contamination. This is especially true of metallic surfaces, which are vulnerable to air corrosion.

Oxidation resistant coatings are available that will protect the surface against certain kinds of contamination, yet still not interfere with a final solvent cleaning just before bonding.

This article is an edited (by John Packer) version of the introductory lecture given by Owen Brett (Ados Chemical Company) at a 1990 symposium on adhesive technology organised by the Polymer Group of the NZIC.

An article with more emphasis on the theory of adhesion and with an excellent section on the composition of common modern adhesives has recently appeared:
Glen A Rowland, *Adhesives and Adhesion*, CHEM NZ, 1998, No.71, 17-27.