

Materials Science of Adhesives: How to Bond Things Together

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Guest Editors

Abstract

This issue of *MRS Bulletin* provides an overview of the state of the art and emerging trends in the area of adhesives. An adhesive is basically defined by its function, which is to assemble two surfaces together. In order to fulfill this function, the properties of an adhesive must include easy positioning at the interface, rapid and complete bond formation and subsequent hardening, and a bond strength adapted to the specific application (structural, permanent, removable, rigid, or soft). A variety of solutions exist in practice, and their application requires an understanding both of polymer chemistry and materials science. The main families of adhesives, their properties, and their basic design principles will be discussed in the articles in this issue, while this introductory article presents an overview of the functions required of adhesives and future trends.

Keywords: adhesion, adhesives, bonding, fracture, interfaces, mechanical properties, polymers.

Historically, the use of adhesives cannot be dissociated from the use of sealants. Two of the earliest documented uses of natural adhesives (from around 1500 BC) are caulking ships with tar and sealing jars of spices with asphalt by the early Phoenicians. The Olmecs in Central America used natural rubber latex to waterproof woven textiles as early as 1000 BC. The next industrial development of adhesives came with the development of the printing press in the 15th century, which required increased production of paper and therefore of natural glues (to hold the cellulose fibers together) and hydrophobic additives (without which the paper would act as a blotter). Although natural adhesives are still used today for certain applications, modern adhesives are closely linked to the development of synthetic polymers in the 20th century. Current world production of adhesives is on the order of 10 million tons a year, and there are more than 10,000 different adhesives available on the market from a vast number of manufacturers.¹

From a materials science point of view, what defines an adhesive is not its material type (such as a polymer, a metal, or a semiconductor) but its function. In appearance, this function is rather simple and mundane, namely, to bond two surfaces together. However, the choice of an appropriate adhesive system for an application depends on many factors, such as the required adhesive properties (from permanent to temporary applications), the materials to be bonded, the thermo-mechanical properties of the bonded joints, and the processing conditions. Making the proper choice requires knowledge of the physics, mechanics, and chemistry of various materials ranging from metals to polymers, composites, and even skin; their surfaces and bulk properties must also be extensively characterized.

It is necessary to use specific methodologies to characterize the degree of adhesion (i.e., surface and interface properties) and the degree of adherence (i.e., mechanical resistance to shear, peel, and fracture).

Adhesion refers specifically to the strength or areal density of interfacial bonds; adherence is a measure of all the energy dissipated in a volume near the interface during a fracture test. In order to better define what type of materials can be used for these various applications, it is important to keep in mind the function: bonding two surfaces together. This requires that the adhesive start as a liquid (to form the bond easily and completely, even on a rough surface) and have some affinity with the substrates to be bonded. In its final state, the adhesive must be a solid (to resist fracture of the bond). Therefore, all existing adhesives represent technological and scientific solutions for achieving this liquid-to-solid transition.

The only materials that are able to easily undergo this type of transition, either through a chemical reaction or a melting/crystallization process at reasonable temperatures, are polymers. Therefore, all adhesives are polymer-based; their design aims to control both the rate of bond formation and the bond strength (resistance to stress, strain, and brittle fracture).

Except for the case of self-adhesive materials, the raw materials used for adhesives are either reactive monomers or polymers formulated in such a way that they can be easily coated on various substrates. Low viscosity is essential for spreading the adhesive on the surface to achieve the most complete bonding interaction. Then, a physical process (solvent evaporation, temperature cooling) or a chemical process (chain- or step-growth polymerizations, vulcanization, or mild cross-linking) controls the transformation of the adhesive into a bonded joint. The mechanical strength of the formed joint is then related to both the chemical structure of the polymer backbone and the molar mass between physical entanglements or chemical cross-links. The design of the polymer must be related to the adhesive application (from a soft, low-shear-strength polymer for removable pressure-sensitive adhesives to a hard, high-shear-strength, tough polymer for structural adhesives). The large possibilities offered by polymer science lend indispensable versatility to adhesion technology.

From a technological standpoint, the typical specifications for adhesives include:

- The ability to bond a wide range of raw materials (ceramic, polymer, glass, metal, composite, skin, etc.) and allow assemblies of various shapes and dimensions;
- The ability to allow the distribution of stress on the adhesive joint over all of the bonded surface;
- Economical processing; and
- Ease of use (the technology should be usable by anyone).

Some additional specifications, such as electric or thermal conduction, or low permeability to air or water, can be achieved by the specific design of the adhesives and the resulting bonded joints.

This versatility makes adhesive bonding the technology of choice for many applications in which precise positioning and processing speed are crucial and the bond is subjected to relatively low stresses. An example of this versatility is the widespread use of adhesives in the microelectronics industry; as an example, Figure 1 shows the many places that adhesives are used inside a photographic camera.

However, in the case of structural materials, if one compares adhesive bonding with other joining technologies such as riveting, bolting, or welding, some disadvantages of adhesives become apparent. First of all, while modern structural adhesives can achieve, once cured, reasonable levels of yield stress and toughness, there is often no nondestructive way to measure the level of adherence; the only way to evaluate the bond is to fracture it. This is a particularly important drawback when it comes to measuring age-resistance, because once fracture occurs, the sample is no longer available for further aging. Second, adhesive joints generally cannot withstand high temperatures. Their use at elevated temperatures is limited by the poor thermal stability of organic polymers. However, recent progress in polymer chemistry has made possible the continuous use of adhesives at temperatures as high as 300°C.

The first two articles in this issue, by Aymonier and Papon on soft reactive adhesives and by Millington and Shaw on high-temperature adhesives, are focused on adhesives that require careful design of the polymer chemistry at the monomer level. Such careful attention to the functional monomer is essential in achieving the desired performance of the bonded joint and ensures ease of manipulation of the uncured adhesive.

The second two articles are focused on adhesives in which no chemical reaction takes place during bond formation in the liquid state. Pressure-sensitive adhesives (as described by Creton) do not undergo any physical transformation but only work because of adhesion hysteresis. In this case, macromolecular design (chain molecular weight, cross-linking) and formulation are more important than the functional monomer. Hot-melt adhesives (as discussed by Paul) are often based on the controlled crystallization of a specific phase upon cooling. Since this crystallization process can be very fast, relative to most chemical reactions, these types of

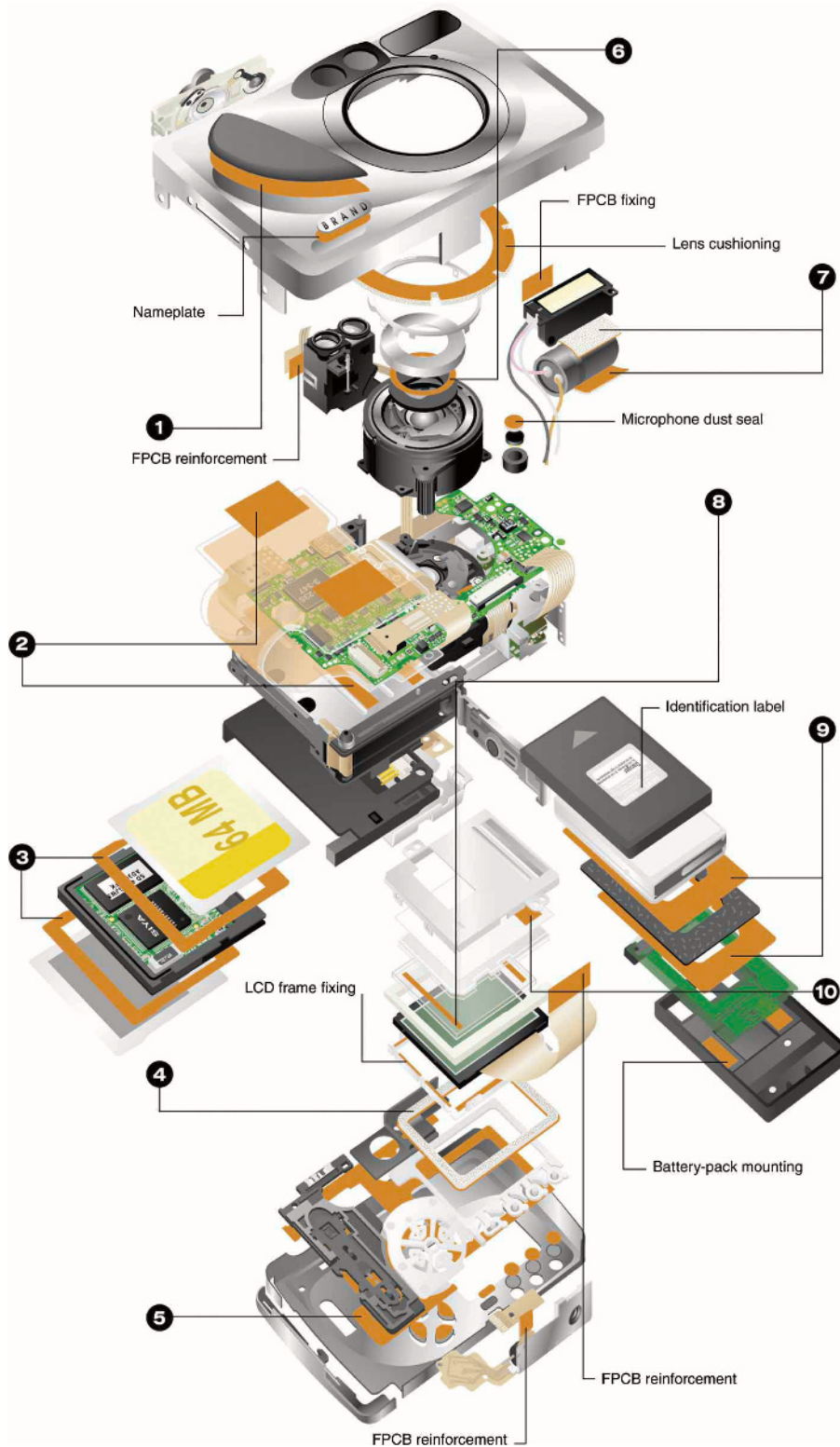


Figure 1. Example of the extensive use of adhesives (in this case, double-sided, pressure-sensitive, polyacrylate-based adhesives) in devices such as the photographic camera shown here. The numbers correspond to types of adhesive tapes used. FPCB = flexible printed circuit board. (Illustration courtesy of tesa AG.)

adhesives are favored where process speed is important.

Finally, the last two articles are more focused on the properties of the adhesive joint, with two examples for which the key to the desired properties is the introduction of a carefully designed second phase at the micron level. In the case of toughened epoxies (as explained by Kinloch), the introduction of micron-sized rubber particles greatly increases the energy dissipation upon crack propagation and makes these adhesives by far the most used type of structural adhesives for high-strength applications. The final article, by Murray et al., provides interesting examples of what the future may have in store for us in terms of functional adhesives, which combine the ease of use and versatility of an adhesive with an additional property such as thermal or electrical conductivity.

Future Trends Reversible Adherence

One emerging trend in adhesive research is control of the reversibility of adherence. A main advantage of structural joints is their high resistance to stress, combined with their strong adherence on various substrates. However, the irreversibility of the viscous-to-solid transition in adhesive bonds precludes, for example, the easy repair of industrial devices or recycling of raw materials. In order to remove the adhesive—that is, to achieve the solid-to-viscous transition—one can imagine including some specific organic moieties in the polymer-based adhesive backbone. These moieties, easily cleaved under external stimulation (e.g., UV-vis irradiation) could induce polymer-chain scission and thus decrease the mechanical resistance of the joint. One application of such a strategy could be in the area of dentistry, to easily and painlessly eliminate a protective acrylic sealant before the treatment of dental decay. Another way to influence the fracture properties of a structural joint could be to use some specific additives that are able to induce, after suitable activation, controlled deterioration of the joint. Some examples have been recently patented (e.g., French patents FR 02 03 095 and FR 03 03 594).

Functional Adhesives

As discussed in more detail in the article by Murray et al., another trend is to combine different functions in the same adhesive. Thermal and electrical conductivity are one example; controlled drug release is another. In the second case, the drug is dissolved or encapsulated in the adhesive (e.g., on a pressure-sensitive

patch) and then released at a controlled rate. In this type of application, the solubility and diffusion coefficient of the drug must be well controlled.

Environmentally Friendly Adhesives

One of the important trends in the 21st century is the drive toward ecologically sound (e.g., recyclable) products. While adhesives, since they are typically used in small amounts, are not at the forefront of this trend, recyclability is likely to become more important in the future.

A lot of so-called “green” adhesives are derived from the biomass, for example, from trees and animal fats. Today, these adhesives are typically used for low-cost applications. However, research based on the chemical modification of biomacromolecules should lead to the design of new adhesives to broaden their usual range of applications. Adhesives derived from the biomass are manufactured from a complicated blend of molecules found in nature, so their chemical structures are poorly defined. There is a push in Europe to purify raw materials to produce adhesives with a well-defined chemical structure. Such adhesives must be designed to perform well and be recyclable while also satisfying the constraints imposed by forthcoming environmental legislation.

Nanoscale Organization Controlling Macroscale Properties

Increasingly, the materials science of polymers uses supramolecular architecture to obtain novel properties. The adhesives industry is not immune to this trend. Beyond the adhesives based on styrenic block copolymers, which have been on the market for two decades, new adhesives will certainly appear that take advantage of supramolecular organization to decouple small-strain viscoelastic properties from large strain and fracture properties.

Mild Polymerization Processes (UV-Visible Irradiation)

Polymerization or cross-linking methods controlled by UV-visible radiation have been under development for several years. Until recently, this technology was limited to transparent substrates joined by adhesives deposited as thin films. Some new formulations are currently proposed that work regardless of the nature of the substrates or the thickness of the adhesive. This technology, called “dark cure,” uses the formation of active species able to initiate polymerization or cross-linking even if the UV irradiation has been stopped. Because of the easy implementation and cure efficiency of such adhesives, many

applications are found in dentistry and in microelectronics.

Pressure-Sensitive Adhesives

In the area of pressure-sensitive adhesives, the high-end applications are focused not so much on improving the ultimate properties in terms of strength but more on the careful control of adhesion. One example is the removable temporary protection for a new automobile during transport from the factory. More futuristic applications may include adhesive products in which adhesion can be switched on and off by a suitable external stimulus such as light, temperature, or an electrical field. Imagine a Band-Aid that could be removed painlessly at will from your skin, while staying well bonded in the shower!

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Kinloch has published more than 190 patents and refereed papers in the areas of adhesion and adhesives, toughened polymers, and the fracture of polymers and fiber composites, and has written and edited seven books in these areas. More than 55 students have obtained their MSc and PhD degrees under his supervision.

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Shaw holds an MSc degree and a PhD degree. He joined the U.K. Ministry of Defense in 1976 to work on various aspects of adhesion science, high-temperature polymers, and toughness enhancement of polymers. In 1991, he transferred to the Materials and Structures Department at the Defense Evaluation and Research Agency (DERA) to lead a small research group engaged in dynamic fatigue studies of adhesively bonded joints. He was then appointed section leader of the Adhesives and Sealants Section in 1992. This section was enlarged the following year to incorporate composite-matrix resin research activities. In 2001, DERA was partially privatized and became QinetiQ.

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