Adhesive Materials

Adhesives, substances used to join other materials together, have been used since prehistoric times. Over the centuries, processing and development methods continued to refine natural adhesives as industry and new uses required materials with strength and adhesion properties beyond previous limits. But by the 1930s, with the development of polymer chemistry, synthetic adhesive materials proliferated and have now replaced natural adhesives in nearly all uses.

Selecting an adhesive depends primarily on the materials to be joined and the conditions under which the bond must hold. Early workers discovered that different adhesives reacted differently to varying conditions of temperature, moisture and clamping time, as well as to the base material's alkalinity or acidity.

Adhesive materials were initially used to join paper and wood, and to fasten the components of weapons and tools. The first crude substances were probably beeswax, rubber sap, shellac, and rosin. Pottery cemented with resin has been found in burial mounds dating before 4000 B.C. Raw materials for other natural adhesives ranged from animal proteins and blood, casein (from milk), starches and starch-derived dextrin to inorganic silicates such as water glass.

Vegetable adhesives, commonly called "pastes," were prepared from tree sap or starches that are soluble or dispersible in water. Ancient Egyptians used flour paste to bind together reed fibers to produce papyrus. Cassava (tapioca) flour cooked with caustic soda was found to make a thick, viscous mixture; and early workers used corn, potato, or rice starch the same way. Vegetable adhesive bonds are strong when they dry, but are easily attacked by mold and fungi and have limited moisture resistance.

Vegetable adhesives also include water-soluble natural gums, such as gum arabic (exuded by acacia trees that were intentionally wounded), algin (a derivative of seaweed), and agar (a colloid of marine plants). Agar is obtained by hot-water extraction, with the resulting solution frozen for purification. Workers made algin by digesting seaweed in alkali, then precipitating the alginic acid (or, conversely, the calcium salt). Vegetable adhesives of this type were most often used on paper products and are still applied on gummed paper and stamps.

Many animals create their own adhesives from mucous body fluids, an ability which, for example, enables insects to fasten eggs to plants and birds to build nests. (The load-carrying capacities of some of these natural adhesives rival those of modern structural adhesives!).

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The material commonly called "glue" is an impure gelatin made from collagen, the principal protein constituent of animal skins, tendons, cartilage, and bones.

Hide or bone glue makers obtained scraps from butchers or tanners. For hide glue, animal skins were washed in water, then soaked in a water/lime solution to leach out nonglue proteins. The treated hides were then washed with a mild acid, which made the collagen soluble, then rinsed again with water before being cooked in large kettles or tubs.

For bone glue, the bones were also washed with water or mild acid, and then crushed before cooking. The resulting glue could be dried and ground into a powder and packaged for later use, or it could be used directly as a liquid. Similar glue was also made from boiled fish skins.

Animal glues have been used for at least 5,000 years. Egyptians used glue 3,300 years ago for woodworking applications; a cedar chest removed from the tomb of Tutankhamen shows extensive use of glue in its construction. Animal-derived glues, as well as sealants made with similar methods, greatly improved the efficiency of wood and paper manufacture. After the fall of the Roman Empire, glue fell into disuse for the manufacture of furniture during the Dark Ages, and was not rediscovered until about the 16th century. The first commercial glue plant was founded in Holland in 1690, and the first glue patent was issued in Britain in 1754 for a process to manufacture fish glue.

Egg and blood albumin have also been used as adhesives that harden on heating. Ancient Aztecs made ritual use of blood as an adhesive. In the first century A.D. the Goths used egg whites mixed with lime to glue coins to the outsides of wooden boxes. Medieval European monks used egg whites to bind gold leaf to their illuminated manuscripts. The albumin bond is very moisture resistant, though it deteriorates with age and is attacked by fungi. Currently, blood-albumin adhesives are used extensively in the manufacture of plywood.

Casein adhesive is made from dried milk curds and lime, mixed cold. The bonds are very water-resistant (superior to the glue made from animal collagen), though they also deteriorate from mold and fungi. The Egyptians used casein glues to build wood furniture and to attach layers of ornamental veneers to wood surfaces. A carving from about 1500 B.C. depicts Egyptians during the reign of Thothmes III gluing a thin piece of veneer onto a sycamore plank. Large-scale commercial manufacture of casein adhesive began in Switzerland and Germany in 1800, and a U.S. patent for waterproof casein cement was granted to C. Luther in 1892.

Yet another type of adhesive found use with structural materials. Mud or dung was used in some of the earliest examples of human-built shelters, and naturally occurring asphalt has been used as an adhesive for structural materials since ancient times. Natural asphalt was used to cement ivory eyes into 6,000-year-old Babylonian statues. Tar and natural asphalt mixed with sand or crushed rock proved strong and durable enough to be used for major construction projects.

Hydraulic cement is a finely ground powder that, when mixed with water, sets to a hard mass resulting from the hydration of the compounds. The hydration process creates submicroscopic crystals or a gel-like material with a high surface area. Cements are used alone (as in grout) or mixed with an inert material called aggregate (such as sand or crushed rock) to form mortar or concrete. Hydraulic cements were first used in ancient Greece and Rome, where people added lime and volcanic ash to water. This cementing material, used in Roman construction 2,000 years ago, was also used in western European building for centuries afterward.

By the turn of the 19th century, workers in England and France began burning nodules of clayey limestone and using that as the base material. Portland cement, a further refinement, was first created by Joseph Aspdin of Leeds, Yorkshire, from a

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mixture of limestone and clay. He patented his material in 1824 and named it portland cement because he believed it resembled portland stone (a limestone building material used in England).

Today's epoxies can be custom formulated for specialized uses, large or small, in commercial and military aviation and in the electronics and automotive industries. (Photo courtesy of Magnolia Plastics, Inc.)

Also in the 19th century, the introduction of rubber and rubber-based products throughout the world brought about a new series of adhesive materials that made great impact on industry. Natural latex had been used as an adhesive by natives, but industrial processing improved its material properties for adhesive uses. Peal and Johnson received British patents in 1791 and 1797, respectively, for the use of natural rubber as an adhesive. Rubber cements — natural rubber (or more recently synthetic rubber) in a solvent — proved to be extremely water resistant and resilient.

Synthetic resins appearing in the first part of the 20th century were generally prepared from raw materials such as urea, phenolics, polyvinyl acetate and polyvinyl alcohol, melamine, resorcinol, polyester, acrylic, epoxy, and polyurethane. Synthetic resins have higher strengths and longer lifetimes than many natural adhesives. Nearly all industries found broader uses for these new and inexpensive substitutes — in automobile and aircraft manufacture, electronics, and medicine. Synthetic adhesives could join together nonporous materials such as plastics, glass, and metals with excellent bond strength unattainable with natural adhesives.

Epoxy resins were developed in the 1950s, creating an adhesive through chemical action rather than through heating, cooling, or the evaporation of a solvent. Epoxies form strong bonds to a variety of materials, including metal and glass. A resin agent containing epoxy groupings is mixed with a separate polymerizing agent just before use. The mixture solidifies into a resin that is insoluble in water and organic solvents, and that will not melt on heating. The epoxy bond shrinks only slightly on hardening, which makes epoxies particularly appropriate for large construction applications.

Epoxies can be formulated to develop hard bonds or flexible ones; some epoxies harden at room temperature, while others require heating. Metal-to-metal bonds with epoxy resins typically have shear strengths of about 3,000 pounds per square inch, though some formulations can have strengths as great as 7,000 psi under temperatures up to 350°F.

About two billion pounds of adhesives are used each year in homes and industry. Annual per capita consumption in the United States is about 40 pounds. Specialized adhesive materials have been developed in enormous variety — for dentistry, optics, electrical applications, packaging, and medicine. Some recent developments include anaerobic adhesives that set in the absence of air, delayed-tack adhesives that can be reactivated even after hardening, conductive adhesives for electrical or thermal applications, encapsulated adhesives activated by pressure, and adhesives that can withstand temperature extremes. The growth of the aircraft, aerospace, and computer industries has placed increased demands on new adhesive materials, forcing high degrees of structural strength, resistance to fatigue, and the ability to withstand exotic environmental conditions — such as deep space — far beyond anything the first users of beeswax and tree pitch could have conceived.

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