AN INVESTIGATION AND RESEARCH REGARDING THE ADHESIVE QUALITIES OF EPOXY RESINS IN ARCHITECTURAL CONSTRUCTION

by

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TABLE OF CONTENTS

Epoxy resins have made remarkable industrial achievements in uses, such as structural adhesive bonding, since their first commercial introduction. They were first introduced commercially in 1947 but the basic epoxy chemical compounds have been known for over a century.[4, 41]

In 1863 a German chemist, Charles Adolphe Wurtz, prepared the first epoxide, "ethylene oxide". He showed that this simple epoxide would readily polymerize. Then he studied some of its reactions. During the next eighty years several chemists learned how to prepare polmeric resinous materials based on Wurtz's earlier studies. The first di-epoxy compound was prepared about 1891 by other German chemists.[20, 38]

The epoxy resins which led to actual development were first synthesized by Pierre Castan in Switzerland and by S.O. Greenlee and Dr. J.S. Long in the United States late in the 1930's.[4]

The first commercial exploration of epoxide resins was begun by Germany in the thirties. The German patent 676117 (1939) describes liquid polyepoxides which can be hardened by a variety of methods. Because of the war there was no corresponding U.S. patent or other information pertaining to liquid polyepoxides.[6]

It was about 1940 that the chemical group's value was recognized. The exploitation of the polyfunctional epoxy was started by this time.[19]

By complete independent research, epoxies were being developed by Ciba Company, Inc. in Switzerland and by Devoe and Raynolds Company, Inc. in the United States. Ciba's approach was in the direction of adhesives and potting resins, resulting in the first Araldite. The first Araldite was introduced into the United States in 1946.

While Devoe and Raynolds' approach was in the direction of surface coatings, paints and varnishes.[18, 53]

The first actual development of epoxy resin was in Switzerland by Ciba Company, Inc.. In June of 1942 Ciba was asked to develop and manufacture the new synthetic resin. The epoxy resin was invented by Dr. Pierre Castan in the late thirties while working as a chemist for Messrs. De Trey Limited, a specialized firm in dental products. The resin was supposed to be especially suitable for the manufacture of dentures. The question was discussed whether Ciba would be interested in taking over production and sale of this synthetic resin for all the fields of application which lay outside the medical ones and especially the dental application.[60]

The resin was then examined by Ciba, especially with regard to its application possibilities as a casting resin and for electrotechnical purposes. These examinations were greatly delayed because of the difficulties in procuring raw materials during the Second World War. Technical difficulties arose particularly from the high adhesion of the resin to the casting molds, which later led to many adhesive uses.[6, 60]

Toward the end of the Second World War, because of the difficulties in procuring technical literature from abroad, few companies were aware of the growing interest in adhesive bonding agents on the basis of synthetic resins in the aircraft industry. Because of this, the new synthetic resin was not investigated for its adhesive value until late in 1944. The testing at this time was prompted by the high adhesion to metals and other materials during the earlier casting tests.[39, 60]

The first adhesive laboratory tests were carried out on November 27, 1944. The synthetic resin, discovered by Dr. Castan, was later designated as an ethoxyline or epoxy resin, which would be suitable as a metal bonding agent.[60]

On July 13, 1945, after thorough investigations of epoxy resin as an adhesive, Ciba Limited filed the first Swiss patent on the bonding of materials, especially metals, with the aid of epoxy resins. This patent has been extended since by further patent applications.[60]

Jones-Dabney Company, now a subsidiary of Devoe and Raynolds Company, discovered the use of epoxy resins in surface coatings, paints and varnishes. Started by William C. Dabney in 1919, the Jones-Dabney Company has seen continual changes in paint technology of which epoxy resin has been a part in the last several years.[61]

Most of the coating materials developed prior to the Second World War had a common characteristic: an ester linkage in the molecule. Though this chemical characteristic was partly responsible for the fact that such materials could be used for coatings, it was the weak point where chemical action, weather, and age deteriorated the paint.[61]

Early in 1939, three men working under Mr. Dabney decided to organize a systematic search for a coating material which did not have the achiles' heel, ester link in it. At that time, it was supposed that this ester link was an essential part of the resin. Dr. J.S. Long and S.O. Greenlee outlined types of the molecules which might hold possibilities. A sketch of the molecular structure desired was drawn and then they proceeded to work backwards in creating it. Basically, they were after a resin that would provide a tough, scuff-proof, light, and chemical resistant coating with adhesion vastly improved over anything then on the market.[18, 61]

After two years research their work led them to compound a resin from epichlorohydrin and bisphenol. After careful study the resin convinced them that it was what they had been looking for. Bisphenol had allowed them to form a polymer, which was thought to be impractical before.[61]

Development of this resin and other epoxy resins that stemmed from it was purely deliberate through every step of the work from early discussions right through the testing period. There was only one piece of luck connected with the undertaking: availability of epichlorohydrin.[61]

At the time of the early epoxy resin investigations, epichlorohydrin had received new interest itself. Shell Chemical Company was in the midst of testing synthetic glycerine processes and supplied samples of the by-product, epichlorohydrin, that formulated the first epoxies. Shell also supplied this material for epoxy resin production.[61]

Despite superior properties of the new materials, it was a more difficult task getting them into production than it had been to work out technology. This was caused by the lack of materials created by the war. Chemical resistance and wear resistance of "Super Marble Floor" epoxy coating made it a strong contender in the market. But wartime restrictions kept the company from making much of this coating.[53, 61]

By this stage, applied research on production methods had become a big item of expense. Lack of equipment, especially new equipment designed for epoxy production, made the work of the development team even tougher. The resin was highly active and reacted exothermically when catalyzed by alkali. One of the principle impurities was a trace of alkali.[61]

Because the word "epoxy" did not appear on any of the papers governing high priority wartime projects, allocations for equipment were not forthcoming. As a result, tests on production conditions had to be sandwiched in between regular runs of alkyds and other materials being made.[61]

Between the years 1944-46 production conditions were found, formulations were perfected, and information on the behavior of the resin was gathered. By 1947 the solid resin was under final tests and salesmen for the company were shown what could be done with it.[5, 61]

Dr. S.O. Greenlee and his associates while at Devoe and Raynolds made several important contributions in the further development of epoxy resins. Between 1948 and 1952 several patents disclosed a variety of processes and products of interest for coatings and adhesives. Dr. Greenlee's research provided the coatings industry with a unique new material, which was described as a "super-phenolic", possessing remarkable adhesion and resistance to chemicals.[6, 61]

The first company outside of Devoe and Raynolds to recognize the terrific potential of epoxies was Shell. Having worked closer to this project than any other organization, it was natural that they were among the first to be licensed and to start their own research program. Shell had a big part in the early successful commercialization of the idea, by supplying epichlorohydrin.[6, 61]

Shell Development Company started their own research program on epoxies and investigated the utility of a large family of chemicals derived from propylene, one of Shell's basic chemical raw materials. The propylene derivatives of greatest interest in epoxies were epichlorohydrin and allyl glycidyl ether. To convert these to resins, Shell chemists discovered new acidic and basic catalysts. Shell proposed monoepoxy compounds as diluents and alumina as a reinforcing filler for casting, potting and adhesive uses.[6]

In the field of plastics, Bakelite was the fourth United States company to begin the manufacture of epoxy resins. Bakelite Company has concentrated on liquid casting resins rather than the solid coating resins and has done much to gain acceptance for epoxies in adhesives, tooling, laminates and potting.[6]

Shell, Bakelite, Ciba and Devoe & Raynolds (now Jones-Dabney) have been the leading manufacturers of epoxide resins.

An agreement between these companies to cross-license epoxy patents covers the original four companies as well as the Reichhold and Dow Corporations. The user will benefit, no matter which one is his supplier, because he may draw upon their pooled basic knowledge of epoxy resin.[6]

With the patents minimized as a competitive factor, the relative success of the producers of epoxy resins, will depend increasingly upon the extent to which they are intergrated. Jones-Dabney Company has a captive outlet for its epoxy coating resins because of their technical background in coatings. Shell, as a manufacturer of both epichlorohydrin and bisphenol A, is well intergrated with regard to raw materials and could become important in the production of polyepoxides. Bakelite has access to epichlorohydrin of the Union Carbon Chemicals Company as well as access to several new manufactures of epoxy resin. The experience gained in marketing several other plastics has given aid to the commercial development of epoxies at Bakelite Company, but Ciba Company maintains its strong position through extensive technical aid to formulators of epoxy. They manufacture bisphenol A as well as a flame-retardant tetrachlorobisphenol A.[6,61]

The Minnesota Mining & Manufacturing Company has also become important in the manufacturing of epoxy resins. The Irvington Varnish Division of Minnesota mining has its own unique mixture derived from cashew-nut oil. The epoxy resin derived from the cashew phenols has a superior impact resistance at room temperature and other desirable characteristics.[6]

The Bordon Company is also producing epoxy from the view-point of a long established manufacture of phenolformaldehyde. Other companies with interest in epoxies include General Mills with its "Versamid" polyamides, Lancaster Chemical Company with its "Lancast A" and Thiokol Corporation with its liquid polysulfides. These materials give epoxy resins flexibility and toughness.[6]

There are a good many more reasons why solid epoxy resin will bear watching. They are probably the most versatile plastic materials ever developed. Epoxy resins have been reacted with or modified with other resins, esterified, molded, used as structural adhesives, for potting and many other uses. It will cure at any normally encountered temperature. Promises for big volume, low-cost uses are shown in the "alloying" with other plastics and the superior characteristics of epoxy resins.[61]

Since World War II the manufacture and sales of epoxy resins have grown tremendously. From nearly zero output in 1949, sales have risen to more than 100 million pounds in 1965. It is estimated that the sales for 1968 will be about 150 million pounds. The epoxy resin's remarkable growth and development in the field of plastics indicates its industrial potential in many varied uses. Although epoxy resins are the newest of the major industrial plastics, its development was a deliberate effort to bring about a better plastic material. Through the energy and skill of teams of men in industrial research, we benefit in new materials and new standards of excellence for the materials which further research will develop.[6, 14]

COMPOSITION OF BASIC EPOXY RESINS

Epoxy resins have found many uses in industry because of their many outstanding qualities, such as adhesion, toughness and chemical resistance. These qualities are reflected by the epoxy resins complex chemical composition.[6]

In common with phenolic and polyester resins, the epoxy resins are thermosetting materials. In the uncured state the thermosetting epoxy resins are either honeycolored liquids or brittle amber thermoplastic solids which become liquid when heated. If the epoxy resin molecules were enlarges ten million times, they might resemble short pieces of thread and would vary in length from about one half an inch in the liquids to several inches in the solids. When converted by a curing agent, the thermosetting epoxy resins become hard, infusible systems. In curing the molecular thread like structures are joined together at the ends and along the sides to form large cross-linked structures. Each epoxy resin molecule is tied to several others, giving it the appearance of a fish net or spider's web but in an irregular pattern. The three dimensional cross-linked network might be visualized in a plane as is shown in figure number one on page ten. This indicates that any directional movement of the molecule is opposed by the cross-linking network of the cured epoxy resin system. These hard, infusible systems may become softened by heating but will never again liquefy without destroying their original characteristics.[1, 4, 6]

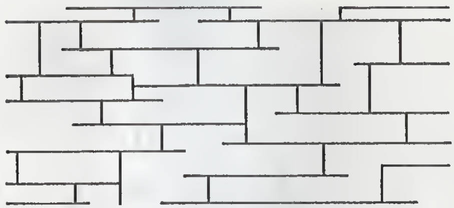
The thermoplastic resins, such as the polyethylenes, acrylics, acetates, polyamides (nylons), polystyrenes and vinyls, may be thought of as permanently fusible compounds composed of long linear chains lying together in three dimensions but not interconnected.

Basically the uncured epoxy resin is a thermoplastic. With the application of heat the brittle solid uncured epoxy resins will also become liquefied. Based on the uncured nature of the solid thermoplastic epoxy resins other thermoplastic materials, such as phenoxy, have been manufactured. These plastic materials are not actually epoxy resins and should not be thought of as such. The thermoplastics or the uncured epoxy resins may be visualized in a plane as is shown in figure number two on page ten. The figure indicates that any directional movement of a molecule is not restricted by cross-linking with the surrounding molecules, as in the cured thermosetting resins shown in figure number one on page ten.[4]

The thermoplastic materials will soften progressively with heat or flow with pressure, whereas the cured thermosetting materials will retain their dimensional stability throughout their design range.[4, 6]

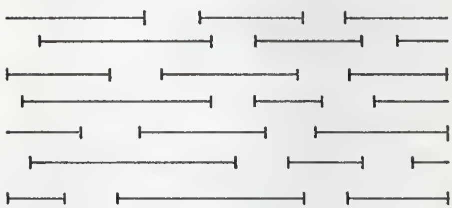
The classification, while justified on the basis of structure, should not be taken as an absolute criterion of performance. Some thermosetting compounds are designed for limited ranges and at higher temperatures they will distort more readily than some of the high-heat-resistant thermoplastic compounds.[4, 6]

In other respects, the two classes of materials will also differ. For instance, thermoplastic materials are formed under heat and pressure into the desired shapes. This is usually not the case with thermosetting compounds, such as epoxy resins. For example, when combining a low viscosity epoxy resin with a suitable fluid curing agent at room temperature and pouring the mixture into a prepared mold, the mold can upon curing be stripped away to reveal a solid, dimensionally stable block of cured resin. There are also other differences which when combined make the thermosetting epoxy resins useful in many applications in which thermoplastics are not chemically suitable.[4]



Symbol Showing Irregular Network of a Cured Epoxy Resin.

Figure No. 1, ref. 4



Symbol Showing the Chain Network of a Thermoplastic Resin.

Figure No. 2, ref. 4

Most of the epoxy resins are produced by the reaction between epichlorohydrin and bisphenol, or similarly by the condensation of phenol, acetone, and epichlorohydrin. These materials serve to produce diglycidyl ether of bisphenol A which is the basic epoxy resin. The most widely used of the liquid epoxy resins are predominantly of this structure. The raw materials for the synthesis are derived from natural gas, crude petroleum or coking by-products.[1, 4]

The epichlorohydrin is a colorless, mobile liquid having an irritating chloroform-like odor. It is an extremely reactive material and is responsible for the actual reactivity of the epoxy resin.[4]

The bisphenol A used in the production of the epoxy resins is produced by the reaction of phenol and acetone. The bisphenol A has been the chief material used in the epoxy resin manufacture because of the availability of phenol and acetone, and because of the ease in which it can be manufactured. There have been several other commercial processes used in the manufacture of the bisphenol. These materials are similar to the bisphenol A and react similarly with the epichlorohydrin to produce epoxy resin.[4, 11]

The actual epoxy resin or diglycidyl ether of bisphenol A is obtained by the reaction of epichlorohydrin with bisphenol A in the presence of certain other chemicals. In the reaction, two parts of the epichlorohydrin are theoretically required for each part of bisphenol A. Although when the 2:1 ratio is employed, the yield is less than ten per cent, with the remaining material being condensation and polymerization products. In order to obtain higher yields, excess epichlorohydrin is employed with the ratio being from 4:1 to 6:1. Then yields of 70 per cent or more are possible. Consequently, with the higher yields, the cost to the consumer is considerably lowered.[4]

Viscosity is one of the characteristics that is important in the manufacturing of epoxy resins. This is important to the consumer also because the viscosity of the uncured resin can impose certain restrictions upon the handling convenience of the formulations. With the use of certain mixed epoxy resins and other available additives, the viscosity can be increased or decreased without serious damage to the desired properties of the cured resin. At the present time epoxy resins are manufactured which range from being thin as water to the brittle solids, in the uncured state.[64]

In the manufacturing process, if liquid resins are desired, the molecule size within the resin must be kept small. To obtain these small molecules and yield the very fluid low viscosity epoxy resins, a great excess of epichlorohydrin is employed in the reaction with the bisphenol A. For the high viscosity resins, the proportion of bisphenol A is much larger. Consequently, the process would be the same for the semi-liquid or the solid epoxy resins except much more bisphenol A would be employed within the reaction.[6]

Although most of the epoxy resins used for purpose of adhesive bonding are derived from epichlorohydrin and bisphenol A, other materials, such as bisphenol F and the tetrachlorobisphenol A may be employed for this class of epoxy resin manufacture. The number of useful reactants for the synthesis and manufacture of epoxy resins for all industrial usages is quite large and varied. Although most of the epoxy resins at the present time are based on the bisphenol A (glycidyl ether), there are other processes being developed, experimented with or employed for the manufacture of epoxy resins. Many of the new processes, as developed at this stage, are not being used in other fields of adhesive bonding but are employed for castings, coatings, and etc.. In the future, many of the new manufacturing processes will become useful products in industry for the purpose of adhesive bonding.

These new epoxy resin materials will replace or add to the present types of epoxy resins because of their manufacturing simplicity, desirable properties, and economic values.[6, 47]

CURE OF THE BASIC EPOXY RESIN

The ability to transform readily from the liquid or thermoplastic state to a tough, hard thermoset solid is one of the valuable characteristics of epoxy resins. This hardening is accomplished by the addition of chemically active material, known as a curing agent. With fast reacting agents, curing of the resin may be accomplished at room temperature. While the slow reacting agents curing will require external heat to accelerate the reaction.[4]

The cure of epoxy resins occurs when the potentially reactive sites within the resin and the curing agent have reacted with one another. The epoxy resin is converted from a group of discrete molecules into huge macromolecules. These are linked together in all three dimensions in such a way that the resin will not remelt or flow upon the application of the heat. The addition of heat will serve only to destroy the cured epoxy resin.[64]

Upon initiation, the curing of the epoxy resin is as irreversible as the boiling of an egg. Just as a three-minute boiled egg will differ from one boiled fifteen minutes, the physical properties of the epoxy resins depend on the extent of the cure. The greater the "density of the crosslinking", the better the final properties of the cured epoxy resin product will be.[6]

The epoxy resins may be cured by two methods, which are catalysis and reactive crosslinking hardeners. The curing of an epoxy resin by means of a catalyst is also known as "homopolymerizing". The catalyst cure of an epoxy resin is brought about by inner reaction between the epoxy resin molecules. While the crosslinking reactive hardeners, which also are known as "copolymerizing" or "heteropolymerizing", causes the resin to cure by crosslinking with other plastic resins. In curing epoxy resins, catalytic and copolymerizing or crosslinking reactions may occur simultaneously or sequentially.

Also, secondary curing agents may be used to effect polymerization through reactive sites other than the epoxy groups present in the molecules of the epoxy resin system. This is usually done through chemical groups which will react and combine to form copolymerized materials, such as the esterized-epoxy resins and phenolic-epoxy resins.[1, 52]

Catalytic cure is a polymerization reaction, in which the catalyst causes an epoxy resin molecule to react and cross-link directly with another epoxy resin molecule. This chain reaction after being started by the catalyst proceeds rapidly until the epoxy resin groups are consumed or become end stopped by impurities.[64]

The catalytic polymerization of epoxy resins may be accomplished with strong bases such as tertiary amines or strong acid materials such as boron trifluoride and its complexes. Because both bases and acids may be used, epoxy resins can be homopolymerized with a variety of catalysis.[6, 38]

In theory, an epoxy resin system should cure and give the same properties no matter which catalyst is employed to cure the epoxy resin. However, this is not the case, because the catalysis differ in reactivity rates and therefore greater or lesser amounts will have to be used to gain the correct cure desired. From this, it can be understood that the amount of catalyst is critical. With under-catalyzing, the system will be undercured, and with over-catalyzing the system will be degraded far below that desired. In an over-catalyzed reaction, the excess or free catalyst will be locked in unreacted as a diluent or will initiate polymerization at so many sites that the resin polymerization will be end-stopped at a low degree of crosslinking. This resin polymerization reaction will be due to the early exhaustion of the unreacted resin before large crosslinked chains are built.[64]

The amount and type of catalyst is usually dictated by the curing time desired. In a system cured with a catalyst, the lesser amount of catalyst is usually preferred to the greater amount of the catalyst. The undercured epoxy resins usually have better qualities than do the overcured or over-catalyzed products. Also, the properties and curing time of the undercured products would remain much more constant from one mix to the next.[64]

Catalysis are usually used in concentrations which range from 1-10 parts per 100 parts of resin by weight. With some catalysis the curing reaction may be achieved at room temperature, while with others a heat cure may be required.[64]

In uses for adhesives the curing catalysis are usually designed to lower the temperature required for the rapid cure of the assembly being bonded. In the earlier adhesives very little attention was given to the fact that many of the acid catalysis seriously deteriorated the materials being bonded or even the adhesives themselves in the adhesive glue line.[47]

The essential part of the catalytically cured structure is the epoxy resin molecule itself. When the resin molecule contains two epoxide groups, this type of homopolymerization leads to a highly crosslinked system. Although, with this reaction the exact amount of the curing agents are critical in forming a fully cured epoxy resin. Also, because of the difficulties which are encountered in controlling the catalytic polymerization reactions with some of the catalysis now available, curing by this method has not been used extensively in industry.[4, 17]

The crosslinking curing agents are distinguished from the catalytic curing agents because the crosslinking curing agents react with the epoxy molecules and are coupled directly into the cured system as structural members of the molecular network.

The crosslinking agents are a vital part of the cured resin. Their characteristics affect the final properties in proportion to their type and the amount present to a much greater extent than do the homopolymerized resins.[41, 64]

There is an optimum amount of crosslinking agent which will assure a complete reaction. If the ratio of the curing agent to the resin in increased or decreased some reduction of the cured resins properties will result. It is often possible for the crosslinking agents to be present in large quantities. These ratios usually range from 1:10 to 1:1 and have an influence upon the cured properties of the epoxy resin.[64]

Resins cured by crosslinking agents are generally referred to as heteropolymerized resins since the cure involves more than one resin. The crosslinking materials which are copolymerized with the epoxy resins are usually called hardeners. Some of the common hardeners for epoxy resins include the aliphatic and aromatic polyamines, polyhydric phenols, polybasic acids, anhydrides and polyhydric alcohols. These hardeners have a wide variety of desirable characteristics and useful physical properties to contribute to the cured resin. The type of epoxy resin or the viscosity of the resin and the specific application will determine which type of hardener to be used.[38]

Heat may be used for the cure of the crosslinked epoxy resin as well as the catalytically cured resin. Generally the solid or high-molecular weight resins have to be melted or softened so they can be molded into the desired shapes. Therefore with the solid resins or the semi-solid resins, usually a less reactive curing agent is used for heat curing. While the liquid or lower molecular weight epoxy resins can use a more reactive hardener or a hardener with an accelerator for cure at room temperature; though the less reactive hardeners can be used by themselves, but heat must be applied for proper cure.

Also, it must be remembered that the uncured epoxy resin is a thermoplastic material and when heat is applied the resin will become thinner and harder to handle. This can be overcome with some epoxy resins by blending two or more resins together or by adding fillers. In general, a heat cured epoxy resin formulation will be closer to the optimum desired. Quite often the resin formulation will be allowed to reach the initial setting of hardening before heat is applied. This is especially good with the liquid epoxy resins. The amount of heat needed for any formulation will depend upon the type of curing agent and/or hardener and the resin formulation used.[17, 38, 42]

The reaction during the curing of epoxy resins is highly exothermic. This means there is a large amount of heat given off no matter whether the polymerization is with other epoxides or by the reaction with a hardener.[6]

Some of the curing agents, such as boron trifluoride of the catalysts and the aliphatic amines of the reactive hardeners, will promote curing at room temperature. Because of the reactivity of these curing agents, they will start to cure at a relatively slow rate but as the temperature rises the reaction is speeded up until the cure is complete. From an industrial production point of view, the fast curing time is welcome but other problems are presented. As long as the reacting adhesive is in a thin layer the heat will generally be absorbed by the adherends in contact. Also the surface area of the epoxy resin adhesive is quite large in comparison to the volume used, so the heat will usually only be enough to bring about an excellent cure. The material which is still in the pot for the next bonding operation is also curing; but it can not disperse the heat, causing the heat to rise to fast and to high, thereby giving a very short pot life and possibly destroying the epoxy resin adhesive remaining. The pot life can be extended by retarding the cure with the use of refrigeration.[6, 64]

The best results usually come in a two stage cure. In the first stage, the epoxy resin makes an initial set or thicking by the interconnection of the smaller molecules. This initial set or polymerization takes place at room temperature or when moderate heat is applied. Then the temperature is substantially raised and the second stage or polymerization takes place. In the reaction the interconnected smaller molecules are joined together to form large interconnected molecules. When this polymerization is completed, the epoxy resin is transformed from the thermoplastic state to a tough, hard thermoset solid.[6]

Besides improving industrial production, the two stage cure will bring about improved crosslinking and thereby a better final product. In many cases, the adjustment of the amounts of the two blended curing agents can produce slight increases or decreases in the gel time and the cure time.[6]

Sometimes the two stage type of cure will not be compatible with a particular curing agent. When this happens and the curing rate of reaction is slow, an accelerator is needed to decrease the reaction time. These accelerators may be either non-curing reagents or catalysts. Many accelerators, although used trace amounts, will produce gross change in the physical properties of the cured resin because they act directly on the reaction mechanisms. This is true for anhydride cures because the amount of the anhydride curing agent will depend upon the presence or absence of an accelerator.[64]

The "latent" curing agents have received considerable interest for some time. These are curing agents which when incorporated into the epoxy resins will provide a pot life of from three to six months at room temperature but will cure when the temperature is elevated. They are also known as single container or one-component epoxy-curing agent systems.[4, 64]

These curing systems are used for only limited applications because the system often sacrifices some of the desired, valuable properties. The properties, of the two container systems usually possess better formulation possibilities than so the "latent" single container systems. Some other disadvantages associated with the single container system are high curing temperatures or long cure time, poor heat stability, and high cost.[64]

One of the new latent type curing agents which has had much attention is the amineloaded molecular sieves. Molecular sieves are synthetic zeolite crystals which have internal cavities with carefully controlled entrance aperture sizes. With proper techniques, the amine curing agents are mixed with and absorbed by the molecular sieves. Then the epoxy resin is compounded with the amineloaded sieves; but curing does not take place because the amine and the resin do not make contact. This is because the resin can not enter the sieve, but when heat is applied the amine then escapes from the sieves and preceeds to cure the epoxy resin. The molecular sieve compounded epoxy resin has a high degree of latency and do not contain the disadvantages of other latent curing agents. Therefore, they may find considerable use in the future for the layman as well as in industry. The only resulting disadvantage at the present time for the one-component systems containing molecular sieves is that of cost. The molecular sieves are expensive materials.[64]

At the present time there are a large number of basic epoxy resins, curing agents, and numerous additives; such as diluents, fillers, flexibilizers and reinforcements. The selection of a curing agent for a particular application involves complexities and experimentation because of the enormous number of formulation possibilities. This selection can only be solved through the valuable equipment, modern techniques and the vast knowledge of the chemists in the plastics production industry.[64]

With familiarization of the curing mechanisms, immense possibilities in the curing of the epoxy resins may be brought about. The future epoxy resins will find an even greater number of uses in industry because of their outstanding qualities. These qualities are reflected by the complex chemical composition of the cured epoxy resins.[4, 47]

ADDITIVES AND REINFORCEMENTS

In addition to the large number of epoxy resin and curing agent combinations, there are numerous additives and reinforcements which may be used to improve the epoxy resin formulation. These range from flexibilizing materials to fibrous reinforcements and offer a wide range of possible formulations for a given application.[4]

Listed below are the types of modifying agents used in epoxy resin formulations.

1. Fillers ------------ to add strength, bulk and reduce the over-all cost.
2. Colorants ---------- to add integral color to the end product.
3. Reinforcements ----- to add impact, tensile strength, etc..
4. Thixotropic agents - to increase viscosity of the resin.
5. Diluents ----------- to decrease viscosity of the resin.
6. Plasticizers ------- to soften the cured resin.
7. Flexibilizers ------ to make the cured resin more flexible.
8. Resinous modifiers - to add desirable properties by combining other plastic resins.[4, 6]

Fillers

Fillers are inert solid particles which are incorporated into the epoxy resin in varying proportions to achieve properties for a particular application. The ideal filler improves the resin composition in properties, such as increased adhesion, lower shrinkage, increased thermal conductivity, heat resistance, hardness alteration, lower thermal expansion, and/or changes the handling characteristics, without serious impairment of the resins desirable properties.[6]

The connotation that fillers are "cheap extenders", to make a less expensive product has handicapped their use and delayed important improvements of fillers and filler compositions. A consideration of these composition's and their properties has provided a better understanding of the form and function of each component of an adhesive formulation.[2, 21]

Fillers may be either organic or inorganic, metallic or nonmetallic. They may be in the form of fibers, powders, granules, textiles, etc. The more common forms are the fibers and powders. Some of the common organic fillers are wood flour, walnut shell flour, cotton flock, carbon black, etc. The more common inorganic fillers are asbestos, glass fibers, silica, metal powders, etc. The fillers employed in the formulation of adhesives can be of several forms. The most common forms are the powders such as aluminum, aluminum oxide, carbon black, and zinc dust. Another form of fillers are the fibers such as the asbestos and glass fibers. These may be in the loose form or in the form of textiles.[2]

Most of the reinforcing fillers are of a fibrous nature. With the exception of glass and asbestos, the fibrous fillers are generally organic compounds. The non-fibrous fillers are usually inorganic compounds. The non-fibrous calcium carbonate, mica, clays, metals, metal oxides, and pigments are often used to extent the epoxy resin adhesives. Although these lack the nature of being fibrous, the surface and physical form of these fillers is of great importance in delineating their usefulness.[21]

Since powdered or granule fillers are offered in a wide range of particle sizes, the proper selection has become a specialized science practiced by the formulators. It is necessary to select not only the correct filler, particle shape, size, and absorption characteristics, but also the optimum loading volume.[4]

Recently activity has been centered on diversifying plastics, such as epoxy resin, even more by using new and unusual forms of the existing fillers and reinforcements. There has been discussion on reinforcing plastics by means of fine metal filaments that will provide the high strength, light weight, and heat resistance necessary for space vehicle applications. One manufacturer has produced a line of aluminum fillers in the forms of granules, shreds, pellets, and spherical shapes to be used in epoxy resin and other thermosetting plastics.[21]

These unusual forms of fillers and reinforcements are used to add strength, heat transfer characteristics, and electrical conductivity. These metal fillers can also be used to provide decorative effect to plastic materials where appearance is of importance.[21]

Fillers will also serve to increase the viscosity, especially in an adhesive paste is desired. The increase in viscosity is desirable for some adhesives to reduce the tendency of the composition to crawl or drain off inclined surfaces. A small amount of fibrous filler materials such as asbestos and chopped glass fibers will cause thickening, while the dense, compact, powdered metal oxides and metals may be incorporated to the extent of far more than the resin itself.[6]

In general, the lightweight fillers, such as the uncompressed silica and asbestos, will bring about great increases in viscosity at ratios which are below 25 phr (parts per hundred ratio). The medium-weight fillers, such as powdered aluminum and talc, may be incorporated in ratios up to 300 phr, with ratios for casting purposes as high as 900 phr sometimes being employed. The smaller the particle size, (giving greater surface area per weight ratio) the more easily the filler will be to incorporate and the less tendency for it to settle. With large particles and heavier materials for fillers, there will be pronounced settling because of a lesser surface area per weight ratio. Lightweight secondary fillers are often employed as thixotropic (thickening) agents to prevent settling of the primary heavier filler material. If the heavier filler is thoroughly milled into the resin in advance of application, the secondary fillers usually will not be needed. Reactive diluents (to lower the viscosity) may be employed to accommodate higher filler loading volumes, but this is most often used for casting purposes.[4]

In general, fillers are not expected to increase the strength of the cured epoxy resin. Though some fillers, such as the metallic oxides, mineral powders, and some fibrous compositions, do provide some reinforcement. Most fillers will reduce impact resistance; fibrous fillers, such as the short-fiber asbestos, will usually reinforce the cured resin by improving the impact resistance. Both fibrous and non-fibrous fillers will improve the compressive yield strength, but will usually reduce the tensile strength, ultimate compressive strength, and compressive fatigue strength. The compressive yield strength can be sufficiently improved with a high filler loading of alumina or iron oxide. These fillers are preferred for applications where hard surfaces and unyielding structures are needed. These same fillers will lower the tensile strength tremendously. All epoxy resins, filled or unfilled, suffer fatigue, and may fail at a fraction of a single load value when the loading is repeated. These factors must be taken into account in formulating epoxy resin for severe-stress applications.[4, 6]

Most fillers will reduce impact resistance, especially the nonfibrous fillers. The fibrous fillers, such as the short fiber asbestos will somewhat improve the impact resistance, while the impact resistance strength is considerably improved with the use of glass fiber fillers.[4, 6]

Abrasion resistance is increased tremendously with the use of a small percent of graphite as a filler material. Nylon, titanium dioxide, and molybdenm disulfide are effective abrasive fillers, but in a lesser degree than the graphite. While the metal fillers, such as aluminum and iron oxide, are harmful where abrasion is a factor.[6]

Fillers will slow the curing reaction and reduce the exotherm because of their diluting effect. For a composition of epoxy resin containing 75 percent filler, the diluting effect will lower the heat buildup by about one-fourth of that for an unfilled composition. The heat buildup is due to the insulating qualities of the epoxy resin.[4, 6]

While the added fillers often increase the thermal conductivity of the resin composition, thereby dissipating the heat buildup. In general, most plastics are excellent thermal insulators and very poor conductors. For this reason thermal conductivity depends upon the type of filler and in what form it is used. In general, the metal fillers offer the best thermal conductivity, especially if they are in the form of shreds, needles, or filaments. This is because the filler particles can make direct contact in the resin composition, thereby the heat buildup is spread and dissipated more rapidly.[6]

Heat resistance may be improved by the use of certain fillers, but there is very little indication that the heat distortion temperature can be increased by fillers, and in many cases the heat distortion temperature may be reduced. This depends primarily on the type of resin, hardener, and filler within the composition. Generally, the heat distortion temperature will be raised slightly by the use of certain fillers.[4, 6]

Most fillers will reduce the coefficient of thermal expansion because of their bulk effect. Unless the filler material has a negative coefficient of thermal expansion, as do certain of the ceramics.[4]

Thermal coefficient of expansion is important during the functioning life of the cured epoxy resin as well as in its manufacture. When the sole problem is low temperatures, internal plasticizers may be a solution. If the problem is thermal cycling between room and elevated temperatures, it becomes necessary to reduce thermal expansion by incorporating fillers into the epoxy resin composition. The fillers alone have lower coefficients than the unfilled cured epoxy resin. When epoxy resin and fillers are incorporated, intermediate coefficients of thermal expansion result, which is somewhat higher on a weight basis, but somewhat lower on a volume basis.[6]

The metal fillers have moderately high thermal coefficients of expansion, while silica and calcium carbonate have a low coefficient as compared to the epoxy resin itself. One expensive material, lithium aluminum silicate, actually has a negative coefficient of a $-6 \times 10^{6}/^{\circ}C$..[6]

Synthetic resins other than epoxy resins, may be used as fillers or extenders, but they are generally considered as resinous modifiers rather than fillers. For this reason, they will be discussed later.[4]

Fillers containing a high percentage of chemically combined water should be avoided. The only other principal restriction is that the filler material should be neutral or slightly basic and in general nonreactive with the resin or the curing agent. When this is not possible, the effect must be considered and calculations made to determine the amount of the curing agent to be used. If used correctly, fillers that have a tendency to slightly react and cure the epoxy resin may be used advantageously. Some of the clays used as fillers are highly alkaline and can accelerate or even catalyze the curing reaction. Most fillers used conform to the above restrictions, and the curing agent-epoxy resin ratio is based on the resin content only.[4]

The loading volumes of the fillers with epoxy resin will depend upon several important factors. Some of the more important factors are listed below.

1. Handling characteristics - (upper limits of permissible viscosity).
2. System limits - (each particle must be thoroughly wetted).
3. Ultimate properties - (the special improvements to be expected of the filler in the cured resin).[4]

Fillers may be used with epoxy resin as extenders to lower the overall cost; but this procedure often leads to adhesive formulations lacking in the necessary properties desired for a particular application. The formulation of epoxy resin compounds incorporating fillers for adhesive purposes is a complex and specialized field, which often involves considerations unique to a given application.[2, 4]

Coloring Additives

There is a close association between color and plastics. However, there is no simple procedure to the problem of selecting one single pigment system over another. The colorants and the colorant systems for epoxy resins as for other plastics, must be carefully selected for the requirements desired. Some of the most common requirements are weather resistance, heat resistance, chemical resistance, lightfastness, migration, and dispersion.[46]

Coloring additives or fillers, such as dyes and pigments, are used to color resins. Since the liquid epoxy resin is an excellent wetting agent, it is often possible to incorporate the coloring agent by mechanical stirring, but with some compounds it is necessary to grind the coloring agent into the system with a ball mill or other similar device. Generally in the mixing of the dry powdered colorants or colorants that do not disperse into the resin easily, make the grinding operation necessary.

The dry powdered colorants have a tendency to form lumps in the resin if only mixed by the mechanical stirring process.[4, 46]

Some colorants are promoters (catalysis) and oxidizing agents which cause certain epoxy resins to cure upon mixing. While some of the colorants are active antioxidants and thereby may inhibit the cure of the epoxy resin. In using a certain colorant, it must be determined to what degree the colorant will inhibit or accelerate the cure. Moisture must also be considered because a colorant containing moisture will effect curing and physical properties of the epoxy resin. Any reactions between the colorants and the epoxy resin, curing agents, and other special additives must be known before final selection of the formulation.[46]

Quite often when colorants have a tendency to react with and cure the epoxy resin or where specific coloration is desired, the liquid resin is supplied in a natural state for the user to add the coloring agent as desired.[46]

Generally the completeness of mixing can be determined visually, especially if different colors of the colorant are added, with one color for the curing agents and another for the epoxy resin. An example of this is having one black (carbon black) and the other white (titanium dioxide), so upon mixing the final color is gray. When the components are different colorwise, a safe rule is to mix to a homogeneous color and then continue mixing for at least an equal length of time.[4, 6]

Some colorants have a tendency to settle because of weight or coarseness. When this problem is encountered usually a resin thickening (thixotropic) agent is used to thicken the resin and help suspend the colorant. Also, a grinding device can reduce the particle size of the colorant, thereby giving more surface area and better suspend the colorant. Many of the pigments are difficult to disperse in epoxy resin and for this reason are uneconomical.[46]

Paste concentrates and dry powder colorants are the two basic types of colorants for use in epoxy resins. The paste concentrates (wet) are widely used for coloring epoxy resins because they give a complete color dispersion and color development. These concentrates are generally compounded in a grinding device. In the grinding process the colorant is usually in a powder form, then mixed with a liquid or paste grinding vehicle or carrier. It is important that this carrier be of the same chemical type as the resin to be colored, so as not to adversely affect the cured properties of the epoxy resin. The colorant dispersions vary in viscosity from a pourable resin to a heavy paste, this depends on the grinding vehicle and the proportion of solid particles in the paste concentrate. The wet paste concentrates are not usually used if good dispersion of the colorant can be obtained with the dry powdered pigments.[46]

The dry powdered colorants can be used to color epoxy resin if the liquid resin, filler, and other additives are blended in special blending or mixing equipment. When more than one dry colorant is available to choose from with each having desired color and properties, it is best to pick the one that disperses most easily in the resin being used. The dry colorant process is less expensive than the paste concentrates, if used on a large scale. Other than the dispersion difficulty the end result is the same.[4, 46]

The dry colorant process is considered to be the least expensive coloring method. Precolored resin from the manufacturer is more expensive and the paste concentrates are considered to be most expensive. Competitive situations can change this breakdown. The more important factors to be considered are inventory cost, material waste, and completion time. Other considerations for selecting a method for coloring are quality, service, and physical characteristics of the colorant and of the finished product.[46]

There are several key characteristics in colorant selection. These key characteristics can be divided into two groups, the performance characteristics and the resistance characteristics. The performance characteristics are the colorant's brightness, hiding power, tinctorial strength, and transparency. The resistance characteristics are heat resistance, weather resistance, chemical resistance, lightfastness, and migration resistance of the colorant.[46]

Colorants can be divided into two basic classifications, which are inorganic and organic colorants. The key characteristics of the inorganic and organic pigments can differ considerably. Because of the individual characteristics of each basic type of pigment, there must be a careful evaluation of the pigments before using as a colorant.[6]

The inorganic pigments can be divided into the natural and the synthetic groups. Metallic oxides, sulfides, etc., comprise the synthetic inorganic pigments. The natural inorganic pigments are mined and then refined into the finished colorant. The more heat resistant inorganic pigments are finely ground mixtures of inorganic materials that have been calcined at high temperatures. The chrome yellows, chrome oranges, iron blues, and molydates are exceptions, which are calcined at much lower temperatures, occasionally below 250 degrees Fahrenheit.[46]

Inorganic pigments are insoluble in the resins but some, such as the iron blues, can produce translucent shades when used in low concentrations. Some of the synthetic inorganic pigments will produce bright colors when used in high concentrations. In general, they are not as bright as the colors produced with organic compounds.[46]

The basic advantages of inorganic colorants are their excellent resistance to heat, light, and migration. The chemical resistance of the inorganic colorants is generally good, but varies within the colorant groups.

They also have lower oil adsorption, better weather resistance, and have considerably less antioxidation effect than the organic pigments.[46]

The organic pigments are basically divided into two classes: lakes and toners. The toners, are of two types: insoluble organic toners and lake toners. The organic toners are insoluble in epoxy resin, but free from the salt forming groups. While the lake toners are usually pure, water-insoluble heavy metal salts of dyes without fillers or substrates of ordinary lakes. Lakes are water-insoluble heavy metal salts or other dye complexes precipitated upon or admixed with a filler or base.[46]

Dyes are natural or synthetic organic chemicals which are soluble in most of the common solvents. Dyes give bright, strong, and transparent colors by going into solution with the resin or hardener. The color effect produced by dyes are distinctly different than from organic or inorganic pigments. The dyes possess a wide color range, good transparency, high tinctorial strength, and a low level of specific gravity.[6, 46]

In comparing colorants the organic pigments have good brightness and brilliance, but the colors generally are not as bright as those obtained from dyes. The tinctorial power of the organic pigments is not as good as from the dyes, but is considerably better than from the inorganic pigments. Organic pigments have a low specific gravity and have a greater resistance to migration than the dyes. Oil absorption is higher with most organic pigments than with inorganic pigments. Generally less colorant is needed with the organic pigments than with the inorganic pigments. Translucent colors can be made with organic pigments and dyes at low concentrations with excellent dispersion. Also the oxidation-reduction condition has to be considered. Most of the organic colorants can be bleached (oxidized) or reduced in intensity, while the inorganic pigments are usually stable to the oxidation effect.[6, 46]

In selecting a colorant it is usually not possible to produce a desired color from one colorant. Therefore, different colorants are blended together and frequently a colorant from one of the classifications is mixed with colorants from another. Colorants must be properly evaluated because each one acts differently in a different media. Also, each resin or hardener has its own peculiarity, causing the colorant to act differently.[46]

Clarity and color of the resin are prime factors in limiting the colorant selection. Epoxy resins have a tendency to turn amber or yellow color with age. The hardener system is also capable of varying the resin color from clear or light amber to dark brown. This usually can be overcome with a variety of colorants, such as carbon black, titanium dioxide white, cadmium yellows, oranges, and reds, chrome greens, the iron earth colorants, etc.. It is important with many of the epoxy resins that the colorants have a hiding or masking effect. Currently many epoxy resins powder or chalk on the surface upon exposure. Any absorbing action or stabilizing effect of the pigment is advantageous. Other colorant requirements are good lightfastness, excellent dispersibility, and moderate-to-high heat resistance.[6, 46]

Consideration of cost, service, quality, inventory, and physical characteristics of a resin or colorant may dictate one of several routes in which colorants can find their way into a finished product.[46]

Reinforcements

The properties of epoxy resin may be improved by a variety of inert solid reinforcing materials. Fibrous reinforcements are in the form of cloth, mat, chopped strands, or staple. These fibrous reinforcing materials may be mineral, vegetable, synthetic, or metallic in nature. Their common virtue is high tenacity in the fiber direction.[6]

The most common reinforcement for epoxy resins is fiber glass which gives an increased tensile, compressive, flexural, and impact strength. It also improves the heat resistance, reduces shrinkage and thermal expansion. Also, the epoxy resin has tremendous adhesion to glass, thereby giving excellent bonding strength.[6]

Fibrous filaments of glass are formed from a relatively soda-free lime-aluminumborosilicate glass. Fibrous glass for reinforcing thermoset plastics is referred to as "ECC" grade glass. The "E" is for high electrical resistance, "C" for continous filament, and the final "C" for chemical grade. The continous filament "C" can be replaced with "S" for staple fiber, but the staple fibers have less strength and are usually used for insulation batts and not for plastics reinforcements.[6]

Glass fibers are considerably stronger than most other reinforcing materials. It has many of the same characteristics of bulk glass, but some of the properties are modified. The mechanical strengths are increased, while the chemical resistance is reduced. Regardless of the filament diameter, the tensile strength is about 400,000 psi.. Though the fiber strength on a commercial basic is usually about 250,000 psi., because of damage to the fibers during the manufacturing and handling operation.[37]

Glass fibers are manufactured by heating the glass, which is usually in the form of marbles and then drawing it through a small electric crucible called a "bushing". The bushing usually has 204 or sometimes 102 holes in the bottom for the molten glass to pass through. The fibers made by this process are continous filaments with the diameters ranging from 0.00012 to 0.00075 inches. These glass fiber filaments are easily damaged, and loses much of their strength when subjected to even the slight abrasion of the sizing, spinning, and weaving operations.

To protect the 204 or 102 filaments, they are coated with a liquid sizing material. This protects the many filaments and also holds the filaments together to form a "strand" or "sliver", as they are sometimes called. The liquid sizing material used in this process is also known as a "binder". After the strand is formed, it is then wound onto a forming device and cured in a hot-air oven before being converted into other forms.[6]

For the woven fabrics, the protective binder material is used for protection against abrasion and also acts as a lubricant for the weaving process. This is later burned off (heat-cleaned) and the "coupling agent" is applied to the fabric. This coupling agent is a protectant for the glass fibers, but also promotes properties for good adhesion of the epoxy resin and the glass fibers. When the fiber glass strands are to be used as reinforcing, other than woven fabric, the sizing material or binder is replaced by the coupling agent.[37]

After the glass filaments have been made into strands or slivers; next they are made into "rovings" or "yarns". A roving is produced by giving about 60 strands a slight twist to hold them together. Rovings and yarns are further processed into mats and woven fabrics. The strands may also be cut into small pieces to form chopped strands or multidirectionally applied in layers to form mats, etc..[6, 37]

The reinforcing properties of fiber glass cloth is affected by the weave of the cloth. The oldest of the cloth weaves is the plain or square weave. Two other cloth weaves that have found uses as a plastics reinforcement are the leno and satin weaves. Still another important cloth weave, which is similar to the square weave, is the basket weave. Brief descriptions of these different weaves are listed on the next page.[6]

1. Square or plain weave - warp and filling threads of the same yarn cross alternately.

2. Basket weave ---------- two warp and two filling threads, with pairs crossing alternately.

3. Leno weave ------------ warp threads are locked in to place by smaller interlacing fill threads.

4. Satin weave ----------- one filling thread goes across several warp threads before interlacing the warp threads.[6]

Glass cloth can be woven from rovings as well as from yarn. The woven rovings, or roving cloth is a much coarser cloth which eliminates the yarn spinning process. These stiff, heavy fabrics are less expensive and also lowers the labor cost.[6]

The fabricator need not always do the resin impregnation of the fiber glass cloth himself. "Prepreg", which is a glass cloth impregnated with one of several resins can be purchased. The resin is left in a state of incomplete cure (B-staged), so that it is not tacky. When heated under moderate pressure, the prepreg softens, becomes somewhat tacky and cures completely. Uniformity and convenience are the chief advantages of the products.[6, 41]

The prepregs are manufactured by impregnating glass cloth with epoxy resin and a high-temperature or latent curing agent. When stored away from heat, the prepregs may have a shelf life of several months. Some of the epoxy resin prepregs must be kept under refrigeration to prevent premature hardening.[6, 41]

The prepregs are stiff, therefore restricted to planes or simple curvatures. Prepreg glass cloth tapes, for wrapping around pipes and as adhesives, have gained many uses.[6]

The fiber glass cloth, for adhesive prepregs, is generally referred to as a carrier. The adhesive prepregs have found special uses.

These special uses are where the coefficient of thermal expansion of the adhesive layer must be brought into line with that of the materials to be bonded, or when the joint must serve at the same time as a positive insulating layer between the parts.[41]

Other forms of reinforcement from fiber glass are chopped strands and milled fibers. Chopped strands are manufactured by passing continuous strands from the forming package through a cutter which chops them into predetermined lengths, usually from one-quarter to one-half inch. The chopped strands type of reinforcement is a low cost form. Its usually used in the manufacture of molding compounds.[48]

Milled fibers are manufactured from continuous strands from the forming package, which are hammermilled into small nodules of filaments glass. These glass fibers are usually available in nominal lengths, which range from one-sixteenth to one-thirty secondth of an inch in length. They are mainly used for anti-crazing filler reinforcement in casting resins and in epoxy resin adhesives where they give increased body and dimensional stability to the adhesive joint.[37]

A recent development in the manufacture of fiber glass is the continuous "hollow" glass filaments. They are produced by a special manufacturing process and are gathered similarly into a bundle forming a multi-filament strand or sliver. The treatment and handling characteristics are similar to the ordinary solid glass filaments. These hollow fibers give for equal thickness about a forty percent weight savings over the solid fibers. These hollow fibers also provide improved dielectric and thermal properties.[37]

Glass flakes have been used as a reinforcement for thermosetting plastics, such as epoxy resin. They are manufactured by the extrusion of molten glass through slits, thereby forming the glass flakes or platelets.

These glass flakes offer several advantages which are close packing to give higher strength; lower cost form of reinforcement; multi-directional reinforcement; and resistance to solvents, moisture, etc..[6]

Asbestos is a material that has been used both as a reinforcement and a filler for epoxy resin. Asbestos is a group of fibrous materials that occur in many different forms throughout the world. Incombustibility and its unique fiber structure are the basic physical characteristics that give asbestos commercial value. Because of the fiber structure, asbestos can be separated into filaments or fibers of high tensile strength, which can be mixed with materials or made into yarn, cloth, etc..[15]

The incombustibility of asbestos has made it one of the foremost materials for problems of flame and heat resistance. Other important properties of asbestos is its excellent insulation and thermal characteristics, corrosion resistance, high impact resistance, stiffness and good dimensional stability. Because of these desirable properties they have found increased usage as a plastics reinforcement.[15]

There are six different types of asbestos materials, each has a unique fiber structure and individual chemical and physical properties. Of the six types of asbestos, four have found use as reinforcing agents and fillers in the plastics industry. These four types of asbestos are Chrysotile, Crocidolite, Amosite, and Anthophyllite.[15, 32]

Chrysotile asbestos is a hydrated magnesium silicate. It is superior to other types of asbestos for textile processing and many other purposes in the plastics industry. Chrysotile is used almost entirely by industry for fibrous asbestos materials. It does have some disadvantages, such as lower chemical resistance and a higher magnetite content than some of the other asbestos.[15]

Chrysotile asbestos is produced in very short fiber lengths to long spinning fibers. The fiber structure and the high tensile strength make Chrysotile an excellent reinforcing agent for epoxy resins. When used as a reinforcing material with epoxy resin and the other thermosetting plastics it exhibits high strength and good flexibility at both room and elevated temperatures. Because of its excellent properties, Chrysotile asbestos reinforced plastics have found many uses in the aerospace field.[15, 32]

Crocidolite, which is known as the "Blue asbestos", because of its blue color is a complex silicate of iron and sodium. It has the highest tensile strength of the asbestos materials and is manufactured into rovings, yarns, woven fabrics, etc.. In spite of its high tensile strength, the Crocidolite asbestos fibers have not gained major acceptance as a reinforcing agent. This is because the fibers have not been properly processed for use as a plastics reinforcement. Recently though, strides have been made to produce suitable Crocidolite fibrous reinforcements.[15, 32]

Amosite asbestos is basically a ferrous silicate. It possesses good tensile strength, but the tensile strength is not as high as Chrysotile or Crocidolite. The heat resistance of Amosite is better than for the Chrysotile or Crocidolite but its fibers are harsh and unsuited for spinning.[32]

The Amosite fiber lengths vary from one-quarter to five inches. Amosite has found little use as a reinforcement for plastics. Recently though, it has been available and may find industrial application because the Amosite is the most economical fiber available for its given length.[15, 32]

Anthophyllite is basically a silicate of magnesium and iron. Its fibers are usually brittle and lack tensile strength, making them unsuitable for woven fabrics, etc.. The advantages of the Anthophyllite asbestos fibers has been its superior electrical properties and excellent chemical resistance.

For this reason it has found use as a filler and reinforcement for the thermosetting plastics and the thermoplastics as well. The fibers from Anthophyllite asbestos have been used with such plastics as epoxy resin, to manufacture non-corrosive pipe, acid and alkali storage tanks, and similar units for use with chemicals.[15]

The most important factor in the use of asbestos fibers is that they retain high tensile strength at elevated temperatures. Another important factor is the fineness of the asbestos fibers. Asbestos fibers are of a smaller diameter than most other materials used as reinforcing agents. These fiber diameters may be as small as 0.0000018 inch, which gives much surface area for a higher resin to reinforcement bond.[15]

Metal fibers have been used as reinforcements for epoxy resin. For mass casting, three-fourths to two inch fibers have been used, while the shorter metal fibers of one-fourth inch are preferred for the flocking of the face coat. Both aluminum and steel fibers have also been employed. When using them the physical properties improve with the increasing of the fiber length but the handling is difficult.[6]

Metal wire mesh of aluminum and steel have also been employed as a reinforcement and have provided improved heat distribution because of its continuity, as do the metal fiber of the epoxy-alloys.[6]

Generally both the metal wire mesh and the metal fiber epoxy resin-alloys have found use in high temperature epoxy resin compositions. Their advantages are in the tooling applications.[6]

Viscosity

Viscosity is that property of fluids by which they offer resistance to flow or any change in the arrangement of their molecules. Controlling of the viscosity is important because the required cured properties of the epoxy resin will impose restrictions upon the handling convenience and often the control cannot be obtained by changes in the formulation.[3, 13]

The more viscous adhesives may be found most advantageous for use with items having irregular bonding surfaces or where there are broad tolerances between the surfaces to be bonded. However, for close tolerances and smoothness of the surface, an adhesive with a lower viscosity may be more desirable despite the possibility of lower strength.[13]

To increase the viscosity or thicken epoxy resins is accomplished by the use of "thixotropic agents". The thixotropic agents are finely divided particles which can clot or temperarily thicken a liquid epoxy resin, so that it will not drain from an inclined or even a vertical surface. They may be porous granules such as the colloidal silicas, bentonite platelets such as mica, or short fibers such as chopped fiber glass or asbestos. Because of their porous and noncompact shapes, they are able to make contact with each other even when a very low per cent is present. With the contacts between the particles webs are formed which immobilize the liquid; but stirring or vibration will break the web structure formed so the composition can be poured or brushed. The effectiveness of the materials used as thixotropic agents vary considerably.[6]

For the liquid epoxy resins, the best acceptance has been with the use of the colloidal silicas. Because of their high surface area, these porous particles tend to link together forming short fibers.

These short fibers in turn forms the web like structure. But new short fibers are formed as soon as the mix is applied and left undisturbed.[6]

Chemically the colloidal silicas are similar to sand, but they are expensive ingredients, in the price range of the epoxy resins. Usually though, only two to ten percent of the colloidal silicas are needed for the desired thickening of liquid epoxy resin. Higher percentages are usually needed though, for a very low viscosity epoxy resin.[6]

Thixotropic agents can also have a secondary function in epoxy resin formulations. Because of the web forming structures of these agents, they can be used for the purpose of suspending or prevent the settling out of the heavy fillers such as iron oxide or steel dust. This two part function of suspension and thickening works well in formulating epoxy resin pastes for adhesive bonding purposes.[6]

To lower the viscosity of the epoxy resins, "diluents" are generally employed. These diluents are free-flowing liquids of very low viscosity. When a sufficient amount of a diluent is added to an epoxy resin formulation the resultant lowered viscosity usually brings about better penetration, better wetting ability and closer tolerances. This especially aids in the formulations for laminating and adhesive bonding. Diluents also makes possible for a larger amount of filler to be incorporated into the resin.[4]

There are basically two types of diluents, the reactive diluent and the nonreactive diluent. The reactive diluents are generally mono-epoxides of a very low viscosity, such as the phenyl glycidyl ether, allyl glycidyl ether, butyl glycidyl ether, or styrene oxide. These very fluid mixtures have the ability to penetrate and wet other materials. When added in the proper proportion to liquid epoxy resins, these reactive diluents reduce the initial viscosity without destruction of the final properties of the cured resin.

An amount of five to ten per cent is best, at this percentage the reactive diluent will bring about a sharp reduction in viscosity. If these reactive diluents are used in concentrations above fifteen per cent, they usually will reduce the strength and solvent resistance of the cured epoxy resin. This is because the high concentration of the reactive diluent lowers the functionalism and thereby less crosslinking upon cure. Also many of these reactive diluents are volatile and some are toxic.[4, 64]

Nonreactive diluents are basically solvents, such as xylene. They may be used in applications where they can be driven off or evaporated prior to or during the curing process. If the nonreactive diluents or solvents are not removed before or during the curing process, they become locked into the cured resin system, thereby considerably lowering the desirably properties of the cured epoxy resin.[64]

There are other means of lowering the viscosity without the use of diluents. The selection of a low viscosity curing agent will often lower the viscosity of the resin without impairment of the final properties.[64]

Another method is the use of heat. Heat may be used when the pot life of the epoxy resin and/or the exotherm characteristics during the cure permit. Before and during the curing process the epoxy resin is basically a thermoplastic, therefore the addition of heat will lower the viscosity, but will act as a curing catalyst. For this reason, heat often cannot be used with the room temperature curing agents.[64]

In general, diluents and solvents are avoided because they tend to decrease many of the desirable cured properties, such as chemical resistance and thermal stability, and to increase the potential for skin irritation. They also may reduce the compatibility of the resin with certain adherends in bonding.[4]

Plasticizers and Flexibilizers

The excellent properties of most epoxy resins, combined with their compatibility with a wide range of modifying agents, have brought about the development of epoxy resins with greater impact resistance and flexibility. With this they still retained the valuable properties of the rigid system, having excellent chemical resistance, good electrical properties, ease of cure, etc..[4]

Epoxy resins have excellent properties, but when unmodified, they tend to be hard and brittle. If subjected to sharp impact or flexing action they may crack or break. In a brittle state the cured epoxy resin also has a low peel strength. The flexibilizing modifiers are used to increase the epoxy resin's toughness. Toughness is the opposite of brittleness and is dependent upon both the tensile strength and the elongation (strain). The flexibilizing materials incorporated into epoxy resin generally lessen the brittleness by improving the elongation characteristics and thereby making a tougher material. This generally can be accomplished without lowering the tensile strength too much.[6]

The materials used to bring about a higher flexibility to the epoxy resin may be divided into two groups: "flexibilizers" and "plasticizers". The flexibilizers are mono- or polyfunctional compounds which react by crosslinking with the epoxy resin and become an intergral part of the cured resin system. While the plasticizers are those compounds which are nonreactive when combined with the epoxy resin. They may be considered as inert resinous or monomeric fillers.[4]

Plasticizers for the epoxy resins has met with little success. The more common monomeric plasticizers are for vinyls and rubbers.

These monomeric plasticizers are generally incompatible with epoxy resin. They tend to separate from the system during the cure and during the aging process. When retained the result is only a slight reduction in rigidity. Depolymerized rubber has been tried and found unsatisfactory. The viscosity of the liquid epoxy resin increased when as little as ten per cent was used. When larger volumes of the rubber was used in an epoxy-solvent system, the physical properties of the cured resin were not very good.[4, 6]

A few nonreactive monomeric plasticizers have been used in adhesive formulations, but they are not in general use. Considerable work has to be directed toward developing a suitable plasticizer for epoxy resin before they will find general usage.[4]

Monofunctional flexibilizers have been more successful than plasticizers in use with epoxy resins. These flexibilizers generally contain a single epoxy group as the reactive point for crosslinking.[4]

Materials such as epoxyidized vegetable oils impart modest flexibility to the cured resin systems. The flexibility is achieved by the action of longer molecules, with greater spacing between them. Under imposed loads this permits a freer movement of the cross-linked structure. These compounds do not separate during cure because they do react at one point. These materials act also as reactive diluents in that they sharply reduce the viscosities of the mix. They will degrade the ultimate properties of the cured resin, when used in high percentages. They find use in adhesive and laminating formulations when used in lower volumes of about twenty per cent. These materials also find use in casting formulations to improve low-temperature impact resistance.[4]

The greatest success in imparting toughness and flexibility to the epoxy resins has been through the use of other resins or semiresinous materials.

Many synthetic resins are capable of direct reaction with the epoxy resin and thereby serve as the curing agent. In this way more flexibility is built into the cured resin molecule.[4, 6]

The most important of these materials for use as flexibilizing and curing agents are polyamide resins, polysulfide resins, fatty diamines, and certain of the polyester resins. These materials are representative as flexibilizing agents. Also some of the glycols, isocyanates, polymerized fatty acids, etc. have limited use as flexibilizers.[4, 6]

The considerations involved in the formulation of an epoxy resin system containing a polyfunctional flexibilizer is much more complicated than for the formulation of the rigid epoxy resin system. The proper flexibilizer or combination of flexibilizers have to be considered. Also, some of the polyfunctional flexibilizers are curing agents and therefore add further complications in selecting the correct ratios to bring about the optimum epoxy resin compound. Similar to the rigid epoxy resin systems, a variety of fillers, diluents, and other modifiers may be incorporated into these epoxy resin systems.[4]

High percentages of these flexibilizers can be used to produce extremely flexible rubberlike compounds. With the lower percentage of flexibilizing materials, a more resilient impact-resistant epoxy resin is produced. Within this range it is possible to formulate adhesives, coatings, etc..[4]

Some of the polyfunctional flexibilizers will reduce the exotherms and shrinkage. In turn,this reduces the internal strain during cure. Also, the addition of flexibilizers improves the adhesive properties of the epoxy resin. This improvement is in room temperature shear strengths, peel strengths, and the adhesion to the flexible plastics. There is an improvement in lower temperature performance also.[4]

Problems that have been presented with the use of flexibilizers are low tear strength with the higher ratios of the flexibilizers, imbrittlement with aging, and loss of strength at higher temperatures. In the case of the heat-distortion temperature opposing flexibility, certain properties can be achieved only at the expense of other properties. With the flexibilizer usage at lower percentages, the reduction in the heat-destortion temperature is not severe. This performance at elevated temperatures depends primarily on the amount of flexibilizer incorporated into the resin system.[4]

The polyamide resins are described here as flexibilizers but they may be considered as nonirritating polyamine curing agents for epoxy resins. They are viscous, brown liquids with a complex structure, which is different from the common nylon-type polyamides. The cured resin system with the use of polyamides is tough and flexible. They usually provide a higher tensile strength and heat distortion temperature; but a lower elongation than some of the other flexibilizers, such as the polysulfide resins.[4, 6]

It is not the amides but rather the contained amine groups which act to cure the epoxy resins. The resin system need no additional curing agents, when the polyamide resins are used in weight ratios of 0.5/1 to 1/1. In lesser amounts, an amine curing agent should be added.[6]

The chemical as well as the physical considerations limit the mixture ratio variations for the polyamide flexibilizing and curing agents. The optimum values vary from resin to resin. These ratios can be increased with a greater amount of polyamide to achieve greater flexibility.[4]

Several polysulfide polymers useful as flexibilizers for epoxy resins are available commercially. They are viscous, colorless liquids. The commercial resins differ from the ones used as flexibilizers primarily in crosslinking, molecular weight, and viscosities.[4]

The curing reactions of polysulfide with epoxy resin is by addition. This in turn forms longer, more flexible molecules within the epoxy resin. Because of this reaction, the crosslinking of the epoxy resin and the polysulfide resin is not a complete cure. The reaction within a few days will gel the epoxy resin leaving it unworkable and inadequately cured. Therefore curing agents are used with the flexibilized epoxy resin as though no polysulfide resin was present. A typical formulation would involve one hundred per cent or less of the polysulfide resin flexibilizer. Upon using a curing agent the crosslinking is prompt, giving a more flexible and resilient product than the unmodified epoxy resin.[4, 6]

The fatty diamines are used in quantities of about 70 per cent, and react similar to other amine curing agents. The melting point of the fatty diamines is just above room temperature, therefore they must be mixed hot. Once they are melted, they are very fluid. The material has the appearance of a yellow soapy paste at room temperature. Thorough mixing is required at temperatures of about 125 degrees fahrenheit. After mixing, the composition is usually cooled to room temperature for longer pot life. Postcures of 300 degrees fahrenheit may be used without affecting flexibility of the resin.[4]

When using the fatty diamines in ratios of 70 per cent, they have a lower chemical resistance as compared with some of the other epoxy resin systems. With the use of a secondary curing agent to replace a portion of the fatty diamine, it is possible to achieve wide gradation in physical properties and flexibility.[4]

The fatty diamines provide good strength for adhesion at lower temperatures. They also show good performance under vibration and thermal shock. The fatty diamines do not have optimum properties at high temperatures and are usually used in formulations where high temperatures are not encountered.[4]

Caution should be exercised in using the fatty diamines because they are skin-sensitizing agents. Like the unmodified amines they may cause dermatitis.[4]

Possibly the most versatile of flexibilizers are the polyester resins. These flexibilizers differ from those previously discussed, in that it is possible to formulate the polyesters which are nonreactive with epoxy resin at low temperatures; but will react and crosslink with the epoxy resin when a curing agent is added. While other polyester formulations may act as curing agents similar to the polyamides.[4]

As flexibilizers, the more complex polyesters are of use, because of the longer molecular chains. Certain of these polyesters will crosslink into the epoxy resin system during anhydride or amine cure. Many will not react unless catalyzed.[4]

A typical flexibilizer or curing agent composed of the complex long-molecular-chain polyester resins will yield a cured epoxy resin which is tough and impact resistant. The chemical resistance and electrical properties of the composition will usually be below that obtainable with the unmodified epoxy resin system. In both cases, the amount of polyester resins can be varied for specific properties in diifferent applications.[4]

The less complex polyesters having a shorter-molecular-chain may be used as resinous modifiers (extending fillers) for the epoxy resin formulations. These polyesters give much less flexibility to the cured epoxy resin system and therefore are used for the purpose of extending the formulations and possibly lowering the material cost.[4]

Flexibilizers have made the epoxy resin a more useful material in industry by improving desirable properties, particularly in greater toughness, stronger adhesion and less shrinkage.

Flexibilizers have also given improved low temperature performance, increased impact resistance, and better thermal expansion characteristics. These desirable properties provide the formulator with epoxy resins capable of fulfilling requirements not obtainable with the unmodified epoxy resin systems.[4]

Resin Modifiers

Epoxy resins are compatible with many other synthetic resins. These synthetic resins are used in epoxy resin to modify the properties of the cured epoxy system. As an example, phenolic resins have been used to increase the heat distortion temperatures of the epoxy resin system. Other resins have been used to increase flexibility, impact strength, and thermal shock resistance. When the desired properties and compatibility warrant it, the lower priced synthetic resins may be used in fairly high percentages to reduce the over-all cost of the epoxy resin system.[4, 6]

The best results are obtained with resins which react and crosslink with the epoxy resin rather than acting as inert fillers or extenders. In the presence of a catalyst some of the phenolic resins and their intermediates will react with the epoxy resins and cure them. Bisphenol A is one of the most common hardeners or curing agents for epoxy resins. Many others have been suggested as crosslinking agents for epoxy resins. These usually react with epoxy by directly crosslinking with them. The phenolic resins have had much commercial value in the adhesives, coatings, and castings field. Because of the close parallel between the epoxy resin and the phenolic resin in properties and uses, they are used extensively as resinous modifiers for each other.[4]

Listed below are several other of the synthetic resins that are used as resinous modifiers for epoxy resin.

1. Aniline formaldehyde resins (A/F) - coatings field.
2. Fluorocarbons --------------------- coatings field.
3. Furfural resins ------------------ coatings field.
4. Isocyanates (polyurethanes) ------- adhesives field.
5. Melamine resins ------------------ coatings field.
6. Polyester resins ----------------- coatings field.
7. Silicone resins ------------------ coatings and electrical potting field.
8. Urea resins ---------------------- coatings field.
9. Vinyl resins --------------------- adhesives field.[4, 6]

Also epoxy resin has been used as a resinous modifier to upgrade many of these same synthetic resins. In the coatings field, the epoxy resin has been used as an upgrading agent for the phenolics, melamines, ureas, vinyls, furanes, polyesters, fluorocarbons and the asphaltic materials.[4]

The resinous modifiers are important to the plastics industry. Whether it be the epoxy resin used as a resinous modifier for other resins or the other synthetic resins used as resinous modifiers with epoxy resin. The purpose is to bring about more desirable and more useful properties at a lower cost.[4]

PROPERTIES OF EPOXY RESIN

An excellent balance of outstanding properties are possessed by epoxy resins which accounts for their wide use in formulations for structural and non-structural adhesives.[52]

The more important of these properties are:

1. Versatility
2. Handling characteristics
3. Toughness
4. High adhesion
5. Low shrinkage
6. Thermal characteristics
7. Inertness[4]

Versatility

Versatility is an important property of the epoxy resin adhesives in that many varied formulations can be used in industy due to the numerous curing agents available. Also there are many different commercial or experimental types of epoxy resins available, of which are prepared from several base chemical sources. From these numerous resins and curing agents the epoxy resin adhesive properties may be varied over a wide range of curing cycles.[4, 64]

These versatile properties may be varied over a wider range by incorporating other additives and/or reinforcements into the uncured resin system. These modifiers are fillers, colorants, reinforcements, thixotropic agents (thickening), diluents (to lower viscosity), plasticizers (to soften), flexibilizers, and resinous modifiers (other plastic resins).[4, 6]

In the epoxy resin adhesives, these additives and reinforcements serve to enhance the adhesives properties or to bring about desired properties not possessed by the epoxy resin adhesive.[4, 6]

The epoxy resins are versatile in that they are compatible with a wide variety of other thermoplastic and thermosetting resins. Because of this compatibility other plastic resins have been used as curing agents, flexibilizers, extenders, etc. for the epoxy resin adhesives. Also, epoxy resins have been used as stabilizers and modifiers for other plastic resins to bring about more desirable properties.[49]

Because of the number of resins, curing agents, and other additives or modifiers, it is possible by varying the quantity and type of each material to obtain many variations in pot working life, cure rate, and adhesive properties.[49]

Besides the variations in pot working life and cure rate due to the number of resins, curing agents, and modifiers; further versatility can be brought about with temperature control during mixing and curing. For example, refrigeration after mixing will prolong pot working life. While the application of heat during cure will shorten the curing time.[6, 16]

Another important variation in epoxy resin adhesives is that of the actual adhesive forms. Most of the general-purpose epoxy resin adhesives are two-component systems with viscosities which range from water-thin liquids to thick, stiff pastes. Other forms of these adhesives are solid sticks, granules, powders, and films or tapes. These are usually one-component adhesives which are combinations of resins with a latent or "B-staged" (partially reacted) curing agent. When heated, these adhesives soften to a liquid or a paste state and the curing reaction is started.[17]

Epoxy resin adhesives will bond to a very wide variety of materials such as plastics, metals, ceramics, glass, vulcanized rubber, cork, leather, textiles, etc.. About the only materials that epoxy resin adhesives do not bond with great strength is some of the heavy metals and a few of the thermoplastics.[17, 41]

Another versatile trait of the epoxy resin adhesives is their ability to react at or near room temperature with or without applied pressure to give good adhesive bonding strengths. The room-temperature curing methods for these adhesives has found many applications in industry.[38]

Due to the widely diversified properties of the cured epoxy resin adhesive systems, a wide range of specifications can be engineered for industrial use.[4]

Handling Characteristics

Good handling characteristics is another important quality for many of the epoxy resin adhesive formulations. Many epoxy resin adhesive formulations can be worked and cured at room temperature; and those which can not be worked at room temperature require only moderate heat during mixing and curing. Many of the one-component or ready prepared epoxy resin adhesives need no mixing and only have to be applied and cured with moderate heat.[4, 26]

For the two-component adhesive formulations, where the curing agents have to be added to the resins, the pot-working life and the curing time are important. Basically the curing agents may be classified as cold-setting, which cure at room temperature and hot-setting, which require external heat for proper curing of the epoxy resin.[6]

The pot-working life, especially for the cold setting curing agents, depends to some extent on the size and the shape of the containers that the epoxy resin adhesive is mixed in. Generally, the more reactive cold setting curing agents have to be mixed in small or shallow containers, because of poor heat dissipation from the reaction of the cure.[6]

The curing cycle of an epoxy resin usually runs parallel to the pot life of that material. The fast curing formulations have a short pot working life, while the slow or sluggish curing formulations have a long pot working life. Many of the slow curing agents require an application of heat for satisfactory cure.[16]

With proper selection of the curing agents and correct use of modifying materials, the cure of the resin can be accomplished in almost any specified time period. This may range from a few minutes to several days. Existing room temperature and the amount of heat applied to the epoxy resin mix will also have bearing on the curing time. Heat acts as a catalyst and will shorten the curing time considerably. In many cases, pot working life, and cure schedules can be accomodated to the production situation without adversely influencing the properties of the cured epoxy resin adhesive formulation.[4]

The two-component liquid epoxy resin adhesives are available in a wide range of viscosities and degrees of reactivity. The liquid epoxy resin adhesives are available to allow easy incorporation of fillers, other additives, and reinforcements.[38]

Epoxy resins have indefinite shelf life, before the curing agent is applied to the resin, unless the epoxy resin has not been manufactured correctly or contains caustic materials. The ratio of curing agent to resin is not as critical as with many of the thermosetting plastics. Although, it should be held fairly close to the empirically determined optimum amount for best results.

If too much or too little curing agent is present, the desired properties may be reduced, so weighing of the resin and curing agent should be done with care. In general however, a small percentage of error in either direction can be tolerated in most applications, and a few of the curing agents permit quite a wide margin in the ratio of curing agent and the resin.[4]

An advantage in the handling of most epoxy resin adhesives is the absence of volatile by-products during cure. This makes the joining of large pieces, such as sandwich panels, possible with complete safety.[38]

A few of the epoxy resin adhesives contain solvents or nonreactive diluents to lower the resins viscosity. For these epoxy resin adhesives containing solvents, the solvent must be evaporated by pre-drying after application. If the solvents are not removed before or during the curing process, the final properties of the adhesive are lowered considerably.[41, 64]

In using the two-component systems for epoxy resin adhesives requires the handling and mixing of the two-components, the resin and the curing agent. Generally, the materials used in the various epoxy resin adhesive formulations do not present a serious health hazard. Though, there are a few materials used in some of the formulations that should be handled cautiously. These may be handled or mixed and applied with complete safety if certain (adequate) precautionary steps are observed.[52]

These precautionary steps are listed as the following:

1. Use only in well ventilated areas.
2. Prevent skin contact with the resin mix.
3. Wear protective clothing on anticipated contact.
4. Protect eyes from caustic curing agents.
5. Maintain personal hygiene and good housekeeping standards.
6. Remember solvents, which are sometimes used as diluents, can be a fire hazard.[52]

When the epoxy resin adhesives are supplied in a prepared to use one-component system; the resin, curing agent and any additives are already mixed. The one-component adhesives are combinations of resins with latent curing agents which are inert at room temperature, but when heated the adhesives turns to a liquid or paste state and the curing reaction is started. In some of the one-component latent curing agent systems, the reaction may be started with moisture rather than heat or a combination of moisture and heat. These adhesives are usually in the form of liquid or pastes and can be of value for room temperature cures. In some of the specialized one-component systems, the resins and special curing agents are "B-staged". These are mixtures in which the resin and the curing agent are partically reacted to a room temperature-stable solid which is still fusible or thermoplastic when heated. The heating process causes the curing agent to react and finish the curing cycle. Usually, these materials are applied to preheated surfaces or applied to cold surfaces, which are then heated.[17, 36]

The two-component epoxy resin adhesives are usually in the form of liquids or pastes, while the one-component systems have a wider variety of adhesive forms, which can range from liquids to hard solids. Some of the forms of the solid adhesives are solid sticks, granules, powders, films or tapes, and fiber glass impregnated tapes.[17]

Generally the one-component epoxy resin adhesives can be applied directly to the adherends with no further preparation of the adhesives. These materials, in the form of liquids or pastes, permit easy application by spatula, brush, or roll-coating with a minimum of clean-up and waste. Some of these adhesives are thixotropic and thereby maintain form and position during the curing cycle. Also, adhesive thickness can be controlled where loose fitting parts are to join.[26, 36]

The granule and powdered epoxy resin adhesives allow a sprinkling production technique as opposed to the paste spreading method. These materials have been used to improve uniformity of thickness as well as simplifying production techniques.[17]

Toughness

Toughness is another important quality of the rigid epoxy resin adhesive formulations. When properly modified, the cured epoxy resins are approximately seven times tougher than phenolic resins. Toughness of the epoxy resin adhesives has been attributed to the greater distance between cross-linking points of the epoxy resin molecules.[4]

Although the epoxy resins are much tougher than the phenolic resins, they are still quite brittle if not properly modified with suitable flexibilizers or flexibilizing curing agents. Toughness is the opposite of brittleness; so the amount of flexibilizing modifier used in an epoxy resin formulation is quite important. Although hard brittleness is a problem, soft brittleness may also be a problem as far as strength of the adhesive material is concerned. If a formulation contains too much flexibilizing modifier, the formulation becomes soft cheesy brittle or like swiss cheese. When this happens, the resulting material is of no use because the tensile strength is very low and the material breaks with the slightest bend. If the ratio of the stress to strain is not within a reasonable balance, the material is considered to be brittle. As such, a material may have high tensile stress with low strain or a large amount of strain but low tensile stress. Somewhere in between, combining stress (strength) and strain (elongation), are the tough rigid adhesive compositions needed for most industrial applications.[6]

The toughness that is now shown in many of the industrial epoxy resin adhesives is brought about through other synthetic resins, which have a direct reaction with the epoxy resins. Thereby building toughness directly into the epoxy resin molecules.[6]

Some of the more important of these materials are the polyamide resins, polysulfide resins, and certain of the polyester resins. As an example, the polyamide resins are used as curing agents for the epoxy resin adhesives. Used in proper proportions, they impart the flexibility for the strain characteristics. While the epoxy resin gives the high tensile strength to produce an adhesive formulation with tremendous toughness.[4, 6]

The improved toughness of epoxy resin adhesives is needed to give the adhesive bonded joint greater peel strength, distribute the stress loading and stress concentrations due to thermal expansion of dissimilar bonded materials.[4]

High Adhesion

High adhesion is one of the most outstanding properties of epoxy resins. Their adhesive strength is brought about by the polarity of the molecules in the epoxy resin. This is also true for the cured resin system. The polarity of the groups within the epoxy resin molecules creates electromagnetic bonding forces between the molecule and the adjoining surfaces. The epoxy resins have high specific adhesion to metals, glass, ceramics, and most other materials except for a few of the thermoplastics and heavy metals. The epoxy resin adhesives can be formulated to give mixes of low viscosity, with excellent wetting, spreading, and penetrating action. When the epoxy resin adhesive is cured from a liquid or paste state to a solid state, there is very slight shrinkage. Therefore, the bonds initially established upon contact are preserved.[4, 6]

Consequently, the bond is stronger because there is less strain with in the glue line. Unlike the other adhesives, the epoxy resins give off no condensation by-products upon cure, such as volatile solvents or water, which make the assembly-line bonding with only contact pressures possible.[4, 6]

On a strength-to-weight basis epoxy resin compares favorably with those of other materials. When properly modified or reinforced, the epoxy resins are much stronger than most other materials on a strength-to-weight basis. Because of the epoxy resin's strength-to-weight basis, the excellent adhesion, and other desirable production characteristics, they have found uses in the aircraft industry.[6, 17]

The cohesive strength within the glue line and the adhesion of the epoxy resin adhesive to other materials is often so great that failure under stress occurs in one of the adherends, rather than in the epoxy resin adhesive or at the interface. This often happens with such materials as glass, aluminum, concrete, and wood.[6]

Many epoxy resin adhesive bonded joints have resisted shear stresses as high as 5,000 psi (pounds per square inch). While with steel to steel bonds it is possible under special conditions to obtain shear strengths of over 12,000 psi. Epoxy resin adhesives can be formulated with tensile strengths of more than 10,000 psi, flexural strengths of as much as 14,000 psi, and compressive yield strengths as high as 15,000 psi. Because of their strengths, epoxy resin adhesives are excellent structural adhesives. In many cases, they are superior to well established conventional methods of metal-joining, such as rivets, bolts, and welding.[4, 16]

Because of the high bonding strength and the relative ease of application of the epoxy resin adhesives, they have been established in many applications for bonding similar and dissimilar materials.[6, 38]

For bonding such dissimilar materials as plastics and metal, wood and metal, rubber and ceramics, etc., epoxy resin adhesives are unsurpassed by any other adhesive or fastening device. As with the similar materials, the dissimilar adherends, when bonded, need only a small amount of pressure or no pressure at all to obtain satisfactory bonds.[6, 38]

Low Shrinkage

The shrinkage of the epoxy resin upon cure is only a fraction of that of many adhesives. Epoxy resins differ from many of the thermosetting compounds in that during cure they give off no by-products and in the liquid state, the epoxy resins are highly associated to that of the cured resin. Cure of epoxy resins is by direct addition; and shrinkage is usually less than two per cent for the unmodified systems. This indicates that very little internal rearrangement of the molecules is necessary. The phenolic resins and the polyester resins, have reactions which give off condensation by-products upon cure and consequently have much higher shrinkage. With the proper modifiers, inorganic fillers within an epoxy resin formulation, the shrinkage upon cure can be further reduced to a fraction of one per cent. Also by bulk displacement, the filler materials in epoxy resin adhesives can possible improve bond strengths as much as 50 to 100 per cent by reducing shrinkage in the bonded joint.[4, 6]

Another important factor in shrinkage is heat. Epoxy resins have a high coefficient of thermal expansion, therefore heat can cause shrinkage problems in the curing of the adhesive bonded joints. Often the heat used with or produced by the curing reaction of epoxy resin adhesives will cause a differential thermal expansion between the adherends and the adhesive.

Thereby, upon cooling to room temperature after cure, internal stresses are developed due to the resin's shrinkage. The degree of shrinkage, of course, will depend upon the amount of heat used during the curing reaction and the volume or area of the adhesive bonded joint. Certain inorganic filler materials incorporated into the epoxy resin adhesive can be used to lower the shrinkage problem associated with heat. Epoxy resins can be cured usually at room temperature or with only moderate heat, therefore shrinkage and internal stresses due to the heat during cure is usually not a serious problem.[4, 6]

Thermal Characteristics

The thermal characteristics associated with the curing and with the use of the cured epoxy resin adhesives are important. The more important of these thermal characteristics are the thermal coefficient of expansion, thermal conductivity, service temperatures, and flammability.[4, 6]

A high thermal coefficient of expansion is characteristic of plastic materials. Plastic materials, such as the epoxy resins, typically expand, per-unit of temperature increase several times as much as metals. Thermal expansion, as previously discussed in connection with shrinkage of the epoxy resin adhesives, is important during the functioning life-time of the bonded parts as well as in its manufacture.[6, 16]

In the curing of epoxy resins thermal expansion results in two ways. First, heat is evolved "internally," by the curing reaction and the other is the heat evolved "externally", by the room temperature or directly applied heat to ensure thorough and/or faster curing.[4, 6]

Generally, the more reactive the curing agent, the greater the heat evolved during the curing process. While the slow reacting curing agents usually require directly applied or external heat sources.

This is to insure proper cure. This problem is best solved by using a curing agent with intermediate reactivity. The curing agents with intermediate reactivity gives more flexible control of the curing reaction and heat dissipation. This is particularly important where there is extreme differences between the coefficients of thermal expansion of the adhesive and the adherends.[4, 6]

The use of certain filler materials will slow the curing reaction and reduce the curing exotherm because of their diluting effect. In some cases, the metal filler materials will lessen curing exotherms and slow reactions by an increase in thermal conductivity, which helps dispense the evolved heat. This depends primarily on the type of fillers and their loading with the adhesive.[4, 41]

Many of the structural epoxy resin adhesive bonded joints must stand extreme temperature changes during its functioning life time. For example, the changes of the seasons of the year for weather exposed adhesive bonded joints can bring temperature changes of over a hundred-degrees-fahrenheit. Many of the industrial applications have much more severe conditions in temperatures and temperature cycling. These thermal effects can be destuctive to the rigid adhesive bonded joints where there is extreme differences in the thermal expansion characteristics of the adhesive and the adherends.[4,6]

For the most ideal conditions, the coefficient of thermal expansion of the epoxy resin adhesive should match that of the adherends. The filler materials are the most effective means in reducing the thermal coefficient of expansion of these adhesives. Fillers with low coefficient of thermal expansion, when mixed with the adhesive gives intermediate thermal expansion characteristics. Often though, because of the great difference between the coefficient of thermal expansion of the adhesive and the adherends, it is not possible to use ample filler materials without destroying other important properties. In these cases, more flexible epoxy resin adhesives should be used.[4]

Resinous modifiers in the form of flexibilizers and flexibilizing curing agents have done much to relieve the temperature cycling problems in epoxy resin adhesive bonding. These particular materials, when incorporated with or without fillers, can produce rubber-like flexible epoxy resin adhesives or the tough rigid adhesives of great strength. These flexibilizing materials absorb the internal stresses due to the expansion of thermal cycling and curing.[4, 6]

Also epoxy resin adhesive tapes and films, generally on a carrier material, such as fiber glass cloth have been used for the purpose of controlling thermal expansion. These materials are usually of the solid-latent or B-staged (partically cured to a dry state) type of epoxy resin adhesives. Their advantage is in that they absorb and spread the internal stresses of thermal expansion. This though, may be somewhat self-defeating, since they usually require high temperatures for completion of the curing cycle.[4, 41]

Low thermal conductivity of the epoxy resin adhesives can be a problem as well as an aid, especially in the curing process. Because of the insulating properties, often the internal exotherm upon curing of the epoxy resin adhesive is not readily dissipated. For this reason and for the adding of other desirable properties, the conductive metal fillers are often used. Generally though, because of the large surface area of the adhesive glue line, the exotherm buildup is readily absorbed by the adherends, especially if the adherends are good conductors.[6]

The epoxy resin adhesives also have low maximum service temperatures. In contrast with a number of structural materials in common use, epoxies, as most thermosetting plastics in general are best used at temperatures below the wood-char point of about 400 degrees fahrenheit. This is only an approximate statement, due to the varied conditions of actual use and the different combinations of temperature affected properties.[16]

The general purpose two-component epoxy resin adhesives are limited in heat resistance to about 350 degrees fahrenheit; depending on the resin, curing agent and curing procedure. While the more sophisticated adhesives composed of the highly cross-linked epoxy resins, such as both one-component and two-component systems, when properly cured may have heat resistant temperatures as high as 500 to 600 degrees fahrenheit.[35, 44]

Many of the one-component epoxy resin systems require curing at elevated temperatures of 350 degrees fahrenheit or higher. Both of the one or two-component systems usually give better heat resistance when they are cured with the aid of applied external heat. Also, many of the fast reacting curing systems do not initate complete cure because of cross-linking blockage during cure.[6, 38]

Epoxy resin curing reactions, unlike those of the polyesters are a step-by-step process and require more stringent conditions for "full" cure.[38]

Superior properties, such as inertness and mechanical strengths, are best realized when the resin is cured only with thorough cross-linking or the molecules. This is why some systems have better properties, such as heat resistance or high service temperatures and better mechanical strengths.[38]

Another important item in the heat resistance and service temperatures is that of the modifying materials. Many of the modifying materials, such as the flexibilizers, diluents and certain other additives tend to lower the overall service temperatures of the epoxy resin adhesives.[6, 17]

This is partially due to the fact that many of these materials themselves have lower service temperatures. Also, these materials often bring about incomplete cure by blockage of the internal crosslinking of the resin molecules. Some additives, such as the heat resistant phenolics, when properly incorporated can bring about higher service temperatures for the epoxy resin adhesives.[6, 17]

Much development has been directed towards boosting the heat resistance and service temperature of epoxy resins. With this, several new curing agents and resins have been developed which offer good strength retention at 500 to 600 degrees fahrenheit. With proper uses of these adhesives and other modifying materials, most problems of high service temperatures can be solved.[44, 35]

Epoxy resins, as other plastics, may be grouped with organic materials in the sense that they can be destroyed by fire. The epoxy resins though, through a special manufacturing process, can be produced which are "self-flame-extinguishing". By self-flame-extinguishing, if they should be consumed by flames, as soon as the flame source is removed the flaming epoxy resin will discontinue to burn. Presently epoxy resins can be manufactured with the use of bromine and/or chlorine to produce the self-extinguishing characteristics, while still retaining their other valuable properties. There are several of these adhesive products produced for use where fire may be a problem or where building codes require such materials.[4, 57]

Inertness

When properly cured the epoxy resins are very inert chemically. The tight cross-linking and composition of its molecules make the cured epoxy resin system invulnerable to caustic attack, extremely resistant to acids, and insensitive to water or moisture. This accounts for their rapid advance in the coatings field. This also aids the resin system in being effective barriers to heat and electrical current. Some of the other thermosetting plastics, such as the phenolic resins and the polyester resins, are easily broken down or disintergrated in present of certain caustics. For this reason, the chemical inertness of the epoxy resins is an important quality. This is enhanced by the dense, closely packed structure of the resinous mass, which is extremely resistant to the action of solvents.[4, 6, 11]

The inertness of epoxy resins can be a disadvantage as well as an advantage in adhesive bonding. Because of the cured epoxy resins extreme resistance to solvents, they are difficult, to almost impossible, to remove from adhering surfaces. Once cured, the epoxy resin must be soaked in special solvents for several days, even then the job may be very difficult. If the adherends are metals or other heat resistant materials, the easiest method may be to use heat for destruction of the epoxy resin. Often, it is less expensive to scrap the bonded parts. This problem is usually due to careless handling and can be eliminated upon recognition of the epoxy resins adhesive values and inertness.[4]

ADHESIVE BONDING WITH EPOXY RESINS

There are a great many obvious applications of adhesive bonding, such as labelings on materials, thin facing materials to plastics sandwich cores, and others. For these applications, adhesive bonding is the only logical joining method. The use of adhesives may offer many advantages even in cases where there is a choice of bonding methods. Some of the more outstanding of these advantages are listed below.[2, 34]

1. The joining of dissimilar materials.
2. The joining of thin metals together or to other materials.
3. The joining without piercing the adherends.
4. The joined parts provide for uniformly distributed stresses.
5. The joined parts are sealed against liquids and corrosion.
6. The adhesive joining of parts often provides for design simplification.
7. The joining of metals can be electrically insulated.
8. The joined parts often provide vibration damping and resistance.
9. The joined parts can give smoother surfaces and contours.
10. The joining of materials with adhesives often gives reduced production costs.[2, 12, 34]

Any particular epoxy resin adhesive formulation, or even a particular form of the same formulation, will have certain limitations. It is for this reason that the epoxy resins, as well as other adhesives, are formulated to meet specific application requirements. There are many ways in which a formulation or form of the same formulation can cause production difficulties. Some of the more important production difficulties that are often encountered are listed on the following page.[34]

1. Too short a shelf life or pot working life.

2. The wrong form for a particular production application procedure.

3. Curing time is to slow for a particular assembly production equipment.

4. Requirements of pressure and/or heat not applicable to existing production equipment.

5. Adhesive chemically reacts to deteriorate the adherends, or to weaken the adhesive bond.

6. The wrong kind of strength properties, such as high peel strength where high shear strength is needed, and vice versa.

7. Poor resistance to heat or other environment to which the bond is exposed.

8. Too high of a quality for a particular application, therefore too expensive for production.[12]

The particular problems as listed above do not necessarily exclude adhesive bonding with epoxy resins. These problems can generally be solved by proper evaluation and careful selection of the adhesive formulation for the specific application requirements. Often the problem is in the joint itself and not necessarily the epoxy resin adhesive being used. In this case usually redesigning the particular adherends to be bonded will yield satisfactory bonding requirements. For example, if the problem is in the peel strength being to low, possibly the parts design should be changed to bring about less peel stress and more shear stress. Problems of this type are common and can be solved by properly analysing the adhesive joint to be bonded. Also stress testing of experimental specimens is necessary for most structural applications.[5, 34]

There are problems that do exclude adhesive bonding. These problems are easily recognized by knowing the properties of epoxy resins and especially the properties for the particular epoxy resin adhesive being used.

The particular applications that might possibly exclude adhesive bonding with epoxy resins are as follows:

1. Insufficient adhesive bonding area of the adherends.

2. Very high service temperatures, which would cause decomposition of the epoxy resin.

3. Adherend composed of materials of which the epoxy resin will form poor bonds (certain thermoplastics and some of the heavier metals).

4. Exposure of the adhesive bond to certain harsh solvents and certain other similar materials.

5. Extreme fluctuation of service temperatures causing deterioration due to thermal expansion.[4, 6]

There is always the possibly, though unusual, that the requirements of the produced materials, production procedure, various strengths, and environmental resistance, may each demand the best that is possible from all epoxy resin adhesives. No one epoxy resin adhesive or any other adhesive can satisfy such a demand. In any adhesive formulation certain of the necessary properties are obtained only at the expense of other properties. There usually has to be compromises which prove satisfactory in a majority of the bonding applications. At the present time many of the designers are "over-designing" or "overspecifying" the required properties of adhesive bonded joints. In the field of adhesive bonding, such practice is not "safety" but is only demanding compromises that are unnecessary. The reason for this may be a poor understanding of the adhesives, such as epoxy resins or a distrust of bonding. Also, there may be a feeling that testing procedures are not completely accurate. A number of standard tests of the adhesive bonds for structural purposes have been defined by the American Society for Testing Materials (ASTM), and military specifications exist for specialized testing of the structural adhesives. There still is a lack of methods for satisfactory evaluation of bond properties on a production basis.[5, 34]

The adhesive suppliers usually have reports based on experimental testing. These are usually determined by general screening tests, such as tensile shear strength at normal or elevated temperatures. These specific strength values for test specimens cannot be readily translated to other geometrical shapes or to different areas of bonding materials. Also, these strengths are determined by short time tests which do not give an indication of behavior under either continuous stress or under different environmental conditions.[34]

The presently envolved methods of quality control of the epoxy resin bonded parts depend highly on statistical testing analysis of results obtained from destructive tests. Ultrasonic and special equipment is used in a few applications. Until a satisfactory method of nondestructive testing has been developed for a rapid and wide spread usage, the quality will actually remain under control of the technicians applying and curing the epoxy resin adhesives.[34]

Recently, there has been a method devised for analysing the time and degree of cure for epoxy resins. This method uses small pieces of the epoxy resin in the form of a thin film or casting which is then used for infrared spectrophotometric analysis. These resin films and castings are under similar conditions, as the epoxy resin is in production. This system directly correlates the degree and rate of cure of the epoxy resins with the physical measurements of the production materials. This method has been primarily used in the casting field but similar devices may soon be produced for use with the epoxy resin adhesives.[33]

The ASTM has established the following tests specifications which are presently being applied to adhesive bonds. They are listed on the next page.

1. Cleavage -------------------------- D1062-51
2. Flexure --------------------------- D1184-55, C393-57T
3. Impact ---------------------------- D950-54
4. Peel or stripping ----------------- D903-49, D-14T
5. Shear (tensile loading) ----------- D1002-53T
6. Shear (compressive loading) -------- D905-49
7. Tack range ------------------------ D1144-51T
8. Tension --------------------------- D897-49, D429-56T
9. Thermal cycling ------------------- D1183-55T, D1057-56T
10. Adhesive Definitions -------------- D907-55[34]

These are methods of quality control which is based primarily on the statistical analysis of destructive testing results. There can be wide variation from the testing to the actual application in a production procedure. It must be realized that these testings are of great importance and in most cases the testing of adhesive bonds are satisfactory.[34]

Classification

Adhesives usage can basically be classified as structural or nonstructural.[2]

The nonstructural adhesives are those which are not expected or not capable of supporting any appreciable loads. These are usually only required to locate parts in an assembly, or to give temporary bonds to specially placed parts. Probably the best definition of the nonstructural adhesives is that they hold by bonding only "dead load" (loading applied only by the weight of the part being held with no external forces) and should never have live loading applied, unless the adhesive is actually capable of such loading.

In this case, the adhesive would actually be a structural adhesive.[2]

The structural adhesives are those which are applied where extremely strong bonded joints are required. These types of adhesives can be expected to encounter large stresses tending to separate the parts or cause the joint to fail. The epoxy resins are basically thought of as structural adhesives in that they are capable of holding both "dead" and "live" loads for sustained periods of time.[2]

In the structural adhesives there are two very important qualities to be considered, which are adhesion of the epoxy resin to the adherends and the cohesion with in the glue line between the adherends. In these considerations, the epoxy resin adhesive is excellent. When the epoxy resin is properly cured, the cohesive strength within the glue line is so great and the adhesion to other materials so good, failure under stress often occurs in one of the materials being bonded rather than in the epoxy resin adhesive or at the interface. This often happens with such materials as glass, aluminum, and many of the weaker materials, such as concrete and wood.[6]

Resin Forms

In using epoxy resins for adhesive bonding, first the form of the adhesive must be considered. These adhesives are basically of two forms. They are the two-component epoxy resin systems and the one-component epoxy resin systems.[39]

The one-component epoxy resin systems are ready prepared materials which only have to be applied to the adherends to be bonded.[39]

The two-component formulations are the most widely used of the epoxy resin adhesives. These are termed two-component systems because a hardener is added to the resin before curing will take place.[4]

The two-component epoxy resin systems are basically two types, liquids and pastes. The paste type of epoxy resin adhesives are usually prepared as far as the installation of modifying additives and reinforcements. These have been incorporated during the manufacturing process. These additive materials generally include fillers and thixotropic agents, but any of the additives or reinforcements can be added during the manufacture of the epoxy resin adhesive. The pastes are generally prepared for general purpose applications, such as bonding aluminum, concrete patching, bonding plastics, etc.[4]

The two-component liquid epoxy resins are available in a wide range of viscosities, which makes possible for the individual that is applying the adhesive to prepare his own special epoxy resin adhesive formulation. This is accomplished by adding the additives and/or reinforcements to the resin mix. These may be fillers, flexiblizers, colorants, thixotropic agents, and many others. They are discussed further in the section, "Additives and Reinforcements".[4]

There is an advantage in being able to prepare the epoxy resin mix to suit certain adhesive requirements. This is especially true for the individual or group that understands the properties of the adhesives and the additives to be added to the resin mix. They also have to understand what changes the additives will have on the physical properties of the epoxy resin adhesive. Often the user does not fully realize the change these additives will make on the final cured adhesive, which can create a problem. Sometimes because of the expense of the resin, the fillers will be added in excess. Diluents may also be incorporated so more fillers can be placed in the epoxy resin mix. This usually not only destroys many of the resins valuable properties, but may also destroy the resins adhesive qualities.

It is recommended that the special additives should only be incorporated into the epoxy resin adhesives for structural applications by skilled individuals with experience in using epoxy resin adhesives.[4]

Two-Component Preparation

In the two-component epoxy resin systems, the properties of the cured adhesive joint are very dependent on the thoroughness of the mixing operation and the proportions of the ingredients. If cured bonds are to be obtained which have uniform properties throughout the joint and are uniform from piece to piece, it is necessary that the ingredients be measured and proportioned very accurately and be mixed thoroughly. When specific information is not present on varying the mixing ratios, it is usually satisfactory to weigh the ingredients to within less than one per cent of the recommended weight of each ingredient. In the preparation of rather small batches of adhesive which call for small percentages of certain ingredients, the permissible error in the weighing may be much larger. This depends on the strength required of the bonded joint. But when preparing larger batches for production use, it is desirable to employ accurate scales or precise proportioning pumps in dispensing the ingredients for mixing.[6]

Many of the epoxy resin adhesive compounds are difficult to stir and mix, especially if they are of the paste type. There is always a possibility that a small quantity of the curing agent can remain in the corner of the stirring apparatus and may not be mixed into the mass being stirred. This unmixed portion may be spread on the surface to be bonded, where it may harden prematurely. Thus, the remainder of the mass may be deficient in the curing agent and consequently may cure very slowly or not at all.

Generally though, this problem is only with a very few of the curing agents and is most likely to happen with catalyst type curing agents because of the very small quantities used in the mixing. The result may be a weak or incomplete bond. The most difficult to mix thoroughly are the more viscous adhesive mixtures. Extended mechanical stirring can cause air to be entrapped in the mixture. The air bubbles will act as stress-concentration points in the cured adhesive film. Special machinery for metering, mixing, and dispensing the adhesive can be obtained to avoid the problems of air entrainment and the lack of time when mixing short pot-life adhesives. The special equipment stores the hardener and the primary resin separately, so only enough for immediate use is mixed. The mixing process occurs at the nozzle in order to avoid the presence of catalyzed resin in the machine.[6]

The measuring and mixing of the epoxy resin adhesive components is critical for complete cure and development of desirable properties. The proportioning of the ingredients basically depends on the type of curing agents involved. Some of the curing agents can be varied widely, while others have to be kept within strict ratios or valuable properties are lost. Usually, the manufacturer or supplier will supply the needed information on the accuracy to which a given epoxy resin adhesive should be proportioned and mixed.[4]

Preparing Adherends

Sometimes the epoxy resin adhesives fail to bond properly in seemingly random areas of a bonded joint. An explanation of these inconsistant results is the presence of foreign materials, such as absorbed gases, oil, water, or other waxy materials on the surface of the part. Even if only in one molecular layer in thickness, foreign matter can prevent proper bonding of the adhesive.

For structurally sound adhesive bonded joints; cleaning, handling, and storing techniques are often needed to obtain reproducible results because waxy substances and other foreign materials are often difficult to remove and are not usually visible.[6]

One cleaning method for the weaker and more porous materials is a light sandblasting or abrading the joint area of the adherends with silicon carbide paper. This will create a fresh, clean surface on most of the non-metallic materials. Sandblasting, wire brushing, and roughening with emery cloth are widely used as a preliminary treatment to remove scale and oxides, especially for metallic adherends. With these methods, it is the absence of foreign materials rather than surface roughness which increases bond strength. When bonding metals, one cleaning process recommended in the cleaning procedure is the wiping with a cloth saturated with toluene or methylethyl ketone, followed by trichloroethylene vapor degreasing. In the cleaning process for metals, an acid bath is commonly used to etch the metal surfaces of the adherends prior to adhesive bonding. A typical treatment for aluminum and some of the aluminum alloys is immersion in a sodium dichromate sulfuric acid solution. The temperature of the solution must be about 150 degrees fahrenheit. The metal must be kept in the solution for about ten minutes and then is followed by agitated rinses with cold and/or hot distilled water.[2, 4, 6]

Some metals and metal alloys, such as titanium, stainless steel, and magnesium alloys, require quite elaborate cleaning operations. These cleaning precedures usually involve such materials as solvents, detergents, acid etches, and other chemical applications. The cleaning processes may involve ten or more steps in the cleaning procedure with generally hot and/or cold distilled water rinses between each step for most of the cleaning operations.[2]

When cleaning rubber surfaces for adherends, the surface should be sanded or roughened with a scraper or special sanding. Then the rubber adherend surfaces should be cleaned with a cloth saturated with naphtha and followed by a sulfuric acid immersion. The last step in this cleaning process is thorough washing with distilled water and drying.[2]

The water-drop test is a quick and reliable method of determining surface cleanliness. It has been proven in experiments that good adhesive bonds usually result when a water drop, deposited on the clean surface prior to adhesive application, spreads out into a very thin layer. The water drop would remain in a globular form, if the adherend surface is contaminated with waxy or other similar foreign materials. To avoid leaving a deposit on the surface of the adherend, distilled water should always be used in the test.[2, 6]

Because of the great number of possible adherends, there are a great number of cleaning methods and variations of ordinary cleaning methods. Often elaborate cleaning operations for certain adherends, such as most metals, can be considerably shortened by using specially prepared cleaning materials and chemicals. Generally the best results can be gained by obtaining detailed cleaning recommendations from the manufacturers, or suppliers.[2]

Application

Adhesives for structural bonding are generally supplied as pastes, liquids, sticks, powders, films or tapes. Adhesives are usually applied in liquid form or are liquified at some stage in the bonding process for proper spreading and curing. If liquid adhesives are of low viscosity, they are applied by brush, dip, spray, or roller coating. Higher-viscosity liquids may be applied by spatula, calking gun, or knife. It is possible in some designs to inject the adhesive into the closed joint under pressure.

Film adhesives are one-component systems which are often preimpregnated glass fabrics, the cloth acting as a reinforcement and a carrier. This type is cut to size and laid in place on the joint and is "B-staged" or partically cured, which is usually tack-free to allow easy handling. Automatically the film adhesives assure a uniform-thickness glue line through out the joint. This type is somewhat different from unimpregnated glass-fiber mat or cloth, which can be laid in place after the adhesive has been spread on the part. Under certain circumstances unimpregnated and preimpregnated materials can improve the adhesive load strength while at the same time acting to insulate the joint. In some instances adhesives must be applied to vertical surfaces, and in these cases the tendency of the adhesive to flow downward can be a problem. To allow more time for application and permit more uniform spreading, the use of higher-viscosity or thixotropic paste adhesives can be used.[4, 6, 39]

For a powdered one-component adhesive, the application technique is somewhat different. The powdered epoxy resin adhesives make possible a sprinkling technique, in which the powdered material is sprinkled from specially designed containers. This type of adhesive is usually applied to heated surfaces or to cold surfaces, which are then heated for the final curing.[6, 39]

The stick types of epoxy resin adhesives are applied to hot surfaces. The heated surface liquefies the portion of the stick that is in direct contact with the adherend surface leaving a coating of adhesive. Usually both adherends are then placed in contact with additional heat, which completes the final curing. Both the powdered and the stick adhesives are easily employed with metal adherends because of the heat conductivity of these materials.[6]

A significant effect on the strength of the joint is the uniformity of the film spread on the surface of the adherend to be bonded.

Voids, which act as stress raisers under load and weaken the joint, can be caused by any air entrapped within the adhesive bond. It may be impossible to assemble the joint, without entrapping air in the joint, if the adhesive is not distributed uniformly. If the adhesive lies in ridges along the edges of the joint, it is unlikely that all the air can be squeezed out of the joint. The horizontal flow of the adhesive in this area is slight, since the air is trapped near the center of the bonded area. Accordingly, the bubble can not be eliminated but can be made thinner by pressing the joint. In contrast, the condition of the adhesive being spread thicker in the center of the bonded area will be of great assistance in excluding air from the joint. In this case, before the rest of the areas make contact as the joint is assembled, the mound crests touch first. Thus, excluding the air from the joint as this contact area is spread.[5]

To cover the mating surfaces adequately, sufficient adhesive must be applied. The general recommended glue line for epoxy resin adhesive bonding is .004 to .008 inch in thickness. With approximating these thicknesses there usually will be no significant variations in the bond strength.[5]

Some manufacturers recommend a wider range in the thickness of the adhesive glue line, but this depends primarily on the adherends and the type of epoxy resin adhesive being used. For certain adherend materials, the supplier or manufacture usually gives recommendations on the adhesive glue line thickness.[2]

To insure that no starved areas exist, allowance should always be made for sufficient adhesive squeeze-out. The excess adhesive is sometimes scraped from the adherends for neatness in the finished product. It has been noted in some tests that the squeezed-out adhesive material acts somewhat like a fillet in a welded joint, by helping to reduce stress concentrations.

It is possible to have strength reductions of 15 to 30 per cent, when flash is removed by grinding from butt joints between glass-fiber-reinforced plastic and stainless steel. Most often, it is desirable to allow the flash to remain as a fillet and thereby strengthen the joint.[2, 5]

The application technique, whether it be one or two-component system, depends primarily on the number of adherends to be coated, their shape and size, and the availability of equipment already on hand. With most methods equally good results can be obtained, provided that the proper epoxy resin adhesives are selected, the parts are properly prepared, and the manufacturers' recommendations are followed.[4]

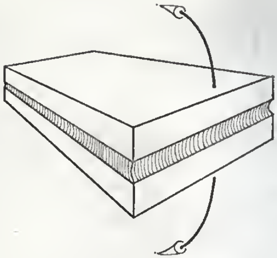
Joint Design

In establishing a design for the construction of an adhesive bonded joint, there should be an understanding of the adhesive, of the adherence to certain fundamentals in the use and of the stresses involved. Basically in adhesive bonded structural design there are two fundamentals that should be observed.

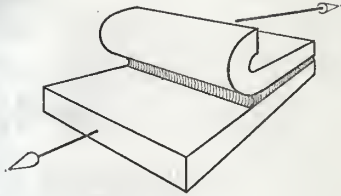
1. Put the stress loading on a maximum area of the bonded joint.
2. Employ good joint geometry in the joint design.[34]

In structural bonding, the four basic types of stresses encountered are tensile, shear, cleavage and peel. The above stresses illustrate the first fundamental. These stresses are shown pictorially in figure number three, page eighty two.[30, 34]

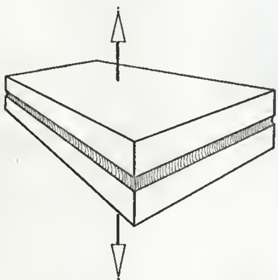
When tensile loading is applied, the force directions are perpendicular to the plane of the joint. Thus, the forces are distributed uniformly over the entire bonded area.



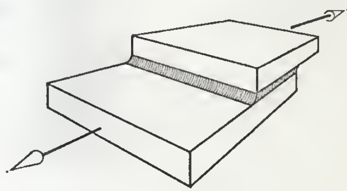
A. Cleavage



B. Peel



C. Tensile



D. Shear

Types of Basic Structural Bonding Stresses.

Figure No. 3, ref. 30, 34

At the same moment the entire joint is under stress and all the adhesive is at work at the same time. When using this type of bonding no portion of the joint carries more or less than its share of the load.[5, 34]

In shear loading the stress is also distributed uniformly over the entire joint; and all of the adhesive works at the same time. One thing that must be kept in mind is that in shear loading, the stress is parallel to the plane of the joint. Because this type of bonding is more practical to structurally apply it is most frequently used.[5, 34]

In using cleavage loading, not all of the adhesive is at work at the same time. When applying force, one side of the joint is under great stress while the opposite side is under no loading stress. For this reason, this type of joint cannot be as strong as a joint of comparable area under tensile or shear loading, and is not advisable for structural uses.[34]

In using peel loading, the stress is confined to a very fine line at the edge of the joint. Because of this, very little of the adhesive contributes to the strength. Most adhesive is under no load stress and for this reason, this type of joint design should be avoided.[34]

Joint Geometry

Rarely will a joint be subjected to only one stress as indicated in the section of maximum area. Usually in practice, there is a combination of several different types of stresses. Distortion of adherends under load, in some cases, will introduce secondary stresses. When this happens the second fundamental, favorable joint geometry, becomes important. The following are typical joints used in adhesive bonding. These are listed on the next page.

1. Lap joints
2. Butt joints
3. Stiffener joints
4. Corner joints
5. Coaxial joints
6. Gap joints
7. Fillet joints[2, 34]

Lap Joints. The lap (or shear) joint will be the most frequently used in adhesive joint design. This is because most bonds involve thin gage material, which are difficult to join by any other design except the lap. Also, lap joints are very practical and applicable to adhesive bonding.[2, 34]

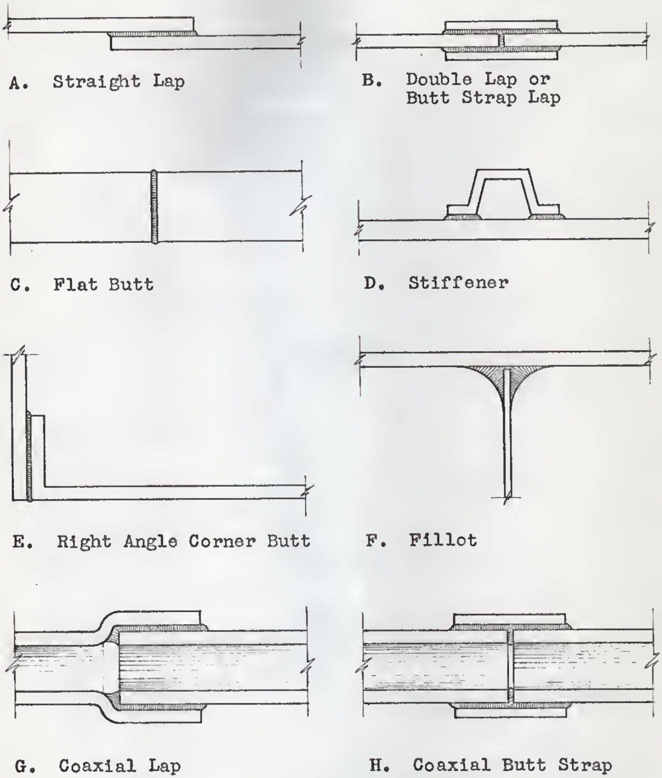
Shear forces are not in line in lap joints because of the offset structure of the design. This may result in the introduction of cleavage and peel stresses, which should be avoided if possible.[34]

When under moderate load, distortion of the joint may occur because the bond area will pivot normal to the load. An element of cleavage is introducted at this point. When an extreme load is applied, causing fatigue, definite bending of the material at the edges of the bond takes place. Because material distortion results in secondary stresses, peel stresses are introduced. When this occurs the joint should be redesigned for maximum strength. Three alternates are suggested as follows:

1. Redesigning the joint, to bring the load on the adherends in line.
2. Making the adherends more rigid near the bonding area to minimize cleavage.
3. Making the edges of the bond area more flexible for better conformance, thus minimizing peel. [34]

There are different types of lap joints that can be used more efficiently than the straight lap joint. The beveled single-lap joint is more efficient because it allows bending of the joint edge when distortion occurs under stress. The double-butt lap joint places the adhesive line in the same plane as the shear stress on the adherends and requires machining which is not always feasible with thin-gage materials. The double-scarf lap joints have better resistance to bending forces than double-butt lap joints, but it also presents machining problems. The most practical joint is the joggle lap joint. Because of the placement of the adhesive line in the same plane as the shear stress on the adherends, the application of pressure for curing is easily accomplished and the joints can be formed by simple operations. The double lap or butt strap joint is still another possibility. This joint employs the use of two-strap type secondary adherends, which places the two adhesive lines in the same plane as the shear stress on the primary adherends. Generally, the total secondary adherends cross-sectional area should be greater or at least equal to the cross-sectional area of the primary adherends. The two adhesive lines also must be of the same thickness or eccentric loading will develop, causing premature failure of the joint. Because of this, the joint can be difficult to construct. Figure four on page eighty six gives pictorial examples of several joint design possibilities.[5, 31]

Butt Joints. Being weak in cleavage is the disadvantage of the straight butt joint. But in the case where two flat, rigid rod ends are butt-joined with an adhesive; any bending of the rods can, through leverage, exert tremendous cleavage forces on the joint. Because of this, recessed joints such as landed scarf tongue and groove, conventional tongue and groove, and scarf tongue and groove are recommended.



Typical Joints For Adhesive Bonding With Epoxy Resins.

Figure No. 4, ref. 2, 5, 34, 43

Adequate clearance to facilitate machining and assembling operations are required by this type of joint. Thus, for butt joint assembly, adhesives with void-filling properties are required.[2, 34]

Groove joints and landed scarf tongue have the advantage of acting as stops, which can be utilized to control the adhesive line thickness. While on the other hand, scarf tongue and groove joints make assembly easier, in that self-aligning takes place when tongue and groove are joined.[34]

Stiffener Joints. The problems of "oil canning", waviness and flutter are usually encountered where large areas of thin gage materials are used. Stiffening of such surfaces is a desired property; which can be efficiently and economically accomplished by adhesive bonding stiffening members to the large areas. When attaching the stiffening members to thin metal sheets, common in aircraft construction, the sheets deflect in service and peel stresses are exerted on the adhesives. Minimum difficulty from peel will result, if the flanges on the stiffening section can deflect with the sheet. Either reducing the stiffness of the flange on the stiffening section or increasing the stiffness of the flange will result in improvement.[34]

T-sections, hat sections and corrugated backing are several types of stiffening members, which are commonly used. The bonding of the T-sections is the simplest to accomplish. The more commonly used are the hat sections because they have excellent rigidity. For excellent flatness over the entire area, corrugated sections bonded to the facings give the best results.[34]

Corner Joints. It is possible to adhesive bond the corners of products made of light gage steel or cored sandwich panels by some joint redesign. Because it produces either cleavage or peel stresses, the usual right-angle butt joint used for mechanical attaching is not applicable for adhesive bonding.

But by using the supplementary corner reinforcement attachments, the panel construction design can have adhesive bonding and also sealed joints. Slip and right-angle support joints are the typical designs for adhesive bonding. These joints will give the resultant structure and increased degree of rigidity.[34]

The use of a supplementary corner extrusion is best in a slip joint. This extrusion can be as heavy as the desired rigidity demands. The edges of the part are bonded into the slip joint. A variation from the slip joint is the use of exterior and interior right angle supports. However, it must be kept in mind that this method requires indexing fixtures until adhesive is cured.[34]

Because of the complicated pressure fixtures required, film adhesives for these applications are not too successful. Adhesives with void-filling properties, such as epoxy resin containing much filler materials, are frequently used. The heat-curing epoxy adhesive can be used but it depends upon the heat resistance of the components being bonded.[34]

Rigid corner joints are used when joining rigid members, like storm doors or decorative frames, and can also be adhesive bonded. Because of inherent racking or twisting stresses butt joints can not be used in these cases. Woodworking adhesive joint design, such as end lap, mortise and tenon, and mitered joint with spline, can be utilized in order to make available the required bond area to resist such stresses.[34]

End lap joints are simple to apply but require machining. For this type of application adhesives requiring pressure can be utilized. Mortise and tenon is an excellent type of joint, but also requires machining. If the members being bonded are hollow extrusions a mitered joint with spline should be considered.

Usually the spline is die cast to loosely fit the interior of the extrusion. In the above case, a void-filling adhesive is also indicated.[34]

Coaxial Joints. The coaxial joints are used to attach tubing or pipes. These joints usually require the use of either gap-filling adhesives or close tolerances on the adhesive line thickness dimensions. Excessive clearances of the adherends should be avoided for these joints, or the joint will be considerably weakened.[2]

The coaxial joints may be divided into basically two classifications; which are lap and butt strap. These joints are shown in pictorial form in figure four on page eighty six.[2]

Gap Joints. The gap joints are considered to be joints fabricated with very thick adhesive lines. They may be of any configuration in joint design. In these joints, generally the adhesive is required to fill large voids in the joint construction. These joints usually have reduced strength, due to the internal development of stresses such as cure shrinkage and thermal expansion. These problems may be partially reduced by using highly filled epoxy resin adhesives. Eccentric loading is also another important problem with the gap joints, especially for the lap type of gap joint. Basically, the gap joints should not be used in highly stressed applications.[2]

Fillet Joints. The honeycomb core sandwich constructions have brought about the use of fillet joints. Since the honeycomb cells are manufactured of very thin materials, they provide quite small cross-sectional areas for bonding to the skins. For this reason, unless the sides of the cell walls are employed in the bonding, weak facing-to-core bonds will result. In the fillet joints the adhesive forms a fillet, fastening the skins to the sides of the cell walls. The compact triangular-shaped "T" fillets are the most efficient. A typical joint is shown in figure four on page eighty six.[2, 43]

The epoxy resin adhesives can develop terrific strengths, but only if applied in a correct manner. There must be complete consideration of the stresses to be placed on the bonded joint, thereby bringing about the configuration design. The joint design should utilize the maximum area, while at the same time using the epoxy resin adhesive and cohesive strength to the highest degree, through the use of good joint geometry.[5]

USES OF EPOXY RESIN ADHESIVES

The epoxy resin adhesives have established several substantial uses in architectural construction. Although many of these uses do not have the glamorous connotation as usually attributed to plastics uses, they still are very important and justifies their use in architectural construction. Probably the most publicized and accepted use of the epoxy resin adhesives is in the flooring field; where they have been used as a mortar to bind together a variety of aggregate materials, to establish durable and decorative floorings. Also, the aggregate-epoxy resin mixes have been used to make decorative panels, facings for masonry building units, and a variety of similar building materials. In the same area the epoxy resin mortars have been used in bonding together masonry units, such as concrete block and ornamental tiles.[45]

Because of the epoxy resin adhesives strength and durability they have found many uses in concrete construction and repair. Fresh new concrete can be bonded to old concrete and damaged concrete structures can be repaired, giving joints stronger than the concrete itself.[59]

Among other uses are the construction of sandwich panels and bonding of dissimilar materials to concrete, masonry, steel, etc.. Many uses in the bonding of similar and dissimilar materials at the present time are in experimental stages.[2]

Epoxy Resin Mortars

The epoxy resin mortars may be used to construct terrazzo floorings. These are filled epoxy resin formulations containing stone chips. This epoxy resin terrazzo material compares favorably with the conventional type.[40]

In comparison with conventional terrazzo flooring, the epoxy resin mortar replaces the portland cement as a binder or matrix for the sand and marble chips. Then the epoxy terrazzo composition is simply spread on the floor to be covered, in layers from 1/4" to 3/8" in thickness. After the placement, it can be hand or power trowelled for even spreading. It is then usually left overnight to cure and ground to a smooth surface the next day. From the original 1/4" to 3/8", it is ground down to approximately 1/8" thickness, as contrasted to the two to three inches thickness required for conventional cement based terrazzo.[14, 40]

There is a large weight saving in using epoxy terrazzo instead of the conventional cement terrazzo. This is because of the lightness in weight of epoxy resins; and the fact that it requires neither as thick an application nor as heavy a subflooring as conventional terrazzo does. Consequently, this gives wide possibilities for using the epoxy resin terrazzo on the upper floors of the high rise buildings which previously could not sustain the large weight load of the convention terrazzo materials. Also the reduced expense, due to the weight savings can result in epoxy resin terrazzo's use in remodeling existing buildings.[54]

Other assets of this epoxy resin material include more flexible and decorative design through easy coloring of the epoxy resin binder and its adhesive values for vertical surfaces.[8, 40]

Because of the chemical resistance of the epoxy resin, the terrazzo can be applied to bathrooms, laboratory floors, and other similar applications. Also, with the epoxy resins toughness, the terrazzo does not crack as easily as conventional cement terrazzo. With these valuable properties, the epoxy resin terrazzo should find many new applications as well as replace some applications of the conventional cement terrazzo.[40, 45]

Also, these epoxy resin terrazzo compositions can be purchased in the form of tiles. These are manufactured in nine inch by nine inch dimensions, with thickness generally 1/8" or 3/16". The terrazzo tiles are similar to the epoxy resin terrazzo's applied at the construction site, except these may be bonded to floors or walls in a similar manner as the conventional asphalt, asbestos, or vinyl tiles. With this installation, flexibility and their decorative appearance, many interesting applications should be available in the near future.[40]

Similar to the epoxy resin terrazzos, epoxy resin aggregate mixes are also being used to prepare wall panels. They can be smooth, marble like surfaces or have a rough exposed stone aggregate appearance. These panels are manufactured similar to the terrazzo, except the finish surface does not have to be ground smooth. Through the selection of proper formulations, aggregate types and aggregate sizes, a wide variety of designs are possible. To further enhance the panels appearance, there are a great variety of colorants and fillers which can be incorporated into the epoxy resin adhesive binder.[14, 54]

With proper reinforcements and panel thickness, the decorative panels can be self supporting for either exterior or interior construction applications. These panels may also be backed with hardboard, particle board, cement asbestos board, plywood, and various insulating boards. Another special fabrication would be use of the terrazzo like panels as facings for sandwich panels, which could be used in curtain wall constructions.[54]

Another use for these terrazzo like materials is for use as counter tops, furniture tops, window sills, or stair steps. These materials would be in the self supporting state, constructed in possibly thicker sections for fabrication in smooth marble-like finishes.

While these uses, such as furniture tops and window sills, would be primarily for decorative purposes, chemical-resistant slabs formed with epoxy resin adhesive binders serve functional purposes in laboratory furniture.[54]

Other significant applications of epoxy resin adhesives are for fastening marble or tile to wall surfaces. Many epoxy resin mixtures with decorative qualities can be obtained by use of decorative stone chips, glass beads, cruched tile, and many others. These compositions are well suited for site application work as well as for the factory applied finishes of concrete block and structural tiles. Practically any suitable material can be bonded to these masonry building materials as well as many other similar building materials at the point of manufacture, so that the masonry unit when set in place provides a finished interior or exterior wall surface of pleasing design.[45]

Epoxy resin mortars or aggregate binding formulations are also finding uses in the area of industrial floorings. There are several hard-surface floor toppings which involve the use of epoxy resins. Non-skid surfaced toppings which involve the use of epoxy resins, are made by applying a 1/8" to 1/4" layer of the epoxy resin formulation to a floor base and evenly spreading abrasive materials over the resin surface before curing takes place. Some of the materials commonly used for these high-friction toppings are fine particles of flint, aluminum oxide, silcon carbide, emery or sand.[8, 9]

Smooth epoxy resin toppings for surfacing and finishing are used for protection against heavy traffic and stains due to chemical spills. These toppings are produced by blending dry salt free sand and white portland cement with epoxy resin formulations. This composition is trowelled over a base floor or wall surface primed usually with an epoxy resin primer, to a thickness which may range from 1/8 inch to 1/4 inch. These surface toppings may be colored by adding colorants directly to the composition before application.[8, 9]

Basically, the epoxy resin mortars or aggregate binding formulations can replace most of the commonly known uses for the conventional cement mortars. Except for heat resistance and material expense, these epoxy resin compositions give a much greater range of desirable properties than is possible to obtain from the conventional cement mortar materials.[14]

One unusual use for epoxy resin adhesives is its use as a mortar to bond together masonry units. The epoxy resin mortars have successfully been used for this purpose. Because of the strength of the epoxy resin, these mortars have strengths that exceed the usual masonry units. It is estimated that the strength of these epoxy resin mortars is about twenty times as strong as conventional mortar.[9, 55]

Because of the expense of the material, maximum economy can be best gained by using a mortar bead or layer of just enough to make the joint only 1/16" thick when the blocks are set into position. The best result with the epoxy resin mortar have been in using an 1/8" joint rather than the 1/16" layered joints. These mortar joint requirements produce a mortar joint which eliminates tooling and lessens the probability of leaving mortar droppings, which would have to be cleaned away later. The epoxy resin mortars produce a completely waterproof joint because of their inertness. In order to obtain the joints, the horizonal and vertical face shell areas of each block should be ground, to afford the mortar layer an even, uniform contact with the block. This is especially true for the 1/16" mortar joints.[55,56]

It has been estimated from experimental trials by the manufacturer and block producers; that horizontal face shells can be ground on a machine grinder at an approximate rate of two hundred, eight inch concrete blocks per hour. This in turn gives an approximate cost of about three or four cents per unit.

Though the horizontal surfaces can be ground quite easily, it is some what more difficult to grind the vertical surfaces of the joint faces on a machine grinder.[56]

Generally, the critical part of the block is the horizontal face shells. Usually the top and bottom bed face shells have been formed by a flat plate, creating a smooth surface, and it can be used, if the deviation in height of any block does not exceed half the thickness of the desired 1/16" or 1/8" of the mortar joint. In the 15 inch length grinding is not required. Variations in the gradation of the aggregates used in the concrete block will determine the amount of grinding which is necessary to give the even, uniform contact between the joint faces which is desired.[56, 63]

The mixed epoxy resin mortar can be applied to the block face shells with a trowel, putty knife or caulking gun. These epoxy resin mortars are usually in two-component forms which can be mixed in a disposable pail with an electric mixer or mixing paddle. One particular manufacturer of the mortar uses a disposable plastic bag for the mixing, which also serves as an extruder tool for application. When finished or emptied the bag is discarded. A caulking-type gun is probably the most expedient method of applying the mortar. This is because the mason laying the block can apply an even head of mortar completely along the length of the wall to be laid with block. Also, the vertcal joint faces of several of the block can have the mortar applied before the actual installation. This primarily eliminates the length of time for mortar application, which is very time consuming in masonry construction. Actually the speed of construction with the use of the epoxy resin mortar would actually be limited only by the mason's ability to lift and place the concrete blocks manually into position for bonding.[55, 56]

It is possible that the epoxy resin mortars, because of their strength, might have a high potential use for concrete block masonry tilt-up panels. This would have considerable bearing on the strength, weight and/or possible reinforcement of the individual concrete blocks.[8, 56]

The high strength, impermeability, and durability of the epoxy resin mortars should be popular for use in basement wall construction with concrete blocks. Also, because of the shrinkage involved with ordinary masonry cement, there is often much cracking within the joints. The epoxy mortar would eliminate this problem because of its almost nonexistant shrinkage and great adhesive strength.[56]

Besides being used for installation of ordinary concrete block, the epoxy resin mortars usually can be used with a variety of other masonry units, such as decorative concrete screen blocks, decorative clay screen units, brick, stone, terrazzo, ceramic tile, glass, wood and metals. Because the mortar is not restricted to general repair jobs, it can be used to install abutments and preformed curbings, decorative curtain walls, and precast concrete materials other than ordinary block, such as panels and beams.[24, 45, 62]

One of the main disadvantages that presently exists is the expense of the epoxy resin mortar. Although, only a fraction of the epoxy resin mortar is needed in comparison to the conventional cement mortars, it still is expensive. This is greatly offset by the savings in construction time, when the mason fully understands the handling properties of this new mortar material. Based on the present standards of employing masons, this would be benefical to the mason but not for the employer. So with this new type of masonry construction, there will have to be an adjustment of the present standards for masonry construction to justify the use of these new materials. This possibly will not be brought about for several years.[56, 63]

Another disadvantage, other than the expense of installation of the masonry units, is the objections to the new epoxy resin mortars from the standpoint of plant production of the masonry units. Many of the producers state that the thin 1/16 inch or 1/8 inch joints do not allow enough for manufacturing variations in the masonry units. A thicker mortar bed would be economically unfeasible in meeting competition, based on the present economical standards. Possibly with new techniques in masonry unit manufacture, less expensive epoxy resin mortars, and a gained familiarity of its use by the masons, the new mortar materials should find many applications in the future.[56, 63]

Concrete Construction and Repair

A relatively new field which shows considerable promise in the future, is the application of epoxy resin adhesives in concrete construction and repair. Because of their properties, the epoxy resins when properly compounded and applied will solve a wide variety of problems in repairing and constructing concrete. Many of these problems were previously considered very difficult, if not impossible, to solve by conventional techniques.[24, 65]

The first investigations and uses of epoxy resin adhesives with concrete construction and repair was in roadways and bridges. In this area, the epoxy resin adhesives have been very successfully used with considerable savings in time and labor expenses.[24]

The epoxy resin adhesives have been used on concrete structures to bond new concrete to old concrete, to bond precast concrete sections to other concrete, to bond dissimilar materials to concrete, to fill cracks, spalls, and depressions, and bond steel reinforcing dowels or steel reinforcing into concrete slabs.

In the last few years the epoxy resin based adhesives, in liquid, paste, and mortar or grout forms, have proved versatile and easy to use; they form bonds that are much stronger than the concrete itself. Although the expense of epoxy resin is high, many times their use is less than half those of conventional repair methods. Often the use of these adhesives will speed repairs of concrete so that construction continuation or use of the repaired area can be made within a couple of hours.[24, 65]

One particular use of the epoxy resin adhesives have been to bond fresh new concrete toppings to old existing concrete surfaces. In the past the conventional bonding methods have been time consuming and often not to successful. The epoxy resin adhesive formulations permits the bonding of "wet" concrete to cured concrete, forming a permanent joint. Tension, compression, shear, and impact tests show that the bond between new and old concrete is many times stronger and tougher than full cured concrete.[24, 65, 45]

In the process of bonding new concrete to old concrete, the epoxy resin adhesive is applied to the thoroughly cleaned existing concrete bonding face just before the new concrete is poured. In this procedure both the epoxy resin adhesive and the new concrete cure at the same time. With the epoxy resin bonding to both the new and the old concrete. This is possible because the epoxy resin is not effected by water or moisture as many other materials are. In fact, if the old concrete surface is properly coated with the adhesive, it will serve as a waterproofing membrane for the new concrete.[24]

The surfaces of the old concrete to be bonded must be free from contamination. The degree of preparation required to expose a clean adherend surface will depend on previous use, age, and exposure.[24]

Concrete that is impregnated with oil or grease should be sandblasted and/or etched with a dilute acid solution.

After this cleaning process, the surfaces should be flushed with water and thoroughly dried before the adhesive is applied. For ordinary small slab repairs, such as side walks, wire brushing followed by a blast of compressed air to remove dust is usually sufficient.[24]

The fresh concrete applied over the epoxy adhesive should always be a relatively dry mix, with a standard slump of zero to two and a half inches. Coarse aggregates can be used except for feathering the edges. For a smoother surface, a wetter surfacing mix can be used.[24]

The epoxy resin adhesive, that is generally used in the bonding of new concrete to old concrete surfaces, is of the low-viscosity fluid type. This gives good penetration and can be readily applied by brush or sprayed with special equipment.[24]

Bonding of fresh concrete to cured concrete will be an important improvement to pouring and gunniting techniques in concrete construction, as well as in the assembly of precast units in building construction and building maintenance. Other equally important uses of this new adhesive are bonding gypsum plaster to concrete without lath or mechanical keying and the application of sprayed cement asbestos insulation to concrete and steel structures.[45]

Similarly, the epoxy resin adhesives can be applied to construction joints in concrete construction to give stronger and more water resistant joints. This is especially useful for well cured concrete, which is to be bonded to new concrete. The exposed steel reinforcement at and near the joint can be cleaned and coated with adhesive. This will give stronger bonds between the steel reinforcement and the fresh concrete.[24]

In areas where the construction joint reinforcement is not exposed, holes at close intervals can be drilled in alignment with old reinforcement. Then steel dowels coated with epoxy grout are placed in these holes.

Often the actual reinforcement to be used in the new concrete can be coated with the paste epoxy resin grout adhesive and placed into the holes. Also the holes are filled with the epoxy resin adhesive grout before the dowel or reinforcement insertion. The purpose is to completely fill the joint and exclude air bubbles, in order to gain the needed strength.[24]

Concrete slabs or similar concrete structures, which have developed small cracks, can be repaired by either pouring or brushing in a liquid epoxy resin adhesive. For wide cracks, the adhesive can be mixed with suitable fillers and/or clean, dry sand and trowelled on like a mortar. Often cracks developingin masonry wall structures can be repaired similarly. The strength and the flexible nature of the bonding agent are sufficient to resist load and temperature stresses, and to prevent failure that might possibly occur at the cracks.[24, 59]

Where spalls, depressions, or broken edges of concrete occur, they can be easily repaired with the aid of epoxy resin adhesives. One method is to coat the area to be repaired with the liquid epoxy resin and then apply fresh concrete to the area. For smaller areas, an epoxy resin mortar can be used by its self for the patching operation. Often broken chunks of concrete can be bonded back in place with the epoxy resin mortars. With the broken chunks bonded in place, existing cracks can be filled later with the epoxy resin mortar. These repairs are equally as strong as the existing concrete, if the bonding operation is correctly executed. These repair methods can be applied to masonry construction as well as concrete. Broken brick, terra cotta, clay tile, concrete block, stone, and many other forms of masonry are often more easily repaired with epoxy resins than concrete itself.[9, 59, 62]

The beautiful varicolored seams that give marble its distinctive appearance can often be a problem. These seams generally contain soft mineral deposits, which are subject to failure. Because the marble represents a sizeable investment, these fractures must be repaired so that the bond will not be readily visible or fail again. Epoxy resin adhesives have been found to be the most effective material for repairing split marble. The adhesive is applied to the fractured surfaces, then the pieces are clamped together until the adhesive has cured.[62]

Because of the small amount of the epoxy resin adhesive required, the joints are almost invisible. A small amount of colorant can be added to the adhesive to match the marble. This further helps to make the joint invisible. These joints are usually stronger than the stone being repaired, with further breakage occuring in locations other than the joints.[62]

The epoxy resin adhesives may be used to bond similar and dissimilar materials to concrete surfaces. A wide variety of precast concrete materials may be bonded to other concrete or masonry parts of a building. For example, the epoxy resin adhesives may be used to bond precast lintels, steps, and a variety of other precast trimmings, with excellent strength and other desirable properties.[62]

Excellent uses of the properties of the epoxy resin adhesives have been made in precast-concrete construction. For example, building roof construction has brought about the use of epoxy resin adhesive bonding of concrete planks to subpurlins, eliminating all metal clips. Uses such as these are few but show the possibilities for future applications in precast-concrete construction.[45]

The epoxy resin adhesives may be used to bond dissimilar materials, such as stone copings and window sills into place.

It can also be used to bond metal thresholds, handrails, lighting fixture bases, and other assorted hardware. Metal flashings and gutterings may be bonded together, or to the building masonry, or to concrete surfaces. It must be remembered in bonding metals that the metals are nonporous and have to be molecularly clean for excellent bonding.[62]

Also in bonding dissimilar materials to masonry and concrete structures, the curtain wall panels, such as sandwich constructions can be easily bonded giving smooth, strong, and weather tight joints. With the masonry and concrete structures this can possibly eliminate many of the complicated fastening devices, thereby giving faster construction and less expense in labor costs. Applications at this time are mostly experimental, but show good possibilities for future construction.[45]

Also, it is important to have sufficient bonding surface area, especially when bonding metals to concrete or other masonry surfaces. This is because usually these materials are weak in comparison with metals. Excellent adhesive bonds can fail due to the concrete or masonry failing, while the adhesive bond is still in tact. This depends primarily on complete understanding of the materials and their strengths in the bonding operations. For example, handrails with one square inch of mounting surface per four or five feet of length can not be bonded to concrete or masonry. While such items as flashings have unlimited bonding surface area, with the possibility of the adhesive being stronger than the material itself. This is especially true of very thin aluminum. These considerations are important with adhesive bonding as well as in other forms of fastening.[62]

Sandwich Panel Construction

Sandwich panels are multilayered constructions formed by bonding two thin, dense load-bearing faces or skins to relatively thick, light, stabilizing core materials. When properly constructed, they are considered to have the greatest strength in proportion to their weight of any solid material now being manufactured. The development of epoxy resin adhesives and other synthetic resin adhesives for joining faces and cores are largely responsible for their growing acceptancc by industry and by a large segment of the general public. Principally, it has been the strength, simplicity, and rigidity combined with minimum weight that has brought increased usage of the sandwich panel constructions.[2]

Basically the construction materials of the epoxy resin adhesive bonded sandwich panels may be divided into three classifications. These are the adhesives, facing materials, and the core materials. The purpose of the adhesive is to bond and distribute the stresses from the core materials to the facing panel materials. While the facings must be high strength materials that will withstand outside fiber stresses. The function of the core is to stiffen and stabilize the two-thin facings. The core material must also transmit the stresses from one of the faces to the other in optimum design.[28]

Not all of the sandwich panels are load-bearing structural materials. Some are designed to carry only their own weight as thermal or acoustical barriers; other as weather shields or firewalls.[28]

Epoxy Resin Adhesive Materials. The bonding qualities of the adhesives used in sandwich panel construction determine, to a large amount, the strength and durability of the panel.

As adhesives, the epoxy resins are the most versatile bonding agents introduced in industry to date. Because of their basic structure which possesses low cure shrinkage, high affinity to wet, and cling to most materials, they develop adhesion to nearly any clean surface with exception of very non-polar adherends. These non-polar adherends are only the heavier metals and a very few of the thermoplastics.[49]

The supported composite films that have been used mostly in the manufacture of the honeycomb sandwich panels are tough, elastomeric adhesive layers bonded to the facing material; with this is a self-filleting but non-tacky paste bonded to the core. A carrier or scrim cloth material separates and supports these two adhesives during the curing process. This concept combines the high peel strength of the elastomeric adhesive and deep filleting characteristics of the epoxy resin adhesive, thereby giving strong, fatigue-resistant honeycomb structures. The disadvantage of this method is the production process. It is long, tedious and costly. Also, there is excess adhesive remaining on the surface of the skin opposite the cell core, which adds weight without contributing to the strength.[27, 43]

The newer development in the bonding of the facings to the honeycomb cores is the use of the unsupported films. These are self-filleting elastomer-modified epoxy resin adhesive formulations which achieve maximum efficiency in designing the glue-line of the honeycomb sandwich constructions. This system eliminates the use of two different adhesives because the unsupported epoxy resin adhesive is strong, flexible, and thereby giving excellent peel strengths. Because these epoxy resin adhesive films are unsupported, all of the adhesive weight is used to form the structural fillets upon cure. In designing sandwich materials with this method they can be made to provide maximum strength to weight ratio, reliability and economy.[43]

Since the foil-thin edges of the honeycomb cell walls adds up to less than fifteen per cent of the area of the facing surfaces, filleting of the adhesive is very important. Generally, a perfect match between all the edges of the cell walls and the skins is impossible, even in flat panels. To increase the mating surfaces enough to obtain optimum structural strength, the core to skin adhesive must form structural fillets between the skin surface and the inside cell walls of the honeycomb core.[27, 43]

In addition to the core-to-face adhesive bonding, a second type of adhesive bond is used in a honeycomb sandwich. This is the joining of the honeycomb core plies together at the crests. The bond is fabricated in the manufacturing process of the core materials. These bonds help to sustain the shear stresses in the core and contributes to its flat-wise compressive strength. Usually, the epoxy resin adhesives are used. Cheaper adhesives of less strength may be used because these bonds are not nearly as highly stressed as the skin-to-core bonds. This is because of the relatively large bonding area presented by the crests of the cells.[28]

Two other types of adhesive bonds important in the sandwich panels are: (1) those between the core and high-density inserts, edgings, or fittings within the panel; and (2) those between the adjacent sections of the cores. The epoxy resin adhesives are especially suitable for both purposes because they tend to form void free adhesive bonds in large thicknesses.[2]

Facing Materials. In an adhesive bonded sandwich, the facing material is the strength giving element and usually defines the strength properties. In selecting a facing material, it generally has to meet the requirements of strength, weight, stiffness and maintenance. The complete sandwich though, obtains its characteristics from all three basic components, which are core material, facing material, and the adhesive.

For example, wood in various forms was the most frequently used material for many years. Now a list of common facing materials include the following: plastics (especially the fibrous glass-reinforced types), metals (mild steel, stainless steel, aluminum, copper magnesium) and some non-metal inorganic materials such as glass or asbestos cement board.[29]

The sandwich panels may have a smooth or textured surface to improve appearance, handling, and ease of possible thermal stresses. Many times the colors involved in the design may dictate a certain facing material; but they seldom have an influence in the structural design. An exception to this is porcelain coatings on metal facings, which usually adds up to 50 per cent in rigidity.[29]

Generally, metals can be used in very thin sheets because of the large surface area and their strength. The thin sheets can bring about two important problems. These two problems are thermal expansion of large areas and lack of stiffness on the surface. These problems can easily be overcome with core stiffeners, heavier secondary facings, more rigid core materials, or by using textured metal facings. When thermal expansion is a major problem, then the two facings must be balanced, otherwise greater shrinkage on one side will product distortion of the other side.[29]

Aluminum is perhaps the most popular metal used as a facing because it represents an excellent compromise between strength, weight, and cost. Aluminum honeycomb cores with aluminum skins or facings joined with epoxy resin adhesives are very common in aircraft structures. Also aluminum is used often as a facing for plastic foam cores. The key properties are high strength-weight ratio and excellent corrosion resistance.[29, 50, 52]

Mild steel is an excellent high-strength, low-cost material, but it must be protected from corrosive elements that commonly exist is normal use.

A variety of coatings have been developed for this purpose such as galvanizing, paintings, vacuum metalizing, porcelain enameling, and laminating with vinyl or polyester films. Porcelain is the most durable of these protecting methods, but requires that the facing be completely shaped before the coating operation.[29]

Stainless steel is a high-cost and relatively heavy facing material. It becomes economical when its strength and corrosion resistance over a wide range of temperatures are considered. The stainless steel has gained much in appearance, due to new coloring methods. This has helped to open a wider consumer market for them. They have been used in construction of exterior panels for modern buildings.[29, 50]

Magnesium alloys may be used where strength to weight ratios are very important in structural sandwich applications. However, they must be handled in a special procedure during their cleaning and bonding operations. Because of the expensive production procedures, these materials have found little use in architectural construction.[2]

Many times metal facings do not fit the application needs as well as plastics do. For the thermosetting plastic facings the most popular reinforcing agent is woven fibrous glass fabric. Often asbestos woven fabrics are used for special applications, such as heat resistance. The more commonly used plastics for impregnating and laminating the fabrics are epoxy resins, polyester resins, phenolic resins, and silicone resins. Within broad limits, many combinations of resins and fabrics have been used to produce plastic laminate faces for sandwich panel constructions. Although these reinforced plastics are quite expensive, they offer desirable properties such as corrosion resistance, high strength-weight ratios, and good dielectric characteristics.

These plastic faced panels have many uses in both structural and non-structural applications. In building construction, they can often be used for decorative purposes. For example, a dramatic paneling material was recently fabricated by dipping paper honeycomb core material into colored epoxy resin adhesive and bonding it to transparent glass-reinforced polyester sheet.[7, 29]

Experimental homes have been built which incorporate metal and reinforced plastic faces on paper honeycomb or foamed plastic core sandwich panels. Cores of foamed plastics work well with laminated plastic or metal faces because the lay-up process tightly locks the facing to the core. With contoured parts, these paneling materials are easy to apply by hand lay-up. These versatile materials have much promise for future homes for a large segment of the public.[58]

Other than metals, asbestos cement board is the most common inorganic material used for the facing of sandwich panels. Its nonflammable characteristic makes it an ideal facing material for firewalls. Paper honeycomb cores impregnated with a cement slurry for fire resistance has been produced into sandwich panels with asbestos cement board faces for building purposes. Moisture resistance of the asbestos cement board sandwich panels is excellent and the board can be worked like wood, although tool wear is high. The chief disadvantage is the high density of the asbestos cement board.[29]

Honeycomb Core Materials. The prefabricated sandwich constructions are usually classified according to their core materials. The most commonly used core materials is probably the "honeycomb" design concept. This design is based on the bee's honeycomb. It uses a minimum of material to the maximum advantage.[2]

The honeycomb design concept developed out of paper honeycomb configuration which has been used for some time as core materials for sandwiched plywood doors and for lightweight, strong, inexpensive shipping containers.[50]

The honeycomb core material may be of such materials as plastic resin impregnated paper, cotton, fiber-glass or asbestos fabric; or it may be an inorganic material such as aluminum, steel, or titanium. The honeycomb core materials carry shear loads and resists compressive and tension loads normal to the faces of the sandwich. It also supports the thin faces, preventing them from buckling under edgewise compressive loads before the yield strength of the face material is reached.[2, 50]

Plastic impregnated fiber-glass and cotton honeycombs are excellent core materials for use where the properties of impregnated plastics, plus the strength of the reinforcing materials, are important. In addition to high strength, they usually have good thermal insulation, good electrical properties and excellent weather resistance.[2, 44, 50]

For structural applications where high strength, resistance to moisture and general weathering are required, the metal honeycomb cores are the most common. The most frequently used metals are aluminum and stainless steel. There has been some development towards the uses of titanium in sandwich panels, especially in aircraft.[50]

Kraft paper honeycomb is one of the most versatile and one of the strongest core materials known on a strength-weight basis. One of its versatile traits is the ease of handling and cutting to size. Where loading is not excessive, it is an excellent low-cost core material. It has good insulating characteristics, but these can be further improved by filling the core cells with various insulating materials. Insulating cell filling materials, such as the foam-in-place plastics and powdered perlite have been used.

Very effective fire barriers can be made by filling the honeycomb cells with lightweight gypsum or portland cement. A disadvantage of this core material is its sensitivity to moisture. For this reason, the sandwich panels must be weather sealed.[28]

Foamed Plastic Core Materials. In addition to the plastic resin-impregnated honeycomb core materials, there are the cellular or foamed plastics. These plastics may be either the thermoplastics or the thermosetting plastics. A list of the rigid plastic foams are: polystyrene, vinyl, urethane, cellulose acetate, phenolic, silicone, urea, and epoxy foams.[28]

All foam plastics have a natural advantage which is their low thermal conductivity. The foam plastics are ideal for sandwich construction because of their good resistance to humidity and many chemicals. They also have good dielectric properties. Another advantage is the foam plastic's density and mechanical properties can be closely controlled in formulating.[28]

Polystyrene plastic foam is of the lightest of rigid sandwich panel cores available. It is available in expandable beads for foam-in-place applications or in precast planks. This material is an effective insulator for sandwich construction. It is especially good where there is an extreme difference in temperature and humidity. Because of its closed cell structure, it does not soak up condensation.[22, 28]

The rigid urethane foams are closed-cell structures, which have many desirable properties. Some of their more outstanding advantages are high strength-weight ratio, low thermal conductivity, and good chemical resistance.[7]

The phenolic foams are a low cost core material with a wide range of densities. Although the strength of this material is low, it can be combined with paper honeycomb cores to take advantage of thc best physical properties of each material.

Generally, a sandwich prefabricated in this manner is of low cost and has excellent thermal and acoustical insulation; plus good structural strength, especially if it is bonded with epoxy resin adhesives.[22, 28]

The epoxy foam cores are finding many uses, which range from plastic tooling to reinforcing inserts and edge filling materials for the aluminum honeycomb panels. They have excellent dimensional stability, high structural strength, and are resistant to solvents. When used with metal honeycomb panels such as aluminum, they are foamed in place and serve to stabilize and fill the sandwich core cells. While at the same time they are forming excellent bonds between the facings and the core.[22, 28]

The syntactic plastic foams have found uses in sandwich panels because of their strength giving properties. These foams are mixtures of hollow, microscopic, phenolic spheres (or microballoons) and usually an epoxy resin binder. Cheaper plastic binders, such as the polyesters and phenolics, may be used but usually give lower strengths. By varying the ratio of binder-to-sphere and also by the choice of binders, a wide range of densities are obtained for this foamed core material. The uncured foam is usually a putty-like material which is hand-trowelled onto surfaces or pressed into sandwich core structures. This core material has found greater use, as a core reinforcement, than as an actual core by itself. It adds much strength to the honeycomb core panels.[22, 28]

Several other plastic foams have had limited usage as core materials for the sandwich panels. These are the rigid vinyl foams, cellulose acetate foams, silicone foams, and the phenolic foams. The rigid vinyl foams and the silicone foams have been considered basically to be to expensive for the gained properties. While the cellulose acetate foams have other disadvantages such as flammability.

The phenolic foams are usually brittle and relatively weak. Because of their low cost though, they have found uses as filler materials for the honeycomb cores, thereby providing added insulation to the sandwich panels.[28]

Many other materials have been and are being used for sandwich panel construction. These materials though, usually use adhesives other than the epoxy resin for bonding purposes. An example of a core material that would not be bonded with the epoxy resin adhesives is foam glass. The brittleness of this material requires an adhesive with less strength and greater resilience. Other core materials, that usually use different adhesives, are plywood and hardboard. This is basically because of their thin cross-sections and the porous nature of these materials.[22, 28]

Fabricating Sandwich Panels. The manufacturing process used in the fabricating of adhesive bonded sandwich panels are as follows:

1. Chemically cleaning and preparing the facing materials for the sandwich panel.

2. Applying the adhesive upon the core and/or facing materials.

3. Bonding the core and the facings with heat and/or pressure.[2]

The flat sandwich panel is the most commonly manufactured form and has the largest number of end uses. It is rather simply constructed because it requires little special tooling and can have many integral parts imbedded within the panel, such as conduits, attachment inserts, stiffeners, etc.. Where light weight, stiffness, and flatness are important considerations, such as in partitions, floors, panelings, doors, etc., the light-weight honeycomb or the insulated honeycomb sandwich may be the best solution. Where stiffness and strength are of less importance, usually the plastic foam core material will work well, especially for sound and thermal insulation.[28]

Both the honeycomb and the foamed plastic core materials can be designed for simple or compound curves. The cores of foamed plastic are usually foamed in place to get the desired curved shape. While the honeycomb cores are generally either machined before expansion or the cells of the expanded honeycomb are filled with a removable material and then cut to the desired shape. This procedure, using the expanded honeycomb, may be somewhat expensive. The versatility of form in sandwich panels offers the designer almost unlimited latitude in adapting this type of construction to design requirements.[50]

Because of the low density of most core materials, precautions must be taken in fastening the sandwich panels with bolts or rivets through the panel to prevent crushing of the core material. Generally metal or plastic spacers, or special rivets are used for this purpose.[51]

Experimental Uses

Probably the most outstanding experimental use of epoxy resin adhesive bonding in building construction was in a small office building addition for Gilman Brothers, Inc., a Connecticut plastics manufacturer. Basically the building was built utilizing steel rectangular tubing for columns and beams. While the interior and exterior walls, roof and flooring was composed of sandwich panels. The sandwich panels were constructed with polystyrene foam cores, while the facings were composed of plywood, gypsum boards, and cement asbestos boards. Window and door frames and the other trim materials were constructed of wood. This 1800 square foot structure was economically constructed with epoxy adhesive bonding. No mechanical fasteners, such as screws, nails or bolts were used in the construction. All of the various structural members and elements were bonded with epoxy resin adhesives.[25]

The composite panels forming the walls, roof, and floor areas were assembled at the job site, by bonding the skins or facings to the polystyrene cores, with hand applied epoxy resin adhesives. The building was constructed by bonding the composite panels directly to the tubular steel beams upon which they were seated, and to each other with simple splined butt joints. These composite panels were composed with six inch thick cores for floor and ceiling panels and four inch thick cores for the walls. The continuous unity of the bonded panels added greatly to the rigidity and strength of the whole structure.[25]

With the panels bonded in place, openings for windows, door and skylights were simply cut into the building where desired; then the windows, doors, and skylights were adhesive bonded into the openings provided.[25]

Another experimental use of epoxy resin adhesives for bonding in building construction was in the construction by Mr. A.G. Kimmel, of the Kimmel Engineering Company, in his new plant specializing in structural epoxy resin products at Harrisonville, Missouri. The walls of the building are constructed of 8" X 10" X 16" concrete blocks bonded together with epoxy resin mortar. The window frames and door bucks are constructed of fiber glass reinforced epoxy resin and installed into the masonry openings with epoxy resin adhesives. This is probably the first building construction to use epoxy resin adhesives for bonding window and door frames into masonry openings. With the surface area for bonding purposes, this may well be a practical application in the future.[63]

The most unusual use of epoxy resins and epoxy resin adhesives was in the construction of the lightweight, translucent, arched roof system. The box beam like arches are framed inside with very thin wood members assembled in a jig.

An outer skin, used on all sides, of 1/8 inch fiberglass epoxy resin laminate was bonded to the light framework with epoxy resin adhesives. The result was a very efficient stressed-skin arch or curved beam.[10, 63]

Another interesting fact is that the stressed-skin arches span forty feet and weight about two hundred and fifty pounds each. Each arch is four feet wide and twenty inches thick in the center, which tapers to ten inches thick at the ends. The rise of the arch is five feet at the center, giving the appearance of an airplane wing in cross-section. Because of the lightweight, four men can easily slide the arches into position against the sections already in place.[10, 63]

Each of the stress-skin arched sections are bonded together with epoxy resin adhesives. The sections are also adhesive bonded to the ten inch concrete block walls as they are installed. Besides the epoxy resin adhesive being used to bond these sections into place, they act also as weather protecting sealers.[10, 63]

Several years ago Mr. Lee Frankl, a designer and independent researcher, established a laboratory on Cape Cod to study methods of producing house components that are particularly appropriate for the use of plastics.[23]

During his research Mr. Frankl used several approaches in designing and testing of stress-skin types of plywood sandwich panels with polystyrene foam cores. Some of his experimenting dealt with different shapes of the polystyrene plastic foam. The basic exterior had the appearance of plywood stress-skin panels, but the interior contained configurations of the polystyrene plastic foams. One particular configuration used three inch tubes of foamed polystyrene bonded in place with epoxy resins. While another used the polystyrene foam in a corrugated configuration.

In this way, the maximum depth for thicker sandwich panels was gained without completely filling the cores with the expensive plastic foam. With epoxy resins and similar adhesives, he was able to gain the strongest possible bonds for the bonding area available.[23]

SUMMARY

Although the epoxy resins have been considered to be a relatively new plastic material, they have been known for over a century. Its usefulness was not discovered until late in the nineteen thirties. It was during this time that Pierre Castan in Switzerland and the research team of S.O. Greenlee and J.S. Long in the United States synthesized epoxy resin which led to the actual development in industry.

The epoxy resins were first introduced commercially in 1947 and by 1965 the production had grown to one hundred million pounds. The epoxy resin's remarkable growth and development in the plastics field indicates its industrial potential in many varied uses.

Similar to the phenolic and polyester resins, the epoxy resins are thermosetting materials. In the uncured state, the epoxy resins may range from thin liquids to solid forms which become liquid when heated. When converted by a curing agent, the thermosetting epoxy resins become hard, infusible systems. The basic ingredients used to produce epoxy resins are epichlorohydrin and bisphenol. The reaction between these two materials produces diglycidyl ether of bisphenol, which is the basic epoxy resin. By varying these two basic ingredients different viscosities of the epoxy resin may be produced.

The ability of epoxy resins to transform from the liquid or thermoplastic state to a tough, hard thermoset solid is one of its valuable characteristics. This hardening to a solid state is accomplished by the addition of chemically active curing agents.

Due to industrial interests in the epoxy resins, a large number of curing agents are available. These range from the homopolmerizing catalysts to the copolmerizing or hetropolmerizing through cross-linking with other plastic resins.

The selection of an epoxy resin and curing agent for a particular application involves complexities and experimentation because of the enormous number of formulation possibilities. This selection can only be solved through the valuable equipment, modern techniques, and vast knowledge of the chemists in the plastics production industry.

In addition to the large number of epoxy resin and curing agent combinations, there are numerous additives and reinforcements which may be used to improve the epoxy resin formulation. Many chemical compounds may be used in the development of specific formulations. These chemical compounds vary from viscosity control with diluents and thixotropic agents used in preparing the resin to the fillers, reinforcements, resinous modifiers, colorants, and flexibilizers which give special properties to the end product.

The unmodified epoxy resin-curing agent systems are seldom used commercially. To be of commercial value, modifications are nearly always needed to lower cost, improve handling characteristics, and modify the selected properties.

Each particular epoxy resin formulation will exhibit its own special properties. Thus, through the careful selection of the components, it is possible to formulate systems exactly suited to the specialized industrial applications.

An excellent balance of outstanding properties are possessed by epoxy resins which accounts for their wide use in formulations for structural and non-structural adhesives.

The most important of the epoxy resins excellent properties are versatility, handling characteristics, toughness, high adhesion, low shrinkage, thermal characteristics, and inertness.

With the characterizing properties of epoxy resin adhesives, it should be remembered that one specific property of the cured resin produced with one curing agent, additive, or curing cycle does not necessarily increase all other desirable properties. A specific service environment will dictate certain desirable properties and a specific "optimized" resin system will not be optimum in all properties. It will be a compromise of properties designed to accommodate the specific property requirements. Due to numerous resins, curing agents, and the incorporation of special additives and/or reinforcements, the epoxy resin adhesive formulations can be varied over a wide range of compromised properties. These compromises will usually be based on the service requirements of the adhesive.

The epoxy resin adhesives can develop terrific strengths, but only if applied in a correct manner. There must be complete consideration of the stresses to be placed on the bonded joint and thereby bring about the configuration design. These stresses on an epoxy resin adhesive bonded joint can be classified as shear, tensile, cleavage, and peel. The cleavage and peel stresses involve stress concentrations, therefore should be avoided at all times in high stressed structural joints.

In architectural construction, the epoxy resin adhesives have established several substantial uses. These uses are basically in the areas of masonry and concrete construction and repair. The most widely accepted use of epoxy resins, as an adhesive material, has been in binding of various aggregates together for bonding to floors, walls, panels and masonry units.

In the flooring area, these epoxy resin mortar compositions may range from the smooth ground terrazzo surfaces to the abrasive industrial floor finishes. For wall constructions, panels, and masonry units, the epoxy resin binding mortars may be used to create durable but decorative surfaces for interior or exterior uses. These surfaces may be rough exposed aggregates or the aggregates may be made smooth by grinding. In the same area, the epoxy resin mortars have been used in bonding together various masonry units, such as concrete block, brick, and ornamental tiles.

The epoxy resins adhesive strength and durability has made it an excellent material for adhesive bonding of concrete. The epoxy resin adhesives have been used to bond freshly poured concrete to old concrete surfaces. It has also been used to repair damaged concrete structures, thus giving the repaired joints more strength than the concrete itself. Also, precast concrete parts can be bonded to concrete, giving design flexibility not possible before. Among other uses are the bonding of dissimilar materials to concrete, such as masonry units, metals and plastics.

In architectural construction the sandwich panels have many uses; especially in high-rise structures. Many of these sandwich panels are being prefabricated by bonding the thin facing materials to honeycomb or foamed plastic cores with epoxy resin adhesives. The epoxy resin adhesives make possible the construction of sandwich panels, which have tremendous strength in relation to their weight. Industrially produced, these sandwich panel materials are expected to find many more applications in architectural construction.

Many epoxy resin adhesive bonding applications in architectural construction are presently in the experimental stages. These usually involve the bonding of similar and dissimilar materials for construction site applications.

The success of these experimental applications of epoxy resin adhesive bonding depend primarily on economics and familiarity of bonding procedures by the user. A great number of the experimental applications will find wide usage in the future, when the architect and the builder has a better understanding of the properties of the epoxy resin adhesives.

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AN INVESTIGATION AND RESEARCH REGARDING THE ADHESIVE QUALITIES OF EPOXY RESINS IN ARCHITECTURAL CONSTRUCTION

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The historical aspects of the epoxy resins was first investigated to determine for what purpose the epoxy resins were developed and what persons or industries were involved in its initial discovery. Also, this investigation disclosed that the epoxy resin adhesives have made rapid production development and growth since their introduction in 1947.

The basic resin composition and the curing mechanisms were investigated next. Because of the complexity of the epoxy resin, this study was directed towards a basic understanding of the converting of the liquid or thermoplastic epoxy resins into a tough, hard thermoset solid. From the research on the epoxy resin and its curing, the architect can best utilize this adhesive material from the manufacturers or formulators recommendations. This is because of the enormous number of resin and curing agent combinations, which can only be solved by the valuable equipment, modern techniques and vast knowledge of the chemists in the plastics production industry.

Next the investigation and research brought about the fact that numerous additives, such as fillers, viscosity control agents, flexibilizers, and fibrous reinforcements, may be incorporated to improve the epoxy resin formulation's bonding characteristics. In addition to the large number of epoxy resin and curing agent combinations, the numerous additives and reinforcements give the epoxy resin adhesives an excellent balance of outstanding properties. These outstanding properties of the epoxy resin adhesive are versatility, handling characteristics, toughness, high adhesion, low shrinkage, thermal characteristics, and inertness. These properties account for the epoxy resins wide usage in formulations for structural adhesives.

Further research information revealed that the epoxy resin adhesives can develop terrific strengths but only if applied in a correct manner. The adherends must be thoroughly cleaned and there must be a complete consideration of the stresses to be placed on the bonded joint. By using maximum bonding areas and good joint design, strong durable joints can be constructed, thereby relieving stress concentrations which often cause failure of the joints.

The epoxy resin adhesives have established several substantial uses in architectural construction. This is because of their capacity to bond to a wide variety of similar and dissimilar materials. Presently these uses are in the areas of decorative aggregate based surface covering, mortars for masonry construction, and a variety of adhesives for concrete construction and repair. The epoxy resin adhesives have also been used to fabricate a wide variety of sandwich panels, which are finding many varied uses in architectural construction.

Because of the valuable properties of the epoxy resin adhesives, they are continually finding more uses in architectural construction. For this reason, many of the epoxy resin bonding applications are presently in the experimental stages. A great number of these experimental applications will find substantial usage in the future, when the architect and the builder have a better understanding of the properties of the epoxy resin adhesives.