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A Survey on Epoxy Resins

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ABSTRACT : Many man-made articles are synthesised today to satisfy the industrial needs as per its requirements. Naturally available materials are combined either chemically or mechanically to obtain required product for increased industrial needs. In present time, Plastics have taken over a major share of market due to its reliability, effectiveness, proper strength and economical in manufacturing and consumption. The only negative point of plastic consumption is its waste disposal and its inability to disintegrate naturally or by simple means creating major problem of pollution. Plastics though create immense pollution but are very attractive to the concept of replacement towards metal works. Plastics are mainly characterised by two different types, Thermosetting Plastics and Thermoplastics. One attractive option from the group of Thermosetting Plastics is Epoxy Resin. The versatile characteristics of epoxy and its diversity bring it into the applications of laminated circuit boards, electronic component encapsulations, potting, adhesives, etc. However, the pervasive applications of epoxy are limited by default characteristics like low impact resistance, brittleness and high fracture probability. Now, these limitations are overcome by modifications in their primitive structure increasing their basic properties. This article is presented with brief overview of epoxy resins covering topics of basic epoxy resin, synthesis, modifications, advancements and its industrial applications.

KEYWORDS : Thermosetting Plastic, Epoxy Resin, Natural fibres, Nano-composites, curing, Bisphenol A.

1. INTRODUCTION

Increasing consumer demand with variety, practicability and economical value of product is propelled by increasing technological development leading to discovery and inventions of various production materials with desirable properties on a daily basis. Also, increased pollution over decades has compelled researchers and scientists to develop materials with re-engineered properties to bring balance between consumption and pollution. Much of the attention is provided towards increase in involvement of polymers or plastics for applications such as construction, packaging, furniture, automotive components, etc. Mostly, a thermosetting polymer in the form of resin is preferred these days. A thermosetting resin and a composite when developed, it forms highly cross-linked chains. This structure when undergoes catalysis is unable to go in reverse form and cannot be remoulded, reshaped or reformed. This happens due to high cross-linking density which results in restriction to long chain molecular movement or slippage. This also results in higher flexibility for achieving strength, high rigidity, better thermal and chemical resistance. Thermosetting polymer system mainly comprises of derived components like Melamine Formaldehyde, Phenol Formaldehyde, Polyurethane, Polyesters and Epoxies. Various techniques are available for processing above stated thermosetting polymers. Most favourable throughout the industrial approach is the method of Molding. Some subsets of molding methods are Compression Molding, Transfer Molding and Injection Molding which have typical approaches based on the type of material to be produced and definition of end application of required product. Epoxy resins are concern of the presented article and are discussed below.

1.1 Epoxy :

Epoxy is either any of the basic components or the cured end products of epoxy resins, as well as a colloquial name for Epoxide functional group. An epoxide is a cyclic ether with three-atom ring. This ring approximates as an equilateral triangle which makes it strained, thus highly reactive. Figure 1 shows the epoxide triangular structure. A compound containing the epoxide functional group can be called as epoxy, epoxide, ethoxyline, etc. A polymer formed from

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epoxide precursors is called an epoxy, but such materials do not contain epoxide group or contain only a few residual epoxy groups that remain unreacted in the formation of resin. Most commercially available epoxy resins are oligomers of diglycidyl ether of Bisphenol A. some of the other important epoxy resins are as follows,

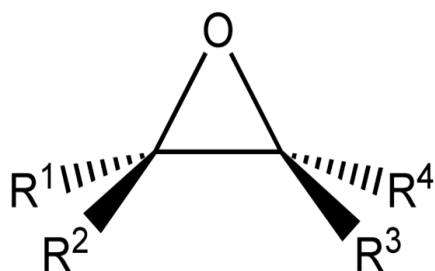


Figure 1. Structure of Epoxide

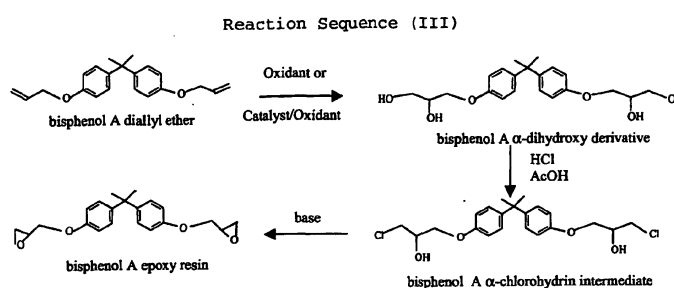


Figure 2. Reaction process of Bisphenol A epoxy resin

1.1.1 Bisphenol A Epoxy Resin :

This resin is produced from combining Epichlorohydrin and Bisphenol A to give Bisphenol A Diglycidyl Ether. Increasing the ratio of Bisphenol A to epichlorohydrin during manufacturing process produces higher molecular weight linear polyethers with glycidyl end groups. This results in production of semi-solid to hard crystalline materials at room temperature depending on the molecular weight achieved. Chemical reaction of this process is given in Figure 2.

1.1.2 Bisphenol F Epoxy Resin :

Bisphenol F may also undergo epoxidation in similar way as that of Bisphenol A. Compared to Bisphenol A Epoxy Resin, these have lower viscosity and higher mean epoxy content per gram. This property helps it to have increased chemical resistance once the resin is cured.

1.1.3 Novolac Epoxy Resin :

Reaction of phenol with formaldehyde and subsequent glycidylation with epichlorohydrin produces epoxidised novolacs such as Epoxy Phenol Novolacs (EPN) and Epoxy Cresol Novolacs (ECN). These are highly viscous to solid resins and have high temperature and chemical resistance but low flexibility.

1.1.4 Aliphatic Epoxy Resin :

Aliphatic Epoxy Resins are typically formed by glycidylation of aliphatic alcohols or polyols. The resulting resins may be monofunctional, difunctional or higher functional with respective examples like Dodecanolglycidyl ether, Butanedioldiglycidyl ether and Trimethylolpropanetriglycidyl ether. These resins display relatively low viscosity at room temperature. These are mainly used to modify the viscosity of other epoxy resins.

1.1.5 Glycidylamine Epoxy Resin :

Glycidylamine Epoxy Resins are higher functionality epoxies which are formed when aromatic amines are reacted with epichlorohydrin. Important industrial grade resin from this category is triglycidyl-p-aminophenol (functionality-3). Resins of this group have low to medium viscosity at room temperature, making them easier to process than EPN and ECN resins.

Like other thermoset resins, epoxy resin primarily shows low fracture toughness, low impact resistance and low resistance to crack initiation and propagation. These and other characteristics can be changed by renewed chemical structure and network achieved after curing. Curing results in 3D (tridimensional) covalent network depending on the extent-density of cross-linking curing kinetics and their chemical composition. This makes it possible to vary the

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mechanical and physical properties of the resin to provide it desired industrial characteristics. Epoxy technologies is known to satisfy variety of non-metallic composite designs in commercial and military, aerospace applications.

II. STRUCTURE AND SYNTHESIS OF EPOXY RESIN

2.1 Structure :

DEGBA, obtained from diglycidyl ether of Bisphenol A is the most commercially successful epoxy resin. The oxirane function group (a three-member ring formed between two carbon atoms and an oxygen atom) forms the main feature of this epoxy structure. Figure 1 shows the oxirane ring of epoxy. The carbon atoms of the ring are electrophile because of different electronegativity of carbon and oxygen. This atomic arrangement thus shows enhanced reactivity. Thus epoxies or epoxy function are highly reactive and usually undergo ring-opening reactions with nucleophiles. Epoxy resins, depending upon its backbone structure, may be low-medium-high viscosity in liquid or solid state.

Most of the world production of epoxy resin is based on reaction between Bisphenol A and epichlorohydrin in presence of basic catalyst. The three basic elements of an epoxy resin formulation that must be considered while selecting a thermoset system are base resin, curatives and the modifiers. When formulating an epoxy resin for an industrial or commercial use, it is important to know what each of these components contributes to the physical properties and mechanical performance of end use product.

2.2 Synthesis of Base Epoxy Resin :

In general terms, an epoxy resin can be considered of as a molecule containing a three-membered ring consisting of one oxygen atom and two carbon atoms. The presence of functional group defines a molecule as an epoxide but the molecular base to which it is attached can vary widely resulting in the yield of various classes of epoxy resins. The commercial success of epoxies is due to the reason that the diversity of molecular structures that can be produced using same chemical process. Epoxy resins are produced from base molecules containing an unsaturated carbon-carbon bond. There are two processes that can be used to convert this double bond into an oxirane ring: Dehydrohalogenation of a halohydrin intermediate or direct peracid epoxidation. Both above stated processes are used to produce commercial epoxy resins but Halohydrin route is more common and is used to produce a wider range of materials. The most important raw material used in production is epichlorohydrin which is used as a precursor for nearly every commercially available epoxy resin except for Cycloaliphatic resins.

III. MODIFICATIONS

The potential use of epoxy thermosets in many high performance applications is limited due to its drawbacks such as low impact resistance, higher possibility of fracture and failure. To overcome these weak points, nearly all epoxy resins are modified or amended with various additives and fillers, some of which are reactive oligomeric compounds, low molecular weight polymer, plasticizers, Nano-fillers, etc. Some property improvements made are by doing,

- Using curing agents, resins and co-monomers to polymer resin with new backbone structure and chemistry.
- Modifications with thermoplastic polymer, elastomers, inorganic particles, fibres like glass, carbon or natural fibres, variable geometry and different sizes.
- Adding reinforcements of different natures to provide additional mechanical energy absorption mechanism in high heat and temperature applications to be fire retardant materials.

3.1 Curing process for Epoxy resin :

As stated, uncured-base epoxy resins have poor mechanical, chemical and heat resistance properties. Good properties overshadowing weak points of resins are obtained by reacting the linear epoxy resin with suitable curatives to form tri-dimensional cross-linked thermoset structures. This process is commonly referred to as Curing or Gelation process which is widely adapted process in production areas. Curing process is basically an exothermic reaction and in some cases produces heat more than required causing thermal degradation of product if reaction is not controlled. Curing can be achieved by reacting an epoxy with itself or by forming a co-polymer with poly-functional curatives or Hardeners. It

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is based on the fact that any molecule containing Hydrogen may react with epoxide group of epoxy resins. Common classes of Hardeners for epoxy resins include amines, acids, acid anhydrides, phenols, alcohols, thiols. Relative reactivity from lower to higher order is approximately in the order of phenol < anhydride < aromatic amine < cycloaliphatic amine < aliphatic amine < thiol.

While some epoxies-hardener combinations will cure at ambient temperature, many require heat supply upto 150~200°C of temperature. Curing temperature should attain the typical Glass Transition temperature (T_g) of fully cured network in order to achieve maximum properties. The epoxy curing reaction may be accelerated by addition of small quantities of accelerators. Tertiary amines, carboxylic acids and alcohols are effective accelerators. One of the most highly effective and commonly used accelerators is Bisphenol A but is now being rapidly replaced due to health conditions on working with it. Some of the curing methods and hardeners are stated as follows,

3.1.1 Homopolymerisation :

Epoxy resin may be reacted with itself in the presence of an anionic catalyst or a cationic catalyst to form cured networks and this process is called as Homopolymerisation. The resulting network contains only ether bridges and exhibit high thermal and chemical resistance.

3.1.2 Amine Hardener :

Polyfunctional primary amines form an important class of epoxy hardeners. Primary amines undergo an addition reaction with the epoxide group to form hydroxyl group and the secondary amine. The secondary amine can further react with an epoxide to form or tertiary amine and an additional hydroxyl group. Amine type will alter both the processing properties like mechanical, temperature and heat resistance of cured copolymer networks.

3.1.3 Anhydride Hardener :

Epoxy resins may be cured with cyclic anhydrides at elevated temperatures. Here, reaction occurs only after opening of anhydride ring. The low viscosity and high latency of anhydride hardeners make them suitable for processing systems which require addition of mineral fillers prior to curing, for example, for high voltage electrical insulators.

3.1.4 Phenol Hardener :

Polyphenols, such as Bisphenol A or novolacs can react with epoxy resins at elevated temperatures (130~180°C) in the presence of a catalyst. The resulting material has ether linkages and display higher chemical and oxidation resistance than typically obtained by curing with amines or anhydrides.

3.1.5 Thiol Hardener :

Thiols, which are also known as Mercaptans contain sulphur which readily reacts with epoxide group even at ambient temperatures. This hardener is useful for applications which cannot undergo heated curing process or very fast curing is required. Thiols have distinctive smell which can be found in bi-component household adhesives.

3.2 Fire retardant Epoxies :

Epoxies, like thermoset resins and polymers which are based on petroleum and are combustible, on exposing to temperatures of the range 300~400°C goes under decomposition releasing smoke, toxic volatiles, soot of organic matrix of cured epoxy laminate. Epoxy resins are made fire retardant by either incorporating it with reactive fire retardant thermoset polymers. End applications which demand the fire retardant property of epoxy resin are electronics (for semiconductor encapsulation and printed wiring boards), transportation (automotive components, aerospace and aircraft, trains), composite structures and furnishing elements. Recently, researchers synthesized epoxy resin by incorporating tris(2-hydroxypropyl)borate (THPB) and OPOSS (octaminophenyl polyhedral oligomeric silsesquioxane) having boron and silicon in the curing system. It was found that there was an increase in Limited Oxygen Index (LOI) value of epoxy resin with improved heat-resistant layer and decrease in release of flammable gases.

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3.3 Natural Fibre-based Epoxy Composites :

Due to availability of knowledge of natural fibres and its productive combinations, the interest and applications of using natural fibres as reinforcements in polymers has increased in the areas of engineering and research field. Study also shows importance on the use of natural, renewable sources for issue of safer environment, waste disposal and depletion of non-renewable sources. Potential substitutes for synthetic fibres among natural resources like vakka, date palm, coir ,oil palm empty fruit bunch, bamboo, hemp, etc. are suggested through studies. Research is also carried out to determine the possibilities of introducing new natural fibres as fillers in polymeric matrix to develop new economic and light weight structural materials. Natural fibres based epoxy resin composite provide unique combination of great versatility, high performance and production at cheaper rates than synthetic thermoplastics. Study also shows that the physical and mechanical properties of epoxy gets improved in maximum number of cases of its incorporation with natural fibres.

IV. ADVANCEMENT IN FIELD OF EPOXY RESIN

4.1 Nano Epoxy Composites :

In current times, one of the most promising approaches in the field of future hi-tech engineering application is development of Nano-particle reinforced polymer composites with appropriate amounts and dispersion of nanoparticles. Research is done rigorously to enhance the epoxy characteristics to overcome its weak points by adding Nano-sized inorganic fillers such as carbon Nanotubes and carbon Nano-fillers. Nano-composites have scope of novel products with increased mechanical properties and anisotropic electrical conductivity. Reinforcement of Nano-fillers in epoxy composites is shown to provide materials possessing properties such as increase in glassy modulus, broadened Glass Transition temperatures, low dielectric constant, etc. Disadvantage occurred is that in some cases Nano-particles showed agglomeration i.e. relocating and locating leads to lowered interfacial interaction of Nano-particles in epoxy resin matrix.

Nano-composites based on nanotechnology have very diverse applications. Currently, 70% of Nano-clay composites structures are employed in applications of food preservation, innovative packaging and processing technology. CNT(carbon nanotubes) epoxy composites are also being used in aero-automotive, electrical and electronics field. Layered silicate epoxy Nano-composite has been exclusively used for insulating materials in heavy applications of automotive and electronics field. Figure 3 shows an example of silica based Nano-composite in epoxy resins.

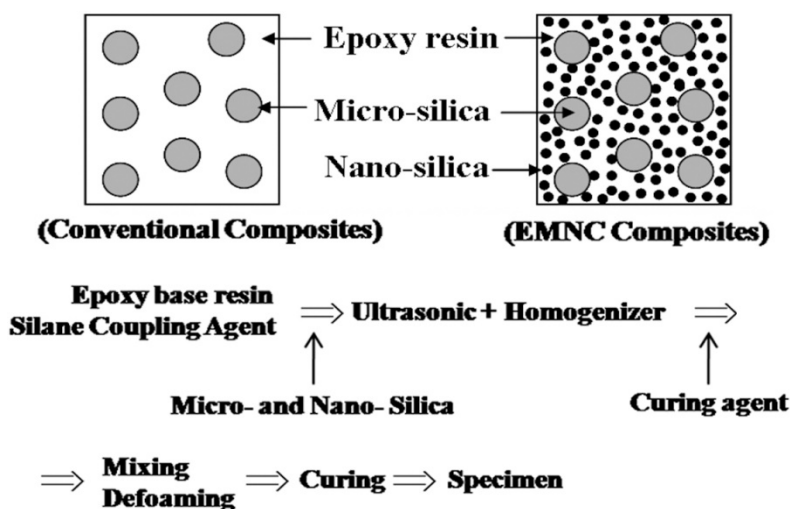


Figure 3. Nano-composite Epoxy material with silica

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4.2 Green or Sustainable Epoxy Resin :

Growing environmental issues, waste disposal and short-coming of sources in recent years have made strides to develop polymers from natural resources such as Bio-polymers. Bio-polymers have advantage of low production cost and its theoretical biodegradability. Bisphenol A is one of the highest volume chemicals produced around the world which also has a major share in production of epoxy resins. With large production, significant amount of Bisphenol A is also released into environment. Bisphenol A has severe impact on human health as it is able to alter human immune and reproductive systems with brain chemistry. The chemical bonds between Bisphenol A are not stable which results in release of polymer itself in small quantities which is toxic and hazardous to environment. Also, Bisphenol A have estrogenic properties. Thus several efforts are being made to replace the traditional DGEBA by bio-based epoxy monomer or oligomer with comparable high performance materials.

DGEBA is derived from Bisphenol A and epichlorohydrin. Thus, the easiest way to produce a partially bio-based DGEBA is to use epichlorohydrin from bio-based glycerol which is an inexpensive and abundant phenol. Above stated bio-based epichlorohydrin is now commercially available in market. For formation of sustainable epoxy resins, natural polyphenols (condensed tannins, lignin) and polysaccharides are most abundantly available renewable natural resources (obtained from forests/agricultural biomass or residues) in large quantities. Previously, bio-based epoxy resins were synthesised from catechin molecule or condensed tannins, one of the repetitive units in natural flavonoid biopolymers with improved thermal and mechanical properties. Also, non-functionalized gallic acid (from hydrolysis of gallotannins), glycerol based epoxy precursors such as glycerol polyglycidyl ether and polyglycerolpolyglycidyl ether are industrially available and are inexpensive for bio-based epoxy resins formulation. Researchers are also interested in epoxidised plant oils and fatty acids as alternative because they display interesting and comparable thermal properties to commercial DGEBA.

V. ADVANTAGES OF EPOXY RESINS

Distinct advantages of cured epoxy resins compared to other traditional thermoplastics and thermoset resins are,

- Minimum shrinkage during curing process.
- Relatively cheaper and abundantly available.
- High moisture and chemical resistance.
- Good electrical and non-magnetic properties.
- Does not have volatile organic compounds.
- It is damage tolerant and anti-corrosive.

VI. DISADVANTAGES OF EPOXY RESINS

- Base resin cannot be directly used for end application and has to be processed and modified.
- Synthetic epoxy resin is not environmental friendly.
- Synthetic epoxy resin has waste disposal problems.

VII. APPLICATIONS OF EPOXY RESINS

Due to inexpensiveness and superior properties, epoxy resins are commercially used in applications as follows,

- Adhesives for general purposes.
- Insulating material for heavy apparatus and di-electric materials as shown in Figure 4.
- Industrial paintings and coatings as shown in Figure 5.
- Fibre reinforced Plastics.
- Solidifying sandy surfaces in oil drilling.
- Making rigid foams and for binders in cements and mortars.

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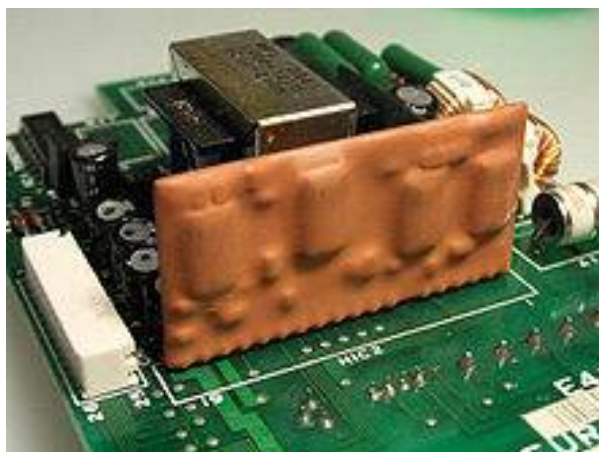


Figure 4. Insulation for Electrical and Electronic devices



Figure 5. Epoxy resins in coating for ceramic floors

VIII. CONCLUSION

Thus, brief information is reviewed over Epoxy Resin in above article. Basic structure and synthesis has been stated and understood. Various modification methods like Curing and Hardener materials have been discussed. Brief overview over importance of Epoxy Resin and Bisphenol A in industrial sector is given. Recent advancements in article like Nano-composites and Green-Sustainable epoxy resins are stated and recent as well as future research in their respective fields are presented. Advantages, disadvantages and commercial applications are stated in above article.

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