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Synthesis And Applications of Bisphenol-A Epoxide Resins A Review

Akshay Shankar[1], Sambhav Maloo[1], and Ankur Upadhyay[#]

[1]Calorx Olive International School, Ranchoddpura, Gujarat, India
[#]Advisor

ABSTRACT

Epoxy resin is a widely used substance for coatings, adhesives, composites, electrical components, LEDs, paintbrush manufacturing, fiber-reinforced plastic materials, and consumer product manufacturing (such as cases, kits, and snowboards). Epoxy resin is highly versatile due to its properties. One of the most commonly used types of epoxy resin is Bisphenol-A Epoxy resin, which is excellent for high-temperature applications, the adhesion of a variety of substrates, compression, bends, electrical insulation, mortar, grouts, adhesion, and high-tensile-strength applications. There are several types and applications of Bisphenol-A epoxy resin. This paper aims to review the types, synthesis, and applications of Bisphenol-A epoxy resin.

Introduction

Resins refer to any organic compound, whether natural or synthetic, that consists of a noncrystalline or viscous liquid substance. They are typically viscous liquids that turn solid after curing. There are many applications for resins, and they are used in almost every aspect of life. Resins are everywhere, from adhesives to paints, electric insulation to structural composites. Resins have the potential to be extremely useful in the future. There are many types of resins, and the most commonly used ones are epoxy resins. Epoxy functional groups, sometimes known as epoxy, are crucial to epoxy resins. They contain a three-membered cyclic ether group commonly called an epoxy group, 1,2-epoxide, or oxirane. Diglycidyl ethers of bisphenol A, which are produced by combining bisphenol A and epichlorohydrin, are the most commonly used epoxy resins. These resins can crosslink with one another or with co-reactants such as amines, acids, phenols, alcohols, and thiols, which are frequently used as hardeners or curatives. A thermosetting polymer with desirable mechanical qualities, high thermal resistance, and chemical resistance is formed when the epoxy cures. Epoxy resins are used in many different things, such as adhesives, composites, electronics, and electrical parts, and there are many different types of epoxy resins.

Epoxy has been utilized since the early 1890s, but only until 1950 was it widely known and utilized. Epoxy began with the discovery of peroxy boric acid and its reaction to olefin by the Russian chemist Nikolai Alexandrovich Prilezhaev. The reaction he found formed epoxides, which are used to form epoxy and polyamine. The first synthesis of epoxy was reported in 1936 by Dr. Pierre Castan from Switzerland and Dr. S. O.. Greenlee from the USA. Although they did not co-invent epoxy, they claimed co-ownership of its discovery. They applied for various patents in the late 1930s. However, both shared credit for developing the diglycidyl ether of bisphenol A. Dr. Pierre allowed his work to be licensed by 'Ciba' in Switzerland. Thus, Ciba became the first company to ever commercialize the production of epoxy resin in the year 1946. (1)

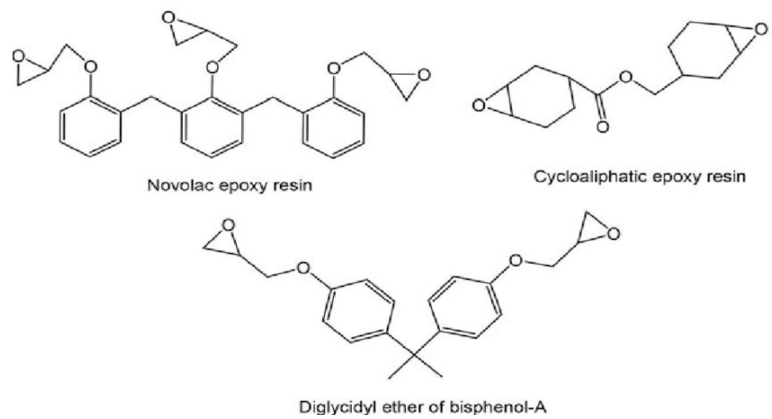


Fig. 1. Structures of various epoxy resins

Synthesis of bisphenol-A Epoxy resins

Bisphenol A epoxy resin is the most widely used epoxy resin. There are many different types of bisphenol A epoxy resins, each with different characteristics and functions. There are mainly five types of these epoxy resins:

Bisphenol-A diglycidyl ether (DGEBA)

Bisphenol-A diglycidyl ether (DGEBA) is a commonly used epoxy resin. DGEBA is a clear or pale-yellow liquid used in commercial plastics (2). It is created by the reaction of bisphenol-A and epichlorohydrin while using a basic catalyst (3). These types of epoxy resins have the lowest molecular weights among epoxy resins. DGEBA-based epoxy resins are widely utilized in various industries and applications due to their desirable properties, such as excellent adhesion, chemical resistance, and mechanical strength. They are commonly used in adhesives, coatings, composite materials, electrical and electronic components, mold making, and most prominently, in the synthesis of polycarbonate plastics.

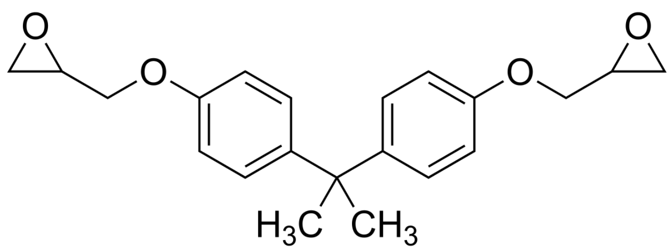


Fig. 2. Structure of DGEBA

Materials
A humidity-protected 500-mL glass reactor was equipped with a mechanical stirrer, dropping funnel, and condenser. Methylyl derivatives of bisphenols (0.11 mol) and 1% (wt% reacted with the weight of methylyl bisphenols) of BF3ET2O, and 10 mol of EC (epichlorohydrin). Additionally, 0.22 mol of NaOH (as a 50% aqueous solution), 50 mL of acetic acid (50% solution), 150 mL of toluene, and hot water (60-80°C).

Synthesis for DGEBA
A humidity-protected 500-mL glass reactor equipped with a mechanical stirrer, dropping funnel, and condenser; purified methylyl derivatives of bisphenols (0.11 mol); 1% (wt% reacted to weight of methylyl bisphenols) of BF3ET2O;

EC (epichlorohydrin) in a quantity of 10 mol; 0.22 mol of NaOH (as 50% aqueous solution); 50 mL of acetic acid (50% solution) for neutralization; 150 mL of toluene; and hot water (60–80°C) used for washing the filtrate. (5)

Novolac Epoxy Resins

Novolac epoxy resin is produced through the reaction of phenol and formaldehyde. These resins exhibit excellent chemical resistance and are widely used in various applications. One notable advantage of novolac epoxy resins is their safety during synthesis and use, as they are free of volatile organic compounds, which means that they can be handled without the need for respirators. Novolac epoxy resins possess high durability and adhesive strength, making them suitable for demanding applications where strong bonding and chemical resistance are required.

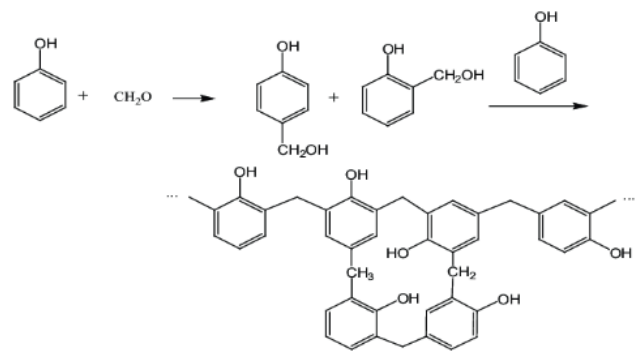


Fig 3. The reaction of phenol and formaldehyde to form the structure of novolac epoxy resin

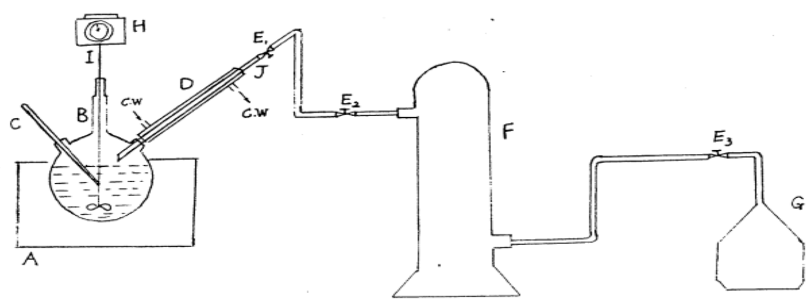
Materials
Diglycidyl Ether of bisphenol A (DGEBA) is recrystallized from an acetone-methanol mixture (20:80, v/v); m.p. 44C Epichlorohydrine (EC) was used as received. AEP was used as a hardener. P-formaldehyde and formalin solutions (37%) were used as received. High-purity acetone, toluene, and pyridine were used as-received. All chemicals were supplied by the Aldrich Chem.

Synthesis
In a humidity-protected 500-mL glass reactor equipped with a mechanical stirrer, dropping funnel, and condenser, the purified methylyl derivatives of bisphenols (0.11 mol) were mixed with 1% (wt% reacted to the weight of methylyl bisphenols) of BF3ET2O and heated at 40C. EC (10 mol) should be gradually added to the reaction mixture during 2 h. The reaction mixture was heated at 65°C for 30 min, cooling to 40C, 0.22 mol of NaOH (as 50% of aqueous solution) was added to the reaction mixture. The temperature of the reaction mixture was increased to 80C for 30 min. After cooling, the mixture was neutralized with 50 mL of acetic acid (50%), 150 mL of toluene was added, and the reaction mixture was filtered to remove sodium salts. The filtrate was washed four times with 150 mL of hot water (60– 80C), toluene was evaporated from the organic layer using a rotary evaporator. The obtained products were viscous liquids (5).

Bisphenol A Diglycidyl Methacrylate (BisGMA):

Bisphenol A diglycidyl methacrylate (BisGMA) is a versatile epoxy resin produced through the reaction of bisphenol A and glycidyl methacrylate. BisGMA is known for its exceptional chemical resistance, making it suitable for applications that require protection against corrosive substances. BisGMA is the safest of all bisphenol-A-based epoxy resins, both during synthesis and usage, as it is low in volatile organic compounds (VOCs), eliminating the need for respirator use during handling. The high durability and adhesive strength of BisGMA make it well suited for demanding applications that require strong bonding and chemical resistance. These properties contribute to its wide utilization in fields such as dental treatments, where it provides structures to caps and crowns by acting as an organic binder.

Materials
0.5 mole of glycidyl methacrylate (GMA), 0.2 moles of Bisphenol A, A 250 ml three-necked flask, nitrogen gas (N2) for bubbling, a temperature-controlled setup to maintain a constant temperature of 60°C, a stirring apparatus, 0.3577 g of dimethyl p-toluidine (DMPT), and 0.0589 g of hydroquinone.



A. ice bath
B. flask
C. thermometer
D. condenser
E_1. value
E_2. value
E_3. value
F. gas dryer
G. N_2 gas cylinder
H. stirring motor
I. glass stirring
J N_2 gas introducing tube

Fig 4. apparatus of BisGMA synthesis

Method
Two or more moles of glycidyl methacrylate were reacted with one mole of bisphenol A (bis(4-hydroxyphenyl)dimethyl methane) or (4,4-Isopropylidenediphenol). The tertiary amine, dimethyl-para-toluidene (DMPT) catalyzes the addition of the phenolic hydroxyl groups to the epoxide groups. The final Bis-GMA synthesis experiment was carried out with 0.5 mole of GMA and 0.2 mole of Bisphenol A in a 250 ml, three necked flask, with continual stirring, N2 bubbling, and the temperature held constant at 60°C. Once the reactants were completely dissolved, 0.3577 g DMPT was added to the flask. After 1 h, a small sample was removed for analysis of the epoxy value, after which 0.0589 g of hydroquinone was added to the reaction mixture. At hours 3, 5, 7, and 9, the samples were withdrawn to determine the epoxy value. After each sampling, 0.3577 g of DMPT was added, except at hour 9. The epoxy value at hour nine indicated that the reaction was complete [6].

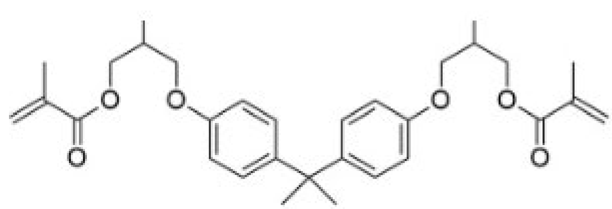


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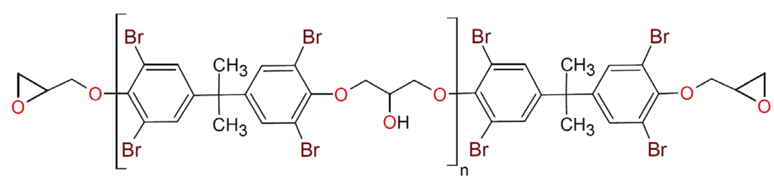
Fig 5. Structure of BisGMA

Brominated epoxy resin

Brominated epoxy resins are a type of epoxy resin that contains bromine atoms, mostly as a result of modifications to bisphenol epoxy resins to add bromine atoms to the structure. Brominated epoxy resins have similar properties to bisphenol epoxy resins, such as great chemical and mechanical resistance, but the unique properties of brominated epoxy resins are their flame retardant properties. The addition of bromine atoms allows for increased flame retardancy, due to which these epoxy resins are used in places where fire safety is vital, such as the aerospace and electronic industries. (7)

Materials
750 cm3 flask, dropping funnel, thermometer, reflux condenser, Tetrabromobisphenol A and Epichlorohydrin to be added in appropriate amounts, isopropanol as an inert process solvent, NaOH, NaCl, hot water to dissolve NaCl, and vacuum distillation equipment that will be used to remove impurities and obtain the resin and the distillate residue.

Synthesis
A 750 cm3 flask was used, along with a dropping funnel, thermometer, and reflux condenser. Appropriate volumes of TBBA and ECH were placed in the flask while isopropanol was used as a solvent that did not react with ECH or TBBA and acted as an inert process solvent. Add 32 wt% of NaOH drop by drop at 50°C for 15 min, after which condensation occurs. After condensation, hot water was added to dissolve the NaCl, and vacuum distillation was used to expel purified volatile products, such as isopropanol. The epoxy resin will be obtained as the distillation residue. (8)



Brominated Bisphenol A Epoxy

Fig 6. Structure of haloganated BPA epoxy

Cycloaliphatic epoxy resins

Cycloaliphatic epoxy resins have a fully saturated molecular structure and aliphatic backbone, which contribute to their outstanding UV stability, weatherability, thermal stability, and electrical characteristics. CAE is extremely vital because it is used with and alongside bisphenol epoxy resin to enhance the properties of Bisphenol epoxy resins (3).

Materials

3′ cyclohexenylmethyl 3-cyclohexenecarboxylate (cyclo-olefin) to react with peracetic acid to produce cycloaliphatic epoxy resin (3′,4′-epoxycyclohexymethyl 3,4 epoxycyclohexane carboxilate [CAE])

Synthesis

The reaction of 3′ cyclohexenylmethyl 3-cyclohexenecarboxylate (cyclo-olefin) with peracetic acid, cycloaliphatic epoxy resin (3′,4′-epoxycyclohexymethyl 3,4 epoxycyclohexane carboxylate [CAE]) was produced. Because CAE often takes the form of a liquid with low viscosity and strong wetting properties—even on oily surfaces—it is frequently used for coating or sizing fibers, along with bisphenol-A. CAE has a fully saturated molecular structure with an aliphatic" backbone. The CAE curing procedure often uses anhydrides that develop during the heating process. Because of its great thermal stability and high resistance to ultraviolet rays, CAE is used to create components for outdoor and high-temperature exposure applications. It is therefore used to enhance the properties of epoxy resin containing bisphenol A to create a heat resistant bisphenol A which can then be used for paints, coats, etc. (9)

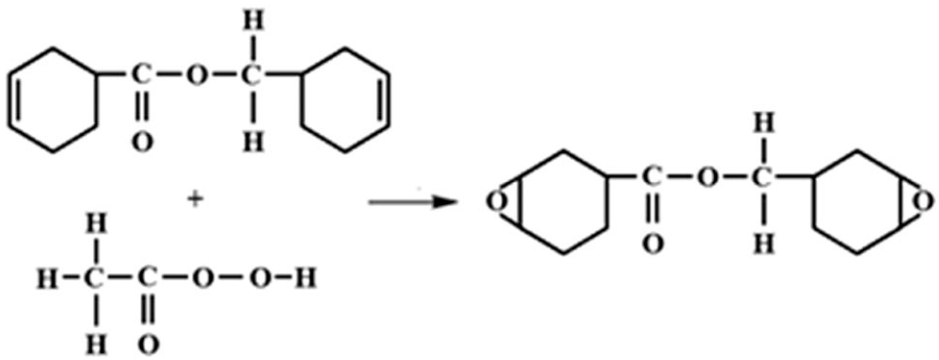


Fig. 7. Formation reaction of GPE-221 from cycloolefin and peracetic acid

Applications

Aerospace was the first commercial field that epoxies could penetrate in the early 1950s. However, it has also been discovered to be extremely useful in other niches. It took over two decades for epoxy resin to obtain the required exposure. Many first questioned the product, which resulted in most commercial failures. The lack of knowledge also managed to do the same. The current epoxy used today has its own formula but is based on the work of Prilezhaev. Thanks to the studies of Dr. Pierre Castan and Dr. S.O. Greenlee, epoxy has further developed and become what it is now. Companies have also contributed to the commercialization of epoxy. Although it may be difficult to explain what epoxy was during those times, they still pushed hard and successfully introduced a new product that revolutionized the market. Epoxy is still very eminent today and will be used in the coming years. Each person plays a role in the epoxy and its history. Scientific minds and entrepreneurs have worked together to make epoxy one of the greatest adhesives today. With previous scientists' efforts, epoxy resin has continued to be pushed toward the market because of its incredibly versatile and beneficial properties. It is also possible to alter the properties of epoxy resins to create materials with desired properties. The following are a few applications of epoxy resins:

Paints and coatings

Because of their unique properties, epoxy resins are widely used in paints and coatings. They have a high chemical resistance, which makes them suitable for heavy-duty anticorrosion coatings. Metal objects such as cans or containers are often coated with epoxy resin, which can prevent rusting. Another property of epoxy resins is that they are highly safe, making them suitable for use as coatings for containers containing acidic substances or foods. For example, storing acidic foods, such as tomatoes, in metallic containers, such as copper or aluminum, can be dangerous as acids react with the metal. However, coating metal containers with epoxy resin can prevent reactions from taking place. Several paints utilize epoxy resin due to its properties such as high corrosion and mechanical resistance, which can provide protection to the painted object; safety, which makes it suitable for everyday use; easy processing and quick drying; affordability, which makes the paints practical; and high toughness and adhesion (3).

Adhesives

One of the biggest applications of epoxy resins is in adhesives. Epoxy resins exhibit strong adhesion, especially towards metals or metallic allows and many other substrates, such as wood and concrete, making them very practical and highly versatile. Epoxy resins have high-strength bonds, and there are high attractive forces between epoxy resins and the substrates, which causes epoxy resins to have very powerful adhesion properties (10). Epoxy resins can function at high temperatures (approximately 150°C) and can be used for both short- and long-term applications. At the same time, many different types of epoxy resins have different properties and cures, owing to which they are incredibly versatile. The curing of epoxy resin does not result in the creation of volatile by-products, and the shrinkage during curing is also relatively low. This, combined with the versatility, safety, affordability, and adhesive strength of resins, makes them a great choice for adhesives. (11)

Construction

Epoxy resins are vital in the construction industry. As mentioned previously, it can be used for adhesives, paints, and coatings, which are integral parts of the construction industry. It is also used to create epoxy resin concrete, which is widely used in construction applications. Epoxy resin helps bond new concrete with old concrete by creating a powerful shear connection between the cured and uncured concrete. Resin mortars have been used in bridges as bedding and have also been used in other such places. Epoxy resin is used to create molds and aid industrial production. It can also be used to create laminates, fixtures, and casts. (12)

Electronics and machinery

Epoxy resins are good insulators, and their toughness can provide protection. Consequently, they are widely used in chemical components to protect circuits from moisture, short circuits, and dust. They are used in motors, generators, insulators, transformers, printed wiring boards (PWB), etc. The structural properties of epoxy resins and their composites make them suitable for machinery. Composite materials are created by combining two or more materials. The composite obtained certain properties from both materials, which means that it is possible to create materials with specific properties using composites. Consequently, it is possible to fabricate composites of epoxy resin to obtain a diverse range of materials that can be useful for machinery. For example, epoxy resin combined with fiberglass produces fiberglass-reinforced resin, which is used to make rotor blades for windmills. Throughout the electronics and machinery industries, epoxy resins are widely used due to their structural and insulative properties. (3)

Aerospace industry

Epoxy resins are utilized in the aerospace industry as adhesives and construction materials. The high adhesive properties and low costs of epoxy resins, as well as their ability to function under a wide range of conditions, make them a popular choice in the aerospace industry. The industry also utilizes fiber-based epoxy resins, which are materials that combine epoxy resins with fibers. Epoxy resin has great strength and durability, and the fiber, typically made of glass or carbon, provides additional strength, making it a highly durable material. Epoxy reinforced with high-strength fibers such as glass, carbon, boron, or Kevlar is strong, durable, and lightweight, which makes it extremely useful for the aerospace industry. (13)

*Other*s

There are several other applications for epoxy resins. It is widely used in art, with many artists using epoxy resin with color to create artwork or other materials such as wood. Clear or colorful epoxy resin can be used to give artwork a glossy finish, or it can be used directly to create artwork. Epoxy resin is also used in biological fields; for For example, vascular grafts utilize epoxy resin.

Epoxy resins are also grealty increasing in the space exploration and space traffic, an increasing number of satellites are being manufactured. Satellites require adhesives and coatings on instruments. Hence, epoxy resins are commonly used as adhesives, coatings, and composite materials for spacecraft and satellite components. Epoxy resins have excellent mechanical properties, low outgassing, and resistance to extreme temperatures. More effective epoxy resins will continue to be researched to meet the demand for space exploration, possibly leading to the development of the most effective material for space exploration. This increase in epoxy demand can be seen in the trend of epoxy resin market size. Epoxy resin had a 23.4 Billion USD market size in 2022, and with a growth rate of 7.22%, it is expected to reach 23.4 Billion USD by 2030. Epoxy resin is a promising field that continues to be explored, yielding great results and advancing all fields universally with its versatility and strength. Accordingly, demand is catching up to the potential of epoxy resins. (14)

Conclusion

This study focused on the classification, synthesis, and application of epoxy resins. It examines various types of epoxy resins and their synthesis methods, highlighting their diverse range of applications in fields such as paints, construction, electronics, and aerospace as coatings, adhesives, and composites. This study aims to provide a comprehensive overview of epoxy resins and their significance in various industries.

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