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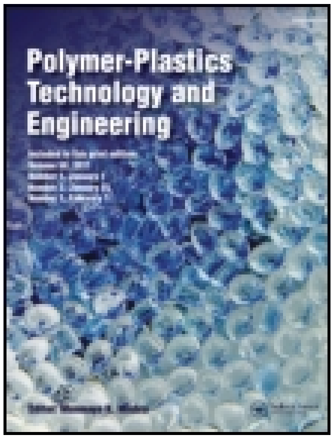

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Synthesis and Modifications of Epoxy Resins and Their Composites: A Review

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Synthesis and Modifications of Epoxy Resins and Their Composites: A Review

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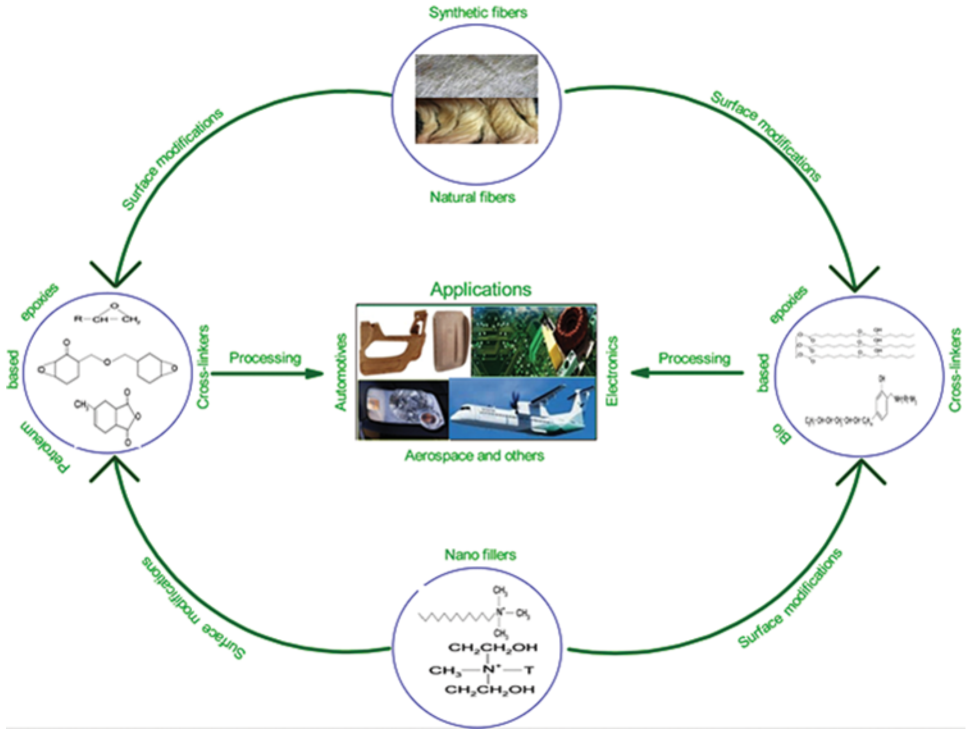
GRAPHICAL ABSTRACT



This article is designed to review the developments in synthesis, modifications, and properties of epoxy monomers derived from both petroleum and renewable resources. It begins with the enhancement in epoxy monomer properties such as mechanical, thermal, adhesive, barrier, etc. by addition of flexible polymer and elastomers. It also explains the role of organic/inorganic fillers on epoxy monomers to achieve the desired properties for outdoor applications. The effects of chemical/physical treatments on fiber are reviewed and their improvements with epoxy monomers are also observed. The authors also suggest for further improvement of epoxy monomers to obtain various eco-friendly high-performance applications.

Keywords Bio-based epoxies; Epoxy polymers; Nanofillers; Natural fibers

INTRODUCTION

The use of lighter materials and reduction of parts in composite development is a concept that has survived since the materials were invented. Polymeric materials with their strength to weight ratios and their functionalities attract

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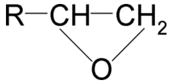


SCH. 1. Epoxide ring.

much attention for the materials world, serving many different industrial applications[1]. Epoxy resins are one of the most important polymeric or semipolymeric materials, part of the thermosetting family; which play an important role in composite materials. They are created using different processing techniques and reinforcing phases. The structure of an epoxy group is shown in Scheme 1; such a chemical structure is also called an oxirane or a glycidyl group[2]. Petroleum-based epoxy monomers are known for superior properties such as tensile strength, high stiffness and excellent electrical strength. These are widely applied in diverse applications in commodity, construction, automotive sectors and aerospace industries due to several desirable properties, such as good mechanical strength, dimensional stability, good wetting ability, fire retardance, excellent chemical resistance and low cure shrinkage[3,4].

The oxirane group of an epoxy monomer reacts with different curing agents such as aliphatic amines, aromatic amines, phenols, thiols, polyamides, amidoamines, anhydrides, thiols, acids and other suitable ring opening compounds; forming rigid thermosetting products[5,6]. The cured epoxies are brittle in nature due to the high degree of cross-linking, and they contribute to weakening epoxy impact strength and other relevant properties[7,8]. Hence, modification of epoxy monomers is necessary to improve their flexibility and toughness as well as thermal properties. Much work has been conducted to reduce brittleness and to improve thermomechanical properties by the incorporation of flexible polymers, inorganic solid particles (nanoparticles), and elastomers[9,10].

Epoxy resin is also used to modify several polymers such as polyurethane or unsaturated polyesters to enhance their physical and chemical attributes. Further, the synthesis, modification, properties and applications of epoxy resins and their curing agents are explained well in two articles[11,12]. Fiber- and nanoparticle-reinforced epoxy composites have generated considerable industrial interest over past decades. These materials have high specific strength-to-weight ratio, low density, and enhanced high modulus, which permits them to contend with selected metals. The primary aim of reinforcing/blending of epoxies is to achieve the desired properties while maintaining low costs. Several approaches for synthesis, modification, properties and applications of epoxy monomers are discussed in this review. This review also highlights the emerging technological knowledge that is leading researchers to prepare epoxy monomers from natural resources such as natural oils and sugars[13,14].

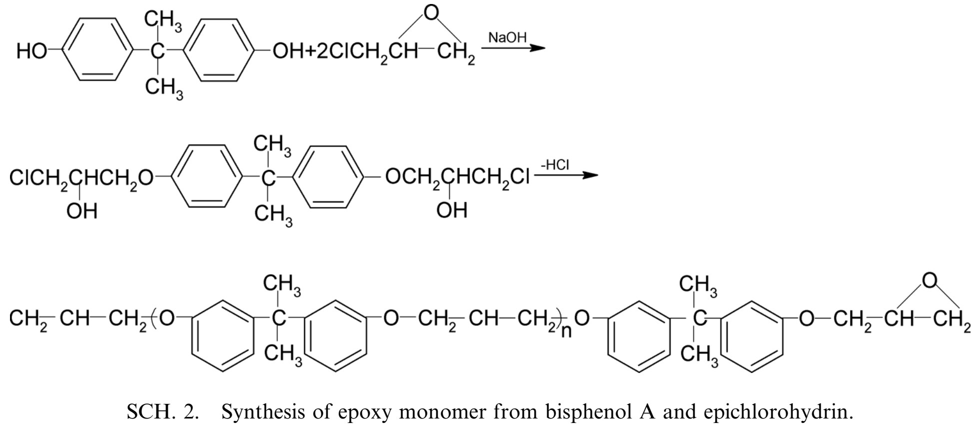
CHEMICAL METHODOLOGIES FOR SYNTHESIS OF EPOXY MONOMERS

Most epoxy monomers are derived from the condensation reaction of epichlorohydrin with aromatic amine, diphenyl methane, polyhydric phenols and polyols, olefinic or polyolefinic compounds, or by peracid epoxidation of olefins, etc. Based on the oxirane ring, epoxy resins are further divided into many categories. Here, we discuss synthesis and preparation of various epoxy monomers.

Di-Functional Epoxy Resins

In 1946, Ciba-Geigy, Ltd. first introduced epoxy resins; today they are everywhere in our daily lives. These resins are synthesized by the condensation reaction of bisphenol A (4,4 (propane-2,2-diyl) diphenol) and epichlorohydrin in the presence of sodium hydroxide catalyst. In 1960, Lee and Neville as well as Wallace[2,3,5], developed the well-known construction of a product called the diglycidyl ether of bisphenol A (DGEBA) (Scheme 2).

Generally, the reaction occurs at 110°C for about 16 h with an excess of epichlorohydrin, and the resulting resin has terminal epoxy groups. Low molecular weight resins



SCH. 2. Synthesis of epoxy monomer from bisphenol A and epichlorohydrin.

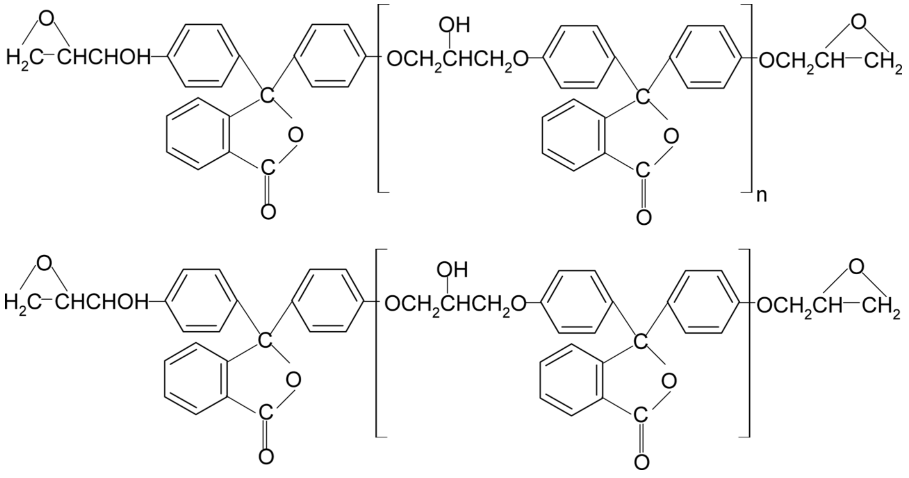


FIG. 1. DGEPP, DGEBF epoxy monomers.

are produced by increasing 10 to 20 mol epichlorohydrin per mol of bisphenol A. Most of the commercial DGEBA epoxies are low in molecular weight with high reactive functional groups and high cross-linking density, which improves the glass transition temperature. High molecular weight resins are generally semisolids, and they need to be melted for compounding. These resins have more hydroxyl groups in their backbones, which provide greater adhesion when cured with hardeners.

Lin et al.[15] have studied different types of di-functional epoxy monomers: 1) bisphenol A (DGEBA), 2) phenolphthalein (DGEPP), and 3) 9,9-bis(4-hydroxyphenyl) fluorine (DGEBF) resins (Figure 1). These resins were cured with trimethoxyboroxine (TMB) hardener, and the order of reactivity of these resins toward hardener was found to be DGEBA ~ DGEBF > DGEPP, respectively. The order of cross-linking density at the same curing conditions was noted to be DGEBA > DGEPP > DGEBF, respectively. High performance epoxy monomers were found by modifying DGEBA with DGEPP and DGEBF. They found that the DGEBA-DGEBF copolymer possessed a high thermal resistance than DGEBA-DGEPP due to aromaticity. Synthesis procedures of epoxy monomers are described next:

1. Diglycidyl ethers of phenolphthalein (DGEPP) were prepared by the reaction of phenolphthalein and epichlorohydrin in the presence of sodium hydroxide catalyst.
2. Diglycidyl ether of 9,9-Bis(4-hydroxyphenyl) fluorene (DGEBF) was prepared from fluorenone and phenol, in the presence of dry hydrogen catalyst and 3-mercaptopropionic acid co-catalyst.

Chen et al.[16] also developed varieties in epoxy resins: 1) bisphenol A (DGEBA), 2) 9,9-bis(4-hydroxyphenyl)fluorine (DGEBF), 3) 3,6-dihydroxyspiro-[fluorene-9,9′-xanthane] (DGEFX), and, 4) l0,l0-bis(4-hydroxyphenyl)anthrone (DGEA) (Figure 2). The authors determined that these polymers exhibited high heat resistance and show better flame resistance when cured with diaminophenylsulfone (DDS) and trimethoxyboroxine (TMB) due to high aromaticity. The glass transition temperature of uncured and cured resins with DDS or TMB was in the order DGEFX > DGEA > DGEBF > DGEBA, respectively, due to an increase in the side chain stiffness. The order of char yield of uncured resins at 700°C was DGEFX > DGEA > DGEBF > DGEBA due to the high level of aromatization.

A brief synthesis procedure of epoxy monomers is mentioned next:

1. Diglycidyl ether of 3,6-Dihydroxyspiro[fluorene-9,Y-xanthane](DGEFX) was prepared from fluorenone and resorcinol with dry hydrogen chloride catalyst.

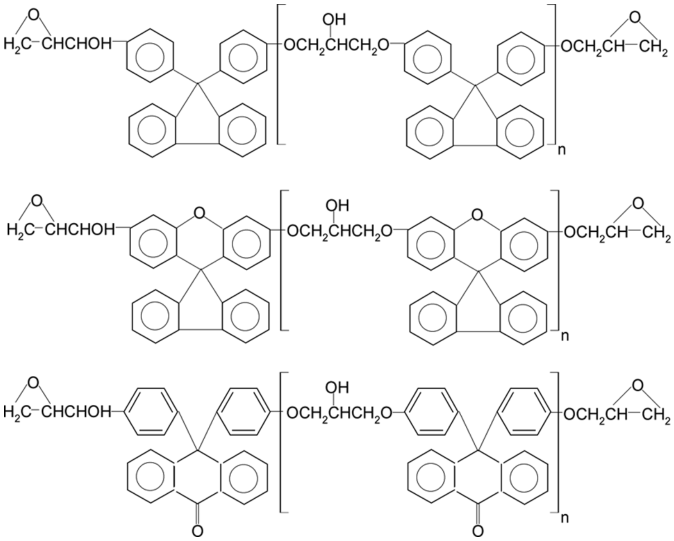
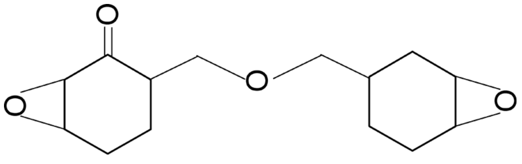
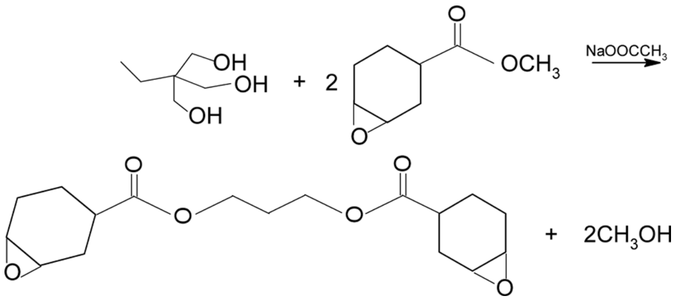


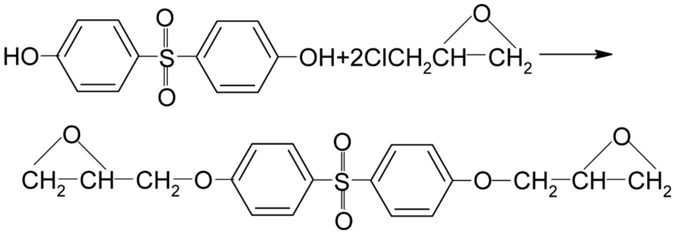
FIG. 2. DGEBF, DGEFX, DGEA epoxy monomers.



SCH. 3. The structure of ERL-4221.



SCH. 4. Preparation of autocatalytic cycloaliphatic epoxy resin (DMTMP).



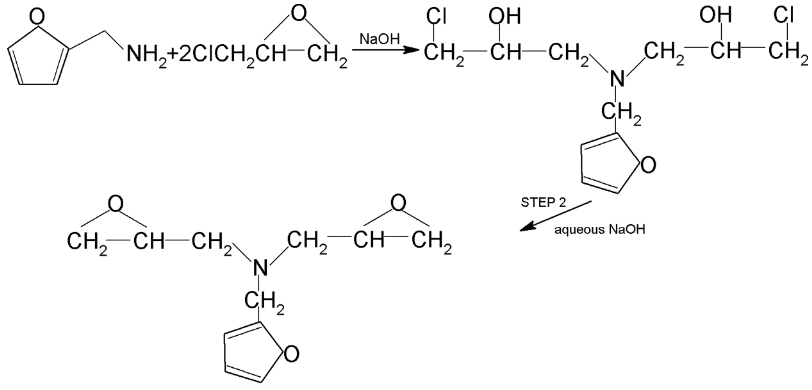
SCH. 5. Synthesis of diglycidylether sulfone monomer (SEP).

2. Diglycidyl ether of 10,10-Bis(4-hydroxyphenyl) anthrone (DGEA) was prepared from anthraquinone and phenol with dry hydrogen catalyst and 3-mercaptopropionic acid co-catalyst.

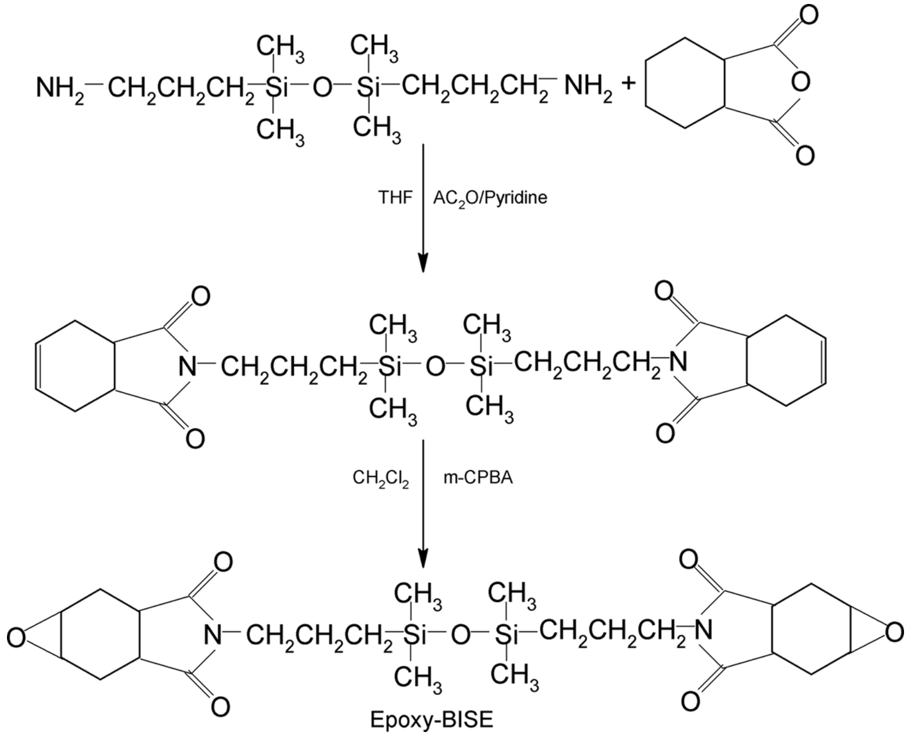
Cycloaliphatc epoxy resin was prepared by Songqi et al.[17], who synthesized by the transesterification of methyl-3,4-epoxy cyclohexane carboxylate and trimethylolpropane. These epoxy resins are chloride-free monomers and highly UV resistant materials because they do not have an epichlorohydrin group and strong UV chromophore groups. The major drawback of these resins exhibit modest reactivity with curing agent due to the epoxide groups present on the rigid rings. Further, they determined that the cycloaliphatic epoxy resins containing hydroxyl groups improve compatibility between resins and curing agents. Based on DSC and TGA studies, cycloaliphatic epoxy resins containing a hydroxyl group (DMTMP) (Scheme 4) system reactivity higher than the commercial cycloaliphatic epoxy 3,4-epoxy cyclohexylmethyl-3,4-epoxy cyclohexane carboxylate (ERL-4221) (Scheme 3) system. They investigated that the decomposition behavior of DMTMP epoxy resin is relatively slow in weight, with a decreasing tendency compared to ERL-4221 epoxy resin.

Chiu et al.[18] reported synthesis of a sulfone-type of epoxy monomer (Scheme 5). Diglycidylether sulfone (DGES) monomer has been prepared from bis(4-hydroxyphenyl) sulfone and epichlorohydrin with the absence of catalyst. The cured DGES material was more thermally stable than the DGEBA due to the formation of sulfate compounds. Glass transition temperature (T_g) was reported as 163.81°C and 111.2°C for DGES and DGEBA epoxy monomer, respectively. The T_g increases from 111.2 to 139.1°C with the incorporation of DGES into DGEBA, due to the establishment of hydrogen bonds between the sulfone group and the hydroxyl group during the ring opening of the oxirane structure.

A novel N,N-diglycidyl-furfurlamine (DGFA) was synthesized by Qiao et al.[19], who synthesized (by a two-step mechanism) the reaction between 2-furfurylamine and epichlorohydrin in the presence of sodium hydroxide catalyst. The two steps were a ring-opening addition reaction between an oxirane ring in epichlorohydrin and DGFA, the product formed through the ring-closing reaction of chlorohydrin groups. The authors found that the cured DGFA (Scheme 6) with methylhexahydrophthalic



SCH. 6. DGFA synthesized by a two-step route.



SCH. 7. Synthesis of imide ring and siloxane containing cycloaliphatic BISE epoxy monomer.

anhydride (MHHPA) possess good mechanical properties and also exhibited thermal remendability. The cracks formed in the cured epoxy monomers were due to the network consisting of two kinds of chemical bonds (i.e., thermally stable cross-linking bonds due to the reaction of epoxide groups with curing agents, and thermally reversible Diels-Alder bonds) and the healing performance of epoxy resins that was well controlled by setting both chemical bonds.

A novel cycloaliphatic epoxy monomer containing imide and siloxane groups were reported by Tao et al.[20]. The 1,3-bis[3-(4,5-epoxy-1,2,3,6-tetrahydrophthalimido)-propyl] tetramethyldisiloxane (BISE) (Scheme 7) epoxy monomer was synthesized in two steps. In the first step, 1,3-Bis[3-(1,2,3,6-tetrahydrophthalimido)-propyl] tetramethyldisiloxane monomer was prepared by the reaction of 1,3-bis(3-aminopropyl)tetramethyldisiloxane and tetrahydrophthalic anhydride. In the second step, cycloaliphatic BISE epoxy resin was prepared by the reaction of 1,3-Bis [3-(1,2,3,6-tetrahydrophthalimido)-propyl] tetramethyldisiloxane with m-chloroperoxybenzoic acid and methylene chloride in the presence of sodium sulfite aqueous solution and sodium bicarbonate. Chemical structures of the epoxies and curing agents are shown in Figure 3. FTIR results confirm the imide ring at 1700 cm^{-1} and siloxane groups at 1351–1354 cm^{-1} and 1067–1076 cm^{-1}, respectively.

It was cured with hexahydromethylphthalic anhydride (HMPA) and hexahydrophthalic anhydride (HHPA), respectively. Already Songqi et al.[17] reported that the cycloaliphatic epoxy resins are thermally more stable than that of a commercial ERL epoxy monomer. The cured BISE epoxy resins are relatively low in glass transition temperatures due to the presence of flexible propyl and siloxane segments in the epoxy backbone. The BISE epoxy resin not only exhibits good strength, but also improves dielectric properties as well as is a highly water resistive material. This is due to the presence of siloxane groups in

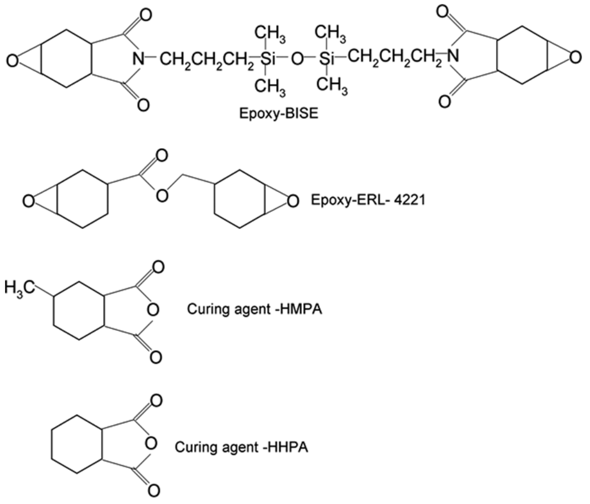
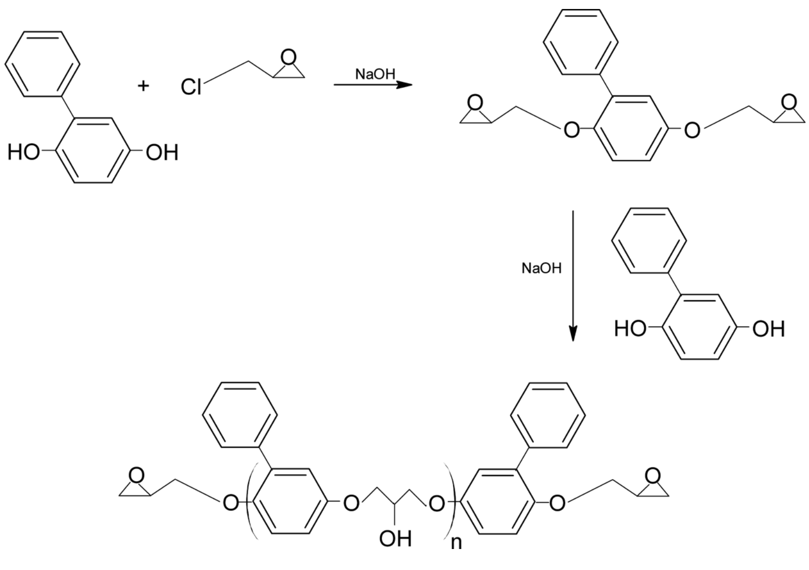


FIG. 3. Chemical structures of the epoxies and curing agents.



SCH. 8. Reaction pathway for the synthesis of epoxy prepolymer.

the epoxy chain length, and these are successfully used in electronic encapsulation applications.

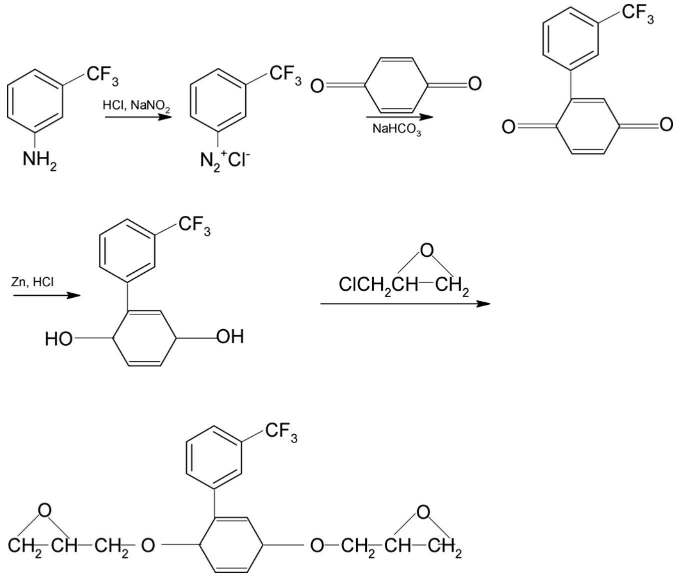
Ridzuan et al.[21] have reported a rigid aromatic-based epoxy resins with the pendant phenyl group (Scheme 8). It was synthesized from the reaction between phenylhydroquinone and epichlorohydrin with sodium hydroxide catalyst. Introducing rigid ring structures into epoxy backbone would induce a higher glass transition temperature (Tg). They concluded that the chemical stability and hardness were improved due to the complicated cross-link network formed during the curing reaction with 4-aminophenyl sulfone.

The epoxy resin containing trifluoromethyl groups has been developed by Z. Liu et al.[22]. The synthesis of (3-trifluoromethyl) phenylhydroquinone epoxy resin (3F-PQE) was followed by three steps:

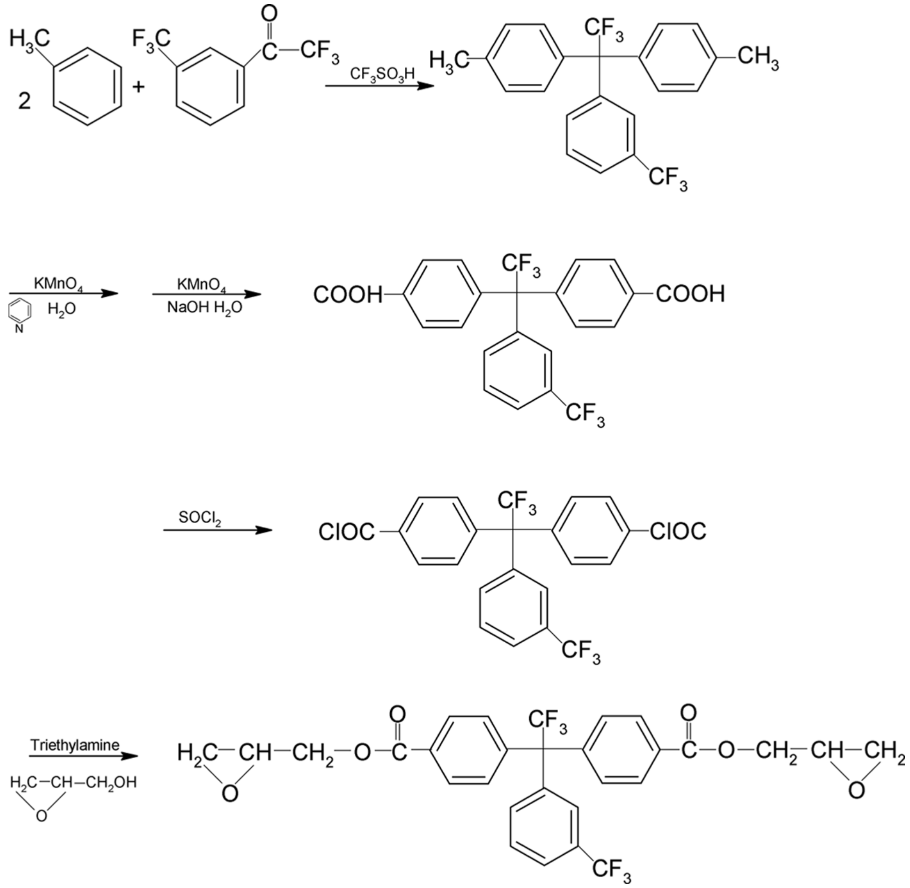
1. Synthesis of (3-trifluoromethyl) benzoquinone (3F-BQ);
2. Synthesis of (3-trifluoromethyl) phenylhydroquinone (3F-PQ); and,
3. Synthesis of (3-trifluoromethyl) phenylhydroquinone epoxy (3F-PQE) monomer (Scheme 9).

The curing studies have been described with four different type functional group curing agents: poly(propylene glycol) bis(2-aminopropy) ether (D230); 2-methylimidazole (2MI); 4, 4-methylene-dianiline (DDM); and, phthalicacidanhydride (PA). From the results, authors found that all cured samples exhibited higher thermal stability in the order: 3F-PQE-DDM > 3F-PQE-2MI > 3F-PQE-D230 > 3F-PQE-PA at 700°C with 21.8, 19.2, 7.7 and 5.3 (wt.%) char, respectively. The 3F-PQE-DDM exhibited the highest T_g (145°C) than the 3F-PQE-2MI, 3F-PQE-D230 and 3F-PQE-PA, respectively. This is due to the presence of rigid aromatic groups in the backbone of DDM-cured epoxy monomer. The authors have found that the succession of the T_gs were in order: 3F-PQE-DDM > 3F-PQE-PA ≈ 3F-PQE-2MI > 3F-PQED230. Moisture absorption of 3F-PQE-DDM and 3F-PQE-PA at 80°C for 24 h was observed to be less than 1 wt.% due to the presence of hydrophobic fluorine atoms in the spine. However, water absorption was found to be greater in the case of 3F-PQED230 and 3F-PQE-2MI due to the presence of aliphatic chain and imidazole group.

Novel fluorinated epoxy monomer has reported by Z. Tao et al.[23], who synthesized 1,1-bis(4-glycidylesterphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane (BGTF) epoxy



SCH. 9. Synthesis route for 3F-PQE epoxy monomer.

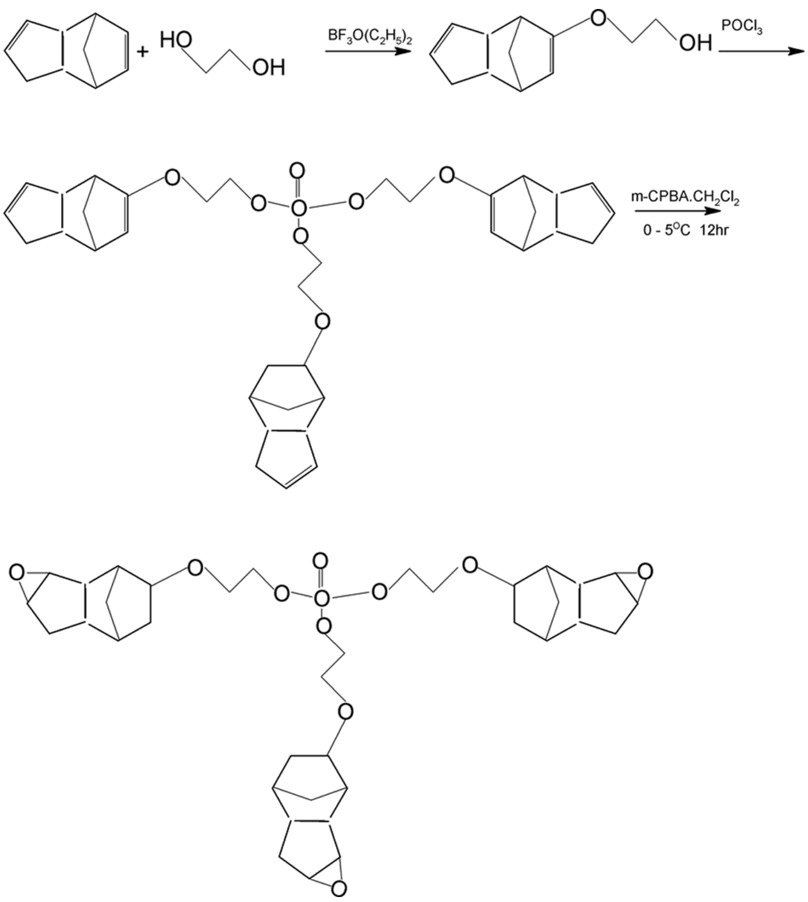


SCH. 10. Synthesis of the fluorinated epoxy compound BGTF.

monomer (Scheme 10) by three steps: 1) 1,1-Bis(4-tolyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane, 2) 1,1-Bis (4-carboxyphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane, and, 3) 1,1-Bis(4-glycidylesterphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane (BGTF). These were cured with hexahydro-4-methylphthalic anhydride (HMPA) and diaminodiphenyl-methane (DDM). The authors found that the viscosity of fluorinated BGTF epoxy monomer was higher than that of DGEBA. The gelation time of epoxy resin systems was found to be in order: BGTF/DDM > DGEBA/DDM ≈ BGTF/HMPA > DGEBA/HMPA. DSC exothermic starting temperatures were in this order: BGTF/DDM < BGTF/HMPA < DGEBA/DDM < DGEBA/HMPA exhibited in 93, 99, 132 and 138°C, respectively. The cured BGTF epoxy resins exhibited excellent mechanical, thermal and glass transition temperature as compared to the cured DGEBA epoxy resins. At 600°C, 47.3 wt.% char yield observed for BGTF/DDM resin and 26.9% of DGEBA/DDM resin and they revealed that improved thermal stability of BGTF/DDM is probably due to the presence of CF3 groups in the polymer backbone. From the results, it is concluded that the cured BGTF epoxy resins exhibited low water absorption and better dielectric properties as compared to the DGEBA epoxy resins. This is due to the existence of hydrophobic fluorine groups in the epoxy resins network.

Tri-functional Epoxy Monomers

The synthesis of a novel tri-functional cycloaliphatic epoxy monomer was reported by Zhang et al.[24] from DCPD as a starting material. Synthesis method was observed by three steps: 1) Synthesis of ethylene glycol monodicyclopentenyl ether, 2) Synthesis of tri-(dicyclopentadiene-oxyethyl)-phosphate, and, 3) Synthesis of epoxide of tri-(dicyclopentadieneoxyethyl)-phosphate (Scheme 11). They also made a comparative study with commercial cycloaliphatic epoxy resin (ERL-4221). Both resins were cured with the hexahydrophthalic anhydride (HHPA). The strong absorption peaks of DCPD were observed at 3047, 1620, and 656 cm^{-1} in FTIR spectrum. Higher char yield observed for tri functional epoxy resins, whereas a more modest value, i.e., 9.3% of char yield has been found in the cured ERL epoxy resins. Results indicated that the higher char yield could be due to the presence



SCH. 11. Synthesis of epoxy monomer starting from DCPD.

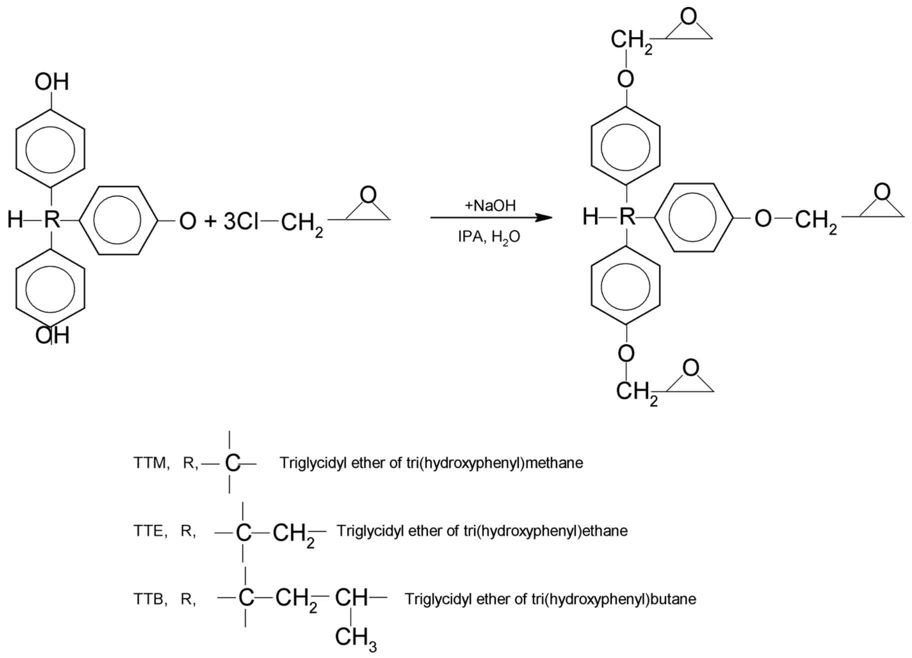
of phosphorus content in tri functional epoxy resins. It is, therefore, proposed that the tri functional cycloaliphatic epoxy resins can be utilized as a packaging material.

Lin et al.[25] synthesized trifunctional epoxy monomers (Scheme 12) from the condensation of triphenol and epichlorohydrin in the presence of sodium hydroxide catalyst. The authors also reported three different type of triphenols (Figure 4) such as tri(hydroxyphenyl) methane, tri(hydroxyphenyl) ethane, and, tri(hydroxyphenyl) butane (THB). These were the condensate products of 4-hydroxybenzaldehyde, chloroacetaldehyde and crotonaldehyde with phenol.

Tetra-Functional Epoxy Monomers

Ayman et al.[26] have reported the preparation of tetra functional epoxy monomers. These monomers were synthesized by the reaction of hydroxyl derivatives with DAK (Diabietyl ketone of resin acid) Diels–Alder adducts and epichlorohydrine in the presence of NaOH catalyst. A hydroxyl derivative of DAK Diels–Alder adducts were prepared by the reaction of diethanolamine (DEA) in the presence of xylene. Diels Alder adducts of DAK are two types: 1) maleodiabietyl ketone (MA/DAK), and, 2) acrylodiabietyl ketone (AA/DAK). These were prepared by the reaction of maleic anhydride and acrylic acid. They also prepared cycloaliphatic-based poly-(amide-imide) hardeners. These hardeners were prepared by the condensation reaction of a ketonic derivative of rosin acid and APA or MPA adducts with polyalklene-polyamines (triethylene tetramine (TETA), pentaethylene hexamine (PEHA)). All tetra functional epoxy resins cured with these poly (amide-imide) hardeners possesses excellent mechanical properties with good durability. The authors concluded that the tetra functional cured epoxy resins can be used as a coating on steel.

Chen et al.[16] have prepared tetra functional epoxy resin of 9,9,10,10-tetrakis (4-hydroxyphenyl) anthracene (TGETA) (Scheme 13) by the condensation reaction of 9,9,10-tri-(p-anisy1)-10-(p-hydroxyphenyl) anthracene and hydro-bromic acid. The authors have also presented a comparative study with di functional and tetra functional epoxy resins. They concluded that the tetra functional cured and uncured epoxy resins show better thermal stability than di functional epoxy monomers due to the presence of high aromaticity. Tetra functional epoxy resins



SCH. 12. General preparation of polyglycidyl ether.

exhibits high heat resistance and better flame resistance with diaminophenylsulfone (DDS) and trimethoxy-boroxine (TMB).

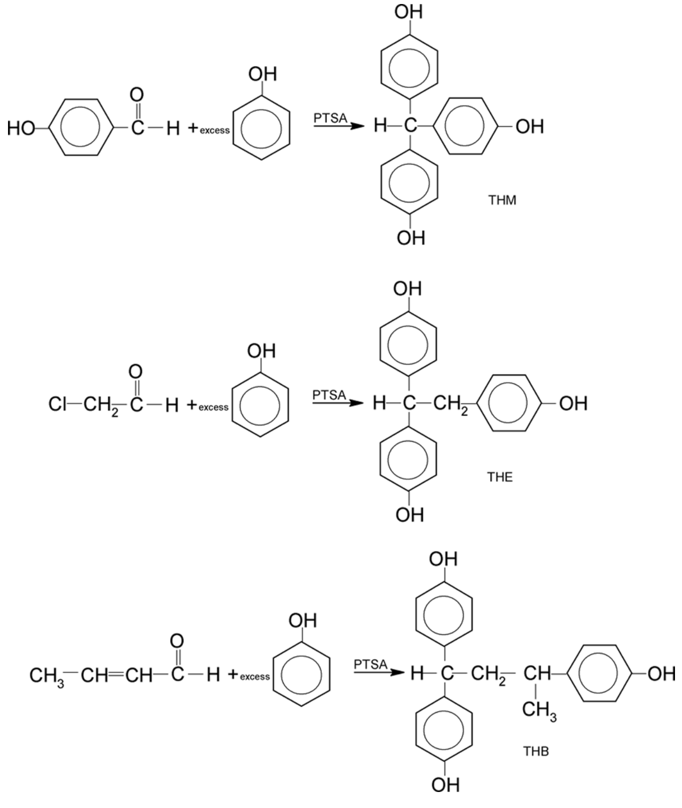


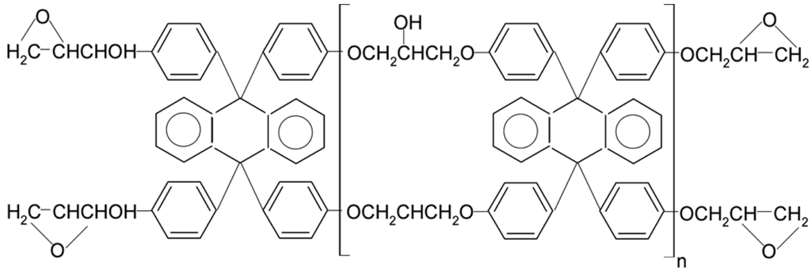
FIG. 4. Schematic diagram of the synthesis of triphenol.

Meenakshi et al.[27] have prepared N,N′–Tetraglycidyloxy 1,1,3,3-tetramethyl siloxane diamine (TG-siloxane) (Figure 5) by the reaction of 1,3-Bis-(aminopropyl) tetra methyl disiloxane and epichlorohydrin in the presence of sodium hydroxide catalyst. The curing was done with diaminodiphenylmethane (DDM) and bis(3-aminophenyl) phenylphosphine oxide (BAPPO) curing agents. The incorporation of siloxane into epoxy resin enhances the thermomechanical and physicochemical properties as compared with the di-functional epoxy resins. Siloxane groups were found at 1105–1100 cm^{-1} in the FTIR spectrum. The authors concluded that the mechanical, thermal, water absorption and fire retardant properties were found to be better for BAPPO-cured systems than DDM.

Multifunctional Epoxy Resins

Multifunctional Bis-ANER (bisphenol A type Novolac epoxy resin) was synthesized by Yanfang et al.[28] from Bis-ANR (Figure 6) and epicholorhydrin in the presence of sodium hydroxide catalyst and 4,4′-diaminodiphenyl sulfone (DDS) as curing agent. The activation energy obtained from the dynamic Kissinger and Flynn–Wall–Ozawa methods, and isothermal Kamal kinetics model of k_1 and k_2 were observed to be 62.7, 67.1, 66.7 and 67.9 KJ/mol, respectively. They concluded that the isothermal curing activation energy values were close to that of the dynamic curing.

Similarly, Guoyuan Pan et al.[29] has described a series of novel Novolac epoxy resin containing naphthalene moiety with different molecular weights. It was synthesized



SCH. 13. Structure of TGETA epoxy monomer.

by the condensation reaction of bisphenol A-naphthaldehyde Novolac resin (bis-NANR) (Scheme 14) with epichlorohydrin. The concluded that the Novolac epoxy resins show better thermal stability and moisture resistance than that of the DGEBA epoxy resin when cured with 4,4′-diaminodiphenyl sulfone (DDS). Naphthalene epoxy systems (Scheme 15) exhibited higher glass transition temperature than phenyl-based system. This is due to the presence of rigid naphthalene in the epoxy backbone. Cured naphthalene epoxy resins shows better moisture resistance than that of BPA epoxy system since hydrophobicity increased with increasing molar ratio of 1-naphthaldehyde to BPA.

Flame-retardant Epoxy Monomers

A various kind of flame-retardant compounds have become of great importance relative to epoxies in order to improve their relative flame retardancy. Several methods can raise the flame retardancy of the epoxy monomer, i.e., (1) additive type flame retardants, which include inorganic nanoparticles; and (2) reactive type flame retardants, which includes phosphorus and nitrogen[30–32]. These include aluminium oxide trihydrate, boron, carbon nanotubes, natural and synthetic fibers[33,34], montmorillonite clays [Sameer et al.[35], nitrogen, phosphorus, polyhedral oligomeric silsequioxanes (POSS)] (Hongyu et al.[36], polyamide, polyimide and silicon compounds (Wang et al.[37], Wenchao et al.[38] and Chen-Feng et al.[39]. These compounds can reduce the high-temperature transfer between the polymer source and heat source, and suppress the smoke during combustion[40,41].

A novel flame-retardant phosphorus-based Novolac epoxy monomers have reported by Muriel et al.[42]. These monomers were prepared by the addition reaction of 9,10-dihydro-9,10-oxa-10-phosphaphenanthrene-10-oxide; 9,10-dihydro-9-aza-10-phosphaphenanthrene-10-oxide (DAPO); and 9,10-dihydro-9,10-oxa-10-phosphaphenanthrene-10-sulfide (DOPS) with epoxy phenolic Novolac monomer in the presence of triethanol amine catalyst. The curing studies of the monomers have been observed in the presence of DICY hardener and Fenuron accelerator. Organo-phosphorus compounds are halogen-free compounds, generating less

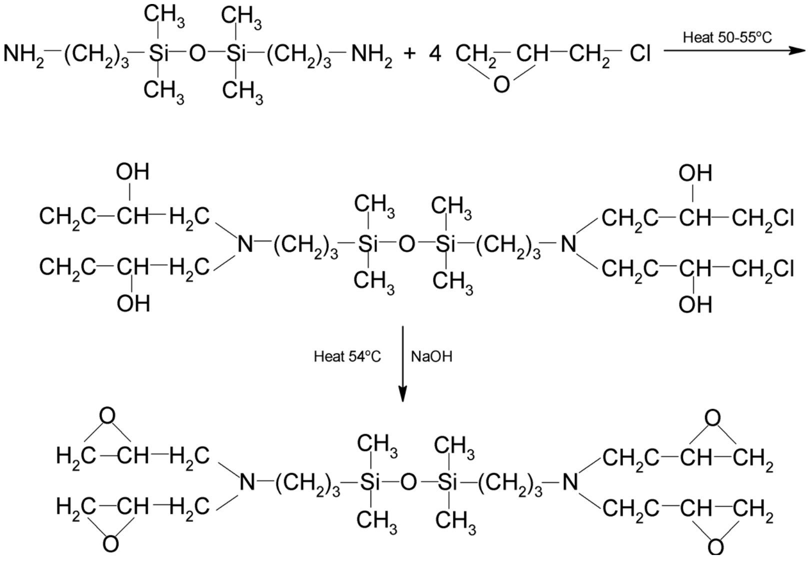


FIG. 5. Synthesis of the tetra functional (TG-siloxane) epoxy monomer.

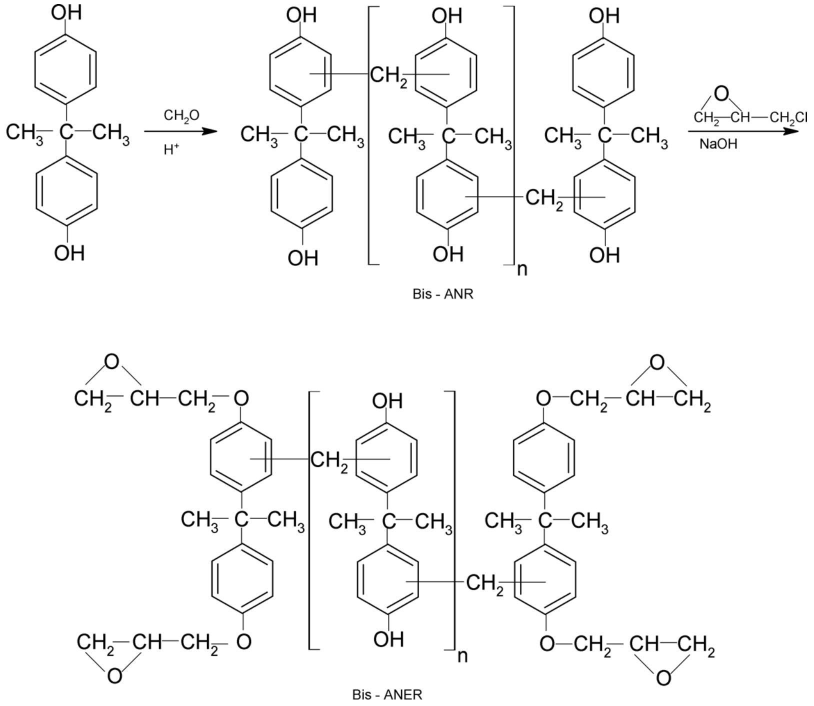
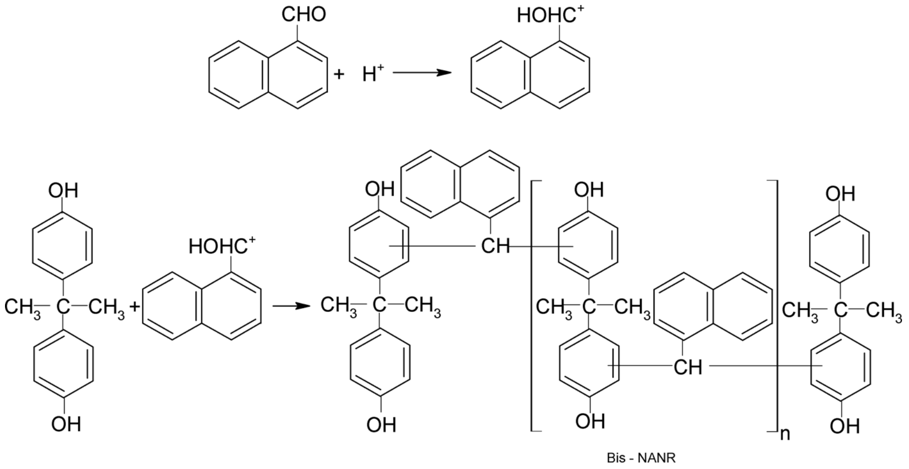


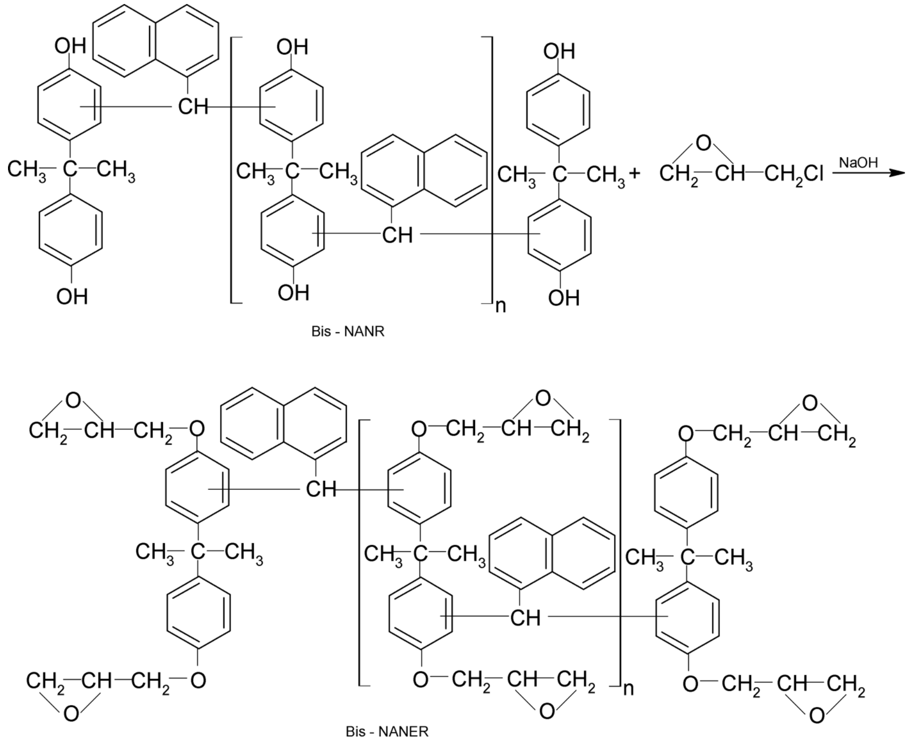
FIG. 6. Synthesis of Bis-ANR and Bis-ANER.

toxic gases and smoke. These groups are permanently bonded to the epoxy resins and exhibit relatively high fire retardancy. The thermal decomposition of epoxy monomers containing DOPO, DOPS and DAPO (Scheme 16) was observed at 700°C to be 31, 32 and 35 wt.%, respectively.

Lin et al.[43] have prepared novel multifunctional phosphorus epoxy monomers, namely $C_{12}P_2$ and $C_{12}P_4$. These monomers were synthesized by the addition reaction of 9,10-dihydro-9-Oxa-10-phosphaphenanthrene 10-oxide (DOPO) (phosphorus content of 2 wt.% and 4 wt.%) and the glycidyl ether of cresol formaldehyde Novolac epoxy monomer. Three different curing agents such as 4,4′-diaminodiphenyl sulfone (DDS), phenol Novolac (PN) or dicyandiamide (DICY) were used in the curing process of epoxy monomer. The authors concluded that the flame retardancy was found to be more in $C_{12}P_4$ (phosphorus content is 4 wt.%) than that of $C_{12}P_2$. The char yield increases with increasing phosphorus content, indicating an increment in flame retardancy.



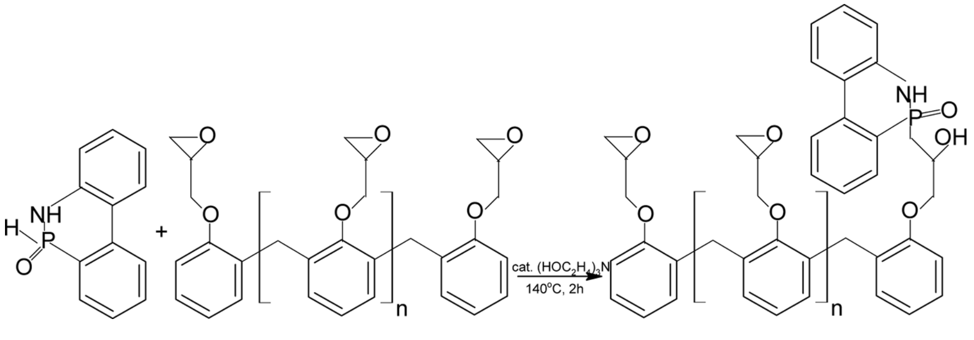
SCH. 14. Schematic diagram of the synthesis of bis-NANR.



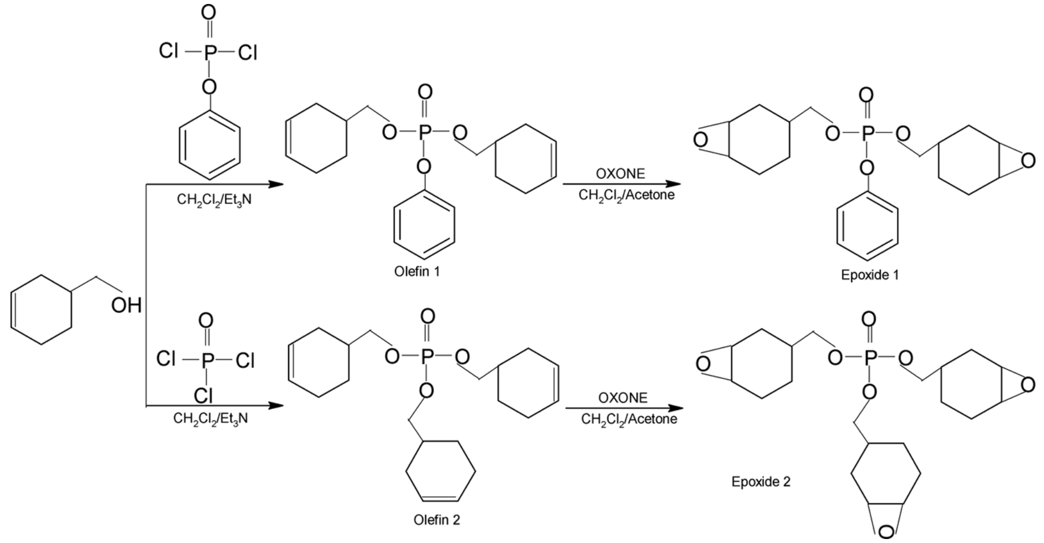
SCH. 15. Schematic diagram of the synthesis of bis-NANER.

The char yields at 700°C were in order $C_{12}P_4$/DICY < $C_{12}P_4$/DDS < $C_{12}P_4$/PN of 27.9, 29.5 and 41%, respectively. The glass transition temperature was observed to be in decreasing order $C_{12}P_4 < C_{12}P_2 < C_{12}$ with all curing agents. This is due to the high rigidity of DOPO leading towards the decrement in cross-link density. A material with LOI of 26 or higher and lower HRR value is placed as a flame-retardant material. LOI values were found to be 38, 33 and 28, respectively, for $C_{12}P_4$/DICY, $C_{12}P_4$/DDS and $C_{12}P_4$/PN. The LOI of $C_{12}P_2$/DICY is higher than $C_{12}P_2$/DDS and C12P2/PN due to the presence of more nitrogen groups. The authors concluded that higher LOI values were obtained with higher phosphorus content. Wanshuang et al.[44] reported phosphorus-containing di- and tri-functional liquid cycloaliphatic epoxy monomers. These monomers were synthesized from olefins by epoxidation to give epoxides. These were cured with HMPA hardener and 2-ethyl-4-methylimidazole accelerator.

The cross-linking density of cured trifunctional Epoxide II (tri(3,4-epoxycyclohexylmethyl)phosphate) was found to be higher by 294% and 64.7% than that of Epoxide I (bis(3,4-epoxycyclohexylmethyl)phenylphosphate) and ERL-4221. They concluded that the T_g-DMA is higher than the Tg-DSC. The T_g values for the three samples were in the order: Epoxide II > ERL-4221 > Epoxide I; obtained from DMA: 227, 191 and 130°C; DSC: 199, 175 and 113°C, respectively. The char yield of phosphate resins was found to be 8 and 12 wt.% low cured Epoxide I and



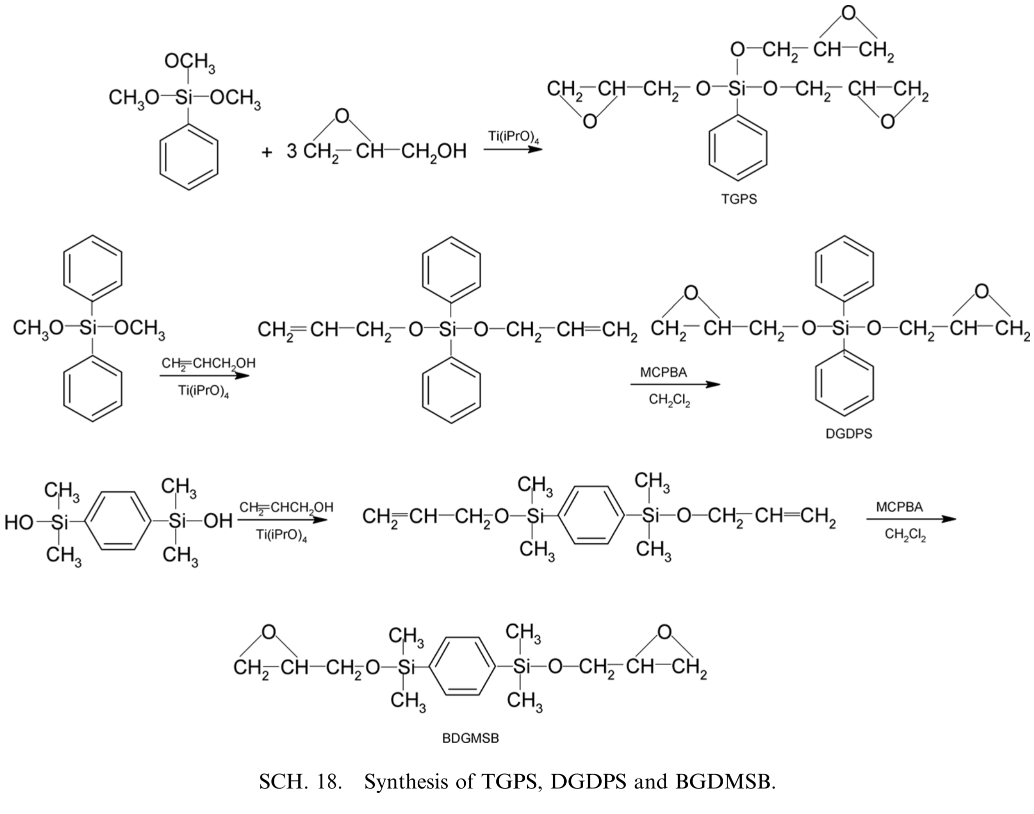
SCH. 16. Functionalization of epoxy phenol Novolac monomer with DAPO.



SCH. 17. Synthesis routes of two phosphorous containing epoxides.

II (Scheme 17), which were much more important than that of ERL-4221. Lin et al.[43] already discussed that the higher phosphorus-containing polymers usually have higher char yield. Synthesized phosphate epoxide II shows 31% LOI, which is higher than ERL-4221 resin.

Mercado et al.[45] have reported two different approaches to introduce silicon atoms into epoxy monomers. First, a new reactive silicon-containing epoxy monomer (Scheme 18) was prepared from diglycidyloxydiphenyl silane (DGDPS), 1,4-bis(glycidyloxydimethyl silyl)-benzene (BGDMSB) and triglycidyloxyphenyl silane (TGPS). Second, silanol with DGEBA was prepared in a chain extension process and designated as $EpSi_{2-1}$ and $EpSi_{3-2}$. These glycidyl epoxy monomers were cured with



SCH. 18. Synthesis of TGPS, DGDPS and BGDMSB.

4,4′-diaminodiphenylmethane (DDS). The glass transition temperature (T_g) of cured silicon epoxy was in the order of $EpSi_{2\text{-}1} > EpSi_{3\text{-}2} >$ TGPS > DGDPS > BGDMSB, BGDMSB, respectively.

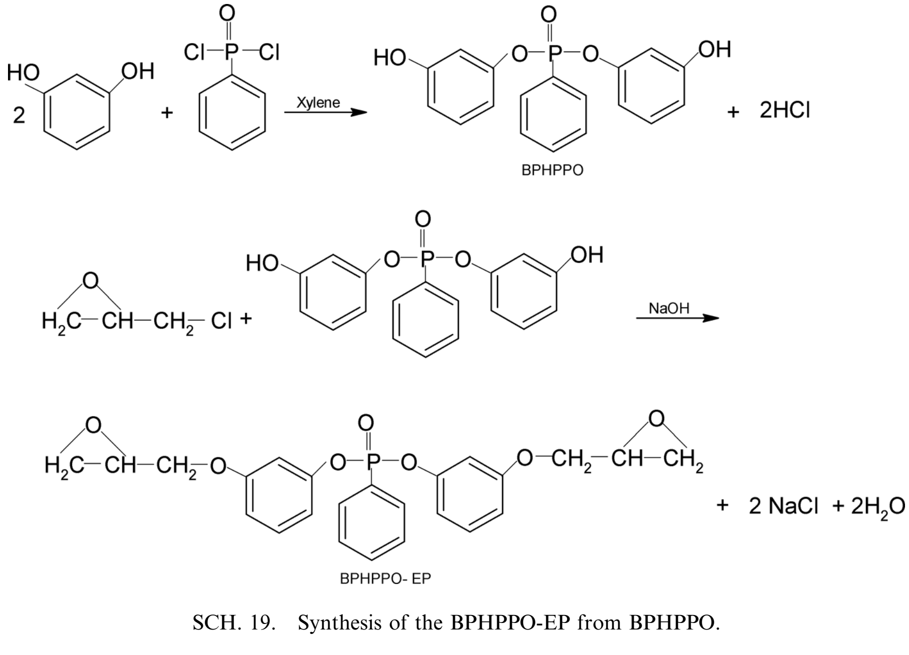
From the results, the authors concluded that the T_g of EpSi material was found to be higher than that of DGDPS, TGPS and BGDMSB monomers due to the presence of aromatic moieties, which restrict the segmental mobility. The T_g of TGPS is higher than that of DGDPS because trifunctional monomers having a high cross-linking density than that of difunctional monomers. However, BGDMSB shows very low T_g value which may be due to the presence of higher flexible segments of Si-O and Si-C units in the backbone. They also concluded that the thermal decomposition of cured silicon containing epoxy resins were low and to be noted in the order of $EpSi_{3\text{-}2} < EpSi_{2\text{-}1} <$ TGPS ≈ BGDMSB < DGDPS. BGDMSB showed 33.5% LOI value which was better than the all other cured epoxy monomers. This is due to the presence of SiO and SiC groups in the chain backbone generally had high flame resistance.

Ren et al.[46] reported synthesis of bis-phenoxy (3-hydroxy) phenyl phosphine oxide epoxy monomer (BPHPPO-EP) (Scheme 19) by the condensation reaction of bis-phenoxy (3-hydroxy) phenyl phosphine oxide (BPHPPO) and epichlorohydrin. The phosphorus atoms present in the BPHPPO-EP increases the flame retardancy property with 34% LOI.

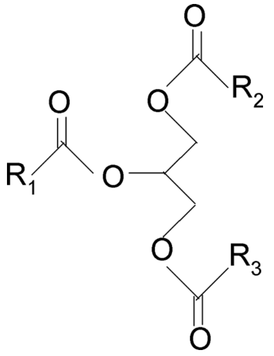
Advanced naphthalene containing epoxy monomer was prepared by Wang and Lee[47] and showed better flame retardancy as well as higher thermal stability than the DGEBA epoxy monomer. A novel epoxy acrylate containing phosphorus and nitrogen flame-retardant monomer (POPHA) was synthesized by allowing the phosphorus oxychloride to react with piperazine and 2-hydroxyethyl acrylate (Xiaodong et al.[31]). The phosphonate flame-retardant epoxy monomer degrades at 260–300°C and formed phosphoric acid, reacts with epoxy acrylate monomer and forms complex phosphorus rich char. It protects the residue from oxygen and heat, resulting in higher char residue at high temperature; and it also helps to decrease in the peak heat release rate (PHRR) of the monomer. The authors concluded that the incorporation of POPHA into EA improves the thermal stability and increases the LOI value from 21 to 29 with addition 0 to 20 wt.% of POPHA. Similarly, Qiang et al.[48] have reported flame-retardant and smoke suppression epoxy monomer containing poly (melamine-ethoxyphosphinyl-diisocynate) (PMPC). PMPC is a combination of phosphorus and nitrogen compounds, which helps to reduce the emissions from smoke and poisonous gases during a fire.

Renewable Resources-Based Epoxy Monomers

Referable to the growing environmental consciousness, sustainability and the depletion of non-renewable resource issues; the biobased epoxies gained very good interest. Recently, petroleum-based epoxies successfully replaced by bio/renewable-based materials developed from sugars, vegetable oils, lignin, furans, etc.[14,49]. The major challenge of biobased polyols is to replace bisphenol A to save our landfill. Here, we have discussed various methods to synthesis the biobased epoxy monomers from renewable resources[50].



SCH. 19. Synthesis of the BPHPPO-EP from BPHPPO.



SCH. 20. Structure of glyceride.

Biobased Epoxy Networks Derived from Vegetable Oils

The vegetable oils such as castor oil[51], cottonseed oil[52], hemp oil[53], linseed oil[54,55], mustard oil[56], palm oil[57,58], rapeseed oil[59] and soybean oil[60,61] are extensively utilized as a major material in the synthesis various bio-products. Various researchers have been studied, the component parts of vegetable oil such as fatty acids and glycerol ester or triglyceride; for use in oleoresinous production. Many researchers have reported the chemical modification and transformation of triglycerides into polymerizable monomer via epoxidation[62,63]. The glyceride structure is depicted in Scheme 20, where R1, R2 and R3 represent fatty acid chains.

Triglyceride contains several reactive positions of C=C and these sites can modify the triglyceride structure with polymerizable groups to obtain polymerization products. Epoxidation is a commercial important functionalization reaction in organic synthesis involving C=C. Tan and Chow[64] have attempted a comprehensive review on the epoxidation of triglyceride oils, optimization of epoxidation conversion rate and increase the epoxy yield. The epoxidation reaction is carried out in the presence of H_2O_2, glycial acetic acid and a catalyst[65]. H_2O_2 acts as an oxygen donor and glycial acetic acid as an active oxygen carrier in the presence of an organic acid catalyst[66].

Park et al.[51,61] have reported the preparation of epoxy prepolymers from vegetable oils. Solution of soybean oil or castor oil or linseed oil, glacial acetic acid, amberlite and toluene were charged in a four-necked, roundbottom flask equipped with a mechanical stirrer, thermometer sensor, and reflux condenser. The mixture was heated at a constant temperature of 55°C, H_2O_2 was added to it and heated up to 55°C for 7 h. Subsequently, the reaction was separated out and washed with distilled water until pH 7 is passed. The oil phase was dried with anhydrous sodium sulfate and then filtered. Finally, the toluene was removed in a vacuum oven at 80°C. The yield obtained from the reaction was 89%. Epoxidized linseed oil shows a higher level of oxirane groups and it gives three dimensional networks with higher cross-linking densities. The syntheses of various epoxidized vegetable oil-based monomers are shown in Figure 7.

Boquillon and Fringant[67] synthesized different types of epoxidized oils and curing studies has been observed with different curing agents such as anhydrides and amines. Decrease in thermomechanical properties and increase in glass transition temperatures were observed in linseed oil than that of epoxidized soybean oil and castor oil. This is due to the large number of double bonds, which contributes more epoxy groups[58].

Stemmelen et al.[68] synthesized a novel vegetable oil-based polyamine from grapeseed oil (GSO). Polyamine grapeseed oil (AGSO) was used as curing agent for epoxidized linseed oil (ELO) to create a fully biobased mesh. AGSO cured ELO (Figure 8) exhibited very low Tg (−38°C) as

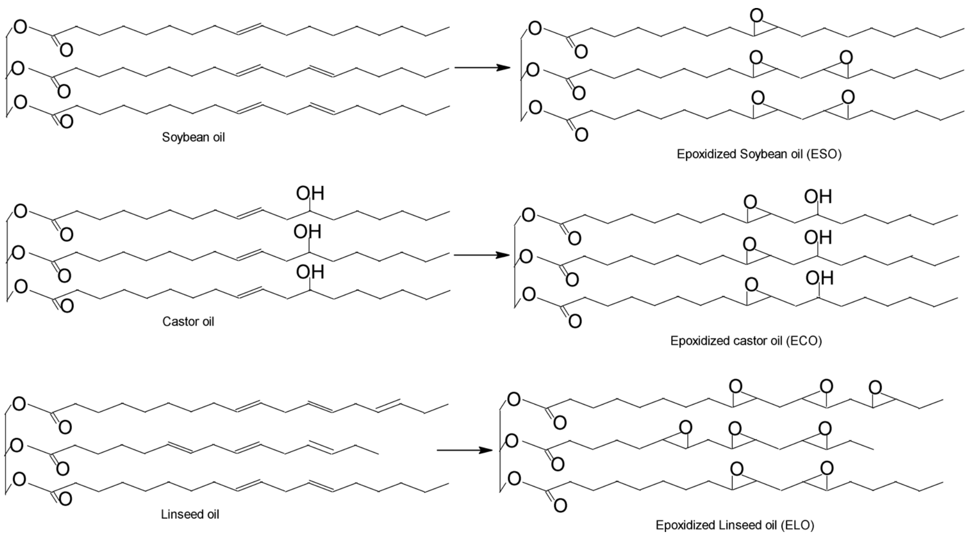


FIG. 7. Epoxidized vegetable oil monomers.

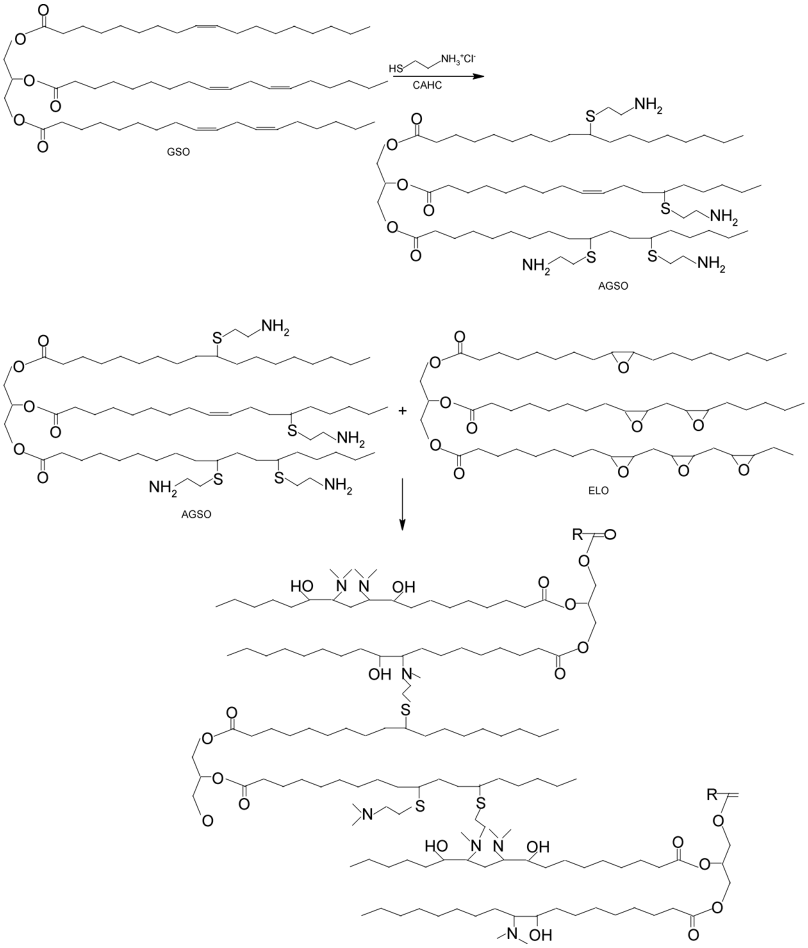


FIG. 8. Synthesis of polyamine grapeseed oil (AGSO); cross-linking reaction between ELO and AGSO.

compared with the anhydride (MTHPA)-cured epoxidized linseed oil ($T_g = 109°C$). This is due to the much higher molecular flexibility of the polyamine grapeseed oil (AGSO).

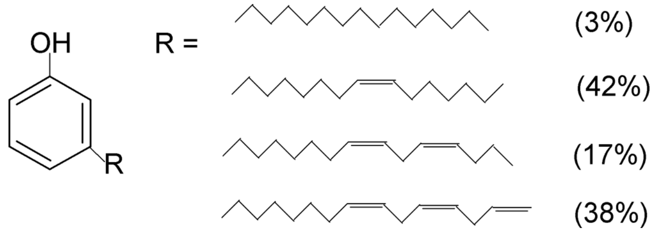
Epoxidation of cottonseed oil was prepared by Srikanth et al.[52] using different liquid inorganic acid catalysts. The effectiveness of catalysts were found in order: sulphuric acid > phosphoric acid > nitric acid > hydrochloric acid. They concluded that the optimum conversion of oxirane groups obtained at 60°C and they also concluded that the acetic acid was superior to the formic acid for the epoxidation of cottonseed oil.

Biobased Epoxy Networks Derived from Cardanol

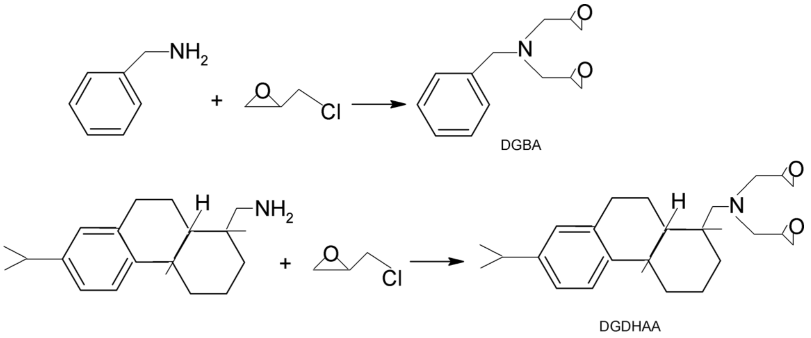
The cardanol was prepared by the vacuum distillation of cashew nut shell liquid (CNSL)[69]. CNSL is a very good alternative to petroleum derived phenols. A Cardanol is a mixture of meta alkylphenols with an unsaturation degree of the aliphatic chain[50,51,61]: 3% 3-(pentadecyl)phenol, 42% 3-(8Z-pentadecenyl)phenol, 17% 3-(8Z,11Z-pentadecadienyl) phenol, and 38% 3-(8Z,11Z,14Z-pentadecatrinyl)phenol; their structures were depicted in Scheme 21. Cardanol exhibiting excellent mechanical and thermal properties due to aliphatic and aromatic structures in their chain and it seems to be the substation of Bisphenol A in the preparation of epoxy monomers[54]. Epoxidized cardanol is commercially available from the Cardolite Co[62].

Biobased Epoxy Networks Derived from Sugar

The growing environmental consciousness BPA is toxic and cause feminizing effects on living creatures, it could be successfully replaced by bio-derived monomers from sugar.



SCH. 21. Structures of cardanol and their compounds.



SCH. 22. Synthesis route for rosin-based epoxy and its twin.

The sugar-based monomers are attached to the glycidyl ether for making cross-linkable epoxy monomer with similar properties of diglycidyl ether bisphenol-A[70]. In another pioneering work, Feng et al.[71] and Fenouillot et al.[72] have reported the synthesis of sugar-based epoxy monomers from sucrose, sorbitol, maltitol and isosorbide.

Epoxy Networks Derived From Sucrose. Sucrose mainly consists of glucose and fructose units, contains a six-member ring of glucose and a five-member ring of fructose. The sucrose-based epoxy monomer i.e., epoxy allyl sucrose (EAS) was synthesized by Sachinvala et al.[73] from epoxidation of octa-O-allyl sucrose. The epoxidation is followed by two steps: 1) Methallylation – it takes place in the presence of aqueous sodium hydroxide and methallyl chloride, and 2) Epoxidation of methallyl intermedium with peracetic acid. They concluded that the glass transition temperature and total heat of cure (ΔH) of EAS/DETA were found to be low as compared with DGEBA/DETA monomer. This is due to the flexible segments present in the EAO chain. Thermal stability of cured EAO exhibited lower temperature than that of DGEBA due to the absence of aromatic rings[66,67].

Biobased Epoxy Networks Derived from Maltitol and Sorbitol. Acierno et al.[74] have reported the multifunctional epoxy monomers such as epoxy metallyl sorbitol (EMS) and epoxy metallyl maltitol (EMM). These were synthesized from sorbitol and maltitol by the epoxidation reaction. They concluded that the storage modulus of EMS and EMM exhibited higher values than that of DGEBA, when cured with DETA at room temperature and the storage modulus of EMO and EMM were quickly falling down with increasing temperature.

Epoxy Networks Derived from Isosorbide. To the environmental and human health concerns, research dissected towards the development of biobased materials. Morrison et al.[75] have replaced bisphenol A by a cyclic aliphatic diol (isosorbide) in the preparation of epoxy monomer. Isosorbide consists of two fused tetrahydrofuran (THF) rings with an obtuse angle ($\approx 120°$) between them. These fused rings of cycloaliphatic diol molecules provide a high stiffness and thermal stability. Recently, Feng et al.[70,71] and Marie et al.[76] synthesized bis-isosorbide diglycidyl ether by heating of isosorbide with 50% sodium hydroxide solution in excess of epichlorohydrin. Isosorbide epoxy monomer showed better tensile properties than that of DGEBA when cured with aliphatic amine hardeners. The glass transition temperature (T_g) of the isosorbide epoxy monomers was lower than that of DGEBA, due to high affinity for water. Isosorbide epoxy monomer was also cured with methyl-5-norbornene-2,3-dicarboxylic anhydride (NMA) with initiator benzyl dimethyl amine (BDMA) to increase the thermal properties[77].

Biobased Epoxy Networks Derived from Rosin

Many researchers have focused on the rosin-based epoxy monomers and their curing agents. Dehydroabietylamine (DHAA) is a derivative of rosin acid, which possesses an aromatic diterpene structure with three rings. Diglycidyl DHAA synthesized by the condensation reaction of DHAA with epichlorohydrin in the presence of sodium hydroxide catalyst[78]. They concluded that the DGDHAA epoxy monomer cured with hexahydrophthalic anhydride (HHPA) shows an enhancement in glass transition temperature. This is due to the presence of bulky fused ring structure in DHAA, which restrict the molecular mobility. Mechanical properties such as tensile and flexural were found to be low for DGDHAA (Scheme 22) as compared with the diglycidyl benzylamine (DGBA) due to the lower in rigidity and the cross-link density.

Recently, Chahinez et al.[79] have prepared biobased epoxy monomer from gallic acid by allylation and followed by epoxidation.

COMBINATION OF EPOXY MONOMERS WITH ORGANIC AND INORGANIC MATERIALS

As said earlier that the epoxies are brittle in nature. However, the modification of epoxy monomers is felt necessary to improve the toughness and thermomechanical properties. Modification of epoxy monomer can be carried out in several ways, such as (i) elastomer modification, (ii) thermoset modification, (iii) thermoplastic modification, (iv) particulate modification, and (v) miscellaneous methods.

Elastomer-Modified Epoxy Monomer

Sultan and McGarry[80] have first reported rubber toughened epoxies to enhance the fracture toughness. They used low molecular weight carboxyl terminated copolymer of butadiene and acrylonitrile. Investigators further attempted on the modification of epoxy monomer using reactive oligomers, and preformed elastomeric particles (instead of reactive oligomers). Many authors have reported the modification of epoxy monomer using suitable rubbers such as carboxyl terminated butadiene acrylonitrile rubber (CTBN)[81], amine terminated butadiene acrylonitrile rubber (ATBN), epoxy terminated butadiene acrylonitrile (ETBN) and hydroxyl terminated polybutadiene liquid rubber (HTPB)[82–84]. Enhancement in toughness of epoxy monomer with elastomers depends on the esterification reaction between them and improves the adherence between them.

The toughening mechanism of rubber-modified epoxy monomers was depending on the particle-size. The most toughening mechanisms are effective in microsized rubber particle mixed with epoxy monomers[85,86]. Long-Cheng et al.[87] have studied the effect of the rubber particle size (0.04 and 1.2 μm) on the deformation mechanism in an epoxy system. They concluded that the microsized, rubber-modified epoxy monomer was enhanced in their fracture toughness and lowered in strength than that of nanosized particles. Kunz et al.[88] have prepared a series of toughened epoxy monomers with very small (<0.1 μm) and larger (0.2–1 μm) particles. They concluded that the larger particles were not more effective than the smaller ones in improving toughness. Unnikrishnan and Thamos[89] and Bagheri et al.[90] have investigated that the mechanical properties are increased with the addition of nanosized rubber particles to the epoxy resins. Hydro and Pearson[91] have incorporated three different types of nanosized commercial triblock copolymers into epoxy monomer, which shows an improvement in fracture toughness.

Wise et al.[92] have reported the precipitated liquid rubber (two CTBN and one ATBN) amine-cured epoxy polymers with variable cross-link density. The toughened epoxy monomer was prepared by adding liquid rubber and an equal stoichiometric ratio of hardener into a molten epoxy monomer at 60°C with mechanical shaking. The resultant mixture was thoroughly stirred, cast in a mold and cured at required temperatures. They concluded that the addition of CTBN rubbers into aromatic amine-cured epoxy resins increases the rate of the epoxy–amine reaction due to the catalytic effect of the CTBN carboxyl groups.

Liquid ATBN-modified epoxy monomer was prepared by Chikhi et al.[93] for increasing the toughness when cured with polyaminoimidazoline hardener. They concluded that the acrylonitrile containing 16% of ATBN copolymer exhibited the better impact properties than that of the unmodified epoxy monomer. Ramos et al.[94] have prepared CTBN-modified epoxy monomers and improvements observed in the impact properties as compared with the unfilled rubber epoxy monomer. Other authors such as Raju et al.[95] have studied CTBN-modified DGEBA epoxy resin, which was cured with an anhydride hardener. The rate of conversion was found to be diminished with increasing CTBN copolymer content due to the dilution effect and increase in viscosity.

They concluded that there is a diminution in the T_g and storage modulus properties of CTBN-modified epoxy monomer due to the reduction in the cross-linking density and flexibility in the epoxy network. Ozturk et al.[96] have reported that the HTPB toughened epoxy monomer, exhibited an improvement in thermal and mechanical properties. Moreover, Dinesh et al.[97] have reported maleated depolymerized natural rubber (MDPR)-modified DGEBA epoxy monomer. MDPR was prepared by grafting of maleic anhydride on depolymerized rubber. The addition of MDPR to epoxy monomer could not alter the glass transition temperature (T_g), tensile and flexural properties. Authors concluded that the MDPR-modified epoxy monomer exhibited better impact properties than that of the unmodified epoxy monomer due to the cross-linking of maleic anhydride.

An approach to improve the toughening of epoxy monomers was investigated by Xiaodong et al.[98] by modifying it with a series of chain-extended urea (U-TPBn) containing hydroxyl-terminated polybutadiene. From the resuts, they concluded that the fracture toughness increases by 400 times than that of the neat epoxy monomer cured with dicyanodiamide. From the last two decades, several approaches have been used to improve the strength and toughness of epoxy monomers using rubber as fillers. Recently, Yang et al.[99] have reported nanorubber-modified epoxy monomers, which was cured by adding the stoichiometric amounts of diethyl toluene diamine hardener.

They concluded that the nanorubber-modified epoxy monomer exhibited better tensile strength as compared with the neat epoxy monomer. Further, authors also concluded that there is no much diminution of glass transition temperature in nanorubber-modified epoxy. Other authors, Long et al.[100] have reported multiscale rubber particles (the phase-separatio nformed submicron liquid rubber (LR) and preformed nanoscale-powered rubber (PR) particles) to balance the toughness and thermal resistance of epoxy composites.

Thermoset-Modified Epoxy Monomers

Unsaturated Polyester Toughened Epoxy Monomers

The toughness of the epoxy resin has been improved by the formation of interpenetrating polymer networks (IPNs)[8,9]. These resins can be used as fillers in epoxy due to their low manufacturing cost, easy processing, high molecular weight and low densities. The low viscosity of unsaturated polyester resins improve the processability, the mechanical and fracture properties of the epoxy resins[10–12]. Varada et al.[101] have studied the miscibility of epoxy/unsaturated polyester blends by viscosity, ultrasonic velocity, and refractive methods. Yeng et al.[102] have reported that the compatibility and interaction behavior of IPNs based on unsaturated polyester/epoxy.

They concluded that the IPNs exhibited excellent compatibility with the epoxy monomer, due to the reaction between hydrogen bonds present in cured epoxy resin with polymer containing carbonyl groups in unsaturated polyester. Still, compatibility decreases and phase separation occurred in the IPN containing more than 30% unsaturated polyester. Moreover, the glass transition temperatures of IPNs were found to decrease with increasing unsaturated polyester content, due to increase in chain mobility and they were found to diminish in the inter polymer hydrogen bonding. Hydroxyl-terminated polyesters were used to modify the epoxy monomer to enhance the fracture properties[10]. It was prepared by the reaction of sebacic acid in excess of propylene glycol in the presence of xylene. They concluded that the toughness of the epoxy/polyester blends increases with the addition of polyester due to phase separation.

Chinnakkannu et al.[12] have prepared unsaturated polyester toughened epoxy composites, by the incorporation of 5, 10 and 15 wt.% unsaturated polyester to epoxy monomer by mechanical mixing followed by ultrasonication. They concluded that the incorporation of unsaturated polyester in to epoxy monomer improves the thermal stability and impact strength to a certain extent. However, the mechanical properties of Epoxy/UPE were found to decrease with increasing UPE content. This is due to the formation of chain entanglement in the UP–epoxy matrix system. The T_g of the epoxy system was found to be decrease with increasing of UP resin due to the chain lengthening and flexibility behavior of UPE resin, which leads to decrease in the effective cross-link density. Authors also found that the improvements in thermal stability and degradation temperature in UP-toughened epoxy resin, due the cross-linked network structure of the UP – epoxy system. The residue content at 798°C was observed to be 20.4 wt.% and 28.2 wt.% for epoxy and UP (10%) toughened epoxy respectively.

Viswanath et al.[103] have reported the hyperbranched polyesters (HBPE) to modify DGBA epoxy monomer. HBPE monomer was synthesized by the condensation reaction of 2,2-bis (hydroxymethyl) propionic acid (bis-MPA) and triethanol amine. Modified DGEBA/HBPE monomers were cured with diethylenetriamine hardener (Figure 9). There is no much improvement in the thermal and electrical properties were observed with the addition of 1, 2, and 5 wt.% HBPE to epoxy monomer. However, a great enhancement in the mechanical properties was found, tensile strength of cured DGEBA and 1, 2 and 3 wt.% modified HBPE epoxy monomers were found to be 27.7, 38.4, 44 and 67.3 MPa, respectively, whereas, impact strength was reported to be 6.85, 6.39, 7.15 and 22.9 J/m, respectively.

Vinyl Ester-Toughened Epoxy Monomer

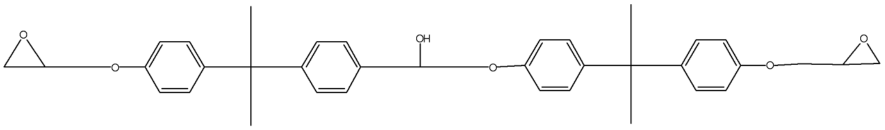
Chinnakkannu et al.[104] have used vinyl esters to modify the epoxy resins, to improve the fracture toughness without any loss mechanical and thermal properties of epoxy monomers because of its flexibility, high thermal, high moisture resistance, and good dielectric properties[104]. Incorporation of 5, 10 and 15% vinyl ester oligomer into epoxy monomer enhances the mechanical properties due to the formation of vinyl ester oligomer-epoxy IPN and the formation of the complicated cross-linked network. Thermal properties of the epoxy monomer decrease with increasing the vinyl ester oligomer concentration. This is due to the chain lengthening and the flexibility behavior of vinyl ester oligomer resin, which in turn decreases the effective cross-link density.

Polyurethane Blends with Epoxy Monomer

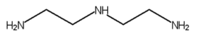
Polyurethane was first made in 1937 by German researchers, Otto Bayer and his coworkers. It was synthesized by the exothermic reaction between alcohols with two or more reactive hydroxyl (-OH) groups per molecules (diols, triols, polyols) and isocyanates that have more than one reactive isocyanate group (-NCO) per molecule (diisocyanates, polyisocyanates)[13]. Polyurethane (PU) is widely accepted as a industrial polymeric material and used as an impact modifier for improving toughness, impact strength, resistance to UV light, flexibility, abrasion, oil and tear resistant, hardness and many more[105–107].

Ahmad et al.[108] have developed a linseed oil-based polyurethane for anti-corrosive coating applications. Further, Anand et al.[109] have developed the inter cross-linked networks (ICN)-based siliconized polyurethane/epoxy coatings, for improving the toughness, thermal and mechanical, and corrosion resistance properties. Hydroxyl terminated polydimethylsiloxane (HTPDMS) was used as a silane cross-linker with dibutyltindilaurate (DBTL) catalyst. Mechanical properties were found to be more with the incorporation of 10 wt.% of PU and silicone due to the toughening of brittle epoxy system.

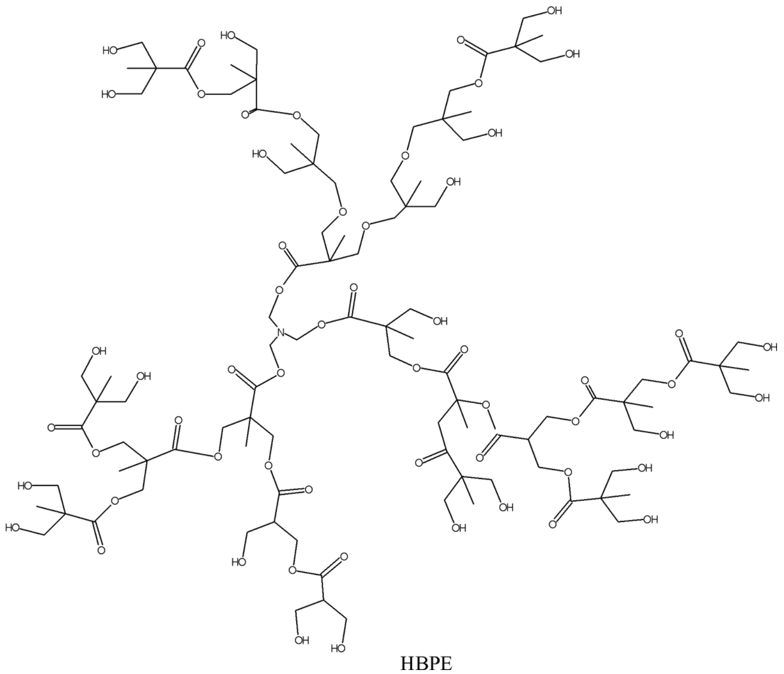
The incorporation of PU into unmodified epoxy/UP coating systems reduces the thermal stability due to the



Diglycidyl ether of bisphenol A



Diethylenetriamine



HBPE

FIG. 9. Structure of DGEBA, DETA and HBPE.

presence of thermally weak urethane linkages, whereas, the incorporation of 10 wt.% silicon into PU-modified epoxy/UP systems improves their thermal stability due to the partial ionic nature, high bond energy and thermal stability of -Si-O-Si- linkage. Mahesh et al.[110] have also reported ICNs-based bismaleimide (BMI)-modified polyurethane–epoxy monomers and cured with 4,4-diaminodiphenylmethane. From the investigations, the authors concluded that the incorporation of polyurethane into epoxy increases mechanical strength.

Furthermore, the incorporation of BMI into polyurethane-modified epoxy systems shows a drastic enhancement in tensile, flexural strengths, and thermal stability while the minor diminution in glass transition temperature and impact strength has been observed. The diminution of glass transition temperature (T_g) in BMI-modified PU-epoxy systems may be due to the increase in the chain length and reduction in the cross-link density. Moreover, thermal stability of an epoxy/PU system decreases with increasing PU content, which may be due to the presence of thermally weak urethane linkages in the epoxy backbone. However, an enhancement in thermal properties in BMI-modified PU/epoxy system has been observed, which may be attributed to the presence of the rigid phenyl group with the heterocyclic ring structure.

Recently, Wang et al.[111] reported aromatic and phenol hydroxyl terminated polyurethane-modified DGEBA epoxy monomers. They concluded that the modified epoxy monomer exhibits higher glass transition temperature than that of epoxy resin containing polyurethane with amine groups. Bakar et al.[112] have proved that the higher isocyanate content polyurethane shows improvements in fracture toughness and mechanical properties. Biobased DGEBS epoxy monomer and hyperbranched polyurethane (HBPU) were synthesized from Mesua Ferrea L. (Ceylon Ironwood) seed oil by Gautham et al.[113] and modified with HBPU. The authors have found that the HBPE-modified epoxy monomer shows better improvements in tensile strength, elongation at break, and impact resistance as compared with respect to the epoxy monomer. They also concluded that the thermal degradation of HBPE-modified epoxy monomer could not exhibit any improvements[114].

Miscellaneous Thermoset Blends with Epoxy Monomer

Jingwen et al.[115] have reported cyanate ester/epoxy monomer cured with acetylacetone cobalt (II) for cryogenic engineering applications due to their excellent mechanical properties, good radiation resistance, long pot-life, very low moisture absorption and cost-effective property. Epoxy monomers are modified with maleimides[116] provides a great enhancement in the thermal stability due to the formation of high cross-linking density, and imide groups provides higher char yield in the condensed phase.

Thermoplastic Modified Epoxy Monomer

The damage tolerance of epoxy monomers (e.g., impact, fatigue, etc.) is generally tuned by the incorporation of thermoplastic polymers into it. The major advantages of thermoplastic-modified epoxy monomers typically possess high Young's moduli, higher fracture toughness and fracture energy as compared with the unmodified epoxy monomer. However, some of the elastomer- and thermoset-toughened modified epoxy monomers are typically shown to decrease in thermal and mechanical properties[117]. Thermoplastics are alternative tougheners to modify brittle epoxies without compromising other properties.

Several authors[118–120] have reported that the thermoplastic toughened epoxies form homogeneous blends in the uncured state and undergo phase separation on curing. Some of the thermoplastics are widely used as self-healing agents in epoxy monomers, to protect it from the structural damages[121]. The frequently used thermoplastics are poly (amide-ester)[122,123], poly (acrylonitrile-co-butadiene-co-styrene) (ABS)[124], poly (aryl ether ketone), polybutadiene (PB)[125], Polybutylene terephthalate (PBT)[126], polycarbonate (PC)[126], poly (ether ether ketone) (PEEK)[127,128], poly (etherimide) (PEI)[129], poly (ether sulfone) (PES)[130], poly (methyl methacrylate) (PMMA)[131,132], poly (phenylene oxide), etc. Some of the most frequently used thermoplastic modifiers are discussed next.

Poly (Ether Sulfone)-Toughened Epoxy Monomers

Alessi et al.[133] have reported the physical ageing phenomenon of epoxy monomers in order to reduce its brittleness and damage tolerance. The physical ageing of the system is strongly depends on the thermodynamic status and the environmental conditions. This is protected by the introduction of engineering thermoplastic toughening agents in to epoxy monomers. The polyethersulphone was used to modify the epoxy monomer in order to study their thermal, mechanical and morphological behavior. They concluded that toughened cured samples showed an increase of the glass transition temperature and the fracture toughness as compared with the epoxy resin. This is due to the excellent adhesion between the PES terminal OH groups and the epoxy monomer. After 1 week and 1 month of hot water immersion, hydrothermal ageing enhancement in thermal properties was observed with the formation of different cross-linking degrees. Brooker et al.[134] concluded that the addition of 35 wt.% PES to the epoxy monomer increases the fracture toughness from 0.688 to 1.11 MPa. Similarly, the impact strength increases from 215 to 530 J/m.

Phase separation of PES toughened epoxy system have reported by Kim and Kookheon[135]. Viscosity gradually increases with time when PES mixed with epoxy monomer, because of the growth in molecular weight of the epoxy matrix and it suddenly decrease when the homogeneous mixture phase separates into epoxy-rich and PES rich phases. At medium viscosity, the storage modulus increase upon phase separation. Results found that the changes in viscosity caused by the phase separation of PES from the epoxy monomer. There are several factors affecting the morphology of PES-modified epoxy system at the interphase, including the competition between the curing rate and the rate of phase separation, viscosity, the thermodynamic characteristics of the constituents of the blend and the gelation time[136].

Polyetherimide-Toughened Epoxy Monomers

The mechanical properties of the cured toughened epoxy monomer depends on the phase separation. It has been generally observed between the two polymer components in a cured state[137]. Yu-xin et al.[138] have reported PEI-modified epoxy monomers for cryogenic applications to avoid the microcracks formation of aging on cryogenic fuel tanks. The impact strength of 1.5 wt.% PEI-toughened epoxy monomer at room and cryogenic temperature increases more than that of unmodified epoxy monomer. The storage modulus of PEI/epoxy monomer drastically increased as compared with the unmodified epoxy monomer from 3900 to 5025 MPa. This is due to the good interfacial bonding between the PEI and the epoxy matrix.

Poly (Ether Ether Ketone) Toughened Epoxy Monomers

Bejoy et al.[139] have found melt mixing of poly (ether ether ketone) (PEEK) /epoxy blends for high performance applications. PEEK is a semicrystalline engineering thermoplastic polymer with excellent thermomechanical properties. It is difficult to blend with epoxy monomers even at high temperatures due to its semicrystalline nature. Hence, it is necessary to it make as amorphous material to improve the processability. The pendent groups on the PEEK like sphenolphthalein poly (ether ether ketone) (PEK-C) was used for toughening epoxy monomer. They concluded that both the rate of the reaction and cure temperature were found to decrease as with the increase in PEEK content.

Similarly, Bejoy et al.[127] already explained that the storage modulus decreased in the 30 wt.% PEEK/epoxy system, due to the decrease in cross-link density in another pioneering work. Bejoy et al.[140] also concluded that the mechanical and thermal properties of the PEI/epoxy blends did not show much increment as compared with the unmodified epoxy monomer. This is due to complicated chain formation with the reduction in cross-link density of the blends, which confirmed by FTIR specrtoscopy.

Miscellaneous Thermoplastic Toughened Epoxy Monomers

Nishar et al.[141] have prepared Poly (styrene-co-acrylonitrile) (SAN) toughened epoxy monomer in order to get improved mechanical and thermal properties. They concluded that the storage modulus and glass transition temperature (T_g) of 10 wt.% SAN/epoxy are slightly lower than that of the epoxy monomer. This is due to the reduction in cross-link density. The water uptake behavior of poly (styrene-co-allylalcohol) (PScoPA) toughened epoxy system have studied by Salazar et al.[142]. They indicated that the addition of thermoplastic modifier reduces the rate of deterioration in fracture toughness in the aged samples. Nicolas et al.[143] have reported the modification of the curing behavior and the phase separation process for syndiotactic polystyrene toughened epoxy system.

Syndiotactic polystyrene (sPS) is an engineering semicrystalline thermoplastic polymer have a high elastic modulus, low dielectric constant and good processability. They investigated that the phase separation in DGEBA/hardener/sPS system is complicated due to the possible crystallization of sPS, and concluded that the reaction rate for sPS-containing blends increased due the phase separation. Rajasekaran and Alagar[144] have examined the mechanical and dynamic properties of bismaleimide-modified polysulfone epoxy systems. They found that the mechanical properties increased for the polysulfone-toughened epoxy and bismaleimide-toughened polysulfone epoxy systems. This is due rigid aromatic molecular structure of polysulfone and the establishment of a cross-linked network between the bismaleimides and epoxy systems. The authors also concluded that the polysulfone-toughened epoxy systems exhibit higher Tg than that of unmodified epoxy, due to lower cross-link density; and bismaleimide-toughened polysulfone epoxy systems exhibit lower Tg value due to increased cross-link density.

Epoxy Nanocomposites

Polymer nanocomposites have added a fresh number of advantages due to its superior properties such as modulus, strength, toughness, barrier, durability and flame retardancy, electrical properties etc.[145], which are mainly due to the low density and ease of processability. In polymer nanocomposites, the filler has at least one dimension on the nanometer scale (<100 nm). The nanoscale is considered, where the dimensions of filler particles, platelets, and fibers are in the size range of 1–100 nm. Many authors have reported various polymer matrix with nanoparticles such as aluminum oxide[146], boron carbide[147], calcium carbonate[148], carbon nanotubes[149], cellulose nanofibers[150,151], clays[152], fly ash[153], graphene[154], nanostructured oil palm ash[155], silica[156], silver[157], tungsten disulfide[158], and so on[159–163].

Clay-Modified Epoxy Nanocomposites

Clays have been widely used as nanofillers for the preparation of polymer nanocomposites. Lately, there has been a growing interest for the development of polymer nanocomposites due to their properties improved drastically as compared to the conventional filled polymers[162]. Clay minerals belong to silicate groups with layered structure known as layered silicates. Layered silicate clay offers two-dimensional expandable interlayer space for intercalating guest species.

Recent years, a broad range of nanoclays incorporated into epoxy monomer to enhance their mechanical properties[164–166]. The large amounts of nanoclays are very much difficult to achieve good dispersion within a polymer matrix due to the hydrophilic nature of clays. In order to make them very good dispersion within a hydrophobic matrix, nanoclays must be treated with some hydrophobic surfactants by the exchange of metal ions in the inter gallery regions with alkylammonium ions[167]. These alkylammonium ions are creating surface functionalities on nanoclays, thereby improving their chemical compatibility/interactions with matrix, leading to enhanced dispersion.

Unmodified and modified epoxy-based layered silicate nanocomposites were prepared[168–170]. They concluded that the modified epoxy nanoclay composites exhibit better thermal, mechanical, and barrier property than that of unmodified epoxy. This may be due to better compatibility between epoxy monomer and nanoclay. They also found that the glass transition temperature (T_g) of nanocomposites was found to be lower than that of neat cured epoxy monomer. Mohan et al.[171] have also reported that the higher curing temperature increases the mechanical properties of the epoxy.

Miyagawa et al.[172] have reported modified biobased epoxy monomers. They synthesized epoxidized linseed oil (ELO) for the modification of petroleum-based DGEBF epoxy monomer; by using anhydride curing agent. The glass transition temperature (Tg) and heat deflection temperature (HDT) of ELO epoxy monomers were decreased with increasing the ELO content due to the weakening of cross-link density. Moreover, the glassy nature of cured DGEBF epoxy monomer exhibit lower impact strength due to high cross-link density and exhibits constant impact strength after modification of DGEDF with ELO. They also concluded that the addition of nanoparticles to the biobased epoxy network exhibited higher storage modulus, lower glass transition temperature, and HDT as compared to the neat epoxy containing the same amount of biobased modifier. This is due to the plasticizing effect of the organic content of the organoclay.

The fracture behavior of silane-treated nanoclay epoxy composites have been reported by Sung-Rok et al.[173]. The fracture toughness of silane-treated clay epoxy nanocomposites was 82% higher than that of untreated clay epoxy nanocomposites. This may be attributed to the clay silane treatment, which is primarily due to the improvement in interfacial bonding between epoxy and silane treated clay that suppressed debonding at the interface. The author also examined the temperature effect on tensile properties at different conditions −30, 25, 40 and 70°C, and found that the tensile strength decreased as increasing with the temperature and the tensile strengths of the silane treated samples were more eminent than that of untreated samples for all temperatures except 70°C.

This is imputable to the good dispersion of the silane treated clay in epoxy and improvement in interface adhesive strength between epoxy and clay layers. The excellent dispersion of nanoclays in a polymer matrix is achieved by two possible approaches: the mechanical and the ultrasonication dispersion methods of the surface-modified or unmodified nanoclays. Several authors[174,175] have reported that ultrasonicated/sonicated epoxy nanocomposites exhibits great improvements on the thermal and mechanical properties than shear/mechanical mixing.

Carbon Tube-Modified Epoxy Nanocomposites

The carbon nanotubes (CNTs) and multiwalled carbon nanotubes (MWCNTs) are one-dimensional sp^2 carbon nanomaterials, exhibit high elastic modulus and high strength; that effect on the preparation and properties of epoxy nanocomposites[176–179]. The properties of polymer nanocomposites depend on the dispersion of nanoparticles and the interaction between nanoparticles, as discussed earlier. The mechanical properties of CNT/polymer nanocomposites depend on the good interfacial adhesion between the polymer matrix and CNTs[180,181]. The deviation in the number of walls causes important variations on the nanotube diameter, which in turn involve the characteristics of nanocomposites[182–185]. Xiao-Feng et al.[186] have modified epoxy monomers with low CNTs content; they concluded that the mechanical properties of epoxy nanocomposites increased, while toughness and flexural strength decreased as compared with the neat epoxy resin. However, viscosity increases with the addition of CNTs content, due to their higher specific surface area.

Jin et al.[187] have prepared the epoxy nanocomposites with various surfaces treated carbon nanotubes. With the help of surface modifications, hydrophilic CNTs modified as hydrophobic substrates. The effect of surface modification of CNTs improves the dispersion and interactions between CNTs and epoxy matrix. They concluded that the thermal and mechanical behavior of CNTs epoxy nanocomposites increased with the surface treatments due to the uniform dispersion of CNTs in epoxy matrix[188].

Philip et al.[189] have reported a novel method to produce high volume/weight fraction nanocomposites with vertically aligned CNTs using shear pressing. They concluded that the shear pressing epoxy nanocomposites containing 32 wt.% CNTs exhibit high tensile strength of 402 MPa and high Young's modulus of 22.3 GPa. Toshio et al.[190] have prepared CNTs/epoxy nanocomposites using a hot melt prepreg method. The resultant nanocomposites exhibit higher Young's modulus and tensile strength than that of composites produced using conventional CNT/epoxy mixing buckypapers method.

The water consumption behavior of the epoxy resin does not vary with the addition of CNTs/MWCNTs up to an optimum weight fraction loading[191,192]. There is a significant diminution in glass transition temperature and storage modulus of the aged epoxy nanocomposites with increasing water content as compared with the epoxy monomer. This is due to the presence of different mechanisms of water immersion and interaction with the epoxy matrix. The authors also explained the water absorption interactions of nanocomposites between the nanomaterials and epoxy monomer by two types. Type I water diffuses into the polymer matrix and breaks the hydrogen bonds resulting in increased chain segment mobility and plasticization. This is because of the diminution of the glass transition temperature, mechanical strength and elastic modulus in the epoxy nanocomposites. Type II is associated with water molecules, which forms multiple hydrogen bonds with the resin network and does not significantly contribute to the plasticization. For this reason, Type II bound water does not behave as a plasticizer, and it promotes the recovery of the mechanical properties of the nanocomposites by establishing a secondary cross-link network with the epoxy monomer.

Graphene/Graphite-Modified Epoxy Nanocomposites

Graphite belongs to the carbon family, and the carbon atoms are arranged in a honeycomb lattice. In comparison with other fillers, graphite and graphene are cheaper and exhibit good thermal stability, high thermal conductivity, excellent heating performance and resistance to chemical corrosion with epoxy monomers[193–195]. Graphene is a kind of two-dimensional nanostructured sp^2 carbon material[196] and can be described as one atom thick layer of graphite[197]. It is not exclusively applied for energy storage materials; also be utilized as a flame retardant material in polymer nanocomposites to enhance flame retardant property due to its unique two-dimensional atomic carbon sheet structure[198]. Swetha et al.[199] has observed improvements in the mechanical properties; electrical conductivity of graphite nanoplatelet (GNP)/epoxy nanocomposite was achieved using both the 3 roll milling and sonication combined with high-speed shear mixing technique than other conventional process.

Shan et al.[200] examined the effects of graphene nanosheets (GNS) on thermal stability and flame retardancy of epoxy resin (ER). These graphene sheets are used as filler in epoxy monomer to replace CNTs due to their modest cost, high specific surface area seems like CNTs and processing is very much easier because of low viscosity. The authors concluded that the GNS epoxy nanocomposites shows an enhancement in their thermal stability. This is due to the GNS helps to promote ER to form char and the char residue of ER/GNS increased with the increase of GNS content. They also concluded that with the incorporation of 3 wt.% of GNS increased the LOI value of ER from 15.7 to 21.0 and reduced the total heat release from 33.37 to 28.20 kJ/m^2. This is due to the interaction between GNS and ER matrix hindering the mobility in the polymer segments near the interface of ER chains.

Miscellaneous Modified Epoxy Nanocomposites

Balakrishnan et al.[201] and Ratna et al.[202] have reported three-phase rubber-toughened epoxy nanocomposites. They observed that the phase separation between rubber particles and epoxy, which decreases the glass transition temperature. Several researchers have reported the SiO_2 modified and unmodified epoxy nanocomposites[203–206]. The 3% SiO_2-incorporated epoxy nanocomposites exhibit better mechanical, thermal properties, and tribological properties than that of neat epoxy monomer due to better interfacial adhesion. The nano-SiO_2 perpetrated by the silane coupling agent and tetraethyl orthosilicate reaction mechanism is shown in Figure Figure 10.

Lei et al.[207] have prepared TiO_2-modified epoxy nanocomposites. The TiO_2 nanoparticles were modified by diblock copolymers such as poly (methyl methacrylate)-b-polystyrene (PMMA-b-PS) via reversible addition-fragmentation chain transfer (RAFT) polymerization. They concluded that the mechanical and thermal properties of grafted TiO_2 (Scheme 23) epoxy nanocomposites were drastically increased as compared to the neat epoxy monomer. General conclusion remarks are given in Table 1 for composites consisting of different nanofillers.

Fiber-Reinforced Epoxy Composites

Reinforcements are thin rodlike structures that provides the stiffness and strength to the composites[1]. The most common reinforcements used in the composite industry are synthetic and natural fibers. The widely used synthetic fiber materials in fiber-reinforced plastics (FRP) are glass, carbon, aramid, and boron. These fiber-reinforced composites have been widely applied in aerospace structures and ship constructions due to their high specific strengths[215–218]. Glass fibers are the cheapest among all other types of synthetic fibers[219–221]. The properties of synthetic fibers are presented in Table 2.

The increasing demand of biodegradable, sustainable, and recyclable materials, the natural fibers are widely applied to make low-cost, polymer-reinforced composites by replacing synthetic fibers[230]. Natural (agriculture-based) fibers are extracted from plants and are classified into several classes, depending on the role of the plant[231,232]. Few types of natural fibers are discussed here.

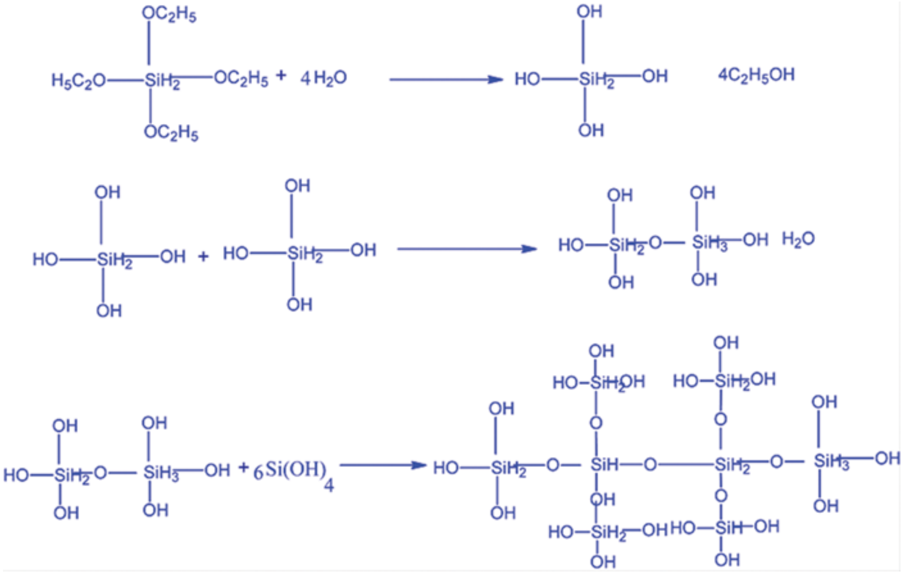
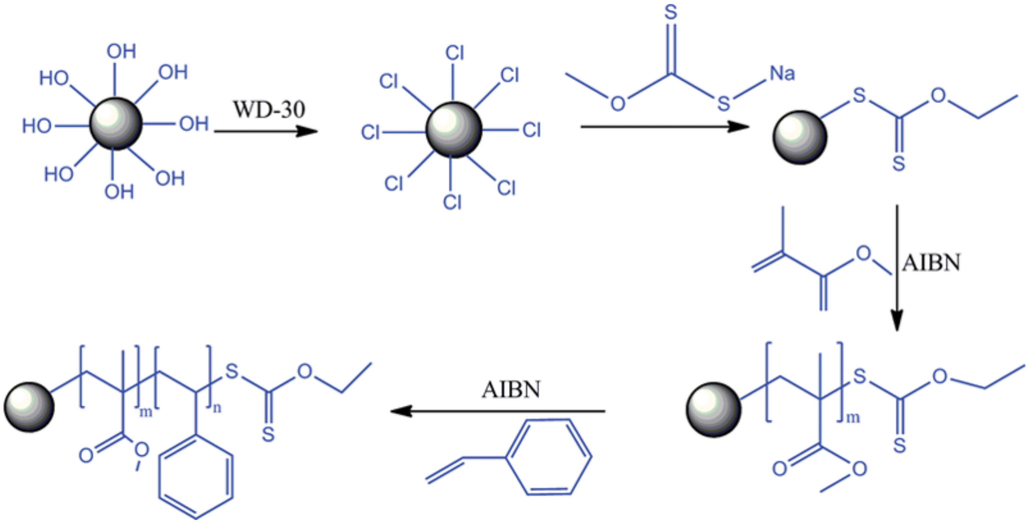


FIG. 10. The hydrolyzation and condensation of TEOS.



SCH. 23. The processes used in this study for the surface modification of TiO_2.

Fruit-based fibers are extracted from the fruit of the plants, which are light and hairy. Some examples of fruit fibers are coconut[233] and oil palm fruit bunch fiber[234]. Fibers with better strength are found in the stem of the plant[235]. Some examples of such fibers are flax[236], hemp[237], jute[238] and kenaf fiber[239]. These fibers are dominating some of the synthetic fibers in various ways. Fibers extracted from the leaves, are rough and sturdy, and they are called as leaf fibers. Examples of leaf fibers are sisal[240], pineapple[241] and banana fiber[242].

When determining the properties of natural fibers, one has to keep in mind that the properties natural products are strongly influenced by their growing environment. Temperature, humidity, composition of the soil, and the air can affect the top of the plant, the durability of its fibers, density, etc. Plant-based fibers do not produce any environmental issue matters and easily processable as compared with the synthetic fibers. The low density natural fibers offer superior properties, such as mechanical strength, wettability, and thermal; which are found to be better than that of the some synthetic fibers[231]. Nevertheless, the chief disadvantages of natural fibers in composites are the poor adhesion between fiber and polymeric material and the relative high moisture sorption[243]. Thus, chemical/physical treatments are necessary to improve the surface attributes of natural fibers for improving the interfacial interactions between fiber and polymeric material[244].

The major techniques may be summarized as follows[230,232,245]:

- Acetylation treatment: The fibers are absorbed in a solution consisting of 250 mL toluene, 125 mL acetic anhydride and a modest quantity of catalyst perchloric acid (60%) at a temperature of 60°C and 1 to 3 h. After modification, the fiber was washed periodically with distilled water until acid free[246].
- Alkali treatment (also called mercerization): The fibers are soaked in a solution containing NaOH at room temperature for 4 h; subsequently, the NaOH-treated fibers were washed several times with distilled water containing a few drops of acetic acid to neutralize the excess sodium hydroxide, followed by thorough rinsing with distilled water. The fibers were then dried in an oven at 105°C for 24 h[247,248].
- Autoclave treatment: The treatment was run during 30 min at three different pressures (0.5 bar at 112°C; 1 bar at 120°C; 2 bars at 134°C)[249].
- Benzoylation: fibers were soaked in a mixture of NaOH and 50 ml of benzoylchloride solution for 15 min. Finally fibers were removed from solution and washed thoroughly with water. Subsequently, the fibers were soaked in ethanol for 1 h to remove the unreacted benzoylchloride, finally washed with water and dried[250,251].
- Dewaxing: The fibers are immersed with a 1:2 mixture of ethanol and benzene for 72 h at 50°C. Followed by washing with distilled water and air drying to get defatted fibers[252].
- Furfuryl alcohol treatment: The fibers are soaked in the furfuryl alcohol at 100°C for 4 h in a reactor with an outlet and inlet for passage of N_2 gas. The excess of FA was removed by soxhlet extraction using ethanol for 8 h. Then, the fibers were dried for approximately 24 h at 45°C[253].
- NaOCl Treatment: the fibers are soaked in 100 ml of 0.4% NaOCl (v/v, in glacial acetic acid) for about 2 h at 85°C. Finally treated fibers were cleaned with distilled water and dried under vacuum for 2 h[233].

TABLE 1
Mechanical and thermal properties of DGEBA nanocomposites

Matrix	Nanofiller type	Particle diameter	Modification type	Weight fraction (%)	Tensile modulus (GPa)	Impact strength (J/m^2)	Glass transition temperature (°C)	References
DGEBA	Silica	23 nm	Organosilane	30	5.53	1257		208
DGEBA	Silica	74 nm	Organosilane	30	5.6	1027		208
DGEBA	Silica	170 nm	Organosilane	30	5.78	1851		208
DGEBA	Silica	130 nm	4.6 wt% CTBN	8.5	2.89	241		209
DGEBA	Silica	130 nm	5.1 wt% CSRIII	11	3.5	1851		209
DGEBA	MMT		Octadecyl ammonium ion	1	2.7		150	210
DGEBF	Graphine oxide	2 μm		1		580	146	211
DGEBA	Silica	20 nm		2	3.95	175.97	159	212
DGEBA	MMT		Na	0.75	2.78			201
DGEBA	SiO_2		Silane coupling agent	3	3.83	5500		203
DGEBA + 3%TEOS + 2%KH550	SiO_2	20 nm	Silane coupling agent			12900	129	204
DGEBA	Zirconium		GPTMS	1	2.15			213
DGEBA	Zirconium		Calcination at 600°C	1	2.49		67	213
DGEBA	MWCNT		$H_2SO_4 + HNO_3$	0.5	3.73		94	214
DGEBA	TiO_2	10–100 nm	(PMMA-b-PS	1		23100		207
DGEBA	MWCNT		Silane coupling agent	0.3	0.6		87.9	184

TABLE 2
Physical properties of synthetic fibers

Material	Density (g/cc)	Tensile modulus (GPa)	Tensile strength (σ) (GPa)	Specific Modulus (E/ρ)	Specific Strength	Melting point (°C)	%Elongation at Break	References
Glass fiber	2.5–2.56	66–73	1.7–3.5	27	1.35	1540+	2.5–3.2	216,221–224
Carbon	1.8–1.9	130–400	1.7–2.6	140–200	0.9–1.5	>3500	0.8–1.5	215,224–226
Boron	2.6	400	3.5	155	1.3	2300	—	222,227
Kevlar	1.4–1.45	80–130	2.71–3	55.5–89.5	1.9	500	2.5–3.5	215,226,228,229

- Peroxide treatment: Dicumyl peroxide (DCP) was selected as oxidants to treat the fiber surface. The fibers are immersed in a DCP acetone solution (6% concentration) for 1.5 h and washed with acetone, and then dried at 60°C in the oven for 4 h to remove excessive solvent[254].
- Permanganate treatment: Potassium permanganate ($KMnO_4$) was selected as oxidants to modify the fiber surface. The fibers are immersed in a permanganate acetone solution for 2 min, cleaned with acetone, and then dried at 60°C in the oven for 4 h to remove excessive solvent[255].
- Plasma treatment: The fibers are placed between the electrodes and passed at various plasma powers (100–300 W) for 2 min. The surface modification properties are depending on the treatment conditions. In all treatments, gentle wind (20.9% oxygen, 79.1% nitrogen, and relative humidity <3 ppm) and argon (99.995% purity) were practiced as a process gas[256].
- Silent treatment of sisal fiber: the fibers usually are absorbed in a solution containing of the silane coupling agent with the mixture of 6 wt.% silane mixed ethanol/ water mix in the proportion of 6:4. The fibers were allowed to endure for 1 hour, subsequently the ethanol-water was drained away and the fibers were dried in air for half an hour, followed by drying in oven[257,258]. Some of the major properties of natural fibers are depicted in Table 3.

However, with the incorporation of synthetic and natural fibers into epoxy monomers are to improve the mechanical, thermal, barrier and electrical properties[230,221,259–261]. For the last few decades, these composites have been attracted a great interest in the industries and trade goods. Besides, the composite manufacturing industries are looking for plant-based, fiber-reinforced composites for many applications such as automotive and aerospace components due to their light weight, high intensity, and low price. Some of the properties of various fiber-reinforced epoxy composites are shown in Table 4.

TABLE 3
General properties of natural fibers

Material	Density (g/cc)	Cellulose (wt %)	Lignin (wt %)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Moist content (wt %)	References
Banana	1.3	63–64	5	540		3	10–12	219–221,230,259
Coir	1.15–1.2	32–45	40–45	140–593	4–6	25–30	8	219–221,230–232,259
Cotton	1.5–1.6	85–90		287–597	5.5–12.6	7–8	7.85–8.5	219–221,230–232,259
Flax	1.4–1.5	71	2.2	500–1500	27.6	2.7–3.2	8–12	219–221,230–232,235,259
Hemp	1.14–1.48	70–74	3.7–5.7	550–900	30–70	1.6–1.8	6.2–12	219–221,230–232,235,259
Jute	1.3–1.46	61.1–71.5	12–13	393–773	26.5	1.5–1.8	12.5–13.7	219–221,230–232,235,259
Kneaf		45–57	8–13	930	53			219,231,232,235,259
Oil palm fiber	0.77–1.55	42.7–65	13.2–25	50–400	0.57–9	2.5–18		219,232,234,259,259
Pineapple		70–82	5–12.7	640		2.4	11.8	219–221,230,232,259
Ramie	1.5	68.6–76.2	0.6–0.7	400–938	61.4–128	3.6–3.8	7.5–17	219–221,230–232,259
Sisal	1.03–1.5	66–78	10–14	511–680	9.4–22	2.0–4	10–22	219–221,230–232,259

TABLE 4
Mechanical and thermal properties of fiber-reinforced composites

Matrix	Curing agent	Fiber	Filler/Fiber type	Surface modification	Fiber loading (wt %)	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength	Glass transition temperature (Tg °C)	Elongation at break (%)	References
DGEBA	DETA/TETA/DDS					35–100	3000–6000	120–190	2800–1720	120–250 J/m	67–150	1–6	12,199, 262–264
DGEBA	Diethylenetriamine	sisal	Long	NaOH + GLYMO	40			79	6500				265
DGEBA	HY5052	Flax	Long	NaOH	40	133	28000	218	17700				266
DGEBF	TETA	Carbon	Long		40	871	28000						267
DGEBA	FR251	RCFpaper	20 μm		46			137.1	5500				268
DGEBA		Jute	Long		48	110	4450	55.8	3020	4.875 J/m^2			269
DGEBA		oil palm EFB	Long		55	46.1	1020						270
DGEBA	A062	Jute	Bi directional long		40	45.5	3890				80.1		271
DGEBA	Piperidine	E2 glass	Long		64.2	1089.4	51000	1564.7	48100			2.36	272
DGEBA	HY591	coir pith/nylon three layers		NaOH		12.5		106.52		359.88 J/m			273
Epoxy		Agave		NaOH		41.2	270	63.5	3850	167 J/m			274
Epoxy		Sugar palm		NaOH	10	50	3800						275
Epoxy		Phormiumtenax fibers	Short		20	26.5	4400	69	4800				276
Epoxy		Phormiumtenax fibers	Long		20	62	6250	92	7200				276
Epoxy		Kneaf	Long	NaOH	38–41			300–350	6800–9800				277
Epoxy		Banana	Short	NaOH		33.6	1680	69.03	13220	12.25 J/m^2			278
Epoxy	HY951	Abaca/jute/glass	Short, long			57	290	12.1	1452	12 J/m^2		18.18	279
Epoxy		Hemp/paper	Unidirectional			134	12468						280
Epoxy		Flax/paper	unidirectional			173	12720						280
Epoxy	H522	Hemp/2.5% lignin nanoparticles	Nonwoven mat		22.46	31.15	5110	86.16	4180	11.50 KJ/m^2			281
Epoxy		Banana/jute	Short			18.96	724	59.84	9170	18.23 KJ/m^2			282

CONCLUSIONS

Epoxy monomers offer a variety of tuneable properties, depending on the method of synthesis and modification, which were used in a wide range of applications. Phosphorus, silicon, and phenol Novolac-based epoxy monomers exhibit higher LOI values with better flame-retardant characteristics and high thermal stabilities due to the presence of aromatic rings in their structure.

With increasing concern about environmental issues, epoxy monomers developed from vegetable oils, isosorbide, gallic acid and rosin, which are categorized as potential future biobased materials are important. Because epoxidized plant-based monomers possess epoxide functional groups along their backbone chains and exhibit the ability to make a three-dimensional elastomeric network when being cured with respective hardeners. On the other hand, these are known to be nontoxic and rigid. These could easily replace petroleum-based epoxy monomers.

Moreover, a number of hydroxyl groups present in plant-based epoxy monomers which offer good adhesion between matrix and reinforcement, resulting towards high toughness, good thermal stability, improves dielectric properties, and less moisture absorption. The modification of epoxy monomers exhibits enhanced mechanical properties and diminution in brittleness. The use of nanoparticles in epoxy monomers has great potential to reduce the weight of the finished composite with good properties such as fiber-reinforced composites. Single-wall and multiwall carbon nanotubes-reinforced epoxy monomers are increasingly used in aerospace components due to their excellent properties.

In recent years, the use of biocomposites reinforced with plant-based fibers has grown significantly due to economically viability, low density, ease of recycling, biodegradability, and good thermal and mechanical properties. These properties make them suitable to replace synthetic fiber-reinforced composites. Interfacial adhesion between plant-based fibers and epoxy matrix will remain the key issue in terms of final properties of the composites. Many authors have highlighted the importance of various types of fiber surface modifications to increase the adhesion between fiber and matrix interface, reduce moisture absorption, and inadequate toughness. Therefore, it is concluded that plant-based, fiber-reinforced epoxy composites are found suitable for use in outdoor applications in the automotive industry, aerospace, agricultural, engineering, and often high-performance applications.

In conclusion, renewable resource-based thermosetting epoxy networks obtained help to protect environment from global warming. As stated earlier, commercial epoxies are synthesized from the condensation reaction between bisphenol A and epichlorohydrin. In some countries, bisphenol A has been declared as a toxic substance that creates human health diseases. Diphenolic acid may be a suitable replacement for Bisphenol A. It is extracted from the condensation reaction of phenol with levulinic acid in the presence of hydrochloric acid. Epichlorohydrin (ECO) may also be replaced by biobased ECO that the Dow Chemical Company, Midland, Michigan initiated and synthesized from glycerin[283]. In recent years, biobased curing agents have become attractive to industry to the extent that perhaps one day they can construct a fully biobased epoxy network.

Phenylkamine is one of the biobased curing agents, developed from cardanol, which is easily replaced by aromatic and aliphatic amine hardeners. Rosin-based curing agents (maleopimaric acid) may also replace the petroleum-based curing agents to form wholly biobased thermosetting resin with high performance[284]. Catalysts are playing important role in developing renewable resource-based epoxy monomers. Liquid inorganic catalysts ($H_2SO_4/HNO_3/HCl$)[52] and transition metal catalysts (Methyl trioxorhenium)[285] are suggestions for future work to increase selectivity, to convert the maximum double bond into oxirane groups, and to reduce reaction time. Biobased epoxies are able to react with 2,4-diamino-6-phenyl-1,3,5-triazine groups to form epoxidized renewable oil-containing benzoxazine monomers of use in high-performance applications.

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