

General Introduction

Highlights

General introduction of epoxies with special emphasis on hyperbranched architecture and their nanocomposites with different nanomaterials is highlighted in this chapter. The prominent role of different reactants or ‘monomers’ for the synthesis of conventional epoxy and hyperbranched epoxy as well as nanomaterials for the fabrication of epoxy nanocomposites are described herein. Different methods for the synthesis of hyperbranched epoxy and fabrication of their nanocomposites are also discussed. Different techniques like analytical, spectroscopic, X-ray diffraction (XRD), microscopic, etc. and testing methods are described for the characterization of hyperbranched epoxy, nanomaterials and their nanocomposites. Properties like physical, mechanical, thermal, electrical, optical, biological, etc. and applications of epoxies and their nanocomposites with hyperbranched architecture are also elaborated. Finally, the scopes, objectives and plans for the present investigation are mentioned at the end of this chapter.

1.1. Introduction

Over the last 25 years hyperbranched polymers are gaining tremendous impetus in several fields of applications where the main credit arises from their structural attributes. The unique characteristics of these novel polymers are their confined globular non-entangled structure, flexibility in tailoring of structural design, large numbers of terminal functional groups with high activity, etc. These result high solubility, low solution and melt viscosity, high reactivity and good compatibility of the resultant polymers.¹ In contrary to the above, hyperbranched epoxy resins are still not gaining their importance over the conventional linear (like, diglycidyl ether of bisphenol-A, DGEBA) based epoxy. Commercial epoxy thermosets like DGEBA, novolac, cycloaliphatic, etc. are widely used because of their overall performance like high mechanical properties, good weather and chemical resistance, low shrinkage on curing, high adhesive strength, etc. They are mainly used as binders for surface coatings and paints along with flexible resins, binders for fiber reinforced plastic (FRP) composites, as adhesives, electrical insulating materials, water proofing materials, flooring materials, and so on.^{2,3} However, many advanced applications are restricted due to their inherent brittleness and low toughness characters. To impart toughness or flexibility to these commercial epoxies, different modifications have been intensively investigated across the globe. These include toughening by blending with different flexible polymers like rubbers,^{4,5} hyperbranched polyesters,^{6,7} etc. Again, their commercial exploration is limited due to processing difficulty, insignificant improvement and high cost to performance ratio. Thus, the research is going on over the last 10 years on designing hyperbranched epoxy to substitute linear commercial one to address the above shortcomings. A variety of hyperbranched epoxies have, therefore, been prepared by various synthetic approaches including end group modification of suitable hyperbranched polymers,^{8,9} polycondensation reaction,¹⁰ functionalization of poly(methyl acrylate) using atom transfer radical polymerization (ATRP)¹¹ and proton transfer polymerization.¹² However, in maximum cases products possess high viscosity and thus, would need dilution with organic solvents, which is detrimental to the environment because of high VOC. In addition, the mechanical performance is not up to the mark mainly due to low crosslinking density.¹³ Thus, desired high performance with such epoxy is rarely found in literature. Therefore, unique structural design is important for obtaining adequate toughness as well as other desired properties and their by can address the shortcomings of conventional epoxy thermosets.

Further, literature witness the inadequacy of performance of polymers including hyperbranched one to suit the demand for their advanced applications. In this milieu, polymer

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nanotechnology is recognized as one of the most promising areas in this century to achieve extraordinary performance. Polymer nanocomposite is defined as an interacting mixture of a polymer matrix with a solid phase material of at least one dimension in nanometer size range. Uniform dispersion of the nanoscale particles produces ultra-large interfacial area per unit volume between the nanoparticles and the polymer matrix. This huge internal interfacial area and the nanoscopic dimension between the domains lead to the formation of a hybrid structure, which fundamentally differentiates polymer nanocomposite from traditionally filled systems. The dramatic improvement in property at very low level of nanomaterial content without noticeable increase in density or weight of the material is the unique feature of polymer nanocomposite. Fabrication of polymer nanocomposite not only improves the properties, but it also provides a new set of desired properties which expand the application area of the virgin polymer. Formation of suitable epoxy nanocomposites with different types of nanomaterials like organically modified nanoclay, functionalized carbon nanotube (CNT), graphene and graphene oxide (GO), etc. resulted noticeable improvement in mechanical, chemical, thermal, barrier, electrical properties, without much affecting the flexibility, elongation at break and impact resistance.¹⁴⁻¹⁶ Various metals like gold, silver, copper, titanium, iron, zinc, etc. and their oxides; and semiconductor quantum dots are also used as nanomaterials to achieve various interesting properties like optical, electrical, antimicrobial, and so on.¹⁷⁻¹⁹ However, such reported epoxy nanocomposites are mainly confined with linear DGEBA based epoxy as the matrix, where the performance especially toughness obtained is not sufficient to address their advanced applications. On the other hand, high performance hyperbranched epoxy nanocomposite is rarely found in literature.²⁰ Therefore, development of tough hyperbranched epoxy thermosets with unique structural design and fabrication of their nanocomposites with different types of nanomaterials may open up a new avenue in the field of high performance epoxy thermoset and hence the subject matter of the present thesis.

1.2. Historical background

It is known that the term hyperbranched polymers was coined by DuPont researchers, Kim and Webster, to define dendritic macromolecules which was prepared by single-step polycondensation of AB₂- type reactants or 'monomers' in late 1980s.²¹ The first prepared hyperbranched polymer was hyperbranched polyphenylene which was warranted as a patent in 1987.²² This polymer was publically presented in 1988 at American Chemical Society Meeting at Los Angeles. Around the same period, Tomalia and Frechet also reported their

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work on highly branched polymers.^{23,24} But the history of hyperbranched polymer is quite long and complex, it can be dated to the end of the nineteenth century, when Berzelius reported the formation of a resin from tartaric acid (A_2B_2 -type 'monomer') and glycerol (B_3 -type 'monomer').²¹ In 1901, Watson Smith also attempted a reaction of phthalic anhydride (A_2 type 'monomer') or phthalic acid (A_2 -type 'monomer') and glycerol (B_3 -type 'monomer') to obtain a hyperbranched polyester.²¹

However, hyperbranched epoxy was first reported in 1999 by Emrick and his group via proton transfer reaction of 1,2,7,8-diepoxyoctane and 1,1,1-tris(hydroxymethyl)ethane to obtain an aliphatic hyperbranched polyether epoxy.¹² In the same year, Chang and Frechet reported a base catalyzed proton transfer polymerization for obtaining an aromatic epoxy from AB_2 'monomer'.²⁵ Subsequently, a variety of hyperbranched epoxy have been reported by various synthetic approaches including end group modification of suitable hyperbranched polymers,^{8, 9} polycondensation reaction,¹⁰ functionalization of poly(methyl acrylate) using ATRP,¹¹ etc. On the other hand, the first attempt to prepare commercial linear epoxy resin from epichlorohydrin was made in 1927 in United States. The credit for the first synthesis of bisphenol A-based linear epoxy resins is shared by both Castan of Switzerland and Greenlee of United States in 1936. Later, Castan's work was licensed by Ciba, Ltd. of Switzerland, which went on to become one of the three major epoxy resin (DGEBA) producers worldwide. Since their first commercial introduction in 1947, epoxy resins have experienced tremendous growth on a commercial scale.

Again, over the last two decades, polymer nanocomposite is rapidly emerging as a multidisciplinary research field for the advancement of polymer by improvement of its performance along with accessing new properties and thereby expanding its applications. Polymer nanocomposites were developed in late 1980s in both commercial research organizations and academic laboratories though the term 'nanocomposite' was first coined by Theng in 1970.^{14,26} The true start of polymer nanocomposites is in 1988 when Toyota first used polymer/layered silicate nanocomposite for the production of their novel car models.¹⁴ However, the term 'nanocomposite' was universally accepted after describing by Komarneni, a very large family of materials involving structures in the nanometer size range (1-100 nm), where the properties are of interest due to the size of the structures, and are typically different from the bulk matrix.²⁷ Later, a number of other companies started to investigate nanocomposites. They also noticed a dramatic expansion of the research and commercial interests in this novel class of materials in broad fields of applications. In the field of epoxy nanocomposites, Lan and Pinnavaia first reported clay reinforced DGEBA based epoxy in

1994.²⁸ In the same year, Wang and Pinnavaia first reported on the self-polymerization of epoxy resin in organophilic smectite clays due to the presence of the alkyl-ammonium ion.²⁹ However, hyperbranched epoxy based nanocomposite was started from the last decade only and the first report came out in 2003.³⁰ However, in recent years research on hyperbranched epoxy based nanocomposites are enlarging tremendously in diversified fields of applications from high performance material to biomaterial.^{17,20}

1.3. Materials and methods

1.3.1. Materials

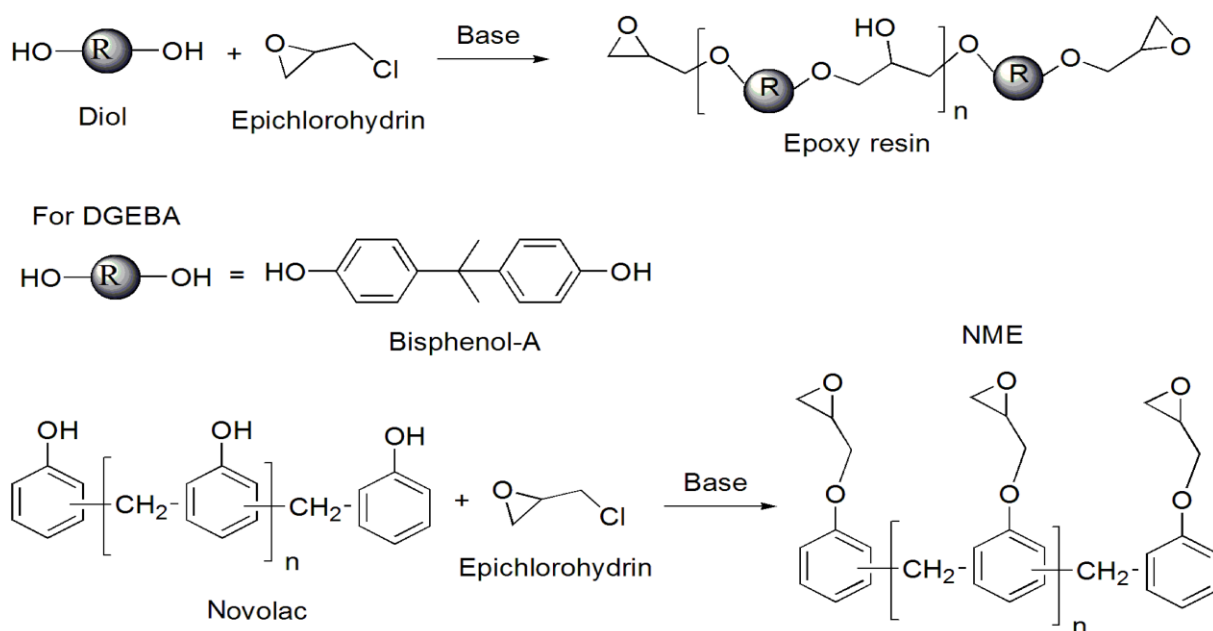
Mainly, commercial interests in nanocomposites have been focused on thermoplastic polymers, so thermosetting nanocomposites are investigated limited extent. However, among the different thermosetting polymers, epoxy is one of the most versatile matrices for the fabrication of nanocomposites with diverse nanomaterials. Again, the large numbers of terminal functional groups with highly active exposed surface functionality of hyperbranched epoxy result high solubility, low solution and melt viscosity, high reactivity and good compatibility with nanomaterials and other additives which help in fabrication of epoxy nanocomposite in terms of easy processing there by resulting significant reinforcement of different properties.

1.3.1.1. Hyperbranched epoxy

Epoxy thermosets are widely used as high performance engineering materials for their overall good performance as stated earlier.^{2,3} Thus, they have a broad range of applications as mentioned in introduction.^{2,3} Epoxy thermosets are mainly three dimensional crosslinked products of epoxy resins and hardeners. Epoxy resins are the reaction products of di/poly-ols with epichlorohydrin (ECH) or other oxirane containing compounds in presence of a base. They have at least two epoxy groups per molecule.³¹ On the other hand, hardeners are proton donor systems of amino, anhydride, phenolic, thiol, etc. containing compounds,³¹ which can react with epoxy resins and transform them to three dimensional network structures under optimal curing and processing conditions. The most frequently used epoxy resin is the polycondensed product of ECH and bisphenol-A (BPA),³¹ known as diglycidyl ether of bisphenol-A (DGEBA) which account for 80-85% of the total worldwide epoxy consumption. Other commercially available conventional epoxy resins are novolac (a condensation product of phenolic compounds with formaldehyde) modified epoxy (NME), cyclo-aliphatic epoxy (CAE), epoxidized oil, etc. General schematic illustration for synthesis

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of epoxy resins from commercially available di- and poly-ols is shown in **Scheme 1.1**. However, used strategies for the synthesis of hyperbranched epoxy resins are slightly different from the synthesis of linear conventional epoxy resins. One of the successful strategies is the synthesis of epoxy terminated hyperbranched polymers through substitution of terminal hydroxyl or carboxylic acid groups of a hyperbranched polymer by epoxy groups.^{8,9} Other approaches are hyperbranched polyethers containing terminal epoxide groups by $A_2 + B_3$ polymerization,¹² polycondensation of multifunctional polyol with diepoxide,¹⁰ functionalization of poly(methyl acrylate) using ATRP,¹¹ etc.



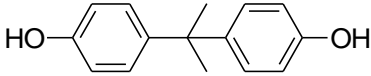
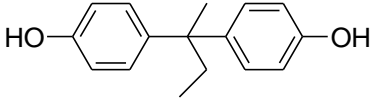
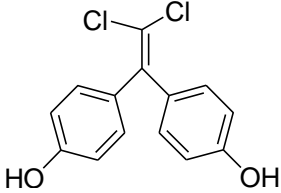
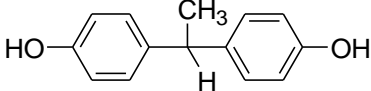
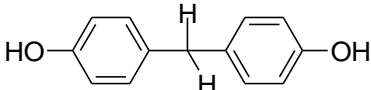
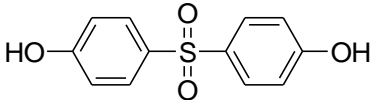
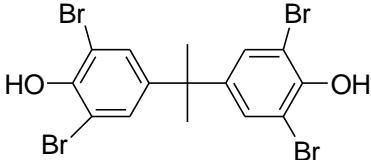
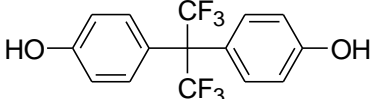
Scheme 1.1: Synthesis of epoxy resins from di/polyols

Di/polyol

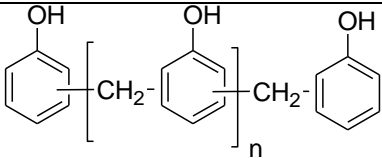
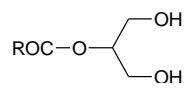

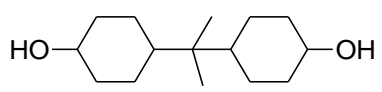
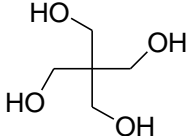
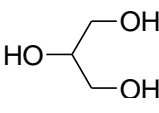
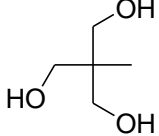
Different types of commercially available di/polyols are used to synthesize epoxy resins depending upon their various applications. As an example, aromatic di/polyols (like BPA, novolac, etc.) are used mainly for obtaining high mechanical strength, thermal stability and good electrical insulation properties. BPA is the most widely used aromatic diol which is manufactured from phenol by reacting with acetone in presence of an acid catalyst.³¹ Aliphatic di/polyols (like ethylene glycol, butane diol, etc.) are used for getting low viscous epoxy binders for surface coatings. Halogenated di/polyols (bisphenol-C, tetrabromo bisphenol-A, etc.) are used to synthesize flame retardant epoxy. A list of di/polyols used for the synthesis of epoxy resins and their applications are given in **Table 1.1**.

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Table 1.1: A list of di/polyols used for the synthesis of epoxy resins and their applications

Name	Structure	Application
Bisphenol-A		High performance general purpose epoxy
Bisphenol-B		High performance epoxy for water proof coatings
Bisphenol-C		Flame retardant high performance epoxy
Bisphenol-E		Resin-injection repair of advanced epoxy composites
Bisphenol-F		High performance solvent free epoxy coatings
Bisphenol-S		High performance fast-drying epoxy glues
Tetrabromo bisphenol-A		In electronic enclosures, flame retardant epoxy
Hexafluoro bisphenol-A		High solid coatings, adhesives and laminates, low dielectric materials
Novolac		High performance thermostable low dielectric epoxy

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Monoglyceride of vegetable oils	 R is hydrocarbon part of fatty acids	Flexible and biodegradable epoxy
Aliphatic diols		Low viscous flexible epoxy
Dehydrogenated bisphenol-A		Weather resistance and color stable epoxy coatings
Pentaerythritol		High performance multifunctional epoxy
Glycerol		For high performance biocompatible hyperbranched epoxy
1,1,1-Tris(hydroxymethyl)ethane		Hyperbranched epoxy

Oxirane ring containing compound

Oxirane ring containing compound is the most important component for the synthesis of epoxy resin by polycondensation with di/polyol or by substitution of other functional groups of a compound. ECH, glycidol, aliphatic and aromatic di/polyepoxides, etc. oxirane containing compounds are used for the synthesis of epoxy resins. A list of these compounds and their corresponding reactants are given in **Table 1.2**.

ECH is an organochloro compound with an oxirane ring which is the most widely used for the synthesis of epoxy resins due to its high reactivity towards active hydrogen

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containing compounds. It is mainly manufactured from allyl chloride by addition of hypochlorous acid followed by treatment with a strong base.³¹ Dow and Solvay demonstrate a biobased process for manufacturing of ECH from glycerol. According to Dow's process, glycerol is first dichlorinated with hydrogen chloride using a carboxylic acid catalyst and then the mixture of dichlorohydroxypropanes is treated with base to form ECH.³²

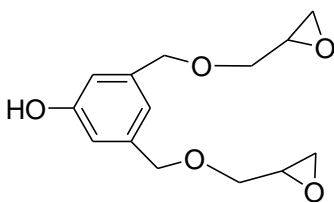
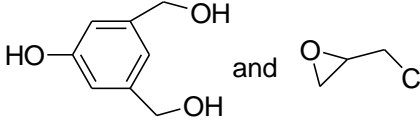
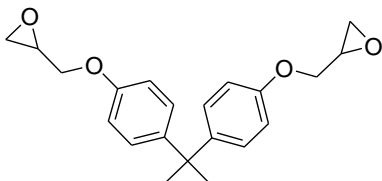
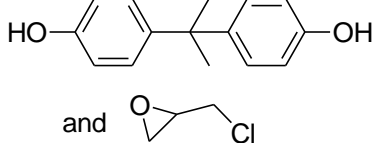
Glycidol is simply prepared by epoxidation of allyl alcohol. It is mainly used to synthesize epoxy resins from di/polyacid chlorides.³³

Di/polyepoxides are mainly used to synthesize high molecular weight as well as hyperbranched epoxy resins through addition,³⁴ atom transfer,¹² and polycondensation reactions.¹⁰ Few of the used aliphatic and aromatic di/polyepoxides are 1,2,7,8-diepoxyoctane, 1,1,1-trihydroxymethylpropane triglycidyl ether, diglycidyl ethers of aliphatic glycols, diepoxy phenol, low molecular weight DGEBA, etc. These compounds are synthesized from di/polyols by condensation reaction with ECH in presence of base.

Table 1.2: A list of oxirane ring containing compounds and their corresponding reactants

Name	Structure	Reactant
Epichlorohydrin		$\text{Cl}-\text{CH}_2-\text{CH}=\text{CH}_2$ or $\text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}$
Glycidol		$\text{HO}-\text{CH}_2-\text{CH}=\text{CH}_2$
1,2,7,8-diepoxyoctane		$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$
1,1,1-Trihydroxymethylpropane triglycidyl ether		$\text{HO}-\text{CH}_2-\text{C}(\text{OH})(\text{CH}_2\text{OH})-\text{CH}_2-\text{OH}$ and $\text{Cl}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2$
Diglycidyl ethers of aliphatic glycols		$\text{HO}-\text{CH}_2-(\text{CH}_2)_n-\text{CH}_2-\text{OH}$ and $\text{Cl}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2$

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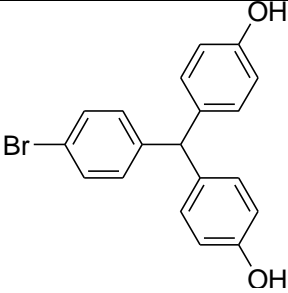
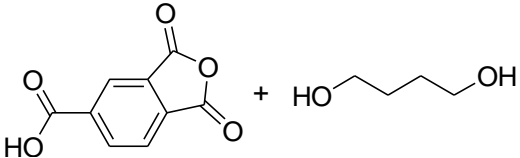
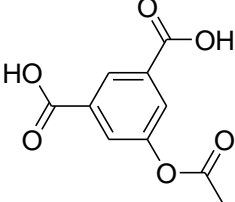
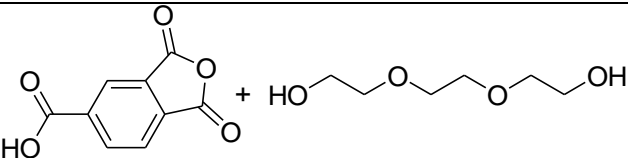
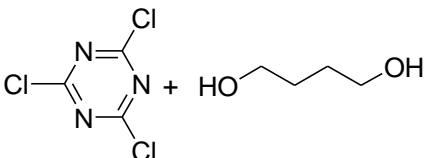
Diepoxy phenol		
Diglycidyl ether of bisphenol-A		

Branch generating units

Synthesis of hyperbranched polymers requires multifunctional reactants as starting materials. Conventional synthesis of hyperbranched polymers used multifunctional AB_x ($x \geq 2$) type 'monomers' in single 'monomer' methodology and $A_x + B_y$ ($x \geq 2$ and $y > 2$) or $AA'_x + BB'_y$ ($x \geq 1$ and $y > 1$) for double or multiple 'monomer' methodology. However, only in few cases multifunctional reactants are utilized for direct synthesis of hyperbranched epoxy resin. Emrick et al. used 1,1,1-tris(hydroxymethyl)ethane as the multifunctional moiety for synthesizing hyperbranched epoxy by proton transfer reaction with 1,2,7,8-diepoxyoctane.¹² Barua et al. synthesized hyperbranched epoxy from glycerol by $A_2 + B_3$ polycondensation reaction with *in-situ* generated DGEBA.¹⁰ The multifunctional polyols which are used to synthesize hyperbranched epoxy are given in **Table 1.2**. In most of the cases hyperbranched epoxy were synthesized by using hyperbranched polymers as core moieties through substitution of terminal hydroxyl or carboxylic acid groups of the core.^{8,9,33,35,36} Whereas, these hyperbranched core moieties were synthesized from different multifunctional reactants by conventional synthetic methods of hyperbranched polymers. A list of hyperbranched core moieties and their corresponding multifunctional reactants are given in **Table 1.3**.

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Table 1.3: A list of hyperbranched core moieties and their corresponding multifunctional reactants

Hyperbranched core moiety	Multifunctional reactant	Reference
Hyperbranched poly(phenylene oxide)		8
Hyperbranched polyester		9
Hyperbranched aromatic polyester		33
Carboxyl-end hyperbranched polyester		35
Hyperbranched polyether		36

Hardener

Hardeners are the most important substances for epoxy resins to achieve well balanced ultimate properties. They transform epoxy resins into thermosets of three dimensional network structures under suitable conditions. These are the bi/polyfunctional active hydrogen containing compounds or proton donor compounds like amine, carboxylic acid, anhydride, thiol, phenol, poly(amido-amine), etc.³¹ The choice of hardeners mainly depends on the final application of the epoxy thermosets. A list of hardeners used for obtaining epoxy thermosets and their various applications are given in **Table 1.4**. Aliphatic amines are mainly used in fast

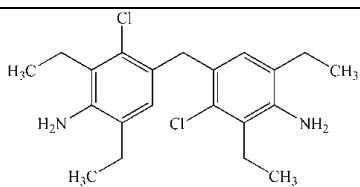
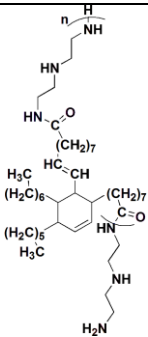
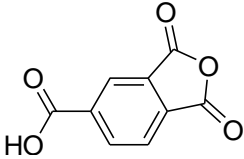
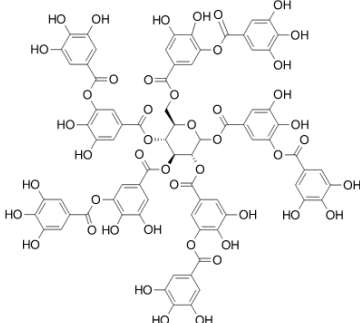
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curing and sealing purposes. Aromatic amines and anhydrides are used for the thermosets with high mechanical strength, thermal stability and low dielectric properties. Vegetable oil-based poly(amido-amine) hardener offers good toughness and high pot life epoxy thermosets.³¹

Table 1.4: A list of hardeners used for the formation of epoxy thermosets and their various applications

Name	Structure	Applications
Diethylene triamine (DETA)		Fast curing at room temperature
Triethylene tetraamine (TETA)		Fast curing at room temperature
Hexamethylene diamine		Thermostable epoxy
Cycloaliphatic amines		Room temperature curable, long pot life, high performance epoxy
Dicyandiamide		Good viscoelastic properties
1-ethyl-3-(3-dimethylaminopropyl) carbodiimide		Fast curable endodontic sealing
Cystamine		Biocompatibility curative
Diamino diphenyl sulfone		Thermostable high performance epoxy thermoset with decrement of curing temperature
Methylaniline		Good physical and dielectric properties
Diamino diphenyl methane		Thermostable high performance epoxy

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		thermoset
4,4-Methylene bis(3-chloro-2,6-diethylaniline)		Good abrasion resistant
Vegetable oil-based poly(amido-amine)		Low temperature curing, tough and biocompatible epoxy thermoset
Trimellitic anhydride		Thermostable high performance epoxy thermoset
Polyphenols like tannic acid		Biocompatible and biodegradable epoxy thermoset

Catalyst

Generally for the synthesis of epoxy resins, ECH is used as an oxirane containing compound and thus, hydrochloric acid (HCl) is the main byproduct for this polycondensation reaction. Thus, a base catalyst, inorganic or organic depending on the reaction medium is used for the synthesis of epoxy resins. The catalyst also increases the reactivity of the di/polyols by removing its active hydrogen. Inorganic bases like sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH), calcium hydroxide (Ca(OH)₂), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), calcium carbonate (CaCO₃), sodium bicarbonate (NaHCO₃), potassium bicarbonate (KHCO₃), lithium bicarbonate (LiHCO₃),

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calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$), etc. are used when water is the reaction medium.^{3,37,38} However, when organic solvents like tetrahydrofuran (THF), acetone, dimethylformamide (DMF), dimethylsulfoxide (DMSO), etc. are used as the reaction media, then organic bases like trialkyl amines, phosphines, etc. are used. Tertiary amines and quaternary ammonium salts are also used as catalysts in polyaddition type reactions, where the addition and dehydrohalogenation reactions are carried out separately.^{37,39}

However, when epoxy resins synthesized from olefinic double bond or unsaturated fatty esters of vegetable oil, epoxidation of the double bond is carried out by four different methods such as (a) epoxidation with percarboxylic acids, catalyzed by acids or by enzymes, (b) epoxidation with organic and inorganic peroxides, catalyzed by transition metal catalyst, (c) epoxidation with halohydrines, using hypohalous acids (HOX) and their salts and (d) epoxidation with molecular oxygen. Industrially more preferred epoxidation is oxidation of double bond by using organic peracids. Formic, acetic, propionic, n-butyric, isobutyric, 3-methylbutanoic, 2,2-dimethylpropanoic, n-valeric, n-caproic, n-heptoic, caprylic, n-nonylic, capric, undecylic, lauric, tridecylic, myristic, pentadecylic, palmitic, margaric and stearic acids are the few examples of such acids. Formic and acetic acids are the most preferred acids out of them because of their ready availability in liquid form at room temperature at relatively low price. Various types of inorganic acid catalysts like H_2SO_4 , HNO_3 , H_3PO_4 and HCl are also used in conjunction with organic acids for the peracid formation.^{40,41}

1.3.1.2. Nanomaterial

Nanomaterials are defined as those that have at least one dimension in the range of 1-100 nm. Depending on their dimension, they can be categorized into three classes: (a) zero, (b) one and (c) two dimensional as shown in **Figure 1.1**.⁴² Properties and interactions of the nanomaterials with different polymer matrices depend on the size, shape and distribution of the nanomaterials. Different types of nanomaterials that are used for the fabrication of polymer nanocomposites are discussed below.

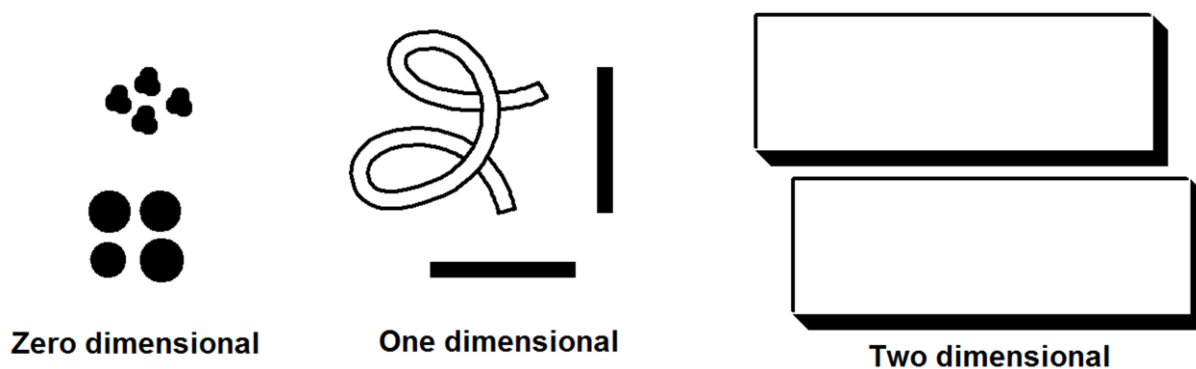


Figure 1.1: Different categories nanomaterials

Zero dimensional nanomaterial

Spherical nanomaterials like quantum dots, spherical metal and silica nanoparticles, nanoclusters, etc. which have all three dimensions in nanometer range (1-100 nm) are included in this category. Semiconductor quantum dots like CdSe, CdS, ZnS, SnTe, etc. are mainly used for their promising optical and electronic properties and thus, polymer nanocomposites with these nanomaterials are used in advanced optoelectronics.⁴³ These semiconductor nanocrystals are mainly obtained by colloidal routes based on controlled precipitation and pyrolysis of organometallic reagents in a hot coordinating solvent.⁴³ Recently, water soluble carbon based quantum dots are largely used for the same purpose because of their easy synthetic procedure and non toxic nature.^{44,45} They are generally oxygenous carbon nanoparticles with a size of less than 10 nm and they are structurally carbonized aromatic clusters with 60-70% carbon and 30-40% oxygen in weight or atomic ratio.⁴⁶ These carbon nanoparticles are mainly synthesized from any carbon precursor by acid oxidation, hydrothermal, direct heating, pyrolysis, etc. processes.⁴⁶

On the other hand, zero dimensional metal nanoparticles like silver, copper, gold, iron etc. and their oxides, sulphides, etc. are mainly used in polymer nanocomposites for antimicrobial, catalysis, sensor, optical, photonic and electronic applications.⁴⁷ In general, these nanoparticles are prepared by wet chemical reduction, reverse micelles, electrochemical and sonochemical techniques, etc. from their corresponding salts.⁴⁷ Wet chemical reduction technique is more popular over the other for the preparation of metal nanoparticles due to easy control of the reaction process and production rate. In wet chemical reduction method, generally reduction of a metal salt from its solution is done. There are three key factors in this reducing process: (i) reducing agent, (ii) solvent medium and (iii) capping agent.⁴⁷ Reducing agents generally used like sodium borohydride, sodium sulfite, ascorbate, hydrazine hydrate,

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elemental hydrogen, dimethylaminoborane, dimethyl formamide, sodium citrate, glucose, fructose, lactose, sucrose, etc. Recently, polyphenolic compounds as plant extracts are largely used in greener reduction process.⁴⁸ In most of the cases water is used as the medium because of its nontoxic and environmentally benign nature. In few cases, of course, organic solvents like ethanol, dimethyl formamide, tetrahydrofuran, dimethyl acetamine, etc. are also employed depending on the metal salts and reducing agents used. However, metal nanoparticles are generally thermodynamically unstable and thus, need a capping agent to stabilize them. They must be arrested during the preparation to produce stable nanoparticles. Surfactants, polyphenolic compounds, organic ligands, polymer matrices, etc. are used for this purpose.

One dimensional nanomaterial

This type of nanomaterials has two dimensions in nanometer range (1-100 nm) and other dimension may be in the range of several hundred nanometers to micrometers. Different nanotubes, nanowires and nanorods like carbon nanotubes, nanocellulose fibers, titanium dioxide nanomaterials, etc. belong to the class of one dimensional nanomaterials.⁴⁹

Carbon nanotube (CNT) is one of the most popular allotropes of carbon. It is a cylindrical nanostructural material constructed with length-to-diameter ratio of 10000:1.⁵⁰ These nanotubes are composed of single and multiple numbers of sp^2 hybridized graphitic carbon layers and classified as single walled (SW) and multi-walled (MW) CNT respectively.³¹ This cylindrical CNT has extraordinary properties, which are valuable for electronics, optics and other fields of materials science. In particular, owing to their exceptional mechanical strength, thermal and electrical conductivity much more interest is found for their uses in polymer nanocomposites. CNT is mainly synthesized by laser ablation, chemical vapor deposition, arc discharge, plasma torch, etc. methods.³¹ Chemical vapor deposition method is the most advantageous over others to obtain nanotubes with minimal impurity and large scale production.⁵¹

Another important example in this category is cellulose nanofibers (CNF). It is a biopolymer which consists of β -1-4-linked D-anhydroglucopyranose units. It is highly crystalline and rigid nanomaterial because of its extensive inter/intramolecular hydrogen bonding between the molecules and thus, it exhibits high stiffness and strength. CNF is mainly obtained from native cellulose fibers by an acid hydrolysis (by sulfuric or hydrochloric acids) and the native fibers are isolated from any cellulose containing source including wood based fibers through high temperature, pressure and velocity impact homogenization, along with grinding or microfluidization. The dimensions of the nanofiber

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depend on the cellulose source materials and conditions for hydrolysis. CNF is widely used in polymer nanocomposites for reinforcement of polymer matrices as well as biological applications like drug delivery, protein immobilization, etc.⁵²

Two dimensional nanomaterial

This type of nanomaterials has only one dimension in nanometer range (1-100 nm) and other two dimensions may be in the range of several hundred nanometers to micrometers. These kinds of materials are multi-layered nano thin films or sheets like structure where only thickness is in nanometer range like nanoclays or layered silicates, graphene, etc.

Nanoclays or layered silicates are the most widely used nanomaterials because of their easy availability, ultra large surface area and good intercalation chemistry. Nanoclays are basically nanometer sized hydrous aluminum phyllosilicates thin platelets or sheets with layered structure. The most commonly used nanoclays are montmorillonite (MMT), hectorite, saponite, etc. They are generally obtained from nature through different physical and chemical transformations.³¹ Among different nanoclays, MMT is the most admired in both industries and academia for the preparation of polymer nanocomposites because of its easy availability and larger structure. It belongs to 2:1 phyllosilicate, means it has two tetrahedral sheets of silica sandwiching a central octahedral sheet of aluminum.³¹ MMT is plate-shaped clay with an average dimension of approximately one micrometer with thickness of 1 nm. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ and thus, it is hydrophilic in nature. Thus, to render the hydrophobic character for enabling its dispersion in the organophilic polymer matrices for the fabrication of nanocomposites, MMT is organically modified, either by surface functionalization or by cation exchange process.^{31,53,54} The most commonly used organic cation for the modification of organo nanoclay is the alkylammonium species like quaternary ammonium compounds containing alkyl, phenyl, benzyl and pyridyl groups. The modification process also increases the interlayer spacing between the clay galleries which allows the polymeric chains to enter into galleries to make strong interaction with the platelets. Thus, incorporation of this modified clay into various polymers, properties like mechanical, thermal, physical, barrier, etc. are significantly enhanced.⁵⁵

Another most popular two dimensional nanomaterial is graphene. It is one of the hottest materials of the decade in the scientific community because of its unique mechanical, electrical and optical properties.⁵⁶ It is a crystalline allotrope of carbon, where the carbon atoms are densely packed in a regular sp^2 -bonded atomic-scale of chicken wire (hexagonal)

pattern. It can also be described as a one-atom thick layer of graphite. Graphene is mainly manufactured from graphite by mechanical, chemical, solvent or sonic exfoliation or by reduction of graphene oxides. Reduced graphene oxide (RGO) is more admired than graphene itself for polymer nanocomposites. RGO exhibits similar attributes as that of graphene, however, it contains some oxygen functionalities of graphene oxide (GO) which is obtained by oxidation of graphite. These polar functionalities are very important for dispersion of RGO by different polar-polar interactions with the polymer matrices by formation of nanocomposites. RGO can also be obtained easily by the reduction of GO using sodium borohydride, hydroquinone, hydrazine or by green approach using plant extract containing polyphenolic compounds.⁵⁵ GO can be easily prepared from graphite by oxidizing with potassium permanganate or dichromate in presence of sulfuric acid.^{56,57}

1.3.2. Methods

1.3.2.1. Hyperbranched epoxy

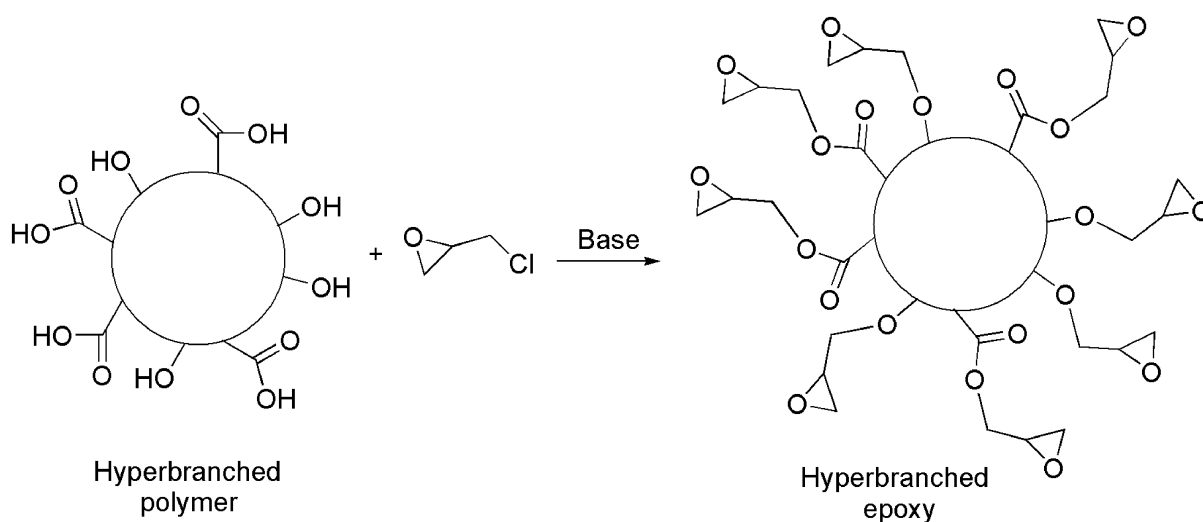
Epoxy resins (mainly DGEBA) are generally synthesized by either taffy or by fusion process. In taffy process for the synthesis of DGEBA, BPA is directly reacted with calculated excess amount of ECH in the presence of a stoichiometric amount of NaOH in aqueous solution and the molecular weight of the resin is controlled by the mole ratio of ECH to BPA. Thus, the process involves two phases, one organic phase that contains the reactants (BPA and ECH) and product (epoxy resin), and another aqueous phase that contains byproduct (NaCl). As the product (resin) is formed, the organic phase becomes more viscous, which is similar to taffy and thus, it is known as the “taffy process”. The product is recovered by separating the desired organic phase from the aqueous phase. The excess or unreacted ECH and trace amount of water are removed by vacuum drying or by distillation after washing the product with water. On the other hand, in fusion process high molecular weight epoxy resin is produced from low molecular weight liquid epoxy resin by reacting with additional BPA. The reaction proceeds via a step-growth polymerization process and hence it is also referred as advancement process. It is much more efficient to make high molecular weight epoxy resin for industries. In this process the hydroxyl groups of BPA are reacted with stoichiometric excess of low molecular weight epoxy resin or polyepoxide in the presence of a catalyst at 150-190 °C. The catalysts mainly used for this process are basic inorganic reagents, like NaOH, KOH, Na₂CO₃, LiOH, and quaternary ammonium salts. The reaction can be carried out with or without solvents. Isolation of the polymerized product is also easier than taffy process since removal of NaCl is not necessary.

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However, for the synthesis of hyperbranched epoxy, these processes are rarely used. Only in few cases taffy or fusion type processes are utilized where hyperbranched epoxies are synthesized by polycondensation reaction. The numbers of synthesized hyperbranched epoxy resins are also limited compared to other hyperbranched polymers due to the unavailability of AB_n type or other multifunctional moieties for the synthesis of hyperbranched epoxy. Thus, most of the strategies used for the synthesis of hyperbranched epoxy resins are slightly different from the approaches for general hyperbranched polymers. The approaches used in maximum cases for the synthesis of hyperbranched epoxy resins are end group modification of suitable hyperbranched polymers and proton transfer polymerization. Sometimes, hyperbranched epoxy are also synthesized by polycondensation reaction and functionalization of poly(methyl acrylate) using ATRP.

End group modification of suitable hyperbranched polymer

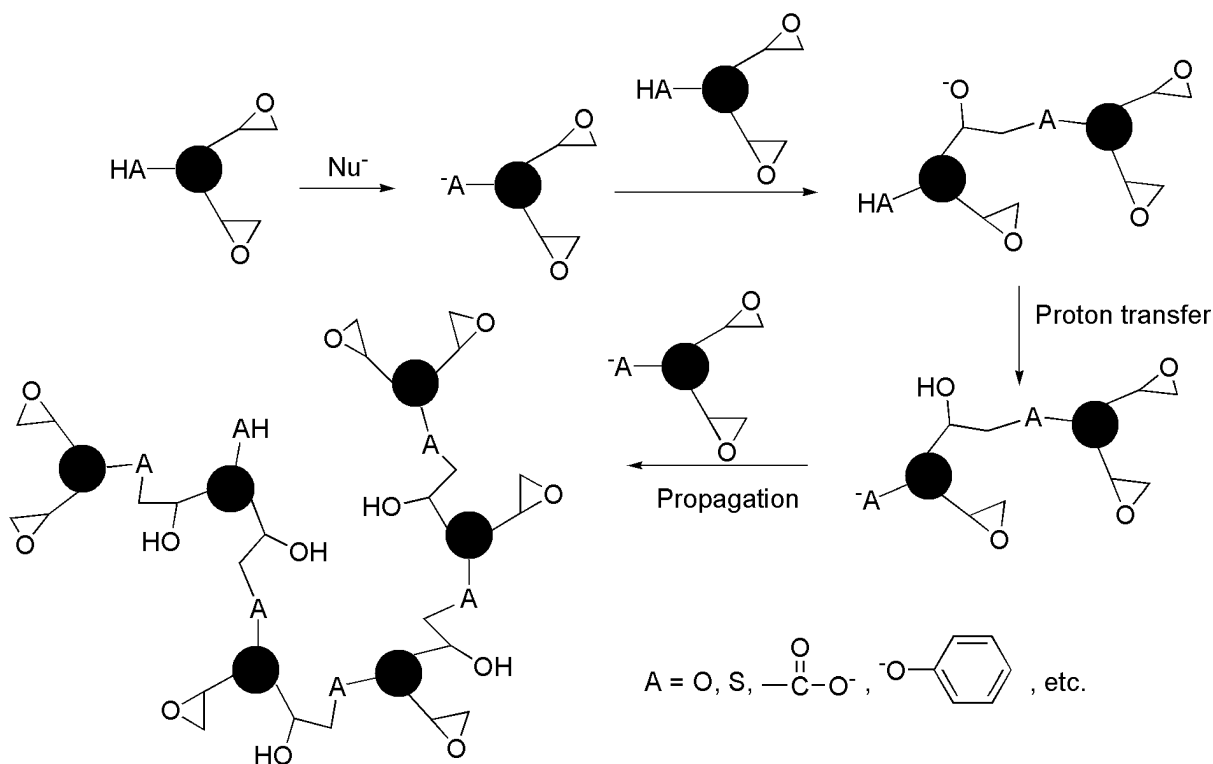
This is the most successful approach for the synthesis of hyperbranched epoxy resins. In this process hyperbranched epoxy resins are synthesized from hyperbranched polymers like polyesters, polyethers, etc. which contain large numbers of hydroxyl or carboxylic acid as end functional groups.^{8,9,35} In the first step hyperbranched polyesters or polyethers are synthesized from different multifunctional reactants (as given in **Table 1.3**) by conventional method of hyperbranched polymer synthesis like self-condensation of AB_n type reactants, $A_2 + B_3$ type polycondensation reaction, etc. In the second step epoxy end terminated hyperbranched polyesters or polyethers are synthesized by the substitution of end functional groups with excess epichlorohydrin in presence of a catalyst like tetra alkyl ammonium halides or inorganic bases as shown in **Scheme 1.2**. The substitution reaction is carried out at 115-120 °C in presence of organic solvent or water.¹³ Sometimes the carboxylic acid end functional hyperbranched polyesters are converted into polymeric acid chloride by reaction with thionyl chloride. Then the epoxy end functionalized hyperbranched polyester is obtained by the reaction of polymeric acid chloride with glycidol at room temperature in presence of a dry organic solvent like THF.³³



Scheme 1.2: Synthesis of hyperbranched epoxy by end group modification of a hyperbranched polymer

Proton transfer polymerization

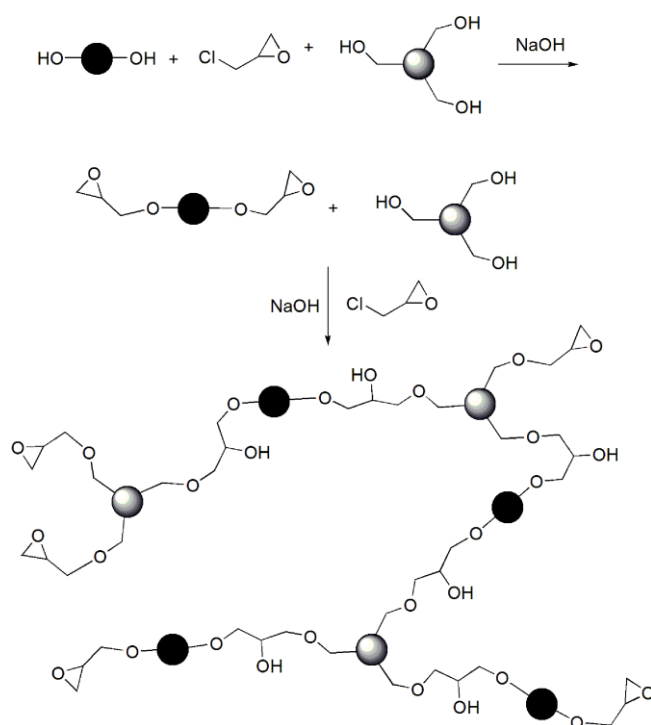
The concept of proton transfer polymerization for the synthesis of hyperbranched epoxy was used by Frechet and co-workers in 1999.¹² In this polymerization, each propagation step involves a proton transfer for the activation of the nucleophile used in epoxide ring opening. Synthesis of hyperbranched epoxy resin by proton transfer mechanism requires AB_n or AB_2 $A_2 + B_3$ type reactants.^{12,58} In case of AB_2 type reactants, one group should contain an active hydrogen proton (like phenolic or thiol containing protons) and the other two should contain epoxide groups. The polymerization is initiated by the addition of a nucleophilic catalyst (like base) to abstract phenolic hydrogen and then, nucleophilic addition to the phenolate anion to an epoxide ring proceeds to generate a dimer containing a secondary alkoxide which undergoes a proton exchange reaction with another AB_2 reactant to produce the phenolate anion. Finally the propagation proceeds by nucleophilic attack of primary alkoxides on epoxide rings to yield the hyperbranched polymer with terminal epoxide groups.⁵⁸ In case of $A_2 + B_3$ reactants, A_2 is a diepoxide and B_3 is triol or vice versa.^{12,59} In this process chloride ion containing compounds like tetra alkyl ammonium chloride (R_4NCl) are used as nucleophilic catalyst. Here initiation is started by nucleophilic attack of chloride ion on an epoxide group of di/triepoxide to produce an alkoxide. Then the proton exchange occurs with one of the hydroxyl groups of di/triol. Finally the propagation proceeds by nucleophilic attack of primary alkoxides on epoxide rings to produce the hyperbranched epoxy.^{12,59} A model reaction for the synthesis of hyperbranched epoxy by proton transfer mechanism is shown in **Scheme 1.3**.



Scheme 1.3: Synthesis of hyperbranched epoxy by proton transfer reaction

Polycondensation reaction

It is slightly similar to taffy or fusion process used for the synthesis of conventional epoxy resins. In this process $A_x + B_y$ ($x \geq 2$ and $y \geq 3$ or vice versa) type 'monomers' are used for the synthesis of hyperbranched epoxy resin where, A_x is a diepoxide like *in-situ* generated DGEBA and B_y is a aliphatic tri/polyol.^{10,36} In the procedure, calculated excess amount of ECH is condensed with BPA and polyol in presence of a base catalyst like NaOH or KOH in aqueous solution at 110-115 °C. In the reaction mixture, first DGEBA (A_2) is generated as the reactivity of BPA is higher than the aliphatic polyol. Finally hyperbranched epoxy is obtained by the reaction between DGEBA and polyol as shown in **Scheme 1.4**. Here the excess ECH also substitutes the terminal hydroxyl groups by epoxy groups and thus, very low epoxy equivalent (large numbers of epoxy groups) containing epoxy was obtained by this process. As aqueous NaOH is the catalyst for the condensation reaction, the recovery and purification of the product is similar to taffy process.



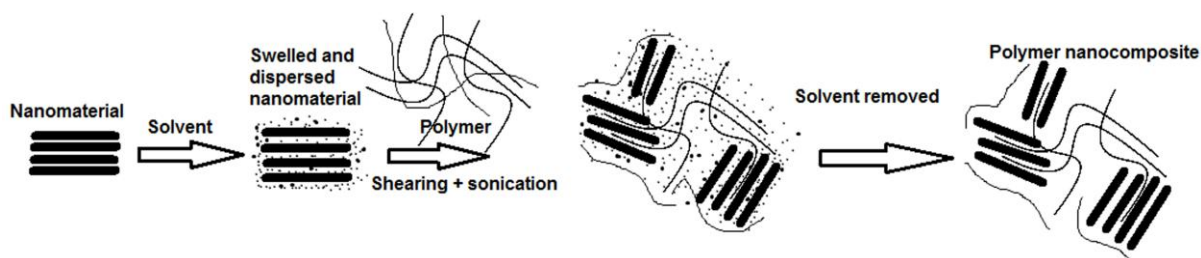
Scheme 1.4: Synthesis of hyperbranched epoxy by polycondensation reaction

1.3.2.2. Polymer nanocomposite

Polymer nanocomposite is a unique mixture of a polymer matrix with a nanomaterial. Nanomaterials are obtained from nature or by different preparative techniques as mentioned earlier in section 1.3.1.2. However, the preparation of polymer nanocomposites by different techniques such as solution, *in-situ*, melt mixing, etc. results uniform dispersion and strong interfacial interactions between the nanomaterials and polymer matrices. These are general techniques for the fabrication of polymer nanocomposites and thus, they are also applicable for the preparation of hyperbranched epoxy nanocomposites.

Solution technique

In this technique a suitable solvent is used to swell and disperse the nanomaterials into the polymer solution. The dispersion is mainly done by high shearing and ultrasonic forces so that polymer chains can penetrate into the layers of the nanomaterials (in case of layered structure) by intercalation or can strongly interact with the nanomaterials (in case of spherical particles) by breaking the aggregates. Then the nanocomposite is formed by precipitation or by evaporation of the solvent.^{60,61} A model diagram for the preparation of polymer nanocomposite by solution technique is shown in **Scheme 1.5**.

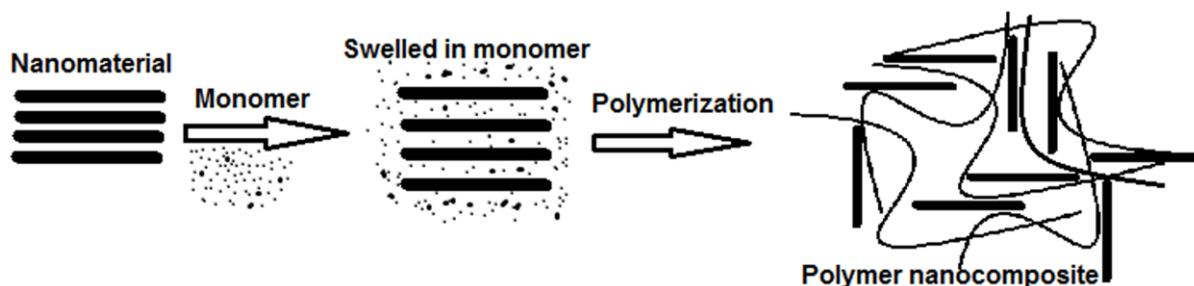


Scheme 1.5: Preparation of polymer nanocomposite by solution technique

However, this technique suffers from some difficulties like high cost due to use of large amount of solvents, phase separation of the materials from solvent, choice and removal of solvent, health hazards and safety associated with the solvents, etc.³¹ Level of interactions between polymers and nanomaterials are also weak in this technique. Thus, in this technique achievement of exfoliated structure for clay or layer silicate based polymer nanocomposites is very difficult.

In-situ technique

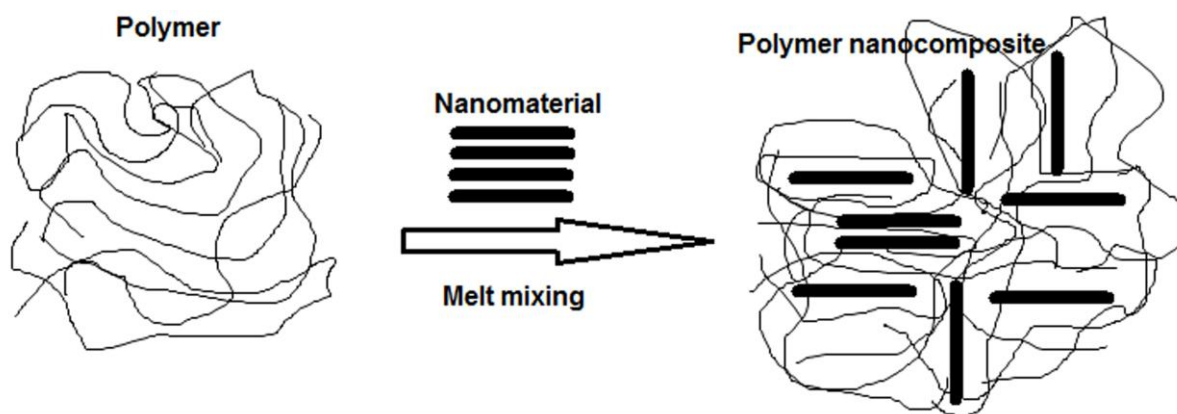
In this technique, first nanomaterials are directly swollen into the liquid ‘monomer’ or prepolymer and then the nanomaterials dispersed reactant is polymerized in presence of an initiator or catalyst. Thus, the interaction level between polymer and nanomaterials is much better in this technique compared to solution technique. This is the most favorable technique for achievement of exfoliated structure in clay or layer silicate based polymer nanocomposites. The ‘monomer’ can migrate into the clay galleries and thus, the polymerization reaction can occur between the intercalated sheets.^{62,63} A model diagram for the preparation of polymer nanocomposite by *in-situ* technique is shown in **Scheme 1.6**. In case of epoxy nanocomposites first, nanomaterials are swollen and dispersed into the liquid epoxy resin and then the nanomaterial dispersed resin is cured in presence of a hardener. Sometimes functionalized nanomaterials like functionalized CNT or GO are used for the formation of strong interaction and stable dispersion *in-situ* epoxy nanocomposites.⁶⁴⁻⁶⁶



Scheme 1.6: Preparation of polymer nanocomposite by *in-situ* technique

Melt mixing technique

Melt mixing technique is a common alternative method, which is particularly used in industries for the fabrication of thermoplastic polymer nanocomposites. In this technique nanomaterials are mixed with molten polymers by twin screw mixers, rollers, injection molding, etc. The process involves the annealing a mixture of polymer and nanomaterial above the softening point of the polymer under shearing force. Amorphous polymers are mainly processed above their glass transition temperatures while the semi-crystalline polymers are processed above their melting temperatures. In case of clay or layered silicate nanomaterials under this condition the polymer can penetrate into the interlayer space and form either an intercalated or an exfoliated nanocomposite.⁶⁷ The level of interaction between polymers and nanomaterials is not as good as that of *in-situ* technique. However, this technique is superior from the solution technique as it eliminates the use of hazardous solvents.³¹ A model diagram for the preparation of polymer nanocomposite by melt mixing technique is shown in **Scheme 1.7**.



Scheme 1.7: Preparation of polymer nanocomposite by melt mixing technique

Besides these techniques, polymer nanocomposites are also prepared by few other techniques like solid-state mechano-chemical or twin-screw pulverisation processes, latex fabrication, template synthesis, coagulation spinning, sol-gel process, plasma treatment, thermal decomposition, etc.⁶⁸⁻⁷²

1.4. Characterization

Different analytical, spectroscopic and microscopic techniques and testing methods are used to characterize the polymers, nanomaterials and nanocomposites by determining their physical and chemical properties, structural features and other attributes. The characterization

techniques for hyperbranched epoxy and its nanocomposites are same as they are for other hyperbranched polymers and polymer nanocomposites.

1.4.1. Hyperbranched epoxy matrix

1.4.1.1. Analytical technique

Different physical properties like epoxy equivalent, hydroxyl value, viscosity, molecular weight, etc. of epoxy resins are determined by different analytical techniques as described below.

Epoxy equivalent

Epoxy equivalent is defined as the number of epoxy functional groups of an epoxy resin, which is expressed as the weight of epoxy resin (in gram) containing 1 equivalent of epoxide group (g/eq.). This value is very important for the calculation of the amount of hardener need for an epoxy to transform into thermoset. The epoxy equivalent is mainly determined by refluxing a known amount of the resin with excess amount of HCl or HBr acid solution and the free acid is back titrated with the standard NaOH or KOH solution using phenolphthalein as an indicator. Most of the cases pyridine is used as a catalyst for this reaction.⁷³ Epoxy equivalent is calculated using the following equation,

$$\text{Epoxy equivalent} = (\text{weight of the sample} \times 1000) / \{(\text{B-S}) \times \text{normality of used KOH}\} \dots (1.1)$$

where, B and S are the volume of NaOH or KOH require for the blank (without sample) and sample solutions respectively.

Hydroxyl value

Hydroxyl value is the measure of the content of hydroxyl functional groups in an epoxy resin. It is defined by the number of milligrams of KOH required to neutralize the acetic acid that binds with 1 g of hydroxyl groups containing epoxy resin. Analytically it is determined by acetylating the epoxy resin with excess amount of acetic anhydride in presence of pyridine catalyst as per the standard test ASTM E222-10. It can also be determined by refluxing with excess maleic anhydride solution using triethyl amine as the catalyst. The excess free acid is back titrated with the standard KOH solution using phenolphthalein as an indicator.⁷⁴ The calculation of the hydroxyl value is done using the following equation,

$$\text{Hydroxyl value} = [56.1 \times (\text{B-S}) \times \text{N}] / \text{Weight of the resin} \dots (1.2)$$

where, B and A are the volume of KOH required for blank (without sample) and sample solutions respectively; and N is the normality of used standardized KOH solution.

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Viscosity

Viscosity is an internal property of epoxy resins that resist to flow. It is very important processing parameter for polymers. Viscosity of the epoxy is mainly measured in its resinous state. The solution viscosity of epoxy can also be measured by suspended level Ubbelodhe viscometer at constant temperature bath using 0.5 wt% solution of the epoxy in a suitable solvent. Measurement of the viscosity is done by comparing the efflux time required to flow through the capillary tube of the viscometer for the resin solution (t) and the used solvent (t_0). The relative viscosity of the solution is calculated from t and t_0 . Finally, the inherent viscosity (in dL/g) of the resin solution is measured from the relative viscosity.

$$\text{Relative viscosity, } \eta_r = \eta/\eta_0 \approx t/t_0 \dots\dots\dots (1.3)$$

$$\text{Inherent viscosity, } \eta_i = (\ln \eta_r)/c \dots\dots\dots (1.4)$$

where, c is the concentration of the resin in gram per deciliter (g/dL).⁷⁵

Whereas, the shear viscosity of epoxy resin is measured using Brookfield viscometer as well as rheometer by applying shear force. In industry the viscosity of the resin is mainly measured with a cup like Zahn cup, Ford cup, Bubble cup, etc.

Molecular weight

It is a very important parameter for determining the properties of polymer. The degree of branching (DB), viscosity, thermal stability, chemical resistance, and mechanical properties of a hyperbranched epoxy depend on its molecular weight.⁷⁶ As the polymers are composed of different length of chains their molecular weights are usually determined as the average values. Two experimentally determined average molecular weights are the number average (M_n) which is calculated from the mole fraction distribution of different sized molecules in a polymer sample, and the weight average (M_w) which is calculated from the weight fraction distribution of different sized molecules. Molecular weight of a polymer is mainly determined by functional group analysis, measurement of colligative properties, gel permeation chromatography (GPC) or by mass spectroscopic analysis.^{31,75}

1.4.1.2. Spectroscopic technique

Spectroscopic techniques like FTIR and NMR are very important for the determination of structural features of a hyperbranched epoxy resin. Presence of different types of functional groups and chemical linkages in an epoxy resin is revealed from FTIR spectroscopy. Presence of epoxide ring and hydroxyl groups, ether linkages, etc. of an epoxy resin is confirmed by assigning the stretching bands at around 915, 3400 and 1250 cm^{-1} respectively

from its FTIR spectrum.³⁶ On the other hand NMR spectroscopy plays an important role to elucidate the structure of the epoxy resin. The presence of different kinds of protons and carbons in different chemical environments is revealed from ¹H NMR and ¹³C NMR spectra. The epoxide protons of an epoxy are observed at chemical shift values around $\delta = 2.8$ and 3.3 ppm in ¹H NMR and $\delta = 43$ and 50 ppm in ¹³C NMR spectra.³⁶ Again, NMR spectroscopy is an important tool for the characterization of hyperbranched epoxy resin since detailed analysis of the spectrum permits extracting of information about degree of branching (DB). According to polymerization mechanism of the hyperbranched polymer and the definition of DB, the resulting polymer should contain dendritic unit (D), linear unit (L) and terminal unit (T). According to Frechet's equation, DB is the ratio of the sum of integration of dendritic and terminal units to the sum of integration of dendritic, linear and terminal units,^{31,36} as given in equation 1.5.

$$DB = (D + T)/(D + L + T) \dots\dots\dots (1.5)$$

UV-visible absorption spectroscopy is also used sometimes to characterize the epoxy resin or thermoset if it contains some UV active functional groups. These functional groups provide particular absorbance peaks in the UV-visible spectrum due to π - π^* and n - π^* transitions. The UV-visible spectroscopy is also used to measure the optical transparency of epoxy thermoset. The percent of transmittance of visible light by the thermoset film is measured using absorbance in the visible range.

1.4.1.3. Testing method

Different testing methods are used to determine the performance like mechanical properties, thermal stability, electrical properties, adhesive strength, flame retardancy, etc. of an epoxy thermoset. The tensile strength and lap-shear tensile adhesive strength of epoxy thermoset is mainly measured by a Universal Testing Machine (UTM) with different load cells and crosshead speeds. The tensile test is performed on rectangular film samples by using the standard test, ASTM D 882. The lap-shear adhesion test is carried out on different substrates like, metal-metal (M-M), wood-wood (W-W) and plastic-plastic (polypropylene sheets) (P-P) adherents by lap-shear test by using the standard test, ASTM D4896-01. The lap-shear tensile strength (MPa) (calculated as the maximum load for rupture per unit bonded area) is directly obtained from UTM. Thermal stability of the epoxy thermoset is measured by thermogravimetric analyzer (TGA) at nitrogen atmosphere. The curing kinetics and transition temperatures like glass transition (T_g) and crystalline melting (T_m) are measured using differential scanning calorimeter (DSC).⁷⁵ The electrical property of the epoxy thermoset is

mainly measured by LCR Hitester instrument up to a frequency of 1MHz at 25 °C. The dielectric constants are calculated by the following equation.

$$C = \epsilon_0 \epsilon_r A / d \dots\dots\dots (1.6)$$

where, C is the capacitance, ϵ_0 is the permittivity of the vacuum, ϵ_r is the permittivity or dielectric constant of the film sample, A is the area of the electrode plates and d is the distance between top and bottom plates i.e. the thickness of the used film. The flame retardancy of epoxy thermosets are generally studied by measuring their limiting oxygen index (LOI) as per the ASTM D2683-77 standard test method. LOI is defined as the minimum volume of O₂ in a mixture of O₂ and N₂ that just supports combustion of the sample. UL-94 is another flame retardant test which conducted to quantify and rank the flame retardancy of epoxy thermoset.

1.4.2. Nanomaterial and nanocomposite

Different types of nanomaterials and their epoxy nanocomposites are mainly characterized by spectroscopic, XRD and microscopic techniques.

1.4.2.1. Spectroscopic technique

UV-visible and FTIR are the main spectroscopic tools to characterize the nanomaterials and their polymer nanocomposites. UV-visible absorption spectroscopy is mainly used to characterize the metal based nanoparticles, quantum dots and their polymeric nanocomposites. Metal based nanoparticles and semiconductor quantum dots are possessed surface plasmon resonance (SPR) peaks. SPR appears at a particular UV-visible region for a specific nanoparticle due to the interaction of the surface electrons with the UV radiation.⁷⁷ This technique is also used to characterize the other nanomaterials which contain UV active functional groups that exhibit a particular peak in the spectrum due to π - π^* and n- π^* transitions.⁵⁵ Presence of different functional groups and chemical linkages of nanomaterials (particularly nanoclay, functionalized nanomaterials like functionalized CNT, GO, etc. and metal oxide nanoparticles) are confirmed by FTIR spectroscopy. Similarly, presence of Si-O, Al-O-Si and Si-O-Si stretching bands in nanoclay (MMT) is confirmed at around 1030, 525 and 450 cm⁻¹ respectively from FTIR spectrum.⁷⁸ Again, after the formation of epoxy nanocomposites, different types of physical and chemical interactions are also predicted from FTIR spectra. The stretching bands of different functional groups of a nanomaterial are shifted to higher or lower values, or the percent of transmittance values are diminished due to these interactions. Besides these two techniques few other spectroscopic techniques like

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photoluminescence (PL), Raman, NMR, etc. are also useful to characterize some special nanomaterials and their polymeric nanocomposites. PL spectroscopy is mainly used for fluorescent or photoluminescent nanomaterials like semiconductor quantum dots, carbon dots, fluorescent nanoparticles, etc. and their nanocomposites. On the other hand Raman spectroscopy is mainly used to characterize the carbon based nanomaterials like CNT, GO, RGO, carbon dot, etc. and their nanocomposites. NMR spectroscopy can also be utilized to elucidate the functionalized nanomaterials like functionalized GO, CNT, carbon dot, etc.

1.4.2.2. XRD analysis

XRD is a powerful tool for structural investigation of a nanomaterial and its polymeric nanocomposite from its orderly arrangements of the atoms or molecules through the interaction with the electromagnetic radiation. If the structure is arranged in an orderly array or a lattice, the radiation is diffracted to many specific directions or angles. Thus, the atomic and molecular structure of the nanomaterial can be identified after measuring the angles and intensities of the diffraction peaks.⁷⁵ The formation of metal and metal oxide nanoparticles are confirmed from their specific crystallographic peaks from XRD analysis.⁷⁹ Again, after the formation of epoxy nanocomposites, the level of interactions and structural attributes are also partially confirmed from XRD study. In metal or metal oxide based epoxy nanocomposites, intensity of the crystallographic peaks of the nanoparticles are diminished after the formation of nanocomposite due to the presence of different physical and chemical interactions with the epoxy matrix.⁸⁰ In case of layered nanomaterials (layered silicate, clay, etc.) beside diminution of the crystallographic peaks, the basal peaks are also shifted to lower values or completely vanished after the formation of epoxy nanocomposite due to large intercalation or exfoliation of the layers of the nanomaterials by epoxy polymeric chains. The increment of the interlayer spacing is calculated from the shifting of the peak using Bragg's equation,

$$2d \sin\theta = n\lambda \dots\dots\dots (1.7)$$

where d is the interlayer distance, θ is the diffraction angle, n is the order of diffraction and λ is the wavelength of X-ray.³¹

1.4.2.3. Microscopic technique

Various electronic microscopes like scanning electron microscope (SEM), transmission electron microscope (TEM), etc. are the most powerful tools to investigate the structural morphology of the nanomaterials and their epoxy nanocomposites.

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SEM is an electron microscope that produces surface images of a sample by scanning it with focused beam of electrons. The electrons interact with atoms in the sample which produces various signals by emitting secondary electrons that are detected by a detector. These secondary electrons provide information about surface topography and composition of the samples. Thus, the SEM micrograph is mainly used to visualize the surface morphology and dispersion pattern of different nanomaterials in the epoxy matrix.

On the other hand, TEM is an electron microscope in which a beam of electrons are transmitted through the ultrathin sample specimen. The transmitted electrons give the internal structural images from the interaction between specimen and the electrons. Thus, TEM is the most important tool to observe the actual structure and state of dispersion of the nanomaterials inside the epoxy matrix as well as to confirm the shape and size of the nanomaterials.

Other important microscopic technique like scanning probe microscopy (SPM) which is mainly used for the application and sensing of very small forces in small material volume and the measurement of in-plane and out-of plane strains with nanometer resolution. In SPM method force interactions or tunnelling current flow are utilized between a probe and a surface to construct a mapping of the geometric and material properties of the sample surface. The two most common methods are scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) that use a sharp tip to measure the tunnelling current and the tip-sample force interactions.

1.4.2.4. Testing method

Different testing methods that are used to determine the performance like mechanical properties, thermal stability, adhesive strength, etc. of an epoxy nanocomposite are same as the testing methods of an epoxy thermoset as described earlier and hence not described again. However, a few biological tests like biodegradation, antimicrobial, etc. for epoxy nanocomposites are described below, as they are not mentioned earlier.

Biodegradation test

Biodegradation test of film sample is mainly done with the help of McFarland turbidity method using different bacterial strains.¹⁷ The bacteria are inoculated in a salt medium in presence of film samples at 37 °C for long time (60-90 days). Bacterial growth in the medium is indicated by the increase in turbidity of the culture medium. The optical density (OD) or absorbance of the bacterial growth is calculated at intervals of every 7-15 days by a

spectrophotometer at wavelength of 620 nm. The weight loss (%) of degraded films is also measured at intervals of every 7-15 days. The changes of OD, weight loss, surface morphology, etc. are compared with a control film sample (without using bacteria).

Antimicrobial test

Antimicrobial test of epoxy nanocomposites is mainly done by well diffusion method and zone of inhibition as well as colony formation unit (CFU) are measured.^{17,19} In this method test microbes are seeded on the surface of the Muller-Hinton agar or potato dextrose agar on Petri dishes. The dispersed nanocomposites are placed into 6 mm diameter wells on the Petri dish. In one well, a standard antibiotic is used as a positive control. Then the zone of inhibition diameters is measured using a transparent ruler after incubation for 24 to 48 h at 37 °C.

1.5. Property

Formation of epoxy nanocomposites significantly improves many properties of pristine epoxy as well as it introduces some new set of interesting properties to the system. A few important properties of epoxy in its resinous as well as thermoset form and after the formation of nanocomposites with different types of nanomaterials are discussed below.

1.5.1. Physical

Physical properties of an epoxy resin are very important in terms of its processing and applications points of view. Due to low molecular weight, epoxy resin possessed low solution as well as melt viscosity and high solubility in most of the organic polar solvents. Again, the hyperbranched structural architecture of epoxy resin with successive branching units, offer some interesting properties in comparison to their linear analog of equivalent mass. Hyperbranched epoxy resin exhibits lower solution and melt viscosity, higher reactivity and solubility compared to the linear analog with equivalent molecular mass due to their non-entangled more compact globular like structure with higher number of end functionalities of the former.^{9,10,36,81} The solubility of the resin increases and the viscosity decreases with the increase in degree of branching (DB).^{31,82} The tree like non-entangled architecture with low hydrodynamic volume of hyperbranched epoxy leads to Newtonian rheological behavior with low viscosity.^{10,31}

1.5.2. Mechanical

Epoxy thermoset exhibits high tensile strength, tensile modulus, hardness, etc. due to its three dimensional crosslinked structure. Further the mechanical properties increases with the structural rigidity. If the epoxy thermoset contains some rigid aromatic moieties in its structure, properties like tensile strength, stiffness and hardness are improved. But, due to inherent brittleness character it possesses low toughness and elongation at break. However, the unique structural design of hyperbranched epoxy imparts adequate toughness as well as other desired mechanical properties.¹⁰ This hyperbranched architecture helps to increase the free volume (the unoccupied space) between the molecules in the three-dimensional network by the steric effect which can able to dissipate the strain and impact energies.⁸³ The non-entangled tree like hyperbranched structure with higher number of end functionalities of hyperbranched epoxy offers better compact three dimensional structure compared to the linear analog. This resulted higher tensile strength, stiffness and hardness than the linear analog. Again, over the last decade literature reported that the mechanical properties of epoxy and hyperbranched epoxy are significantly improved by the incorporation of different types of nanomaterials like clay, CNT, GO, RGO, etc.^{16,20,84-88} Incorporation of essential oil modified OMMT into the hyperbranched epoxy matrix increases tensile strength of the pristine thermoset up to 50%.²⁰ Whereas, the incorporation of carbon based nanomaterials like MWCNT or RGO into the same matrix increases the tensile strength up to 70%.^{87,88} However, the improvements of the mechanical properties are observed up to dose level of >5 wt% of the nanomaterials and in most of the cases elongation at break value decreases due to the imposed restriction in chain motion of the epoxy matrix by the nanomaterials.

1.5.3. Thermal

Three-dimensional crosslinked structure also provides high thermal stability to the epoxy thermoset and it increases with the increase of thermostable aromatic moieties, silicone skeleton, etc. in its structure. Again, the hyperbranched structure of epoxy offers more compact crosslinked structure compared to its linear analog due to its tree like architecture with large numbers of epoxy end functionalities as stated earlier. Thus, hyperbranched epoxy possesses higher thermal stability compared to linear analog with similar structural components. Further, the formation of epoxy nanocomposites with different types of nanomaterials like clay, CNT, RGO, GO, etc. increases the thermal stability of pristine thermoset up to 50 °C. These nanomaterials are acting as a thermal insulator and mass transport barrier to the volatile products generated during decomposition. The segmental

mobility of epoxy chains is also restricted after the formation of nanocomposite which decreases the T_g value and thus, thermal stability increases. Barua et al. reported that the incorporation of *Homalomena aromatica* oil modified OMMT clay into a hyperbranched epoxy increases the initial thermal degradation temperature of pristine thermoset from 255 to 305 °C.²⁰

1.5.4. Optical

The most important optical property of epoxy thermoset is its transparency. Transparency is a property that allows the transmission of visible light through the material. Most of the epoxy thermosets are highly transparent. Again, after the formation of epoxy nanocomposites with different types of nanomaterials, the transparency of the pristine thermoset is not much affected due to the low scattering of light by the well dispersed nanometer size particles as well as the amount of material is generally used very less. Further, a few nanomaterials like quantum dots and metal nanoparticles introduce some interesting optical properties including luminescence or light emitting behavior to the pristine epoxy thermoset. Zou et al. reported a transparent and luminescent epoxy nanocomposite with CdSe quantum dots.⁸⁹ Transparent and light-emitting epoxy nanocomposites containing ZnO quantum dots as encapsulating materials for solid state lighting is reported by Yang et al.⁹⁰ Thus, the transparent and light emitting properties of epoxy nanocomposites offer potential application in the domain of optoelectronics.

1.5.5. Electrical

Electrical properties of polymers and their nanocomposites are commonly associated with the insulating or conducting behavior against flow of current. Most of the polymers behave as insulating materials. Use of low dielectric epoxy thermoset is advantageous, in part, because they adhered well to different substrates including metals over the conventional dielectric materials. However, most of the conventional epoxy thermosets exceed dielectric constant 4.0 due to presence of polar hydroxyl groups and ether linkages in their structures.⁹¹ Whereas, a dielectric constant of 3.0 or less is required in most of the electrical applications as insulator.⁹¹ Thus, different special epoxies like fluorinated, silicone containing, phenol based are used for this purpose. Lin et al. synthesized a 2,6-dimethyl phenol based epoxy thermoset which exhibited dielectric constant 3.1.⁹² Dicyclopentadiene-containing poly(phenylene oxide) novolac and dicyclopentadiene containing epoxy cured thermoset which showed dielectric constant of 2.6 is reported by Hwang et al.⁹³ Novolac based epoxy is also widely

used in many electrical application as it possesses dielectric constant of 3.1.⁹¹ Again, different carbon based conducting nanomaterials are used to enhance electrical conductivity of epoxy thermoset for application in electronics, automotive and aerospace sectors.^{94,95}

1.5.6. Catalytic

Semiconductor quantum dots, carbon dot and metal or metal oxide nanoparticles like TiO₂, ZnO, Cu₂O, etc. are widely used as catalyst, especially as photocatalyst because of their tuneable emissions of light from near-infrared to visible or UV region.⁹⁶⁻⁹⁸ These materials generate electron/hole (e⁻/h⁺) pairs after excitation by the UV, visible or near infrared light. These e⁻/h⁺ pairs react with H₂O and O₂, and produce active oxygen radicals like ·OH, ·O₂⁻ which take part in the catalytic reactions. Sometimes, combination of quantum dots or carbon dot and metal oxide nanoparticles are used for achieving superior catalytic activity.⁹⁸⁻¹⁰⁰ However, the use of these bare nanoparticles causes difficulties in reuse of the catalyst as well as agglomeration generally occurs. Thus, polymer nanocomposites are largely used as heterogeneous catalysts for this purpose.¹⁰¹⁻¹⁰³ High thermo-stability, high mechanical strength and excellent chemical resistance as well as infusible and insoluble nature of epoxy thermoset can also offer it as one of the best matrices amongst other polymers.

1.5.7. Flame retardancy

The flame retardant epoxy thermosets are those which retard or inhibit heating, degradation or decomposition, ignition of flammable gases and combustion with heat generation during burning process. Halogens, phosphorus, Al₂O₃, etc. special element containing epoxy thermoset exhibited flame retardancy. Again, the formation of epoxy nanocomposites with clay, silica, CNT, carbon nanofiber, etc. increases the flame retardant behavior of pristine epoxy thermoset.¹⁰⁴ These nanomaterials are collapsed or formed non-flamable char during the burning process and thus, reduce the heat release rate. The char also prevents the fire spreading by holding the structural integrity of the thermoset.³¹

1.5.8. Gas barrier and chemical resistance

Epoxy thermosets exhibit excellent gas barrier (mainly O₂ and CO₂) property and chemical resistance due to their highly crosslinked network structure and high T_g. Further, these properties are significantly increased after the formation of epoxy nanocomposites.⁸⁴ The nanomaterials provide very high surface area to alter the diffusion path of penetrated gas molecules.³¹ Improvement in gas barrier property of epoxy nanocomposites mainly depends

on the degree of dispersion of nanomaterials into the epoxy matrix and the aspect ratio of the nanomaterials. Thus, high aspect ratio nanomaterials like silica, clay, CNT, graphene, etc. are widely used to enhance the gas barrier property.^{84,105,106} The increase in chemical resistance of epoxy nanocomposites is due to the longer diffusion length.³¹

1.5.9. Biodegradation

Generally epoxy thermosets are non biodegradable in nature due to the presence of insufficient amount of hydrolysable linkages in their structure. However, the epoxy thermosets which are derived from different hydrolysable vegetable oils and polyester backbones or modified with them, exhibit excellent biodegradability.^{107,108} The biodegradation process occurs mainly by four steps viz. water absorption, ester cleavage and formation of oligomer fragments, solubilization of oligomer fragments and ultimately removal of soluble oligomers by microorganisms.³¹ Again, incorporation of nanomaterials especially nanoclay into the epoxy matrices increases biodegradability by acting as catalyst in the biodegradation process.³¹

1.5.10. Antimicrobial

Only a few epoxy thermosets exhibit antimicrobial activity in their pristine form. s-Triazine, phosphorylcholine, etc. containing epoxy thermosets are used in antimicrobial coatings.^{109,110} However, incorporation of few metal or metal oxide nanoparticles like, Ag, Cu, CuO, TiO₂, ZnO, etc. into the epoxy matrices showed excellent antimicrobial activity.^{17,19,87,88} This is due to the fact that metal ions are released from the nanocomposites which strongly interact with the cell surface of the microorganisms. Thus, antimicrobial epoxy nanocomposites are largely used in advanced surface coatings for destructing or inhibiting microbial growth. Formation of epoxy nanocomposites provides stability to the active nanomaterials by uniform dispersion and strong interactions which help in long time utility of the material by slow releasing rate.

1.6. Applications

Epoxy thermosets and their nanocomposites are mainly used in surface coatings and paints, FRP composites, structural adhesive, optoelectronic devices, biomedical, etc. according to their properties and performance. The different applications of epoxy thermoset and its nanocomposites are discussed below.

1.6.1. Surface coating

Surface coating materials are mainly used for the protection of an object from damage by the external attacks and for decoration purpose. Epoxy resins are low viscous, highly soluble in most of the organic solvents and miscible with dyes or pigments as well as with other additives. Further, they have versatile curing systems. Epoxy thermosets also exhibit high mechanical properties, high adhesive strength, high thermal stability, excellent weather and chemical resistance. Thus, epoxy thermosets are the best choice as binder along with a flexible resin for surface coating applications. Epoxy coatings are mainly used for heavy duty service on metal substrates and decorative flooring applications such as terrazzo flooring, chip flooring and colored aggregate flooring. Further, polyester modified epoxies are used as powder coatings for washers, driers and other white goods. Fusion bonded epoxy powder coatings are widely used for corrosion protection of steel pipes and fittings used in the oil and gas industry, potable water transmission pipelines, etc. Epoxy coatings are also used as primers to improve the adhesion of automotive and marine paints, especially on metal surfaces where corrosion or rusting resistance is important. Again, silver and copper based epoxy nanocomposites are widely used in antimicrobial and antifouling surface coatings.^{17,19,111}

1.6.2. FRP composite

FRP composites are the composite systems that are made of polymer matrices reinforced with fibers. Epoxy thermosets are commonly used as matrices in FRP composites due to their high mechanical properties, high adhesive strength and excellent weather and chemical resistance. These composites are also used in the aerospace, automotive, marine, construction industries, ballistic armor, etc. Glass, carbon, Kevlar, boron, etc. fiber reinforced epoxy thermosets are extensively used as structural material in aerospace and automotive industries.¹¹²

1.6.3. Structural adhesive

Epoxy thermosets and their nanocomposites are extensively used as structural or engineering adhesive due to their high performance like high mechanical strength, thermal stability, adhesive strength and chemical resistance.¹¹³ They can also adhere any types of substrates like metal, wood, plastic, glass, stone, etc. These adhesives are used in the construction of automobiles, aircraft, bicycles, golf clubs, boats, skis, snowboards, and other applications where strong bond and high performance are required.

1.6.4. Optoelectronic

Because of their high performance including adhesive strength and electrical insulating character epoxy thermosets are employed in motors, generators, transformers, switchgear, bushings and insulators in the electronic industry. They can also protect the electrical components from short circuiting, dust and moisture. In electronic industry, they are mainly utilized in overmolding integrated circuits, transistors, hybrid circuits, printed circuit boards, etc.⁹¹ Further, the metal nanoparticles, CNT and graphene based epoxy nanocomposites are used for good electrical conducting applications.^{94,95} These nanocomposites are mainly utilized in supercapacitors, electromagnetic interference shielding, electromechanical actuators, transparent conductive coatings, various electrodes, electrostatic dissipation, etc.^{114,115}

Epoxy thermosets are also used in many optical devices including light emitting diodes (LEDs) due to their high transparency and mechanical properties. They are commonly used as encapsulating material and reflector cup in LED to protect the LED chips to damage from external factors and to transmit the light.¹¹⁶ Recently, transparent epoxy/quantum dots nanocomposites seem to be more attractive in LED application because of their interesting color emissions in exposure of UV or visible light.^{89,90}

1.6.5. Biomedical

Biocompatible and fast curable epoxy thermosets confer great attention in biomedical fields, like dental sealing, drug delivery, tissue engineering, etc. In dental sealing epoxy serves as a protective coating that effectively isolates pits and fissures to prevent caries in children and adults.¹¹⁷ Different antibiotic immobilized or antimicrobial epoxy nanocomposites are used as root canal sealers for odontological applications which provide an apical seal so that bacterial penetration into the periradicular tissues can be inhibited.^{118,119} Again, biodegradable and biocompatible flexible epoxy thermosets are used in drug delivery and tissue engineering applications as potent materials.¹²⁰ Different drug and biocide immobilized epoxy nanocomposites are largely utilized as microbial contaminant or infection resistance implantable potential materials.^{20,80,87,88}

Miscellaneous

Besides the above applications, epoxy thermosets are also sometimes used in industrial tooling and composites and in different consumer applications. They are utilized in different

industrial tooling like molds, master models, castings, fixtures, laminates, and other industrial production aids. They are also used in painting art after mixing with different pigments.¹²¹

1.7. Scopes and objectives of the present investigation

From the above discussion, therefore, it is noticed that a lot of scopes present in the field of hyperbranched epoxy and their nanocomposites. In most of the literature, conventional DGEBA is mainly utilized for the fabrication of epoxy nanocomposites. Thus, the shortcomings related to epoxy thermosets like low toughness, flexibility and elongation at break cannot be addressed properly. Again, reports on the synthesis of high performance hyperbranched epoxy are rare in literature. Therefore, development of high performance tough epoxy thermosets and their nanocomposites with different nanomaterials to obtain new set of desired properties as well applications will confer an interesting research arena in the field of material science.

Thus, the main objectives of the present investigation are made as follows.

- i) To synthesize hyperbranched epoxy resins using multifunctional moieties.
- ii) To characterize the synthesized hyperbranched epoxy using different analytical and spectroscopic techniques.
- iii) To evaluate the properties of the synthesized hyperbranched epoxy resins.
- iv) To prepare the nanocomposites of the hyperbranched resins with different nanomaterials like carbon dot, nanoclay and metal oxide decorated nanoclay.
- v) To characterize and evaluate the properties of the prepared nanocomposites using different techniques.
- vi) To optimize the performance of the prepared nanocomposites for their possible potential applications.

1.8. Plan of research

In order to implement and fulfill the objectives, the proposed work has been planned as given below.

- i) A thorough literature survey on the field of hyperbranched epoxy resins and their nanocomposites will be conducted.
- ii) The hyperbranched epoxy resins will be synthesized by polycondensation process using multifunctional moieties with the conventional reactants.
- iii) The synthesized resin will be characterized by using different analytical and spectroscopic techniques such as FTIR, NMR, TGA and DSC.

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- iv) The properties like physical, mechanical, chemical and the dielectric behavior of the hyperbranched epoxy resins will be evaluated.
- v) Hyperbranched epoxy nanocomposites will be prepared by the conventional technique as reported in literature using carbon dot, modified organophilic nanoclay and metal oxide decorated nanoclay.
- vi) The prepared nanocomposites will be characterized by FTIR, UV, XRD, TEM and SEM analyses.
- vii) The special properties like antimicrobial, optical, etc. of the hyperbranched epoxy nanocomposites will be assessed.
- viii) The performance characteristics of the nanocomposites will be investigated by determination of tensile strength, modulus, elongation at break, impact resistance, scratch hardness and adhesive strength.
- ix) The best studied nanocomposite, obtained by optimization of dose of nanomaterials and processing parameters will be utilized for its possible applications.

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