Chapter 2

Synthesis, characterization and properties of hyperbranched epoxy resin

2.1. Introduction

From Chapter 1 it is cleared that the hyperbranched polymers have a lot of potential over their linear analog for a variety of advanced applications in the respective field of material science. The distinctive structure-property relationship of hyperbranched polymers has recently instigated research for different synthetic routes of this novel class of dendritic macromolecules. Their hallmark architectural attribute is a highly branched structure with a large number of peripheral functional groups responsible for their excellent flow and processing properties.\textsuperscript{1-4} The structure of the repeating unit, the nature of their end groups, the degree of branching and the molar mass dictate their final properties. Hyperbranched polymers are attractive because of their easy one step synthetic process in comparison to the dendrimers which require multi-step laborious process. Moreover, the branched architecture of hyperbranched polymers has all the possibilities to mimic the complex macromolecules found in the nature. It is because of its highly branched architecture that offers hyperbranched polymers with different unusual properties that are lacking in their linear counterpart. A few of such unusual properties include low solution and melt viscosity, large number of terminal functional groups for tailoring, high reactivity, high interaction with other polymeric matrix owing to its high surface functionality etc. Moreover, the large number of surface functional groups of hyperbranched polymers offers for its modification to the desired functionality.

In this context, it is pertinent to mention that hyperbranched polymers with s-triazine moiety in their structure have many advantages in practical field of applications.\textsuperscript{5} These include high thermostability, flame retardancy, rigidity and good electronic properties, and so on. Moreover, s-triazine containing cyanuric chloride is relatively a low cost commercially available product with applications attested in various sectors including textiles, plastics and rubber industries.

Thus synthesis of a new hyperbranched polymer with s-triazine unit is an interesting proposition to develop polymeric materials with desirable advanced properties.

Again, epoxy resins are a class of versatile thermosets because of their high strength, low creep, very low or no shrinkage on curing, excellent resistance to corrosion, good adhesion to many substrates, and appropriate electrical properties. These attributes make them applicable in different industries as protective coatings, fibre reinforced plastics, adhesives, binder for composites etc.\textsuperscript{6-9} However, the existing epoxy resins have inherent brittleness character that inhibits their further proliferation into various advanced industrial applications including active surface coatings.\textsuperscript{10} Hence, the synthesis of a new epoxy resin or modification of existing epoxy resins to improve the various performance properties has been the subject of intense investigation throughout the world.\textsuperscript{11-13}

Thus the synthesis of hyperbranched epoxy resin (HBE) with s-triazine unit is expected to be an interesting area of research as it may result lower viscosity, higher solubility, higher thermostability, better adhesive strength and crosslinking due to presence of large numbers of functional end groups compared to its conventional linear analog. Although there are enough reports on synthetic approaches of the conventional epoxy resins, both from petroleum and renewable resources,\textsuperscript{13-16} but the report on hyperbranched epoxy is really rare.\textsuperscript{17,18} Therefore, in the present investigation an interfacial polycondensation will be used to prepare s-triazine based hyperbranched polyether polyol as a core moiety to be utilized for the synthesis of hyperbranched epoxy. The interfacial polycondensation will be carried out by reacting cyanuric chloride with 1,4-butane diol in presence of a phase transfer catalyst (PTC). The synthesis of s-triazine based hyperbranched epoxy resin will be carried out by a simple polycondensation technique using the hyperbranched polyether polyol as the core unit. The polycondensation reaction will be carried out by reacting hyperbranched core moiety, bisphenol A with epichlorohydrin in presence of a base. The synthesized resin would be characterized with various analytical and spectroscopic analyses such as measurements of solubility, solution viscosity, hydroxyl value, epoxy equivalent, and studies of FTIR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, etc. Thus this chapter deals with the synthesis, characterization and properties of hyperbranched epoxy resin.
2.2. Experimental

2.2.1. Materials

Cyanuric chloride (CYC, Fig. 2.1) is an important member of triazine family due to its chemo selective nature; here it is used as a B₃ monomer. CYC was purchased from Merck, Germany. It has m.p. 144-147 ºC, purity 99% and molecular weight (Mₙ) 184.41 g/mol. It was used after recrystallization from chloroform. Cyanuric chloride is relatively cheap and it is mainly used as an intermediate for manufacturing agrochemical, dyestuffs, optical brighteners, tanning agents, softening agents, pharmaceutical building block for plastics and additives.

![Fig. 2.1: Structure of 1,3,5-trichloro triazine (cyanuric chloride)](image)

1,4-butanediol (Fig. 2.2) was obtained from Merck, India. It is a colorless viscous liquid with a molar mass of 90.12 g/mol and density 1.01 g/cm³. The boiling point of the liquid is 235 ºC. It is derived from butane by replacement of two hydrogens with alcohol groups at each end of the chain. It is one of four stable isomers of butane diol. 1,4-butanediol is industrially used as a solvent and in the manufacture of some types of plastics, elastic fibers, polyethers and polyurethanes. Here it is used as a reactive A₂ monomer.

![Fig. 2.2: Structure of 1,4-butane diol](image)

4,4’-Isopropylidene diphenol, bisphenol A (BPA, Fig. 2.3) was obtained from S.D fine chemicals, India. It was recrystallized from toluene before used. The melting point (m.p.) of the purified compound is 157 ºC and molecular weight is (Mₙ) 228.29 g/mol.
BPA is mainly used in the synthesis of epoxy resins and polycarbonates. The polymers made from BPA are used in packaging applications for many foods and drinks items. While the resins are commonly used as lacquers to coat metal products such as food ‘can’, bottle tops and water supply. Some polymers used in dental treatment contain BPA. Here it is used as an aromatic diol (A$_2$ monomer).

Epichlorohydrin (ECH, Fig. 2.4) was obtained from Merck, India. It has a molecular weight of 92.52 g/mol with density of 1.18 g/cm$^3$ and a boiling point of 115 ºC. Epichlorohydrin is mainly used to prepare diglycidyl ether of bisphenol A, a building block in the manufacture of epoxy resins. It is also a precursor to monomer for other resins and polymers.

Epichlorohydrin is also used in paper reinforcement (used for instance in the food industry to manufacture tea bags, coffee filters, and sausage/salami casings) and water purification. Here it is used as a reactant for the synthesis of hyperbranched epoxy.

Cetyltrimethylammonium bromide (CTAB, Fig. 2.5) was obtained from Merck, India. It is a white powdery cationic surfactant and one of the components of the topical antiseptic so called cetrimide. It has a molar mass of 364.45 g/mol with m. p. 237-243 ºC. The cetrimonium cation is an effective antiseptic agent against bacteria and fungi. Its uses include providing a buffer solution for the extraction of DNA. It has been widely used in synthesis of nanoparticles (e.g., spheres, rods, bipyramids). It is also widely used in hair conditioning products. Here CTAB is used here as a phase transfer catalyst (PTC) in the interfacial polycondensation reaction.
Dichloromethane (DCM) was obtained from Merck, India. It is a colorless, volatile liquid with a moderately sweet aroma is widely used as a low boiling solvent. It has a molar mass of 84.94 g/mol, density 1.33 g/cm³ and boiling point of 39.6 ºC. It is miscible with many of the organic solvents though immiscible with water. DCM's volatility and ability to dissolve a wide range of organic compounds makes it a useful solvent for many chemical processes. It is widely used as a paint stripper and a degreaser. In the food industry, it has been used to decaffeinate coffee and tea as well as to prepare extracts of hops and other flavorings. Its volatility has led to its use as an aerosol spray propellant and as a blowing agent for polyurethane foams. It is also used in the garment printing industry for removal of heat-sealed garment transfers. Here it is used as a solvent.

Tetrahydrofuran (THF) was obtained from Merck, India. It has a b.p. of 65-67 ºC, density 0.886-0.88 g/cm³; minimum purity 99.5% and maximum limit of impurities contain Cu 0.0001%, Fe 0.0001%, Pb 0.0001% and non-volatiles substances 0.002%. One of the main applications of THF is as an industrial solvent for poly(vinyl chloride, PVC) and in varnishes. It is an aprotic solvent with a dielectric constant of 7.6. It is a moderately polar solvent and can dissolve a wide range of non-polar and polar compounds. THF is water miscible, and can form solid clathrate hydrate structures with water at low temperature. Here it is used as a solvent.

Toluene was obtained from Merck, India. The toluene has purity of 99.0% with 0.04% water, 0.003% non-volatile matter and 0.0005% sulfur compounds (CS₂) as impurities. The molecular weight (Mw) is 92.14 g/mol, density is 0.860-0.866 g/cm³ at 25 ºC and b.p. is 110-111 ºC. It was purified by distillation and used as a solvent here.

Methanol (MeOH) was obtained from Merck, India. It is the simplest alcohol, and is a light, volatile, colorless, flammable liquid with a distinctive odour very similar to ethanol. It has a molar mass of 32.04 g/mol, density 0.791 g/cm³ and b.p. 65 ºC. At room temperature, it is a polar liquid, and is used as an antifreeze, solvent, fuel, and as a denaturant for ethanol. It is also used for producing biodiesel via transesterification reaction. Here it is used as a solvent and to prepare sodium methoxide.

Pyridine is a basic heterocyclic organic compound which was obtained from Merck, India. It is structurally related to benzene, with one C-H group replaced by a nitrogen atom. It has a molar mass of 79.1 g/mol, density 0.981 g/cm³ and b.p. 115.2 ºC. The pyridine ring occurs in many important compounds, including azines and the vitamins niacin and
pyridoxal. It is a colorless, highly flammable, weakly alkaline, water-soluble liquid with a distinctive, unpleasant fish-like odour. Pyridine is used as a precursor to agrochemicals and pharmaceuticals and is also an important solvent and reagent. Pyridine is miscible with water and virtually all organic solvents. It is a weak basic compound. Most chemical properties of pyridine are typical of a heteroaromatic compound. In organic reactions, pyridine behaves both as a tertiary amine, undergoing protonation, alkylation, acylation, and N-oxidation at the nitrogen atom, and as an aromatic compound, undergoing nucleophilic substitutions. Here it is used as a base catalyst for acetylation reaction.

Acetic anhydride is a chemical compound with the formula (CH₃CO)₂O was obtained from Allied Chemicals Corporation, India. Commonly abbreviated Ac₂O, it is the simplest isolated acid anhydride and is a widely used reagent in organic synthesis. It is a colorless liquid that smells strongly of acetic acid, formed by its reaction with the moisture in the air. It has a molar mass of 102.09 g/mol, density 1.08 g/cm³ and b.p. of 139.8 ºC. Acetic anhydride is a versatile reagent for acetylations of organic substrates. In these conversions, acetic anhydride is viewed as a source of CH₃CO⁺. Ac₂O is mainly used for acetylations leading to commercially significant materials. Alcohols and amines are readily acetylated. The largest application of Ac₂O is for the conversion of cellulose to cellulose acetate, which is a component of photographic film and other coated materials. Similarly it is used in the production of aspirin (acetylsalicylic acid), which is prepared by the acetylation of salicylic acid. It is also used as a wood preservative via autoclave impregnation to make a long lasting timber. Here it is used as an acetylating agent.

Sodium sulphate (anhydrous) was obtained from Merck, India. It has a molecular weight of 142.04 g/mol and density of 2.664 g/cm³. It has a minimum assay of 99.5% and other impurities present are free acid (H₂SO₄) 0.005%, free alkali (NaOH) 0.004%, chloride 0.001%, phosphate 0.002%, ammonium 0.0005%, arsenic 0.00004%, calcium 0.01%, copper 0.0005%, Fe 0.0005%, Pb0.01%, Mg 0.01% and K 0.01%. Sodium sulphate is a very cheap compound. The largest use is as filler in powdered home laundry detergents. The glass industry provides another significant application for sodium sulphate, as the second largest application in Europe. Sodium sulphate is used as a fining agent, to help remove small air bubbles from molten glass. It fluxes the glass, and prevents scum formation of the glass melt during refining. In the laboratory, anhydrous sodium sulphate is widely used as an inert drying agent, for removing traces of water from organic
solutions. It is more efficient, but slower-acting drying agent, than the similar agent magnesium sulphate. It is only effective below about 30 °C, but it can be used with a variety of compounds since it is chemically fairly inert. Here it is used as a desiccant.

Sodium chloride crystals was obtained from Merck, India, it has a molecular weight of 58.44 g/mol. It has a minimum assay of 99.5% with a density of 2.16 g/cm³, b.p. of 1413 °C and m.p. of 801 °C. It has maximum impurities of bromide 0.005%, iodide 0.001%, sulphate 0.002% phosphate 0.0005%, Pb 0.0005%, iron 0.0001%, Mg 0.001% and Ca 0.002%. Sodium chloride is sometimes used as a cheap and safe desiccant because of its hygroscopic properties, making salting an effective method of food preservation historically; the salt draws water out of bacteria through osmotic pressure, keeping it from reproducing, a major source of food spoilage. The industrial uses of salt include, in descending order of quantity consumed, various applications, oil and gas exploration, textiles and dyeing, pulp and paper, metal processing, tanning and leather treatment, and rubber manufacture. Here it is used as a salt.

Sodium hydroxide (NaOH) was obtained from Merck, Mumbai and was used as received. It has molecular weight (Mₚ) 40.0 g/mol and purity > 97%. Here it is used as a catalyst for polycondensation reaction.

Molecular sieve 4A × 1.5 mm was procured from Merck, Mumbai. Its equilibrium capacity for water at 30 °C, 75% relative air humidity is ≥20% and bulk density is 650-700 g/cm³. It is used as a desiccant without any further purification.

Poly(amide amine) hardener (HY 840, Ciba-Geigy, India) was obtained from Hindustan Ciba Geigy Ltd. and used as received. The specifications of the hardener are given in Table 2.1. Here it is used as a curing agent for epoxy resin.

2.2.2. Instruments and methods
FTIR spectra of the polymers were recorded in a FTIR spectrophotometer (Impact-410, Nicolet, USA) using KBr pellet. ¹H NMR and ¹³C NMR spectra were recorded in a Varian 400 MHz NMR spectrometer (Shimadzu, Japan) using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard.
Table 2.1: Technical specification of the hardener

<table>
<thead>
<tr>
<th>Name</th>
<th>Hardener HY 840 (Ciba Geigy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 25 °C (mPas)</td>
<td>10000-25000</td>
</tr>
<tr>
<td>Amine value (eq/kg)</td>
<td>6.6-7.5</td>
</tr>
<tr>
<td>Density at 25 °C (g/cm³)</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The different physical properties such as solubility, solution viscosity, hydroxyl value, epoxy equivalent, drying time etc. of the hyperbranched epoxy resin were determined by following the standard methods.\textsuperscript{19,20} The solubility of the polymers were checked by dissolving a pinch of the polymer sample in about 1 mL of solvent at room temperature and by observing the solubility for consecutive 5 days under the same condition. The solution viscosity of the polymers was measured with 0.5 % (w/v) of polymer solution using Ubbelohde suspended level viscometer at (31 ± 0.5) °C. The hydroxyl value of the polymers was determined by acetylation reaction in presence of pyridine and titrating the unreacted acid with standard aqueous NaOH solution. The epoxy equivalent of the hyperbranched epoxy resin was evaluated by the standard pyridinium chloride method and titrating the remaining HCL with standard alcoholic NaOH solution.

The coating performance of the cured films was evaluated by the determination of different mechanical properties. The mechanical properties such as tensile strength was measured with the help of Universal Testing Machine, UTM (WDW-10, 020891, People’s Republic of China) by using 10 kN load cell at 40 mm/min jaw separation speed. Impact resistance was determined by falling weight impact tester (S.C. Dey Co., Kolkata) as per the standard falling weight method (ASTM D 1037). In this test a weight of 850 g was allowed to fall on the film coated on a mild steel plate from minimum to maximum falling heights. The maximum height was taken as the impact resistance up to which the film was not damaged.

Gloss characteristic of the cured films coated on mild steel plates was evaluated\textsuperscript{19} using a gloss meter (Sheen Instrument Ltd., Model No. 160, UK) at an angle of incidence of 60°. Scratch hardness (ASTM D5178/1991) of the cured films was measured by using scratch tester, (Sheen Instrument Ltd., Model No. 705/1, UK) with stylus accessory and a travel speed of 6 mm/s. The chemical resistance test was performed in a number of different chemical media as per the ASTM D 543-67 standard procedure\textsuperscript{20} by taking weighted
amount of cured epoxy resin films in 250 mL beakers containing 150 mL of the individual chemical medium for specified period of time. The chemical resistance was determined by making observations of visual changes and changes in the weights of the films after the specified period of time.

The solvent resistance test of the cured hyperbranched epoxy resin was determined by evaluating the percent gel fraction as per the standard method. Swelling test was done by immersing weighted amount of the cured films in THF. After 48 h, the weight of the swelled films was taken. Swelling value (%) was determined by differences in weight between the dried film and the swelled film as follows.

\[
\text{Swelling} \text{ (%) } = \left( \frac{W_s - W_d}{W_d} \right) \times 100
\]  

(2.1)

Where, \( W_s \) and \( W_d \) are the weight of the swelled film and the dried film respectively.

The adhesive strength of the cured hyperbranched epoxy resin was measured by lap-shear adhesion test as per the standard ASTM D2339-98 method using surface treated plywood as the substrate. The overlapping zone was 1 × 1 in\(^2\) for each case, the thickness of the adhesive layer within the overlapping area was ca. 0.03-0.05 mm. The plywood substrates were first treated before applying the adhesive layer. Plywood substrates were first washed with acetone and then toluene to remove dirt, grease etc. and subsequently polished with sand paper of grit number 60 (250 mm) followed by washing with toluene (ASTM 906). The cross-cut adhesion test was performed by the standard ASTM D3359-97 method, which was done on coated aluminium strips (150 mm × 50 mm × 0.68 mm) after treatment with chromic-sulphuric acid followed by washing with distilled water.\(^{21}\)

2.2.3. Synthesis of hyperbranched epoxy

Synthesis of hyperbranched polyether polyol

In a round bottom three neck flask equipped with a condenser, a dropping funnel and nitrogen inlet, the required amount of sodium hydroxide (4.95 g, 0.126 mol) and 1,4-butane diol (5.4 g, 0.06 mol) were introduced and 80 mL of doubled distilled water was added to it under stirring condition. The phase transfer catalyst (0.0036 mol, 6 mol % with respect to diol monomer) solution in distilled water (70 mL) was added into the reaction
mixture. Then a solution of cyanuric chloride (7.38 g, 0.04 mol) in dichloromethane (100 mL) was added to the solution at 1-2 °C under vigorous stirring condition. The reaction was continued for about 2 h and then the temperature was raised to 14-15 °C. After 2 h of stirring, the temperature was further raised to 25-26 °C. The reaction was continued for 5 h and then excess diol (5.4 g, 0.06 mol) was added to ensure complete removal of chlorine of cyanuric chloride. The stirring was continued at this condition for another 2 h. Finally, the organic phase was separated from the aqueous phase and the solvent was removed at room temperature under vacuum. The product was then washed thoroughly with distilled water followed by methanol. Further, it was purified by dissolution in acetone and then re-precipitated in water-methanol mixture with little sodium chloride salt. The yield of the sticky mass was about 65%. The purified product was characterized with the help of analytical and spectroscopic techniques such as solubility, solution viscosity, hydroxyl value etc. and FTIR, $^1$H NMR, $^{13}$C NMR etc. respectively.

Synthesis of hyperbranched epoxy

Briefly, hyperbranched polyether polyl (HBP, 20 wt% of total mass of diol compound) and bisphenol A were taken in a three neck round-bottom flask fitted with a condenser and thermometer. Calculated amount of epichlorohydrin (1:1.5 mol ratio of hydroxyl group to epichlorohydrin) was added into it at room temperature under stirring condition. On complete dissolution of HBP and bisphenol A, the system was placed on a preheated oil bath at (54 ± 1) °C. To this reaction mixture 5N aqueous solution of sodium hydroxide (equivalent to hydroxyl groups) was added drop wise for 1 h under stirring condition at constant temperature. After complete addition of sodium hydroxide solution, the reaction mixture was continued for 3 h under aforementioned conditions. The product formed was then separated from the aqueous phase and washed with 15% brine solution followed by washing with distilled water for 3-4 times. The washed product was dried under reduced pressure at 40 °C. The final product obtained was a sticky transparent mass with 59% yield. The purified product was characterized with the help of analytical and spectroscopic techniques such as measurements of solubility, solution viscosity, hydroxyl value, epoxy equivalent etc. and FTIR, $^1$H NMR, $^{13}$C NMR etc. respectively.

The reaction parameters of the polycondensation reaction were optimized with respect to concentration of base, temperature and reaction time by changing only one of
these parameters while all others were kept constant. The yield, solution viscosity and epoxy equivalent were measured in each case to examine the optimum condition for the reaction.

2.2.4. Curing of the resin
Poly(amido amine) was used as the curing agent to harden the hyperbranched epoxy resin. An amount of 50 phr (parts per hundred of resin) of the curing agent was mixed with hyperbranched epoxy resin along with a little amount of THF (to facilitate mixing) by mechanical stirring for 20 min. Then the mixture was cast on glass slides. The films were then degassed under vacuum at room temperature to ensure complete removal of the volatiles. After complete removal of the solvent and volatiles the cast films were cured at 120 °C for a specified period of time followed by post curing at 150 °C for 30 min in a muffle furnace to determine the touch free time (minimum time when no impression appears on touching the film) and hard dry time of the film. Similarly, the films were also cast on mild steel plates (150 mm × 50 mm × 1.6 mm), tin plates (150 mm × 50 mm × 0.4 mm) and glass plates (75 mm × 25 mm × 1.75 mm) for impact resistance, gloss and chemical resistance tests, respectively. The average dry thickness of the films was 40-45 µm as measured by a pen tester (Sheen instrument Ltd., UK) in all the cases.

2.3. Results and Discussion
2.3.1. Synthesis of hyperbranched polyether polyol
In earlier reports, a number of s-triazine based hyperbranched aromatic polyethers and polyamines have been synthesized by nucleophilic displacement reaction of chlorine atoms of cyanuric chloride by the phenoxide or primary amine groups of aromatic diols or diamines. However, the resulting polymers were found to be brittle and of low molecular weight. So in the present work, an s-triazine based polyether was interfacially synthesized by using a flexible aliphatic diol, 1,4-butane diol.

Also, it is well known that the interfacial polycondensation of chloro-s-triazine undergoes substitution reaction under mild conditions. Thus, the polymerization of cyanuric chloride with 1,4-butane diol was carried out by interfacial polycondensation reaction using CTAB as the phase transfer catalyst. A probable pathway of the
polymerization reaction in this case is given in Scheme 2.1. The phase transfer catalyst, and the dianion of 1,4-butane diol form a diammonium salt (A), which passes through the interface boundary between the aqueous NaOH phase and the CH₂Cl₂ organic phase. Cyanuric chloride reacts with ‘A’ in the organic phase (Scheme 2.1). Probably, the phase transfer catalyst is freed after reaction and returns back to the aqueous phase to form new salt with the anion of 1,4-butane diol. Thus, the catalyst migrates back and forth across the interface and keeps the necessary concentration of reactants in each phase. So, only a little amount of catalyst is necessary for a successful reaction. Also, as the removal of catalyst from the polymeric product is difficult, the use of an excess of the phase transfer catalyst is undesirable.

Using the interfacial polymerisation reaction, s-triazine based hyperbranched polyether was successfully synthesized by A₂ + B₃ approach from 1,4-butane diol (A₂) and cyanuric chloride (B₃) by nucleophilic displacement polymerization reaction as shown in Scheme 2.1. However, a soluble product without gel formation can only be obtained under highly restricted conditions in an A₂ + B₃ approach, by carrying out the reaction in three stages with varying the reaction temperature. The first chlorine atom in cyanuric chloride has the highest reactivity followed by the second one and the third has the lowest reactivity due to the passivation effect of substituents. This was reported earlier for the nucleophilic substitution of chlorine atoms in 2,4,6-trichloro-s-triazine by different amine compounds.²⁷ The substitution reaction of cyanuric chloride and 1,4-butane diol is, therefore, highly selective with respect to temperature. The first chlorine atom was substituted at 1-2 °C, the second at 14-15 °C leading to mostly linear products, and the third chlorine was replaced at 25-26 °C by a butane diol substituent in the polymerization reaction leading finally to branching. To ensure the complete replacement of chlorine atoms of cyanuric chloride the excess amount of diol was used at the end of the reaction and the unreacted diol was removed during purification process. This step-wise condensation reaction avoids the gel formation in the synthesized hyperbranched polymer, as no gel product was observed under the used reaction conditions of this polymerization process, as confirmed by the solubility test. The variation of the reaction conditions indicate (Table 2.2) that BDMHDAC is the best catalyst at 2:3 molar ratio of cyanuric chloride to 1,4-butane diol in dichloromethane as the organic solvent for a reaction time of 2 h for first step, 2 h for second step, 5 h for the last step, and 2 h extra with excess diol. The other reaction
conditions resulted in lower yields and lower solution viscosity of the resulting polymers (Table 2.2). A shorter reaction time especially in the last step yielded a low viscosity product in low yield probably due to incomplete reaction. It has also been observed that when the temperature of the reaction was higher than the optimum at any stage, or when a two-stage or a single-stage reaction was carried out, low yields and gel products were obtained. This is due to high reactivity of the chlorine atoms of triazine unit toward the aliphatic hydroxyl functional groups of butanediol. Further, high concentration of the reactants leads to fast increase of viscosity of the reaction medium and again, to lower yield of polymer product due to limited diffusion of the monomers to the interphase.

Scheme 2.1: Synthesis of hyperbranched polyether polyol
2.3.2. Synthesis of hyperbranched epoxy resin

The synthesis of hyperbranched epoxy resin in the present work was carried out by a simple polycondensation technique under mild reaction conditions. However, there are reports on end group modification of hyperbranched polymers,\textsuperscript{28-30} proton transfer polymerization,\textsuperscript{17,18} etc. for synthesis of epoxy resin by using complex reaction scheme, toxic organic solvents, high energy and time consuming processes. So, keeping these issues in mind, here a simple, cost-effective and efficient technique has been utilized to synthesize the hyperbranched epoxy resin.

Table 2.2: Reaction conditions and corresponding yield, hydroxyl value and viscosity of hyperbranched polyethers synthesized by interfacial polycondensation technique

<table>
<thead>
<tr>
<th>Phase transfer catalyst</th>
<th>Organic solvent</th>
<th>Mole ratio (B\textsubscript{3}:A\textsubscript{2})</th>
<th>Temperature (±1, °C)</th>
<th>Time (h)</th>
<th>Hydroxyl number\textsuperscript{a} (mg of KOH/g)</th>
<th>% yield</th>
<th>η\textsubscript{inh} (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDMHDAC</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>2:3</td>
<td>1, 14, 25</td>
<td>2, 2, 5, 2</td>
<td>450</td>
<td>65</td>
<td>0.30</td>
</tr>
<tr>
<td>CTAB</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>2:3</td>
<td>1, 14, 25</td>
<td>2, 2, 5, 2</td>
<td>370</td>
<td>43</td>
<td>0.17</td>
</tr>
<tr>
<td>CPB</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>2:3</td>
<td>1, 14, 25</td>
<td>2, 2, 5, 2</td>
<td>290</td>
<td>32</td>
<td>0.07</td>
</tr>
<tr>
<td>TBAB</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>2:3</td>
<td>1, 14, 25</td>
<td>2, 2, 5, 2</td>
<td>380</td>
<td>23</td>
<td>0.18</td>
</tr>
<tr>
<td>CTAB</td>
<td>CHCl\textsubscript{3}</td>
<td>2:3</td>
<td>1, 14, 25</td>
<td>2, 2, 5, 2</td>
<td>280</td>
<td>21</td>
<td>0.06</td>
</tr>
<tr>
<td>CTAB</td>
<td>Toluene</td>
<td>2:3</td>
<td>1, 14, 25</td>
<td>2, 2, 5, 2</td>
<td>290</td>
<td>18</td>
<td>0.04</td>
</tr>
<tr>
<td>CTAB\textsuperscript{b}</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>2:3</td>
<td>1, 14, 25</td>
<td>2, 2, 5, 2</td>
<td>380</td>
<td>35</td>
<td>0.09</td>
</tr>
<tr>
<td>CTAB</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>1:1</td>
<td>1, 14, 25</td>
<td>2, 2, 5, 2</td>
<td>350</td>
<td>24</td>
<td>0.08</td>
</tr>
<tr>
<td>CTAB</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>2:3</td>
<td>25 (one step)</td>
<td>11</td>
<td>340</td>
<td>21</td>
<td>0.10</td>
</tr>
<tr>
<td>CTAB</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>2:3</td>
<td>1, 25, 40</td>
<td>2, 2, 5, 2</td>
<td>363</td>
<td>35</td>
<td>0.11</td>
</tr>
</tbody>
</table>

\textsuperscript{a}hydroxyl number is expressed as ‘mg of KOH/g’, \textsuperscript{b}the diol is polyethyleneglycol

The hyperbranched epoxy resin in the present work was synthesized by adopting a low temperature bulk polycondensation technique. In this process hyperbranched polyol, bisphenol A and epichlorohydrin formed a homogeneous single phase system in the reaction medium. In this polycondensation reaction, initially epichlorohydrin reacts with the hydroxyl group of bisphenol A, as the acidity of the
aromatic hydroxyl is higher than the aliphatic one. However, after complete consumption of bisphenol A, the epichlorohydrin as well as the diglycidyl ether epoxy reacts with some of the hydroxyl groups of hyperbranched polyol. These reactions result the desired hyperbranched epoxy resin as shown in **Scheme 2.2**.

![Scheme 2.2: Synthesis of hyperbranched epoxy resin](image)

The variation of the reaction conditions indicated that the optimum reaction conditions as 5N aqueous base, temperature of (54 ± 1) °C and duration of 3 h. The increase or decrease of these parameters resulted in lower yield, viscosity and higher epoxy equivalent value of the resulting epoxy resin. A longer reaction time than 3h was found not to increase the yield as well as the viscosity. It has also been observed that at higher temperature than (54 ± 1) °C of the reaction and at higher concentration of the base
than 5N resulted yellow coloration of the product. This may be due to the harsh reaction condition which facilitates the other side reactions. The percent yield is almost comparable under the reaction conditions from 5N to 15N of NaOH. The low viscosity at 15N NaOH may be due to the unfavourable reactions conditions which prevent the formation of high molecular weight as in other two cases. The variation of yield and viscosity can be explained in the same way for the other cases. In this case the yield is the highest for 5h of reaction time, which is the best condition for the polymerization to obtain the low viscosity. This also helps in processing of the resin. The various reaction conditions for the synthesis of hyperbranched epoxy resin is shown in the Table 2.3. The whole process of synthesis of hyperbranched epoxy resin is shown in the flow diagram (Scheme 2.3).

**Table 2.3:** Reaction conditions and corresponding yield, epoxy equivalent and viscosity of hyperbranched epoxy resin synthesized by polycondensation and interfacial technique

<table>
<thead>
<tr>
<th>Conc. of NaOH (N)</th>
<th>Temperature (°C)</th>
<th>Reaction time (h)</th>
<th>% yield</th>
<th>Inherent viscosity (dl/g)</th>
<th>Epoxy equivalent (g/eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>65 ± 1</td>
<td>3</td>
<td>57</td>
<td>0.025</td>
<td>311</td>
</tr>
<tr>
<td>5</td>
<td>65 ± 1</td>
<td>3</td>
<td>67</td>
<td>0.037</td>
<td>263</td>
</tr>
<tr>
<td>10</td>
<td>65 ± 1</td>
<td>3</td>
<td>65</td>
<td>0.092</td>
<td>287</td>
</tr>
<tr>
<td>15</td>
<td>65 ± 1</td>
<td>3</td>
<td>66</td>
<td>0.04</td>
<td>281</td>
</tr>
<tr>
<td>5</td>
<td>54 ± 1</td>
<td>3</td>
<td>59</td>
<td>0.07</td>
<td>250</td>
</tr>
<tr>
<td>5</td>
<td>54 ± 1</td>
<td>5</td>
<td>67</td>
<td>0.03</td>
<td>257</td>
</tr>
<tr>
<td>5</td>
<td>54 ± 1</td>
<td>10</td>
<td>63</td>
<td>0.05</td>
<td>270</td>
</tr>
<tr>
<td>5</td>
<td>85 ± 1</td>
<td>3</td>
<td>61</td>
<td>0.053</td>
<td>268</td>
</tr>
<tr>
<td>5</td>
<td>110 ± 1</td>
<td>3</td>
<td>61</td>
<td>0.04</td>
<td>385</td>
</tr>
<tr>
<td>0.001*</td>
<td>25 ± 2</td>
<td>12</td>
<td>&lt;30</td>
<td>0.01</td>
<td>800</td>
</tr>
</tbody>
</table>

* the result obtained from interfacial technique
2.3.3. Characterization of the hyperbranched polymers

2.3.3.1. Physical properties

The physical properties like solubility, solution viscosity, hydroxyl value, epoxy equivalent etc. of the hyperbranched polymers are given in Table 2.4. Both the hyperbranched polymers appear to be colourless, odourless and sticky in nature. From solubility studies it has been found that both the hyperbranched polymers are soluble in most of the common organic solvents like THF, dichloromethane, 1,4-dioxan, chloroform, acetone, DMAC, DMF, DMSO etc., but insoluble in solvents like hydrocarbon solvents, water, methanol, etc. This may be due to the presence of large number of polar hydroxyl and epoxy groups, globular structure of the hyperbranched polymers, ether linkages and flexible aliphatic moieties in the polymer structures.

![Flow diagram](image)

**Scheme 2.3:** Flow diagram of the complete synthetic process of hyperbranched epoxy resin

The low viscosity of the polymers is due to the compact globular non-entangled structure of the hyperbranched polymers with large numbers of end functional groups. The presence of oxirane ring as indicated by epoxy equivalent value of the resin confirmed the formation of hyperbranched epoxy resin. The observed hydroxyl value of the hyperbranched polyether polyl is due to the large number of peripheral –OH groups present in the structure. The hydroxyl value of the hyperbranched epoxy resin is due to the formation of secondary –OH groups on chain extension of the resin as the reaction progress and the presence of unreacted hydroxyl groups in the hyperbranched core unit. These results indicate that all the hydroxyl groups of the core unit are not utilized for the reaction with epichlorohydrin.
**Table 2.4:** Physical properties of the hyperbranched polymers

<table>
<thead>
<tr>
<th>Property</th>
<th>Hyperbranched polyether polyol</th>
<th>Hyperbranched epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Colorless</td>
<td>Colorless</td>
</tr>
<tr>
<td>Inherent viscosity (dl/g)</td>
<td>0.3</td>
<td>0.07</td>
</tr>
<tr>
<td>Hydroxyl value (mg KOH/g)</td>
<td>450</td>
<td>136</td>
</tr>
<tr>
<td>Epoxy Equivalent (g/eq epoxy group)</td>
<td>-</td>
<td>250</td>
</tr>
<tr>
<td>( T_g ) (°C)</td>
<td>-11</td>
<td>5</td>
</tr>
<tr>
<td>( M_W ) (g/mol)</td>
<td>35,500</td>
<td>-</td>
</tr>
<tr>
<td>Touch free time (min)</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Hard dry time (min)</td>
<td>-</td>
<td>30</td>
</tr>
</tbody>
</table>

### 2.3.3.2. FTIR Studies

All the characterizations were performed using the optimum condition based polymer samples. The FTIR spectra of the hyperbranched polyether polyol (Fig. 2.6) showed the vibration of an ether linkage at 1215 cm\(^{-1}\), which supports the formation of ether bonds in the polymer. A broad band at 3275-3395 cm\(^{-1}\) indicates the presence of terminal -OH bonds. The bands at 1557 cm\(^{-1}\) and 1341 cm\(^{-1}\) are due to presence of C-N bond in the triazine ring. The band for C=N bond of the triazine moiety appears at 1418 cm\(^{-1}\) in the IR spectrum of the polymer.\(^{31}\) The absence of aromatic C-Cl band at 735-750 cm\(^{-1}\) indicates that the displacement reaction was completed.\(^{32}\) Absence of chlorine was further confirmed by quantitative estimation of chlorine by Schöniger oxygen combustion method and silver nitrate qualitative test. The bands at 2852 cm\(^{-1}\) and 2922 cm\(^{-1}\) are due to aliphatic C-H stretching of the butane diol moiety.

FTIR spectrum of the synthesized hyperbranched epoxy resin (Fig. 2.6) indicates the presence of -OH stretching absorption band at around 3400 cm\(^{-1}\) and bands at 2950-2850 cm\(^{-1}\) appeared for the aliphatic -CH stretching vibrations. An absorption band at 918 cm\(^{-1}\) is due to the bending vibration of epoxy group which indicates the occurrence of the reaction and formation of epoxy group.\(^{33}\) The bands at 1507 cm\(^{-1}\) is due to the stretching frequency of phenyl group, and the bands at 1565 cm\(^{-1}\), 1346 cm\(^{-1}\) and 750 cm\(^{-1}\) are due to the triazine ring. The band for C=N bond of the triazine moiety appeared at 1422 cm\(^{-1}\) in the IR spectrum of the resin. The bands at 1241 cm\(^{-1}\) and 831 cm\(^{-1}\)
appeared for stretching vibration of aromatic ether and out of plane –CH bending vibration of benzene ring respectively.

![FTIR spectra](image)

**Fig. 2.6:** FTIR spectra of (a) hyperbranched polyether polyol and (b) hyperbranched epoxy

Thus, FTIR spectra of both the hyperbranched polymers confirmed the occurrence of successful reaction to form the polymers.

### 2.3.3.3. \(^1\)H NMR and \(^{13}\)C NMR studies

The structure of the hyperbranched polymers was further supported by NMR studies. The \(^1\)H NMR and \(^{13}\)C NMR spectra of both the hyperbranched polymers showed expected peaks for the different types of protons and carbons respectively in the polymer structure (Figs. 2.7-2.10). Six different peaks appear for the aliphatic -CH\(_2\) protons of butane diol present in the polymer, which confirmed the presence of both side (symmetric) and one side (unsymmetric) substituted diol (Fig. 2.7). The peaks at \(\delta = 4.4\text{-}4.5\) ppm and \(\delta = 1.7\text{-}2.1\) ppm are due to (-O-CH\(_2\)-) protons and (-CH\(_2\)-CH\(_2\)-) protons of symmetrically substituted butane diol (butane diol moiety with both hydroxyl groups reacted with triazine unit) respectively. The peaks at \(\delta = 4.3\text{-}4.5\) ppm, \(\delta = 3.6\text{-}3.7\) ppm, and \(\delta = 1.2\text{-}1.6\) ppm are due to (HO-C*H\(_2\)-) and (HO-CH\(_2\)-C*H\(_2\)-) protons of unsymmetrically substituted butane diol (butane diol moiety with one hydroxyl groups reacted with triazine unit and one free hydroxyl group) within the hyperbranched polyether. The peaks at \(\delta = 3.1\text{-}3.2\) ppm may be due to terminal hydroxyl groups.
\(^1\)H NMR spectrum of the synthesized hyperbranched epoxy resin (Fig. 2.9) is little complicated due to the overlapping of many peaks in the \(\delta = 3.0-4.1\) ppm region.\(^3\) The peaks at \(\delta = 1.24\) (m) and 1.62 (s) ppm are due to the methylene and -CH\(_3\) protons respectively. The \(\delta\) values at 2.7-2.9 ppm and 3.3 ppm are due to the -CH\(_2\) and -CH protons of oxirane ring respectively.\(^{17,35}\) The chemical shift values at \(\delta = 3.5-3.7\) ppm and 4.0-4.1 ppm are due to the different chemical environment based methylene protons as shown in Fig. 2.9. The peaks appeared at \(\delta = 6.7-7.1\) ppm is due to aromatic protons.

Fig. 2.7: \(^1\)H NMR spectrum of hyperbranched polyether polyol

The \(^{13}\)C NMR spectrums of the hyperbranched polymers further supports and confirm the structure of the polymers. All the important peaks were observed in the NMR spectrum for both the cases. The peak at \(\delta = 172.9\) ppm is due to the carbon atoms of tri-substituted triazine unit symmetrically which can be considered as dendritic triazine unit for the hyperbranched polyether (Fig. 2.8). The peak at \(\delta = 172.5\) ppm is due to the carbon of triazine unit substituted with two symmetrically substituted 1,4-butane diol and a terminal 1,4-butane diol which can be considered as linear unit of the hyperbranched polyether. Whereas the peak at \(\delta = 171.9\) ppm results from carbon atoms of the triazine unit substituted with two 1,4-butane diol terminal units which can be considered the
terminal unit of the hyperbranched polyether. The peaks for the carbon atoms of 
symmetrically substituted 1,4-butane diol moiety appear at $\delta = 68.0$-68.6 ppm and $\delta = 
24.2$-25.0 ppm, whereas the peaks for the carbon atoms of unsymmetrically substituted 1,4-
butane diol moiety appear at $\delta = 62.0$ ppm, $\delta = 28.9$-30.9 ppm and $\delta = 25.9$ ppm (Fig. 2.8).
$^{13}$C NMR spectrum of hyperbranched polyether polyol also confirmed the complete 
substitution of chlorine atom of triazine unit, as there is no peak at $\delta = 170$ ppm which 
would correspond to a carbon atom of the triazine moiety bound to chlorine. This is due to 
the addition of an excess amount of 1,4-butane diol at the end of polymerization reaction 
and the extra 2 h of reaction in the last step of interfacial polycondensation.

![Fig. 2.8: $^{13}$C NMR spectrum of hyperbranched polyether polyol](image)

The $^{13}$C NMR spectrum for the hyperbranched epoxy resin is shown in Fig. 2.10. The peak values at $\delta = 25.0$-29.0 ppm are due to the different methylene $\text{-CH}_2$ carbons. The peak at $\delta = 31.1$ ppm is due to the $\text{-CH}_3$ carbon, while the chemical shift values at $\delta = 41.8$ ppm, 45.0 ppm, and 50.0 ppm are due to the aliphatic tertiary carbon, $\text{-CH}_2$ and $\text{-CH}$ carbons of oxirane ring respectively. The peaks at $\delta = 62.5$ ppm and 68.8 ppm are due to 
the methylene carbons directly attached to electronegative oxygen atom (Fig. 2.10). The 
peaks at $\delta = 114.0$-127.8 ppm and 143.0-156.0 ppm appeared for the carbons of benzene 
ring. Three peaks at $\delta = 173.0$-173.3 ppm are due to the symmetrically substituted, di-
substituted and mono-substituted polyol core, which can be considered as dendritic, linear 
and terminal units respectively (Fig. 2.10).
2.3.4. Curing study of the hyperbranched epoxy resin

The crosslinking or curing of the epoxy resin with poly(amido amine) hardener is a nucleophilic addition reaction. The reaction proceeds through the cleavage of the oxirane ring. In this reaction amine groups of the hardener react with the strained epoxy (oxirane
ring) groups of the resin and thereby forming chemical covalent linkages between the resin and the hardener chain molecules under the used conditions. The first step is the reaction between the primary amine hydrogen with the epoxy group, followed by a reaction between the secondary amine hydrogen with another epoxy group. Due to the involvement of an addition reaction, no volatile by-products are formed during the curing of epoxy resin. The driving force of this curing reaction is the release of strain energy of the oxirane ring. The hydroxyl groups generated during crosslinking reaction or preformed of the epoxy resin also take part in curing reaction by reacting with epoxy groups of the other chains in the presence of base poly(amido amine) forming ether bonds, called etherification. However, the etherification reaction competes with the amine-epoxy curing when the reactivity of the amine is low or when there is an excess of epoxy groups. The secondary alcohols formed during curing process can also catalyze the amine-epoxy reactions; this is called ‘autocatalysis’. Thus role of poly(amido amine) hardener is multifold. It acts as a crosslinker, as a base as well as it imparts plasticization effect to the epoxy resin and thereby improves the flexibility of the cured film.

2.3.5. Performance study

The performance characteristics in terms of impact resistance, scratch resistance, gloss, tensile strength and adhesive strength values of the cured hyperbranched epoxy resin are tabulated in Table 2.5. Adhesion studies indicate that the synthesized hyperbranched epoxy thermoset has a good adhesion character with the used substrates (Table 2.5). This may be due the presence of large number of polar hydroxyl, epoxy and ether groups which create strong secondary interactions like hydrogen bonding, polar-polar and polar-induced polar interactions etc. with the treated plywood and aluminium surface. Generally, gloss refers to specular reflection of the light reflected at the same angle of incidence. The gloss generally depends on the quantity of light absorbed or transmitted by the coating surface, which is determined by the smoothness of the surfaces. The high gloss value of the cured epoxy film is due to the adequate dimensional stability and smooth, uniform surface of the cured hyperbranched epoxy network (Table 2.5) and this result is one of the noticeable achievements in this study. The cured epoxy resin is found to possess good scratch hardness resistance which may be due to the presence of rigid aromatic, heterocyclic moieties and good crosslinking density as
indicated by swelling test (Table 2.5). The moderate impact strength of the cured resin indicates the presence of flexible ether linkages and aliphatic moieties present in the resin.

2.3.6. Thermal study
The thermal study of both the hyperbranched polymers was studied with the help of thermogravimetric analysis (TGA). TGA thermogram of hyperbranched polyether showed that the polymer is thermally stable up to a temperature of 150 °C without any decomposition (Fig. 2.11a). The relatively low initial decomposition temperature is due to the presence of thermolabile aliphatic butane diol moieties in the structure. However, the overall thermostability is relatively good due to the presence of thermostable triazine moieties in the structure, which is supported by the amount of residue at 700 °C (3.2 wt%). The polymer is degraded mainly by a two stage degradation pattern (Fig. 2.11a) related first to the degradation of the aliphatic moieties (150-260 °C) followed by the degradation of the aromatic units (370-480 °C).

The initial decomposition temperature (IDT) and 50% decomposition temperature of the cured hyperbranched epoxy were found to be 270 °C and 395 °C, respectively (Fig. 2.11b). The formation of 6 wt% of weight residue at 600 °C was also observed. This high thermostability is due to the presence of thermostable heterocyclic triazine moiety, rigid aromatic moiety and better cross-linking of the resin. The initial 3-4
% weight loss is due to loss of moisture and/or trapped solvent (Fig. 2.11b). The rapid degradation may be because of the presence of linear aliphatic moieties, structural defects in the hyperbranched epoxy resin.

Table 2.5: Performance characteristics of hyperbranched epoxy resin

<table>
<thead>
<tr>
<th>Property</th>
<th>Hyperbranched epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swelling (%)</td>
<td>27</td>
</tr>
<tr>
<td>Gloss* (60º)</td>
<td>82</td>
</tr>
<tr>
<td>Scratch hardness* (kg)</td>
<td>5.5</td>
</tr>
<tr>
<td>Impact strength* (cm)</td>
<td>60</td>
</tr>
<tr>
<td>Tensile strength* (MPa)</td>
<td>8.25</td>
</tr>
<tr>
<td>Cross-cut adhesion*</td>
<td>5B</td>
</tr>
<tr>
<td>Adhesive strength* (N/m)×10¹⁰</td>
<td>0.98</td>
</tr>
</tbody>
</table>

*the values are the mean of three tests

DSC studies of both the hyperbranched polymers were carried out as shown in Fig. 2.12. DSC curve of hyperbranched polyether polyol showed no melting or crystallization peak, which indicate that the polymer is amorphous in nature. The study further indicates that the polymer has a low T_g of -11 ºC, which is a result of the flexibility of the structure.

Fig 2.12: DSC curves of (a) hyperbranched polyether polyol and (b) cured hyperbranched epoxy thermoset
This high flexibility is due to the presence of large number of ether linkages and aliphatic butane diol moieties in the structure of the polymer. However, DSC study of the cured hyperbranched epoxy resin showed a glass transition temperature ($T_g$) of about 5 °C. No other transition peak was observed under the investigated temperature range which indicates absence of any crystalline phase in the thermoset and the material is amorphous in nature.

2.3.7. Chemical resistance

The chemical resistance of the cured hyperbranched epoxy thermoset was studied in various chemical media. The cured coated resin on glass plate of 6 cm × 1 cm × 0.2 cm size was kept in 250 mL beakers containing 150 mL of different chemical media. The media used were water, aqueous sodium hydroxide solution (pH ~7.4), 10% aqueous sodium chloride (w/v) solution, and aqueous hydrochloric acid solution (pH ~6.8). The plates were kept for 20 days at room temperature and changes of masses were determined gravimetrically. The weight losses of the cured samples are shown in Table 2.6.

<table>
<thead>
<tr>
<th>Type of media</th>
<th>Weight reduction after 20 days (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aq. NaOH (pH ~7.4)</td>
<td>0.26</td>
</tr>
<tr>
<td>Aq. HCl (pH ~ 6.8)</td>
<td>0.27</td>
</tr>
<tr>
<td>Aq. NaCl solution (10%, w/v)</td>
<td>0.23</td>
</tr>
<tr>
<td>Water</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The chemical resistance test in various media showed that the epoxy thermoset is highly stable and almost negligible change in the weight was observed. This may be due to the presence of aromatic, heterocyclic moieties and good crosslinking density (low swelling value, Table 2.5) of the cured resin. Further, gel fraction of the cured hyperbranched epoxy was determined by soxhlet extraction technique using THF as the solvent to verify the solvent resistance of the cured resin. The gel fraction was found to be 0.973, indicating sufficient solvent resistance characteristic of the cured hyperbranched epoxy. Thus, the
overall chemical resistance of the hyperbranched epoxy resin is found to be very good.

2.4. Conclusion
From this chapter, it can be concluded that the hyperbranched polyether polyol based hyperbranched epoxy resin is successfully synthesized by a simple polycondensation technique. The properties of the synthesized epoxy resin showed its potentiality to be used as an advanced material such as adhesive or matrix for the preparation of nanocomposites. However, the impact property of the synthesised resin is not up to the mark and needs further modification. The overall performances of the synthesized hyperbranched epoxy resin are found to be adequate and can be used as adhesive and surface coating materials.

Reference


