Chapter 2

Synthesis, characterization and property evaluation of hyperbranched epoxy resins

Highlight

This chapter deals with synthesis, characterization and property evaluation of hyperbranched epoxy resins to address the shortcomings of conventional epoxies. These resins were synthesized from different multifunctional branch generating moieties. The chapter contains three sub-chapters in accordance to the branch generating moieties used for the synthesis of hyperbranched epoxy resins. The first sub-chapter describes a high performance tough hyperbranched epoxy with low dielectric constant, synthesized from pentaerythritol (B_4) as the branch generating moiety. The second sub-chapter deals with another tough high performance hyperbranched epoxy synthesized from low cost liquid triethanolamine (B_3) branch generating moiety to increase the spectrum of applications for hyperbranched epoxy. The last sub-chapter of this chapter demonstrates a bio-degradable tough hyperbranched epoxy from castor oil-based hyperbranched polyester polyol (B_n) branch generating unit to overcome the non-biodegradibilty of conventional epoxy. All three types of hyperbranched epoxy resins were synthesized by the single step polycondensation reaction and cured with poly(amido-amine) hardener.

Parts of this chapter are published in

1. B. De and N. Karak, *RSC Adv*. **5**, 35080-35088, 2015.
2. N. Karak and B. De, Indian Patent: Application No. 786/KOL/2013 dated 28.06.2013.
3. B. De and N. Karak, *J. Mater. Chem. A* **1**, 348-353, 2013.
4. B. De and N. Karak, *J. Chem. Sci*. **126**, 587-595, 2014.
5. B. De, K. Gupta, M. Mandal and N. Karak, *ACS Sustainable Chem. Eng*. **2**, 445-453, 2014.

2A. Pentaerythritol based hyperbranched epoxy

2A.1. Introduction

From the previous chapter it is clear that the inherent characteristics like brittleness and low toughness of linear conventional epoxies restrict their many advanced applications in spite of their many attractive attributes.[1-3] Different modifications of them such as toughened by blending with different flexible polymers like rubbers,[4,5] hyperbranched polyesters,[6,7] etc. are also problematic from commercial exploitation due to the processing difficulties and insignificant improvements in properties as stated in first chapter. Thus, unique structural design is required to impart adequate toughness as well as other desired properties to address the shortcomings of conventional epoxy. The chemical composition, structural architecture and reaction conditions are the key parameters to tune the properties of such novel epoxy resins. In this endeavor, recently hyperbranched epoxy achieved significant attention to the researchers. This is because of the hyperbranched polymers are a novel class of three-dimensional macromolecules, produced by multiplicative growth from a multi-functional core to form repeated branching units. These polymers have also special interest due to their easy synthetic accessibility, low viscosity, high solubility and the presence of large numbers of end functional groups.[8-10] In addition to those, single step synthetic protocol helps their mass scale production and hence can be seen the door of industry easily. While different synthetic approaches to hyperbranched epoxy resins have been reported including end group modification of hyperbranched polymers,[11-13] proton transfer polymerization,[14,15] functionalization of poly(methyl acrylate) using ATRP,[16] etc. all these products were either solid or highly viscous liquids and would need dilution with organic solvent, which is detrimental to the environment due to production of large amount of VOC. In most of the cases the mechanical strength is also found to be low and thus, they are mainly used as a toughener for linear diglycidyl ether of bisphenol-A (DGEBA) based conventional epoxy. Thus, desired high performance hyperbranched epoxy is limited in literature. So, in order to develop high performance tough epoxies, they have to be designed with unique architectural features such as hyperbranched structure with the combination of aliphatic-aromatic moieties which may impart high performance with desired toughness by increasing the free volume between the molecules by their confined geometry.[17]

Thus, in the present work, tough hyperbranched epoxies are synthesized using pentaerythritol as an aliphatic branch generating moiety along with bisphenol-A, an aromatic diol and epichlorohydrin by an $A_2 + B_4$ polycondensation reaction using NaOH as the base catalyst. The presence of aromatic rigid moiety (bisphenol-A) in the hyperbranched epoxies may result high tensile strength like DGEBA. On the other hand, the aliphatic branch generating moiety and ether linkages may increase the elasticity (elongation at break) by plasticizing effect. Thus, the overall toughness of the hyperbranched epoxy thermosets may balance through their own structural architectures. Again, the use of polycondensation reaction helps to recover pure products easily similar to taffy process by using water as the reaction medium as stated in the first chapter. Thus, hyperbranched epoxy thermosets with desired performance are attempted to develop here.

2A.2. Experimental

2A.2.1. Materials

Bisphenol-A (BPA) or 4,4'-(propane-2,2-diyl) diphenol (**Table 1.1**, Chapter 1) is one of the most widely used reactants for the synthesis of epoxy resin (DGEBA) and it provides high mechanical properties, thermal stability and chemical resistance to the thermoset. Thus, here BPA was used as a reactant for the preparation of *in-situ* generated DGEBA epoxy monomer (A_2). BPA was purchased from GS Chemicals, India and it was further purified by recrystallization from toluene prior to use. The melting point (mp) and the molar mass of the purified BPA are 159 °C and 228.29 g/mol respectively.

Epichlorohydrin (ECH) or chloromethyloxirane (**Table 1.2**, Chapter 1) is the most common reactant for the synthesis of epoxy resins. Here it was used for the preparation of A_2 monomer (*in-situ* generated DGEBA) and substitution of end terminal hydroxyl groups to transform into epoxy groups of hyperbranched epoxy resins. ECH was obtained from GS Chemicals, India. It is a colorless liquid of density 1.18 g/cc with molar mass of 92.52 g/mol and boiling point (bp) of 117.9 °C.

Pentaerythritol (PE) or 2,2-bis(hydroxymethyl)-1,3-propanediol (**Table 1.1**, Chapter 1) is one of the common branched generating moieties used for the synthesis of hyperbranched polymers or dendrimers.[18,19] It is a tetraol and thus, here it was used as the B_4 branch generating unit for the synthesis of hyperbranched epoxy resin along with *in-situ* generated DGEBA. It was purchased from Sigma-Aldrich, Germany and was used after re-crystallization from ethanol (EtOH). Purified PE is a white crystalline solid with a molar mass of 136.15 g/mol. The mp of the purified material is 260.5 °C.

Sodium hydroxide (NaOH) was used as a base catalyst for the synthesis of hyperbranched epoxy resins by polycondensation reaction as well as in chemical resistance test for the thermosets. NaOH pellets were obtained from Merck, India. Its molecular weight and density are 40 g/mol and 2.13 g/cc respectively. NaOH was also used to determine epoxy equivalent values of the synthesized epoxy resins.

Hydrochloric acid (HCl) was used to determine the epoxy equivalent values of the synthesized epoxy resins as well as in chemical resistance test for the thermosets. It was obtained from Merck, India with 37% weight by volume in water. The molecular weight of HCl is 36.5 g/mol.

Potassium hydroxide (KOH) was used for the determination of hydroxyl value. The molecular weight, density and mp of KOH are 56.11 g/mol, 2.12 g/cc and 406 °C. KOH pellets were purchased from Merck, India.

Maleic anhydride (**Figure 2A.1**) is an acid anhydride of maleic acid. It is a white solid with molar mass and mp of 98.06 g/mol and 52.8 °C respectively. Here it was used as a reactant for the determination of hydroxyl value. It was acquired from Merck, India.

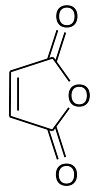


Figure 2A.1: Structure of maleic anhydride

Triethylamine (Et_3N) is a colorless liquid and is commonly used as a base for the organic synthesis. Here it was used as a nucleophilic catalyst with maleic anhydride to determine hydroxyl value. It was obtained from Merck, India. The molar mass, density and bp of triethylamine are 101.19 g/mol, 0.725 g/mL and 88 °C respectively.

Oxalic acid ($C_2H_2O_4$) is an organic dibasic acid. It is a white crystalline solid with molar mass, density and mp of 90.03 g/mol, 1.9 g/cc and 102 °C respectively. Here it was used as the primary standard for standardization of NaOH and KOH solutions. It was acquired from Merck, India.

Poly(amido-amine) (PAA) (**Table 1.4**, Chapter 1) is a non volatile resinous hardener for epoxy resins. It is a polycondensation product of vegetable oil-based dimmer acid with diethylene triamine. Here it was used as a hardener for synthesizing hyperbranched epoxy resins. It was collected from Ciba Giegy, India as trade name HY840. The amine value and the measured viscosity of the hardener are 5-7 eq./kg and 10-14 Pa s.

Sodium chloride (NaCl) is the most widely used common salt. The molar mass, density and mp of NaCl are 58.44 g/mol, 2.16 g/cc and 801 °C respectively. It was purchased from Merck, India. The salt was used to prepare aqueous solution for washing process of the hyperbranched epoxy resins and in chemical resistance test of the thermosets.

Toluene (bp 110.6 °C, molar mass 92.14 g/mol and density 0.86 g/cc), tetrahydrofuran (THF) (bp 66 °C, molar mass 72.11 g/mol and density 0.89 g/cc) and EtOH (bp 78.37 °C, molar mass 46 g/mol and density 0.79 g/cc) solvents were obtained from Merck, India and used after distillation. Here toluene was used for the recrystallization of BPA. THF was used as a processing solvent in small amount for mixing the hardener with hyperbranched epoxy resins. On the other hand EtOH was used in chemical resistance test of the thermosets.

2A.2.2. Characterization

FTIR spectra were recorded by a Nicolet FTIR spectrophotometer (Impact-410, Madison, USA) using KBr pellets. A 400 MHz, Jeol FT-NMR spectrometer was used to record the ^{1}H NMR and ^{13}C NMR spectra of the resins by using TMS as the internal standard and $CDC1_3$ or d_6-DMSO as the solvent. The physical properties such as epoxy equivalent, hydroxyl value, solubility, solution viscosity and swelling value were measured by the standard test methods as reported in the first chapter. The determination of shear viscosities of the resins were done by Bohlin rheometer CVO100 (Malvern, UK). The tensile strength (standard ASTM D 882) and lap-shear tensile adhesive strength of the hyperbranched epoxy thermosets were measured by a Universal Testing Machine (UTM, WDW10, Jinan, China). The tensile test was performed on rectangular sample (size 60 × 10 × 0.3 mm^3) with a 500 N load cell at a crosshead speed of 10 mm/min. Toughness of the thermosets was calculated by integrating the area under the stress-strain curves. The lap-shear adhesion test (as per the standard ASTM D4896-01) was carried out on metal-metal (M-M), wood-wood (W-W) and plastic-plastic (P-P) adherents by lap-shear test (the area of the overlapping zone was 25 × 25 mm^2 and thickness was 0.02-0.03 mm) with a 10 kN load cell at a crosshead speed of 50 mm/min. The lap-shear tensile strength (MPa) (calculated as maximum load per unit bonded area) was obtained directly from UTM. Scratch hardness test (standard ASTM G171) was carried out by scratch hardness tester (Sheen instrument Ltd., UK) on the surface of hyperbranched epoxy thermosets (75 × 25 × 0.3 mm^3). Impact strength of the thermosets was measured by Impact tester (S. C. Dey Co., Kolkata) as per the standard falling weight (ball) method (according to the standard ASTM D 1709). The bending test of the thermosets was done using a mandrel with diameter 1 to 100 mm (as per the standard ASTM D 522). All the tests for the measurement of mechanical properties were repeated for five times and average values were taken as the results. Thermogravimetric analysis (TGA) of the thermosets was done using a PerkinElmer TG4000 with nitrogen flow rate of 30 mL/min and the heating rate of 10 °C/min from 30 to 700 °C. The temperature at which the first weight loss of the thermoset occurred in TGA thermogram was taken as the initial degradation temperature. The dielectric property of the thermoset films (thickness 0.3-0.4 mm) was measured by LCR Hitester instrument (Hioki 3532-50) up to a frequency of 1MHz at 25 °C using the standard method as reported in the first chapter. The chemical resistance test was done in various chemical media such as aqueous HCl (10% by volume), aqueous NaOH (5 wt%), aqueous NaCl (10 wt%), aqueous EtOH (20% by volume) and tap water were used to investigate the effect of these chemicals on the films of thermosets. The films were cut into small pieces (size 15 × 15 × 0.3-0.4 mm^3) and kept in 100 mL glass bottles containing aforesaid media at an ambient temperature (25 °C). The percent of weight loss was measured after 30 days of test. Moisture absorption test was performed by keeping the thermoset (20 × 20 × 0.4 mm^3) in a humid chamber (98% humidity) at 25 °C for 7 days and the percentage of moisture absorbed by the film was calculated from its initials weight.

2A.2.3. Methods

2A.2.3.1. Synthesis of pentaerythritol (PE) based hyperbranched epoxy (PHE) resins

These hyperbranched epoxy resins were synthesized by the polycondensation reaction of BPA and PE (5, 10 and 15 wt% separately with respect to BPA) with ECH (1:2 mole ratio with respect to hydroxyl group) at 110 °C under continuous stirring. An amount of 10.0 g of BPA, 1.0 g of PE (for 10 wt%) and 21.64 g of ECH were taken in two necked round bottom flask equipped with a water condenser and a dropping funnel. The reaction mixture was stirred with a magnetic stirrer. To this reaction mixture 5N aqueous solution of NaOH (4.67 g, equivalent to the hydroxyl group) was added slowly from a dropping funnel. The addition of NaOH solution was started at 60 °C to the reaction mixture and it took about 30 min to reach the temperature 110 °C. After the desired time period the reaction was allowed to settle in a separating funnel and the aqueous layer was separated out from the desired organic layer. Then the organic layer was washed with brine solution followed by distilled water for 2-3 times and dried under vacuum at 70 °C with the help of a rotary evaporator (Eyela, Tokyo, Japan) to get viscous sticky transparent masses. The drying process was done until all the ECH and entrapped water were removed from the resin by checking its constant weight. The epoxy resins for three different reaction times viz. 2 h, 4 h and 6 h were synthesized and coded as PHE2h, PHE4h and PHE6h (yield: ~95%). The epoxy resins with three different wt% of PE viz. 5, 10, 15 wt% were synthesized similarly for 4 h reaction time and coded as PHE5, PHE4h and PHE15 respectively (As PHE4h was also synthesized at same composition under the same conditions).

2A.2.3.2. Preparation of BPA based conventional linear epoxy (SBE)

SBE resin was prepared by the same procedure in absence of branch generating moiety (PE) for comparison purpose. It was prepared by polycondensation reaction between BPA and ECH at 110 °C for 4 h using aqueous NaOH as the base catalyst.

2A.2.3.3. Curing of the resins

The synthesized PHE and SBE resins were cured by mixing homogenously with 50 phr of poly(amido-amine) (PAA) hardener with respect to resin in a glass beaker at room temperature in the presence of little amount of THF solvent (0.5 mL/g). Then the mixtures were uniformly coated on glass plates ($75 \times 25 \times 1.3$ mm^3) and steel plates ($150 \times 50 \times 1.6$ mm^3). The solvent and other volatiles were removed with the help of vacuum for 24 h and the plates were cured at a specific temperature for specified time intervals. The optimization of curing reaction was done by determining swelling values of the cured films (thermosets) immersed in THF for 48 h. The percentage of swelling was determined from the original and equilibrium swelled weight of the film.

2A.3. Results and discussion

2A.3.1. Synthesis and characterization of PHE resins

PHE resins were synthesized by an $A_2 + B_4$ polycondensation reaction. First, DGEBA (A_2) was formed *in-situ* during the reaction as reactivity of hydroxyl groups of BPA is higher than PE due to higher acidic nature of phenolic protons compared to the aliphatic alcoholic protons. The addition of aqueous solution of NaOH was also started at 60 °C to the reaction mixture and it took about 30 min to reach the temperature 110 °C in the procedure. During this period it is expected that BPA was reacted with ECH to produce DGEBA rather than PE. Then hyperbranched epoxy was formed by reaction between DGEBA and PE (B_4) along with the reaction of ECH with free hydroxyl groups of PE, as shown in **Scheme 2A.1**. The structural features of one of the representative resins (PHE4h) of the synthesized epoxies were characterized by FTIR and NMR studies as they possessed similar structural features. The stretching vibrations (ν_{max}/cm^{-1}) in FTIR spectrum (**Figure 2A.2**) are attributed to the following features: 914 (oxirane), 3437 (O-H), 3050 (aromatic C-H), 2965 (aliphatic C-H), 1606 (aromatic C=C), 1241 (C-O) and 1035 (C-C).[20-22] ^{1}H NMR (**Figure 2A.3**) spectrum δ_H (ppm) values indicate the following structural features: 3.3 (1H, oxirane), 2.7 and 2.8 (2H, oxirane), 3.7-3.8 (2H, 4CH_2 of substituted and un-substituted PE), 1.5 (3H, CH_3), 6.8 (4H of BPA), 7.1 (4H of BPA), 4.2 (1H, C*H*OH), 4.0 (2H, CH_2 attached with oxirane), 3.5 (2H, CH_2 attached with PE unit), 4.1 (2H, CH_2 attached with BPA unit), 5.4 and 5.6 (1H, two types of OH).[20-22] In ^{13}C NMR spectrum (**Figure 2A.4**) δ_C (ppm) values were observed at 43 (CH_2, oxirane), 49 (CH, oxirane), 46-47 (central C of PE unit), 114, 127, 143 and 156 (4C, Ph), 31 (CH_3, BPA unit), 41 (C, isopropediene of BPA), 68 (CH_2, PE unit), 51 (CH_2 attached with oxirane) and 62-67 (CH_2-O units and CHOH unit).[20-22] The degree of branching (DB) of the hyperbranched epoxy with variation of time and amount of B_4 reactant was determined from ^{13}C NMR spectra of the synthesized resins. A hyperbranched polymer should content three different types of units: dendritic (D), linear (L) and terminal (T) in its structure as stated in the first chapter. DB is the ratio of the sum of integration of D and T units to the sum of integration of D, L, and T units,[3,10] i.e.,

$$DB = (D + T)/(D + L + T) \quad \text{……} \quad (2A.1)$$

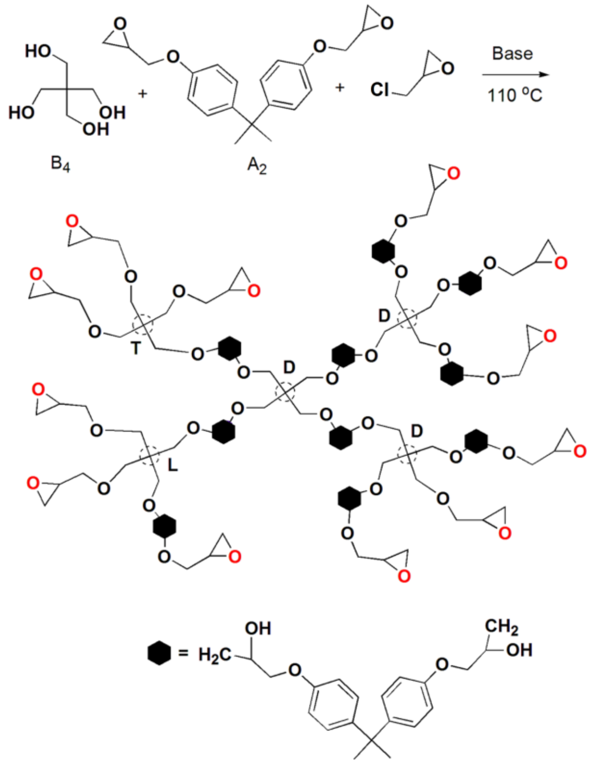
For a hyperbranched polymer this value should be greater than 0.5. In case of synthesized epoxy resins, the units with three and four, two and one hydroxyl group(s) of PE substituted by DGEBA moiety are dendritic (D), linear (L) and (T) units respectively as shown in **Scheme 2A.1**. In ^{13}C NMR spectrum (**Figure 2A.4**) the central carbon atom of PE for these four units of the synthesized resins with different integration values were observed at δ = 46.75, 46.55, 46.40 and 46.20 ppm respectively. The calculated DB from integration values of these peaks for hyperbranched epoxy resins with variation of times and amount of B_4 unit are given in **Table 2A.1**. The highest DB was found at 4 h reaction time with 10 wt% PE (with respect to BPA) due to the fact that under these conditions the highest numbers of dendritic and terminal units were formed (in this case the highest numbers of terminal units were formed as shown in **Table 2A.1**). In case of 2 h reaction time the less numbers of dendritic and terminal units were formed compared to the linear units (the highest numbers of linear units were formed). This is due to the incomplete growth of the structure of the hyperbranched epoxy resin. Whereas, at 6 h reaction time the lowest number of terminal units were formed (**Table 2A.1**). The epoxy resin with 10 wt% PE provides the highest DB among the studied compositions (5-15 wt%). This may be due to the presence of an appropriate ratio of reactants for the formation of the hyperbranched structure of the epoxy resin at this composition. This resulted in both a higher percentage of tri- and tetra- substituted branched units, as well as higher chain end substitution to form terminal epoxides compared to the other two wt% of PE (as shown in **Table 2A.1**). Whereas the decrease in amount of (5 wt%) PE of the epoxy resulted in the lowest numbers of tri- and tetra- substituted internal branched units as well as the terminal epoxides due to incomplete growth of the hyperbranched structure at this composition. On the other hand increase in the amount of (15 wt%) PE of the epoxy the generation of branching units might be prohibited due to the congested nature of the PE moiety.[14,23] Thus, PHE4h exhibited the lowest epoxy equivalent (highest numbers of epoxy groups), hydroxyl, viscosity (solution as well as shear) and specific gravity values as shown in **Table 2A.2**. With the increase of linear units the viscosity and specific gravity values increase as the hydrogen bonding as well as other intermolecular forces are increased. The synthesized hyperbranched epoxy resins are soluble in most of the common organic solvents like MeOH, EtOH, acetone, THF, DMF, DMAc, DMSO, $CHCl_3$, CH_2Cl_2, toluene, xylene, ethyl acetate, etc. due to the hyperbranched architecture and the presence of a large number of functionalities along with combination of aliphatic and aromatic moieties. Whereas, the prepared linear epoxy resin (SBE) is not soluble in toluene, xylene and ethyl acetate. It possessed also high viscosity (both solution and shear) as well as specific gravity values. The epoxy equivalent and hydroxyl value of SBE are lower than the hyperbranched epoxy because of linear structure of the former.

Table 2A.1: The values of D, L and T units (%) and degree of branching (DB) of PHE2h, PHE4h, PHE6h, PHE5 and PHE15 resins

Code	D units (%)	L units (%)	T units (%)	DB
PHE2h	39.82	53.59	6.59	0.46
PHE4h	62.62	21.61	15.77	0.78
PHE6h	64.04	32.02	3.94	0.68
PHE5	41.76	47.40	10.84	0.53
PHE15	59.12	29.0	11.88	0.71

Table 2A.2: Physical property values of PHE2h, PHE4h, PHE6h, PHE5, PHE15 and SBE resins

Parameter	PHE2h	PHE4h	PHE6h	PHE5	PHE15	SBE
Epoxy equivalent (g/eq.)	688	394	583	499	427	254
Hydroxyl value (mg KOH/g)	156	100	220	102	170	98
Solution viscosity (dL/g) at 25 °C	0.046	0.028	0.033	0.038	0.030	0.089
Shear viscosity (Pa s) at 25 °C	9.40	2.99	6.12	7.88	5.03	18.92
Specific gravity at 25 °C	1.19	1.03	1.12	1.16	1.08	1.31



Scheme 2A.1: Synthesis with possible general structure of PHE resins

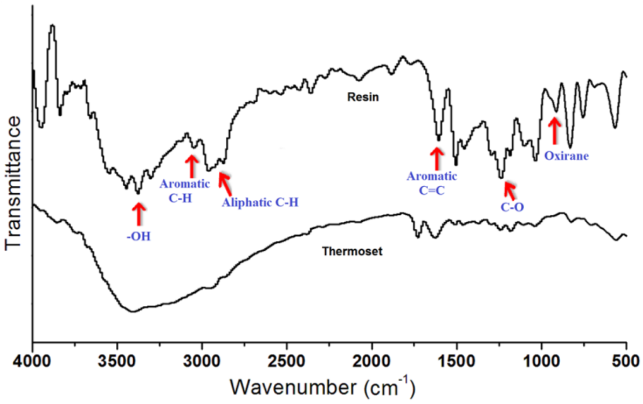


Figure 2A.2: FIIR spectra of PHE4h (resin and thermoset)

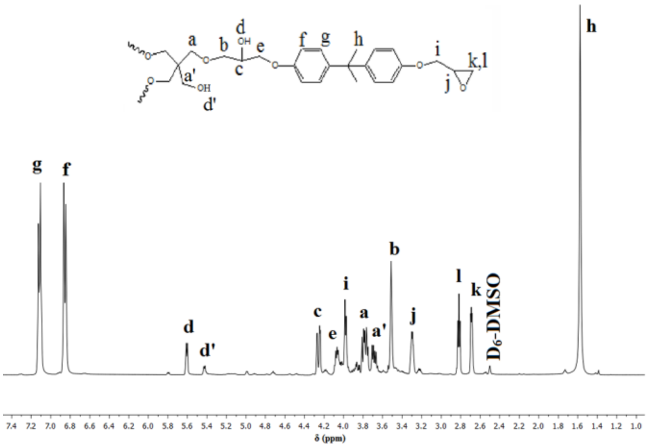


Figure 2A.3: ^{1}H NMR spectrum of PHE4h resin

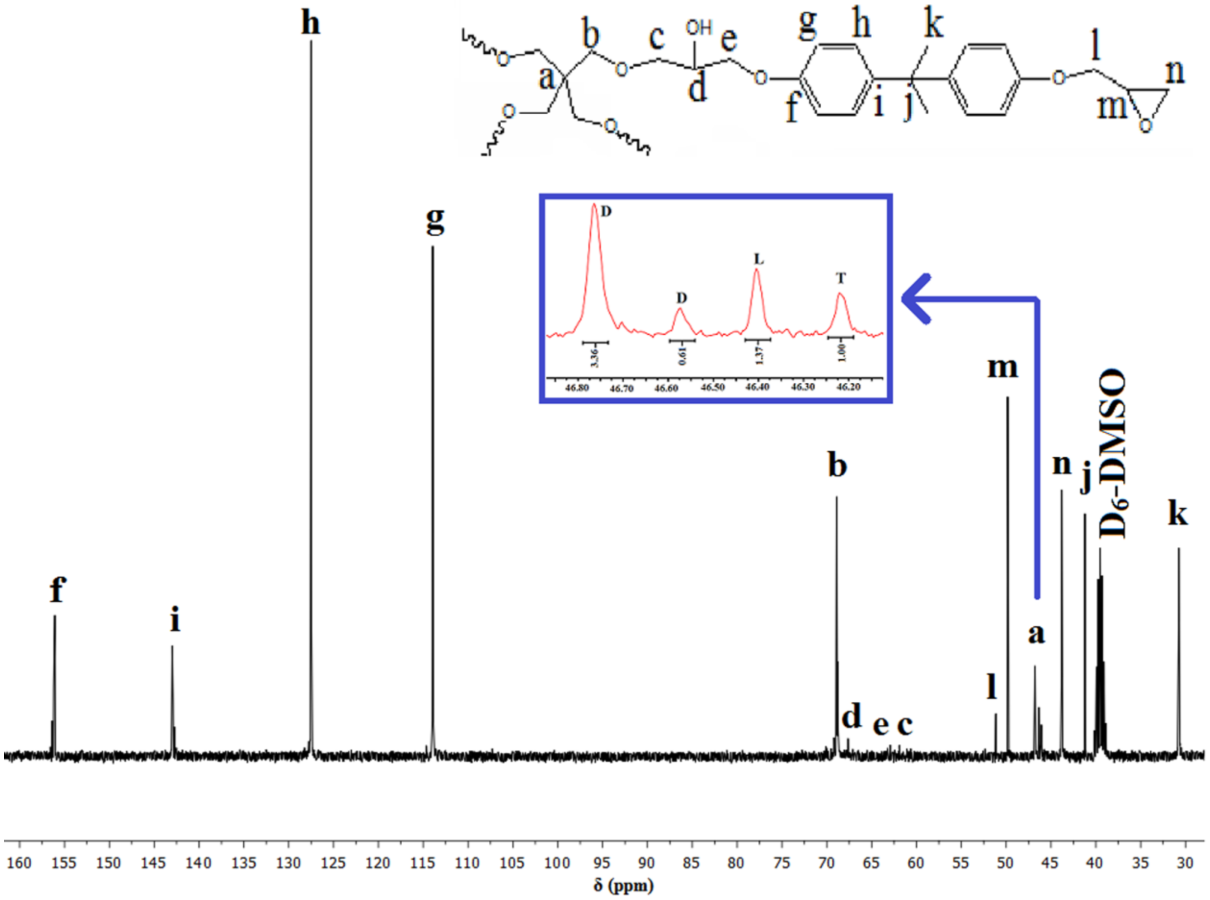


Figure 2A.4: ^{13}C NMR spectrum of PHE4h resin

2A.3.2. Curing study of PHE resins

Curing of PHE2h, PHE4h, PHE6h, PHE5, PHE15 and SBE resins was done under the same conditions for specified period of time (Table 3). According to epoxy equivalent of PHE4h, 50 wt% PAA hardener was required to cure it (as epoxy equivalent weight : amine value = ~400:200). However, in case of other hyperbranched epoxy resins the same amount of hardener was used although they need slight lower amount of hardener as per their epoxy equivalent values. This is for comparison of all thermosets. PHE4h took the lowest time for curing with PAA hardener to attend the swelling value 20-30% (optimum cure) as shown in **Table 2A.3**. This is due to the fact that PHE4h exhibited the highest DB as well as lowest epoxy equivalent. Thus, it has the highest numbers of chain end substitution epoxide groups to react with PAA hardener. Therefore, it formed the best compact three-dimensional network structure which resulted the lowest swelling value. The hyperbranched epoxy resins can also be cured at room temperature (25 °C) and to attend the optimum swelling value PHE4h takes 2-3 days after mixing with the same hardener. After curing the oxirane ring stretching frequency (914 cm^{-1}) of PHE4h in FTIR spectrum (**Figure 2A.2**) was completely vanished or disappeared.

2A.3.3. Mechanical properties of PHE thermosets

The mechanical properties like tensile strength, elongation at break, toughness, impact resistance, scratch hardness and bending values for PHE2h, PHE4h, PHE6h, PHE5, PHE15 and SBE thermosets are given in **Table 2A.3**. From the results, it was found that PHE4h thermoset exhibited the highest tensile strength value. This is due to the fact that PHE4h possessed the highest DB value which resulted the highest numbers of chain end substitution epoxide groups to form denser three-dimensional network structure after curing with PAA hardener as stated above. It also exhibited high value of elongation at break. This is because of the proper combination of aliphatic and aromatic moieties as well the ideal hyperbranched structural architecture. This architecture helps to increase the free volume (the unoccupied space) between the molecules in the three-dimensional network due to confined geometry of the structure.[17] Generally in literature, two types of epoxy thermosets have been reported, one is glassy epoxy thermoset which exhibited high tensile strength (>40 Mpa) with very low elongation at break (<5%) and another is rubbery epoxy thermoset which exhibited low strength (<10 MPa) with relatively high elongation at break (>40%).[24] However, combination of both of these is not found in literature. Whereas, PHE4h thermoset exhibited both high tensile strength (51 MPa) and elongation at break (38%) due to the unique structural combination and geometry. Thus, it also possessed the highest value of toughness (measured by the area under stress-strain curves from **Figure 2A.5**) as well as impact resistance, scratch hardness and bending among the other studied thermosets. However, differences in impact resistance and bending values for all the hyperbranched epoxy thermosets could not be measured as the values reached the highest limit of the instruments for impact resistance (100 cm) and flexibility evaluation (1 mm bending diameter of mandrel). The another reason for the high impact resistance and flexibility of the hyperbranched thermosets beside their aromatic-aliphatic combination and structural architecture is that the presence of different flexible moieties (hydrocarbon chain of hardener and ether linkages of epoxy).[17] The scratch hardness values difference between thermosets of PHE4h and PHE15 could not also be measured as these values also reached the highest limit of the instruments for the scratch hardness (10 kg). On the other hand, linear SBE thermoset exhibited the lowest values of elongation at break as well as toughness though its tensile strength value is high. This is due to its linear structure as well as it contains more amount of rigid aromatic BPA moiety in its structure. Thus, it also possessed the lowest value of impact resistance, scratch hardness and bending. Due to high brittleness and rigidity SBE also exhibited extremely high tensile modulus compared to hyperbranched epoxy thermosets as shown in **Table 2A.3**.

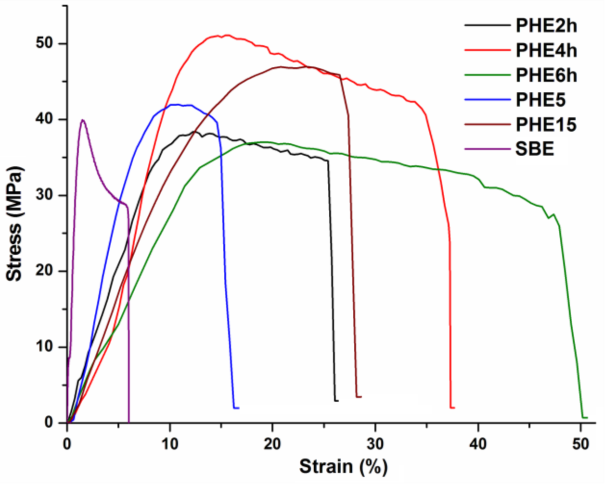


Figure 2A.5: Stress-strain profiles of PHE thermosets

2A.3.4. Adhesive strength of PHE thermosets

The lap-shear tensile adhesive strength values for PHE2h, PHE4h, PHE6h, PHE5, PHE15 and SBE thermosets are given in **Table 2A.3**. PHE4h thermoset exhibited the highest value of adhesive strength among all other thermosets and this is due to the same reason as stated earlier for tensile strength. It has the highest number of end terminal polar groups (due to the highest value of DB) which help to adhere the substrates by strong polar-polar, H-bonding, etc. interactions (W-W) and by physical interlocking (M-M and P-P).[21] However, in case of W-W substrate all the hyperbranched epoxy thermosets showed almost equal adhesive strength due to the failure of the substrate. On the other hand, SBE thermoset possessed poor adhesive strength values for all the three types of substrates compared to hyperbranched thermosets.

Table 2A.3: Performance of PHE2h, PHE4h, PHE6h, PHE5, PHE15 and SBE thermosets

Parameter	PHE2h	PHE4h	PHE6h	PHE5	PHE15	SBE
Curing at 100 °C (min)	60±3	35±2	70±5	50±2	45±2	90±4
Swelling value (%)	29±0.5	22±1.0	31±2.0	28±1.2	24±0.5	26±0.5
Tensile strength (MPa)	38.5±0.5	51±1.5	37±1.0	42±2.0	47±0.5	40±2.0
Elongation at break (%)	26±2.0	37.5±1.6	49±2.0	16±1.2	28±0.8	6±0.8
Toughness (MPa)	785	1432	1308	511	961	181
Modulus (MPa)	411	345	278	665	359	3360
Impact strength (cm)	>100	>100	>100	>100	>100	70
Scratch hardness (kg)	8.0±0.5	>10.0	9.5±0.3	8.5±0.5	>10.0	6.5±0.2
Bending (mm)	<1	<1	<1	>1	>1	3
Initial degradation temperature (°C)	289	296	291	290	292	291
Dielectric constant at 1 MHz (at 25 °C)	3.5±0.06	1.8±0.09	2.5±0.11	3.2±0.04	2.1±0.05	4.2±0.08
Dielectric loss at 1 MHz (at 25 °C)	0.025	0.009	0.015	0.019	0.012	0.033
Moisture absorption at 25 °C (%)	0.32	0.09	0.34	0.19	0.11	0.26
Adhesive strength (M-M) (MPa)	2436±24	3429±17	2258±12	2670±22	2919±18	1028±19
Adhesive strength (W-W) (MPa)	>2840	>2911	>2812	>2865	>2902	1114±8
Adhesive strength (P-P) (MPa)	597±9	789±6	419±11	663±9	708±5	256±12

2A.3.5. Thermal stability of PHE thermosets

TGA thermograms of PHE2h, PHE4h, PHE6h, PHE5, PHE15 and SBE thermosets are shown in **Figure 2A.6**. The initial decomposition (5% weight loss) temperatures of the thermosets are given in **Table 2A.3**. The initial and midpoint (50% weight loss) degradations of the thermosets were found at around 300 and 400 °C respectively. The thermosets were degraded mainly by two step patterns, where the first stage (~300 °C) is related to the degradation of the aliphatic moieties of hyperbranched epoxy (ether and PE moieties) as well as PAA hardener (long chain of fatty acid moieties) and the second stage (~400 °C) is related to the degradation of the aromatic moieties of the hyperbranched epoxy.[20] The degradation patterns and the degradation temperatures of the thermosets were almost the same as their structural units are alike. However, due to the highest crosslinked and compact structure, initial decomposition temperature (296 °C) of PHE4h thermoset was found to be the highest. On the other hand as PHE2h thermoset contents more aromatic moieties in its structure compared to the aliphatic moieties, its second stage degradation temperature (420 °C) and char residue (8%) were found to be slight higher compared to other hyperbranched thermosets.

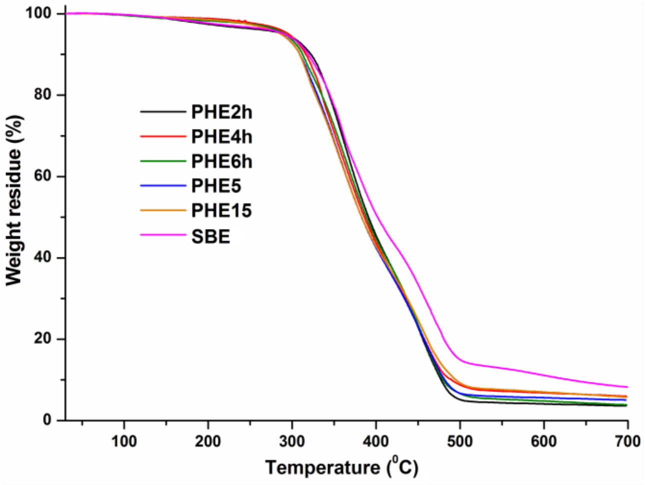


Figure 2A.6: TGA thermograms of PHE thermosets

2A.3.6. Electrical property of PHE thermosets

The dielectric constant and dielectric loss values at 1 MHz frequency and 25 °C for PHE2h, PHE4h, PHE6h, PHE5, PHE15 and SBE thermosets are given in **Table 2A.3**. The variations of dielectric constants with frequency (0.1-1.0 MHz) at 25 °C of the thermosets are shown in **Figure 2A.7**. From the results, it is found that PHE4h exhibited the lowest dielectric constant due to the highest crosslinked and compact structure resulted from its ideal hyperbranched architecture. Here, the synthesized hyperbranched epoxy thermoset possessed comparatively low dielectric constant from any other conventional epoxy thermosets including SBE (4.2), because of the unique hyperbranched structural architecture. Many literature reported that dielectric constant of a polymer can be reduced by increasing its porosity, free volume or by decreasing its polarity.[25,26] In this case, the hyperbranched structural architecture can led to lots of cavities, defects and free spacing among the molecules even after curing.[25,27] The free volume of the thermoset is, therefore, large and the dielectric constant reached a low value (<2.0). This unique architecture may also help to prohibit the hydroxyl groups to restrict the molar polarization at higher frequency which decreases the dielectric constant as well as the dielectric loss. The moisture absorption value (**Table 2A.3**) of the hyperbranched thermoset is very low because of the compact crosslinked structure, which is advantageous for advanced electronics applications.

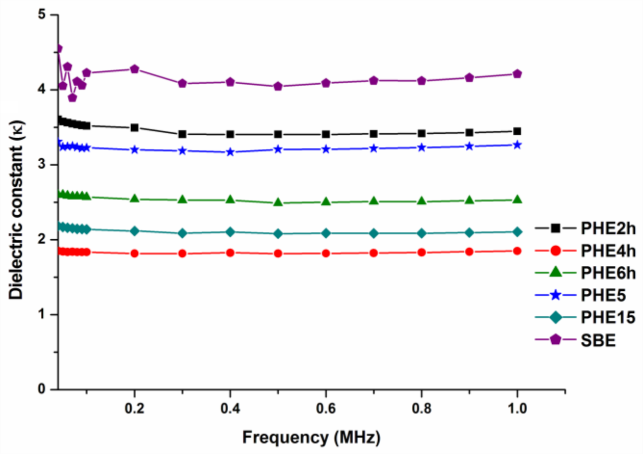


Figure 2A.7: Dielectric constants of PHE thermoset with the variation frequency

2A.3.7. Chemical resistance of PHE thermosets

The results of chemical resistance (percentage of weight loss) for the thermosets in different chemical environments after 30 days of exposure are shown in **Table 2A.4**. An excellent chemical resistance was shown by the thermosets in all the tested media, this is due to the compact and crosslinked structure of the hyperbranched thermosets.[20,21] No weight loss was found for PHE4h and PHE15 thermosets in any studied chemical environment. Only marginal weight loss was found for PHE2h, PHE6h and PHE5 thermosets in basic and acidic medium due to their less compact structure compared to the PHE4h and PHE15 thermosets. On the other hand, due to the lowest compact structure of SBE thermoset, the base and acid resistance were also found to be the lowest.

Table 2A.4: Weight loss (%) of PHE2h, PHE4h, PHE6h, PHE5, PHE15 and SBE thermosets in different chemical media after 30 days of exposure

Chemical medium	PHE2h	PHE4h	PHE6h	PHE5	PHE15	SBE
Aqueous NaOH (5%)	0.64	0	0.30	0.58	0	0.77
Aq. HCl (10%)	1.92	0	0.54	1.69	0	2.34
Aq. NaCl (20%)	0.09	0	0	0.08	0	0.11
Aq. EtOH (20%)	0	0	0	0	0	0
Water	0	0	0	0	0	0

2A.4. Conclusion

Thus, in this study industrially important low viscous hyperbranched epoxy resins were synthesized by a single step A_2 + B_4 polycondensation reaction with the variation of reaction time and amount of B_4 moiety. The structural architecture of the resins was successfully characterized by spectroscopic analyses. High tensile strength, good elongation at break, excellent toughness, high flexibility, good thermal stability, ultra low dielectric constant, excellent adhesive strength and outstanding chemical resistance were achieved for the poly(amido-amine) cured hyperbranched epoxy resin, obtained at 4 h reaction time with 10 wt% B_4 moiety. Thus, the unique hyperbranched architecture with unison of aromatic-aliphatic moieties can offer high performance tough epoxy thermosets to overcome the shortcoming of commercial epoxy thermoset. The studied thermoset can also find a unique position as an ultra low dielectric constant adhesive with low moisture absorption in microelectric industries.

2B. Triethanol amine based hyperbranched epoxy

2B.1. Introduction

In first chapter it is also mentioned that hyperbranched epoxy resins are still not explored widely in spite of their enormous significance over the conventional linear DGEBA based epoxy. This is mainly due to the limitation in conventional reactants as well as performance. In contrary almost all other hyperbranched polymers are well studied in different fields with their attractive attributes. Thus, to increase the spectrum of hyperbranched epoxy different branched generating units are tried to explore. Again, in sub-chapter 2A it is seen that the proper combination of aliphatic-aromatic moieties and unique hyperbranched structural architecture can address the shortcomings of conventional epoxy thermosets. In this chapter, therefore, another branched generating moiety namely triethanol amine is tried to use in order to develop another hyperbranched epoxy to address the shortcomings of DGEBA. The choice of this branch generating unit is due to low cost, easy availability as well as it is a high boiling viscous liquid. Furthermore, triethanolamine is also widely used as a B_3 type of branch generating moiety for the synthesis of different hyperbranched polymers as revealed by the literature.[28-30] In addition, an $A_2 + B_3$ is the most facile and popular approach for the synthesis of hyperbranched polymers including epoxy resins because of the easy availability of the reactants. Thus, in the present work tough high performance hyperbranched epoxy resins were synthesized using $A_2 + B_3$ polycondensation approach, where A_2 is the *in-situ* generated DGEBA and B_3 is an aliphatic triol, triethanol amine.

2B.2. Experimental

2B.2.1. Materials

The chemicals such as BPA, ECH, NaOH, HCl, KOH, maleic anhydride, triethylamine, oxalic acid, PAA hardener, NaCl, toluene, THF and EtOH were utilized for the same purpose as described in sub-chapter 2A, section 2A.2.1.

Triethanolamine (TEA) or tris(2-hydroxyethyl)amine (**Figure 2B.1**) is a viscous colorless triol with a tertiary amine moiety. Here it was used as the B_3 branch generating moiety for the synthesis of hyperbranched epoxy resin along with *in-situ* generated DGEBA. It was obtained from Merck, India and was used after vacuum drying. The molar mass, bp and density of TEA are 149.19 g/mol, 335.4 °C and 1.124 g/ml respectively.

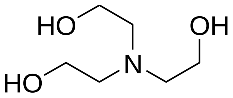
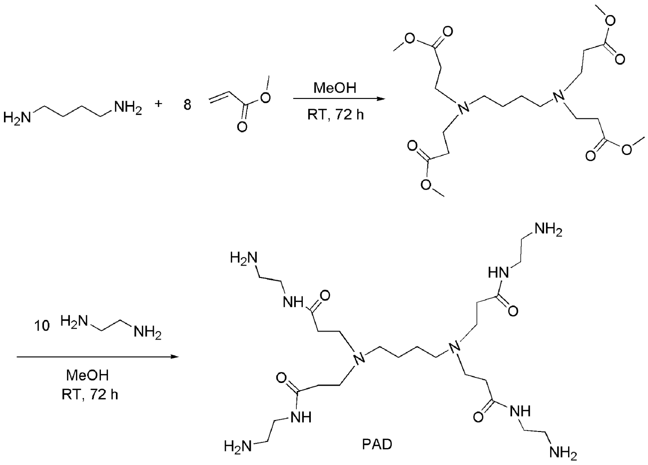


Figure 2B.1: Structure of TEA

Poly(amido-amine) dendrimer is a Michael addition product of acrylates and primary amines. Here the first generation of poly(amido-amine) dendrimer (PAD) was also used as a hardener combined with PAA for achieving of high performance room temperature cured hyperbranched epoxy thermoset. It was prepared by Michael addition reaction of methyl acrylate and aliphatic amines following the literature procedure as shown in **Scheme 2B.1**.[31] Methyl acrylate is a methyl ester of acrylic acid with molar mass, density and bp of 86.09 g/mol, 0.95 g/cc and 80 °C respectively. It was acquired from G. S. Chemical, India. The aliphatic amines like butane 1, 4-diamine (bp 158.6 °C, density 0.877 g/mL) and ethylene diamine (bp 116 °C, density 0.9 g/cc) were purchased from Sigma-Aldrich, Germany. The molar mass of the amines are 88.15 and 60.1 g/mol respectively.



Scheme 2B.1: Preparation of PAD by Michael addition reaction

Methanol (MeOH) solvent (bp 64.7 °C) was obtained from Merck, India and used after distillation. The molar mass and density of the solvent are 32.04 g/mol and 0.79 g/cc respectively. Here it was used as a solvent for Michael addition reaction to synthesize PAD.

2B.2.2. Characterization

The methods for the determination of physical properties such as epoxy equivalent, hydroxyl value, viscosity, etc.; and the characterization and instrumentation procedures are same as described in sub-chapter 2A, section 2A.2.2.

2B.2.3. Methods

2B.2.3.1. Synthesis of triethanol amine (TEA) base hyperbranched epoxy (TAHE) resins

These hyperbranched epoxy resins were synthesized by the same procedure as described for the synthesis of PHE resins, mentioned in sub-chapter 2A, section 2A.2.3.1. Here 10, 20 and 30 wt% (with respect to BPA) of TEA was taken in place of PE and the synthesized epoxy resins are coded as TAHE10, TAHE20 and TAHE30 respectively. The polycondensation reaction was carried out for 4 h and the yield of the resins was found ~97%.

2B.2.3.2. Curing study

TAHE resins were cured with 50 phr PAA hardener by same procedure as described for PHE resins in sub-chapter 2A, section 2A.2.3.3. Again, TAHE20 resin was also cured by the combined hardener of PAA and PAD to obtain room temperature cured high performance thermoset. In the combined hardener system 20 wt% of PAA was taken with 5, 10 and 15 wt% of PAD, separately and the cured thermosets are coded as PAD5, PAD10 and PAD15 respectively.

2B.3. Results and discussion

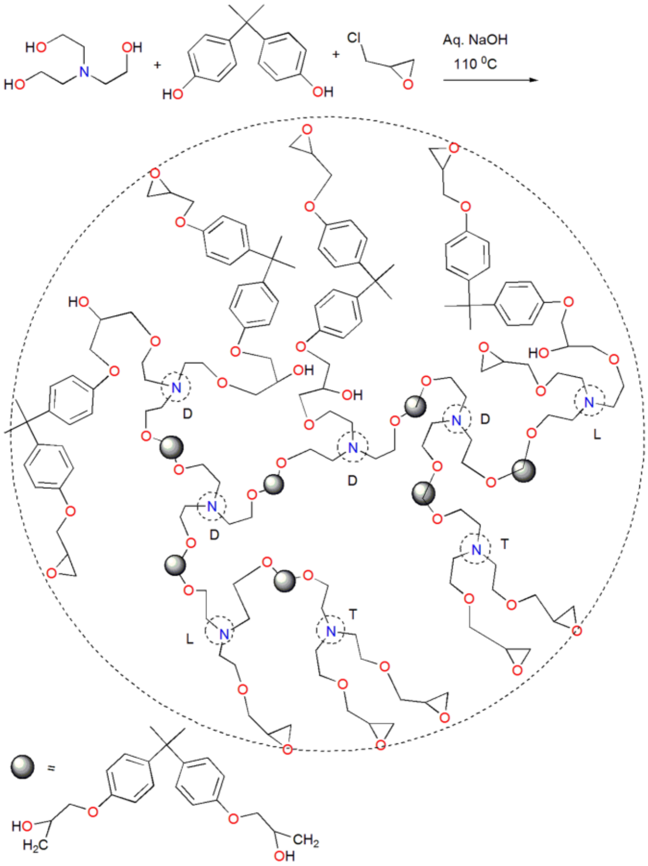
2B.3.1. Synthesis and characterization of TAHE resins

TAHE resins were synthesized by an $A_2 + B_3$ approach. Here also first A_2 monomer i.e., *in-situ* generated DGEBA was formed from the reaction mixture as the reactivity of BPA with ECH was higher than TEA due to higher acidity of phenolic proton as mentioned for PHE resins in sub-chapter 2A, section 2A.3.1. Then the hyperbranched epoxy resins were obtained by the reaction between DGEBA (A_2) and TEA (B_3) along with the reaction of ECH with free hydroxyl groups of TEA, as shown in **Scheme 2B.2**. The hyperbranched structures of one of the representative resin (TAHE10) of the synthesized epoxies were confirmed by NMR studies (**Figure 2B.2** and **Figure 2B.3**). The following structural features were observed from ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si,) spectrum at δ_H (ppm): 3.33 (CH of oxirane ring), 2.73 and 2.89 (CH_2 of oxirane ring), 3.72-3.74 (CH_2OH of TEA), 2.61 (NCH_2 of TEA), 1.62 (CH_3 of BPA), 6.82 and 7.11 (aromatic protons of BPA), 2.19 (-OH), 4.04 and 4.06 ($-OCH_2$) 4.18 (C*H*OH).[20-22] In ^{13}C NMR spectrum, δ_C (ppm, 400 MHz, $CDCl_3$, Me_4Si) were found at 45.95 (CH_2 of oxirane ring), 50.21 (CH of oxirane ring), 113.94, 127.83, 143.90 and 156.30 (aromatic carbon of BPA), 30.99 (CH_3 of BPA), 44.77 (C, isopropediene of BPA), 68.42 and 68.71(OCH_2) 69.87 (CHOH), 41.73 (NCH_2 of TEA), 59.68 (CH_2OH of monosubstituted TEA), 63.69 (CH_2OH of disubstituted TEA), 64.01 (CH_2OH of trisubstituted TEA).[20-22]

These monosubstituted, disubstituted and trisubstituted CH_2OH, carbons of TEA in TAHE resins were represented to terminal (T), linear (L) and dendritic (D) units respectively. From the integration values of these peaks the calculated DB (according to equation 2A.1) of TAHE10, TAHE20 and TAHE30 were found 0.60, 0.79 and 0.51 respectively. DB and the physical properties like epoxy equivalent, hydroxyl value, solubility, viscosity, etc. of the resin obtained at three different wt% of B_3 moiety (TAHE10, TAHE20 and TAHE30) are given in **Table 2B.1**. From this table it can be seen that the epoxy equivalent, hydroxyl value and viscosity of the resins were the lowest in TAHE20. This is due to the presence of an appropriate mole ratio (3:1) of A_2:B_3 reactants in TAHE20, which resulted in both a higher percentage of trisubstituted branched units, as well as higher chain end substitution to form terminal epoxides compared to other two hyperbranched epoxy resins. Thus, the DB was also the highest (0.79). Whereas the decrease of the mole ratio (2:1) of A_2:B_3 in TAHE30 resulted in the lowest trisubstituted internal branched units as well as the lowest terminal epoxides. Even at higher ratio (6:1) in TAHE10 the generation of branching units might be prohibited due to the congested nature of the B_3 monomer.[14,25] The viscosities of the resins were slightly higher than general hyperbranched polymers, which may be due to the presence of high inter- and intra-molecular attraction forces among the polar groups/linkages. As the resins contain a large number of functionalities like epoxy and hydroxyl groups as well as nitrogen linkage, the intra and inter-chain attractions are very high. The TAHE resins were also soluble in most of the common organic solvents such as MeOH, EtOH, acetone, THF, DMF, DMAc, DMSO, $CHCl_3$, CH_2Cl_2, toluene, xylene, ethyl acetate, etc. like PHE resins due to the globular shape and the presence of a large number of functionalities along with combination of aliphatic and aromatic moieties in the structures.

Table 2B.1: Physical properties of TAHE resins

Parameter	TAHE10	TAHE20	TAHE30
Epoxy equivalent (g/eq.)	424	358	599
Hydroxyl value (mg KOH/g)	119	102	144
Viscosity (Pa s) at 40 °C	25.61	22.80	30.61
Degree of branching (DB)	0.60	0.79	0.51



Scheme 2B.2: Synthetic scheme along with possible general structure of TAHE resins

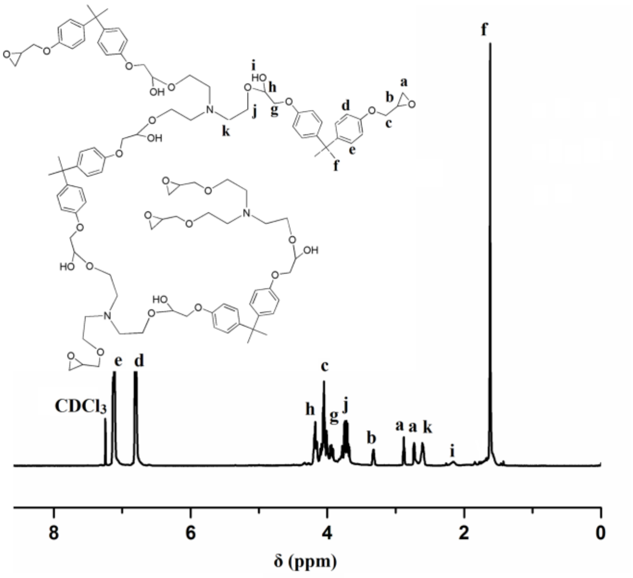


Figure 2B.2: ^{1}H NMR spectrum of TAHE10

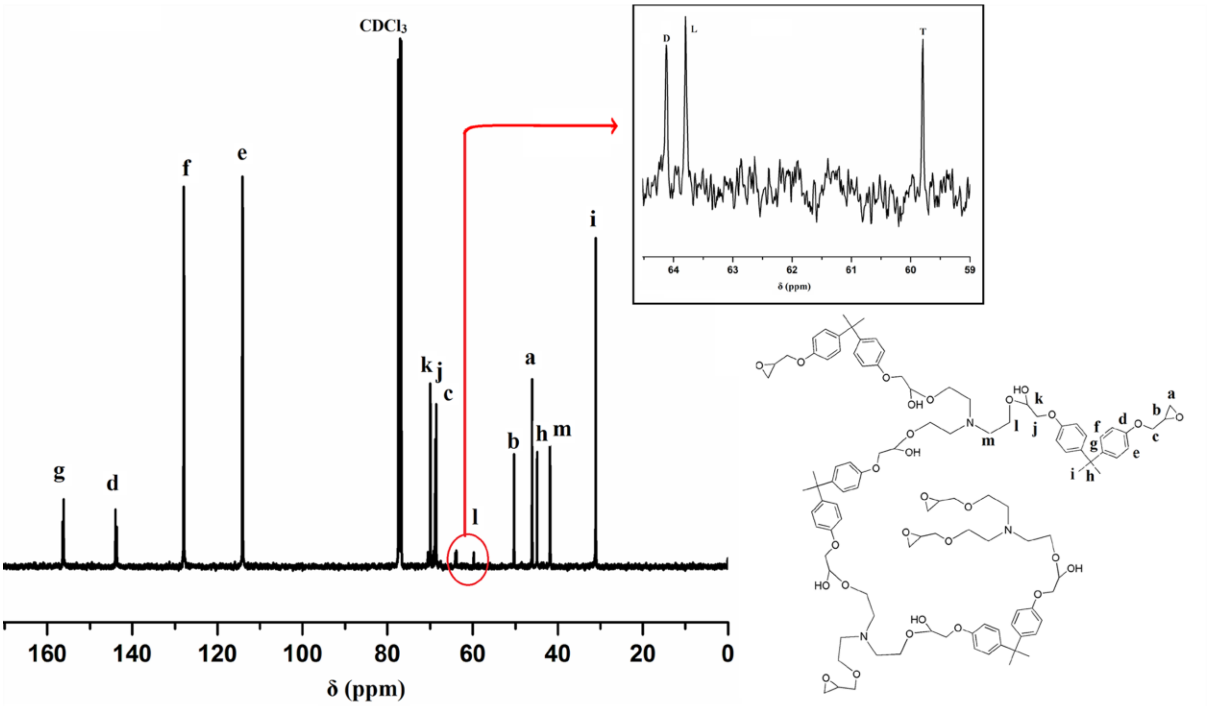


Figure 2B.3: ^{13}C NMR spectrum of TAHE10

2B.3.2. Curing study of TAHE resins

The curing of TAHE resins was carried out at 100 °C with PAA hardener for specified time to obtain the desired swelling values (**Table 2B.2**). From this table, it is found that TAHE20 has the lowest curing time as it has the highest number of epoxide groups. On the other hand TAHE30 has the highest curing time as it has the highest epoxy equivalent, i.e. the lowest number of epoxy groups and also contains the highest amount of the TAE moiety, which decreases the reactivity of the resin due to the presence of electronegative nitrogen atom.

Again, curing of TAHE20 resin was done at room temperature (25 °C) with the combined hardener system of PAA and PAD. The dendritic structure with end functionalities of both the epoxy and PAD facilitate to react rapidly with each other at room temperature. Thus, hyperbranched epoxy cured only with PAD resulted highly rigid and brittle thermoset (coded as OPAD). For combined hardener system PAD was taken 5, 10 and 15 wt% with constant 20 wt% of PAA in each case to optimize the amount of it for the best performance of the thermoset. The decrease in curing time of the thermoset at room temperature was observed with the increase of PAD content. PAD contains 4 primary amine and 4 amide groups. As certain amount of amide groups of PAD were also taken part in the curing reaction, so 10 wt% PAD was found to be the optimum value for curing of the hyperbranched epoxy (calculated from epoxy equivalent of TAHE20; and amine values of PAA and PAD).

Thus, PAD10 get the highest compact crosslinked structure and showed the lowest swelling value (**Table 2B.3**). Both PAD and hyperbranched epoxy have branched structures, so they formed some cyclic compact structure, after curing reaction as shown in **Figure 2B.4**.

Table 2B.2: Performance of TAHE thermosets

Parameter	TAHE10	TAHE20	TAHE30
Curing time at 100 °C (min)	75±2	70±2	85±5
Swelling value (%)	22±0.4	20±0.3	26±0.6
Tensile strength (MPa)	32±0.8	40 ± 1.0	26±0.5
Elongation at break (%)	37.5±2	21±0.8	45.5±1.5
Toughness (MPa)	856	570	850
Scratch hardness (kg)	8.5±0.2	9.0±0.5	8.0±0.5
Impact strength (cm)	>100	>100	>100
Bending dia. (mm)	<1	<1	<1
Adhesion strength (M-M) (MPa)	1987	2662	1638
Adhesion strength (W-W) (MPa)	2224	2680	2056
Initial degradation temperature (°C)	260	267	255

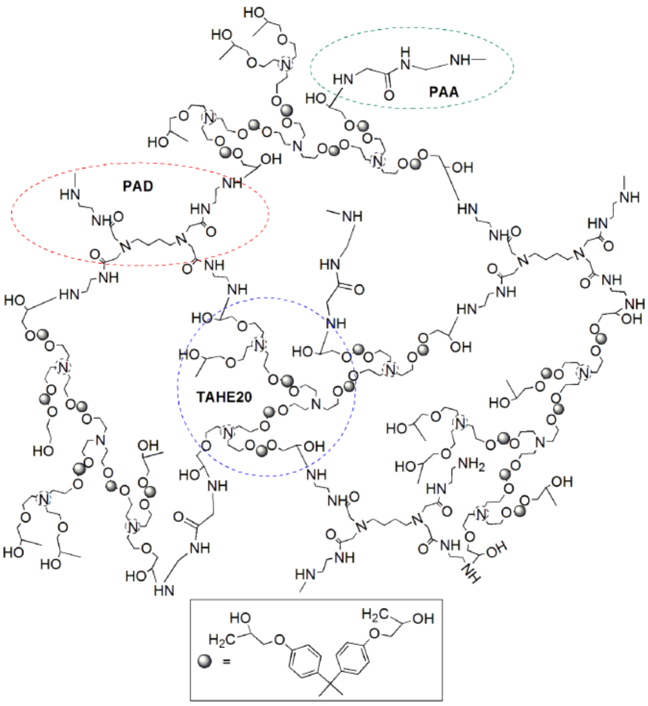


Figure 2B.4: Curing of TAHE20 with combined hardener of PAA and PAD

2B.3.3. Mechanical properties of TAHE thermosets

The stress-strain profiles with toughness of TAHE10, TAHE20 and TAHE30 are shown in **Figure 2B.5**. The toughness value of hyperbranched epoxy thermosets is defined by the integrated area under the stress-strain curve, similar to PHE thermosets. These values obtained for all the three TAHE thermosets were also more than SBE thermoset like PHE thermosets as reported in sub-chapter 2A. SBE thermoset possessed adequate strength but was brittle in nature as its elongation at break value was very low (5%). Whereas, these hyperbranched epoxy thermosets possess both high tensile strength, as well as comparatively higher elongation at break and thus, these are tough materials. This is due to the presence of both aromatic and aliphatic moieties in the structure as well as unique highly branched architecture, which increases the free volume defined as the unoccupied space between molecules in the three-dimensional network (because of the steric effects associated with the large volume) as described in sub-chapter 2A and supported by literature.[17] Thus, the stress-strain curves for these thermosets are like those of ductile materials. As the area under the stress-strain curve of the thermosets was high, more energy was required to fracture the materials. The variations of tensile strength and elongation at break of TAHE10, TAHE20 and TAHE30 are given in **Table 2B.2**. The highest tensile strength and the lowest elongation at break in TAHE20 were due to the presence of the highest numbers of epoxy groups, which resulted in the highest crosslink density with the highest compact structure. Impact resistance test also determines the toughness of the materials and higher impact strength resulted in higher toughness. As the hyperbranched epoxy thermosets possess both aromatic and aliphatic moieties, adequate crosslink density (swelling values are given in **Table 2B.2**) and unique structural architecture, they exhibited high toughness, scratch hardness and impact resistance (**Table 2B.2**) similar to PHE thermosets. The thermosets absorbed the highest limit of impact energy (100 cm, limit of the instrument) because of the presence of flexible moieties (namely aliphatic moieties of epoxy as well as the hardener and flexible ether linkages) in the structure as described in sub-chapter 2A for PHE thermosets and supported by literature.[17] The flexibility of the thermosets was determined by the bending test with the help of a mandrel. The thermosets were highly flexible as they bent up to the lowest diameter of the mandrel (1 mm) without any damage or fracture. The high flexibility of the thermosets was due to the presence of the aliphatic moiety and ether linkages in the structures of the resins as well as PAA hardener that contains flexible aliphatic hydrocarbon which offers the plasticizing effect to the thermosets.

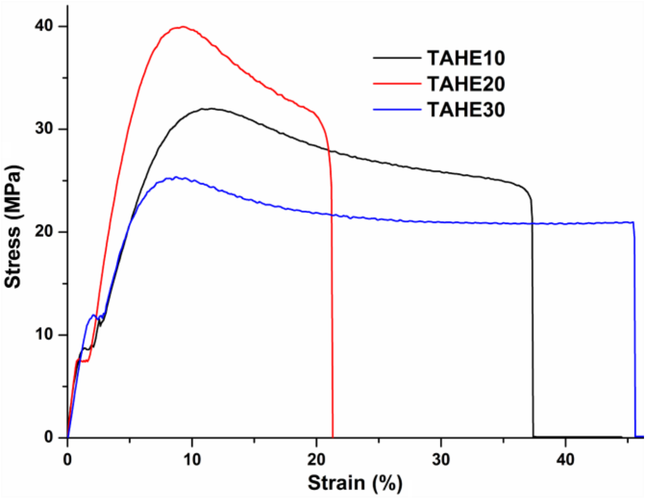


Figure 2B.5: Stress-strain profiles of TAHE thermosets

Again, the combined hardener of PAA and PAD cured TAHE20 thermosets exhibited very high tensile strength with little lower elongation at break (**Table 2B.3**). The dose dependent tensile strength was found on addition of PAD and the value enhanced with the increase of this hardener content. This is due to the formation of compact, rigid and cyclic thermoset of hyperbranched epoxy with PAD as shown in **Figure 2B.4**. Thus, the values of elongation at break and toughness of the thermosets (as determined by integrating the area under stress-strain curves) were decreased with the addition of PAD. However, these values were much higher compared to SBE thermoset (given in sub-chapter 2A, Table 2A.3), because of the hyperbranched architecture of the studied epoxy. The thermosets exhibited very high scratch hardness for their compact crosslinking structure, but the slight decrease in impact resistance with the addition of PAD is due to the formation of rigid cyclic crosslinked structure. PAD10 exhibited the overall best mechanical properties among the combined hardener cured thermosets because of the highest compactness of the crosslinked structure as described in the curing study. OPAD exhibited low scratch hardness as well as low impact resistance (**Table 2B.3**) due to high brittleness character. Thus, it was not possible to obtain the desired film for measurement of tensile strength and elongation at break for this thermoset.

2B.3.4. Adhesive strength of TAHE thermosets

TAHE thermosets exhibited very high adhesive strength (**Table 2B.2**). This is due to the strong interactions of polar -OH, ether and epoxy groups along with the unique branched structural architecture with terminal epoxide groups as well as the polar linkages of the PAA hardener with the wood substrates.[21] Due to the presence of the highest number of epoxide groups in the structure and the high degree of branching TAHE20 showed the highest adhesive strength. The high adhesive strength with the metal substrate is mainly due to physical interlocking with the flexible resins and due to interactions with the strain oxirane ring of the epoxy resin.[21]

In case of combined hardener cured thermosets the adhesive strength (lap shear tensile strength) of TAHE20 increased tremendously with the addition of PAD (**Table 2B.3**). This is due to increase of polar functionalities (nitrogen and oxygen containing groups) along with the secondary hydroxyl groups in the system on addition of PAD. Thus, the polar-polar interactions increase with the cellulosic wood substrate whereas for metal substrate physical interlocking occurs with the hyperbranched epoxy.

Table 2B.3: Performance for the combined hardener of PAA and PAD cured TAHE20 thermosets

Parameter	PAD5	PAD10	PAD15	OPAD
Tensile strength (MPa)	51±2.0	70±1.2	62±1.5	-
Elongation at break (%)	19±0.4	14±0.4	16±0.5	-
Toughness (MPa)	396	438	400	-
Scratch hardness (kg)	9.0±0.2	>10.0	9.5±0.5	5.0±0.5
Impact strength (cm)	95±1	95±2	90±4	60±1
W-W, lap-shear tensile strength (MPa)	>3941	>4226	>4029	>4256
M-M, lap-shear tensile strength (MPa)	5688±7	6064±11	5964±6	7257±12
Dielectric constant at 1 MHz (at 20 °C)	3.22	3.26	3.32	-
Dielectric loss at 1 MHz (at 20 °C)	0.012	0.013	0.014	-
Moisture absorption at 25 °C (%)	0.43	0.11	0.19	0.08
Thermal stability (°C)	256	274	266	-

2B.3.5. Thermal stability of TAHE thermosets

TGA thermograms (**Figure 2B.6**) of hyperbranched epoxy thermosets showed that the thermal stabilities of TAHE10, TAHE20 and TAHE30 were adequately high, as the initial decomposition temperatures (at 5% weight loss) were > 250 °C. From the initial degradation temperature (**Table 2B.2**), it was found that TAHE20 exhibited the highest thermal stability due to the highest crosslinked compact structure.[20,21] The thermosets were degraded mainly by two stage patterns, where the first step is related to the degradation of the aliphatic moieties (~300 °C) and the second stage for the degradation of the aromatic moieties (~400 °C).[20] As all the thermosets have almost same structural units, their degradation patterns were almost the same.

The thermal stability of TAHE20 thermosets after curing with combined hardener system is shown in **Figure 2B.7**. The initials degradation temperatures are given in **Table 2B.3**. The thermal stability of the thermosets was remained same with the addition of PAD. This is due to the similar chemical linkages of both the hardeners. In **Figure 2B.7**, PAD5 shows slightly lower thermostability because of its lower compactness of the crosslinked structure due to the presence of low amount of hardener. Here also in TGA thermograms the initial degradation temperature of the thermosets (~300 °C) is due to the degradation of aliphatic moieties and ether linkages whereas the second degradation (~450 °C) is due to the aromatic moieties and the amide linkages.

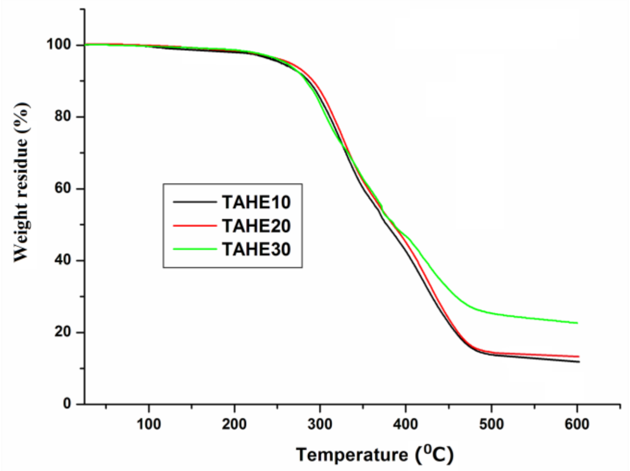


Figure 2B.6: TGA thermograms of TAHE thermosets

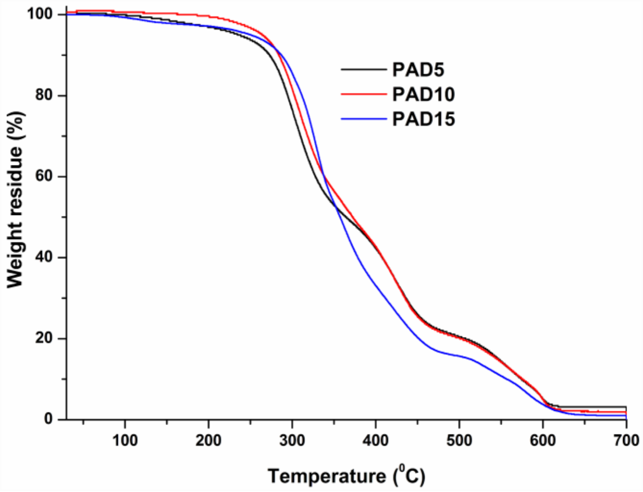


Figure 2B.7: TGA thermograms of combine hardener cured TAHE20 thermosets

2B.3.6. Chemical resistance of TAHE thermoset

The results of chemical resistance of TAHE thermosets in different chemical environments are given in **Table 2B.4**. The thermosets showed excellent aqueous alcohol resistance as well as very good aqueous alkali and acid resistance due to the presence of crosslinked compact hyperbranched structures and strong chemical linkages.[20,21] With the decrease of compactness in TAHE10 and TAHE30, the alkali and acid resistance decreased, though the decrements are marginal.

Table 2B.4: Weight loss (%) of TAHE thermosets in different chemical media after 30 days of exposure

Chemical medium	TAHE10	TAHE20	TAHE30
Aq. HCl (10%)	0.96	0.90	1.03
Aq. NaOH (5%)	1.72	1.48	2.38
Aq. NaCl (15%)	0.54	0.24	0.77
Aq. EtOH (20%)	0	0	0
Pure water	0	0	0

The chemical resistance of TAHE20 thermosets cured with combined hardener system in different chemical environments is shown in **Table 2B.5**. They exhibited excellent chemical resistance even in strong alkali and acid media and no change in aqueous EtOH as well as in fresh water was observed. This is only due to the high compact structure and strong chemical linkages.[20,21] The highest chemical resistance was found in PAD10 among the combined hardener system cured thermosets because, it has the highest crosslinked and compact structure.

Table 2B.5: Weight loss (%) of TAHE20 thermosets cured with combined hardener system in different chemical media after 30 days of exposure

Chemical medium	PAD5	PAD10	PAD15	OPAD
Aq. NaOH (5 %)	1.77	1.24	1.71	1.13
Aq. HCl (10%)	1.04	0.50	0.79	0.38
Aq. NaCl (15%)	0.34	0.25	0.27	0.12
Aq. EtOH (20)	0	0	0	0
Pure water	0	0	0	0

2B.3.7. Electrical property of TAHE20 thermoset

The variation of dielectric constant with frequency of TAHE20 thermosets cured with PAA and combined hardener system is shown in **Figure 2B.8**. The dielectric constant slightly increased with the increase of PAD content because of the increment of total polarity of the thermoset as PAD contains more nitrogen and oxygen containing groups in its structure. Generally epoxy thermoset exhibits dielectric constant slightly higher compared to the other insulating materials because of the generation of secondary hydroxyl groups after curing and also hydroxyl groups in the structure.[32] But here dielectric constant was low compared to SBE thermoset due to the branched unique structure of the epoxy which restricted the molar polarization at higher frequency as well as increased the free volume between the molecules as described in sub-chapter 2A, section 2A.3.6 as well as in literature.[25-27] Because of the high compact crosslinked structure moisture absorption was also very low, which is advantageous for advance electrical applications.

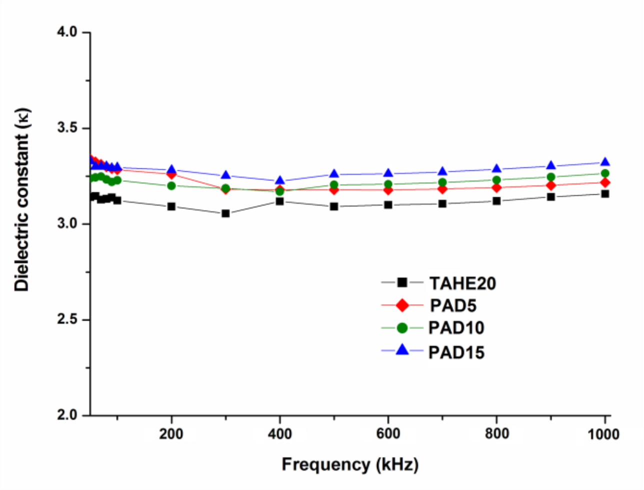


Figure 2B.8: Dielectric constants of TAHE20 thermosets cured with combined hardener system with the variation of frequency

2B.4. Conclusion

Thus, high performance hyperbranched tough epoxy thermosets with excellent adhesive strength and good thermostability were obtained in this study. The industrially important hyperbranched epoxy resins with varying compositions were synthesized by a single step $A_2 + B_3$ polycondensation reaction. The structure of the synthesized hyperbranched epoxy resin was characterized through different analytical and spectroscopic studies. The influence of the B_3 moiety on the performance of the thermosets was noticeable. The overall results indicate that thermosets can be used as a high performance tough epoxy thermoset. Thus, the studied hyperbranched epoxy thermoset could be produced commercially on an industrial scale, particularly from the point of view of its cost performance ratio.

Again, combined hardener cured TAHE20 epoxy has high potential to be used as a room temperature cured high performance epoxy. The resulted thermosets exhibited high tensile strength, good thermal stability, excellent adhesive strength and low dielectric constant. Thus, this low dielectric thermoset might be potentially used for electronic equipments operated under high frequency, electrical packaging, microelectronic devices, etc.

2C. Hyperbranched polyester polyol based epoxy

2C.1. Introduction

From the above two sub-chapters it is clear that the nature of branch generating unit has strong influence on ultimate property of hyperbranched epoxy thermoset. However, such petrochemicals based hyperbranched epoxy as well as commercial epoxy thermosets are suffering from non biodegradability due to absence of sufficient degradable or hydrolysable moieties in their structures. Further, literature supports that vegetable oil based polymers or polymers with ester backbone exhibited excellent biodegradability due to the presence of hydrolysable ester linkages.[33-36] Again, the uses of renewable resources in different fields of application of polymers are increasing day by day because of worldwide improved environmental concerns and depletion of crude oil pool. In addition to above, if the resources are naturally renewable, there will be no scarcity of feed stock as well as they are environment friendly. A large numbers of literature support the uses of different vegetable oils for the synthesis of different polymers including epoxy resin.[35-40] Among the different vegetable oils, castor oil (*Ricinus communis*) is very interesting as it is available easily in large quantity, relatively low cost and has fascination fatty acid composition.[35-37] The oil has approximately 85-95% recinoleic acid which is a 18-carbon containing monounsaturated fatty acid with a hydroxyl functional group on 12th position, as the major component. The presence of hydroxyl functional group in ricinoleic acid imparts polarity to the castor oil.[37] Thus, in order to develop biodegradable high performance epoxy along with toughness, a hyperbranched epoxy was designed from castor oil based polyester polyol. The toughness and biodegradability may be incorporated into the epoxy by blending with polyester resin.[6,7] However, the processing difficulties and the decrement of other mechanical properties are the major problems in that case.

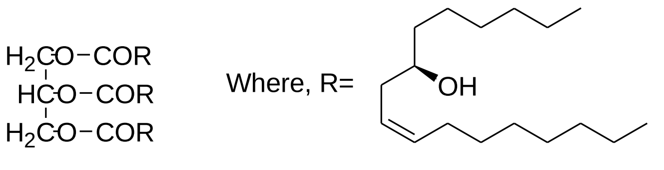
Therefore, in the present work a biodegradable tough hyperbranched epoxy was synthesized by an $A_2 + B_n$ polycondensation reaction between *in-situ* generated DGEBA and castor oil-based hyperbranched polyester polyol. The synthesized epoxies were characterized and properties were evaluated for the poly(amido-amine) cured thermosets.

2C.2. Experimental

2C.2.1. Materials

The chemicals like BPA, ECH, NaOH, HCl, KOH, maleic anhydride, triethylamine, oxalic acid, PAA hardener, NaCl toluene, THF and EtOH are utilized for the same purpose as described in sub-chapter 2A (section 2A.2.1) and 2B (section 2B.2.1).

Castor oil (*Ricinus communis*) is a vegetable oil, which contains different types of unsaturated fatty acids such as recinoleic acid (85-95%), oleic acid (2-6%) and linoleic acid (1-5%). So, approximately 90% of fatty acid chain of the oil contains ricinoleic acid which is a 18 carbon atoms containing monosaturated fatty acid with a hydroxyl functional group on 12th position of the chain (**Figure 2C.1**). Here it was used for the preparation of hyperbranched polyester polyol (HBPP) form its monoglyceride. Castor oil was collected from BD Pharmaceutical Works Pvt. Ltd., India and was used after measuring the acid and hydroxyl values which were found to be 3.7 mg KOH/g and 157 mg KOH/g respectively. It is a pale yellow liquid with bp and density of 313 °C and 0.96 g/cc respectively.



Castor oil

Hydrocarbon part of ricinoleic acid

Figure 2C.1: Structure of castor oil

Glycerol (**Table 1.1**, Chapter 1) is a colorless viscous liquid with three hydroxyl functional groups. Here it was used as a reactant for the preparation of monoglyceride of castor oil. It was obtained from Rankem, India and used after vacuum drying. The molar mass, density and bp of glycerol are 92.09 g/mol, 1.26 g/cc and 290 °C respectively.

2,2-Bis(hydroxyl methyl) propionic acid (bis-MPA) (**Figure 2C.2**) is one of the most widely used AB_2 type monomer for the synthesis of hyperbranched polymers and dendrimers. Here it was utilized along with monoglyceride of castor oil to synthesize hyperbranched polyester polyol (B_n) core moiety for hyperbranched epoxy. It was procured from Alfa Aesar, UK. The mp and molar mass of bis-MPA are 190 °C and 134.13 g/mol respectively.

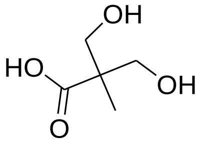


Figure 2C.2: Structure of bis-MPA

Sodium methoxide (NaOMe) is a basic compound with molar mass of 54.02 g/mol. It is a white powder with mp 127 °C. NaOMe was prepared from super dry MeOH and metallic sodium. Here it was used as a catalyst for the preparation of castor oil monoglyceride.

p-Toluene sulfonic acid (PTSA) (**Figure 2C.3**) is a strong organic acid. It is mainly used as a catalyst in organic synthesis. Here it was used as a catalyst for esterification reaction. PTSA was purchased from GS Chemicals, Mumbai, India.

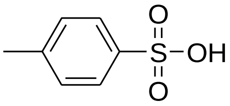


Figure 2C.3: Structure of PTSA

MeOH solvent was obtained from Merck, India and used after distillation as described in previous sub-chapter. Here it was used for the preparation of NaOMe. The super dry methanol was used for obtaining NaOMe.

2C.2.2. Characterization

The methods for the determination of physical properties such as epoxy equivalent, hydroxyl value, viscosity, etc.; and other characterizations and instrumentation procedures are same as described in the sub-chapter 2A, section 2A.2.2. The acid value of the castor oil and hyperbranched polyester polyol (HBPP) was measured by the standard procedure as described in the first chapter. The chemical resistance test of HBPE thermosets was done by the same method as reported for PHE thermosets. However, the effect of alkali solution on the thermosets was done with slight lower concentration of NaOH solution (2 wt%) due to presence of alkali hydrolysable ester groups in HBPE thermosets.

2C.2.3.Methods

2C.2.3.1. Synthesis of hyperbranched polyester polyol based epoxy (HBPE) resins

HBPE resins were synthesized by two steps process. In the first step, the hyperbranched polyester polyol (HBPP) was synthesized from monoglyceride of castor oil. Then HBPE resins were synthesized in the second step by polycondensation reaction of HBPP with BPA and ECH.

Synthesis of HBPP from castor oil

HBPP was synthesized by a two-step method from castor oil. The first step was alcoholysis process in which monoglyceride of castor oil was prepared by reaction of castor oil with glycerol in 1:2 mole ratio at 220 °C using NaOMe as the catalyst (0.05 wt% with respect to oil). The reaction was carried out for 1.5 h and the formation of the product was confirmed by checking the solubility in MeOH at regular interval of time. The reaction was stopped when the reaction product was completely soluble in MeOH at room temperature.[38,41,42]

In the second step, esterification reaction was carried out between monoglyceride and bis-MPA in 1:2 mol ratio at 140 °C using PTSA as the catalyst (0.1wt% with respect to monoglyceride). Briefly, an amount of 12 g of monoglyceride was taken in a three necked round bottom flask equipped with a mechanical stirrer, a thermometer and a nitrogen gas inlet. An amount of 8.64 g of bis-MPA and 0.012 g PTSA were added into the above flask and stirred for about 2 h at 140 °C. Formation of the product was confirmed by determination of acid value of the reaction mixture, which was found to be decreased with time as the reaction proceeded.[38,42] The reaction was stopped when the acid value was found to be below 15.[38,42] The synthesized resin was washed and dried by same procedure as described for PHE in sub-chapter 2A (section 2A.2.3.1). The yield of the final product was about 98% (19.12 g).

Synthesis of HBPE

HBPE resins were synthesized by the polycondensation reaction of HBPP with BPA and ECH at 110 °C for 4 h using aqueous NaOH as the catalyst by same way as described for PHE and TAHE resins in the previous sub-chapters. In a typical procedure, HBPP (2.35 g, hydroxyl value 420 mg KOH/g), BPA (8.03 g, 0.035 mole) and ECH (13.02 g, 0.14 mole) were taken in a two necked round bottom flask equipped with a water condenser and a dropping funnel. The reaction mixture was stirred with a magnetic stirrer. To this reaction mixture a 5 N aqueous solution of NaOH (3.52 g, 0.088 mol) was added very slowly from a dropping funnel (1-1.5 h). After 4 h, the reaction was stopped and allowed to settle in a separating funnel and the aqueous layer was separated out from the desired organic layer. Then the organic layer was washed and dried by similar way as elaborated for PHE and TAHE resins to remove excess ECH and entrapped water. The final product was a viscous sticky transparent light yellow mass with yield 13.26 g (98%). The synthesized resin was coded as HBPE2 (2.0 mol of BPA per hydroxyl group of HBPP). Similarly, HBPE1 and HBPE3 (1.0 and 3.0 mol of BPA per hydroxyl group of HBPP, respectively) were synthesized and found approximately same amount of yield. The amount of polyester (HBPP) was taken 30%, 20% and 10% (approximately) in weight respect to the synthesized resin of HBPE1, HBPE2 and HBPE3 respectively.

2C.2.3.2. Modification of SBE resin by HBPP (MSBE)

BPA based conventional linear epoxy (SBE) was prepared by the same method as described in sub-chapter 2A, section 2A.2.3.2. Then, SBE was physically modified with HBPP for comparison purpose. A 10 wt% of HBPP (with respect to SBE) was mixed homogeneously with SBE resin in the presence of little amount of THF (to facilitate mixing) under stirring at room temperature to obtain the modified product. The physically modified SBE was coded as MSBE.

2C.2.3.3. Curing of the resins

HBPE and MSBE resins were cured with 50 wt% of PAA hardener by the same procedure as described for the PHE resins in sub-chapter 2A, section 2A.2.3.3.

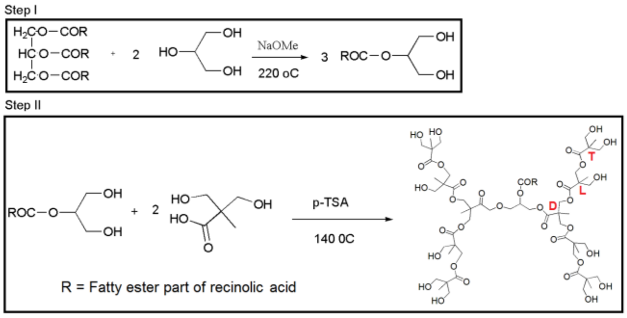
2C.2.3.4. Biodegradation study

Biodegradation study of HBPE and SBE thermosets was done with the help of McFarland Turbidity method using *Pseudomonas aeruginosa* as the bacterial strain.[43] The crude oil contaminated soil of Assam, India was used to isolate the bacterial species. The used salt medium consisted of main constituents (g/L): $(NH_4)_2SO_4$ (1.0), KH_2PO_4 (13.3), $MgSO_4$ (1.3), citric acid (1.7); trace element 10 mL of (g/L): $FeSO_4•7H_2O$ (10), $ZnSO_4•7H_2O$ (2.25), $CuSO_4•5H_2O$ (1), $MnSO_4•5H_2O$ (0.5), $CaCl_2•2H_2O$ (2.0), $Na_2B_4O_7•10H_2O$ (0.23), $(NH_4)_6MO_7O_{24}$ (0.1), HCl (0.1 N, to adjust the pH 7) and dextrose (10 g). 50 mL aliquot of this mineral salt medium was dispensed in a few 100 mL conical flasks. Each flask with polymer films with dimension $2 \times 2 \times 0.03$ cm^3 was taken and the flasks were incubated at 37 °C for 60 days. One of these flasks containing mineral salt medium without any bacterium was used as the control. Increase in turbidity of the culture medium indicates the growth of bacteria in the medium. The optical density (OD) or absorbance of the bacterial growth was calculated at interval of every 15 days at λ_{max} 600 nm. The weight loss (%) of degraded films was measured after 60 days of exposure to the bacterial strain. The experiment was performed in triplicate. The biodegradation study of SBE thermoset was also done by same procedure for comparison purpose.

2C.3. Results and discussion

2C.3.1. Synthesis and characterization of HBPP resin

HBPP was synthesized by a two steps reaction viz. glycerolysis of the oil followed by polycondensation with bis-MPA as shown in **Scheme 2C.1**. In the first step, castor oil undergoes catalytic alcoholysis reaction with glycerol at elevated temperature using NaOMe as a catalyst to obtain the desired monoglyceride. While, the second step was also a catalytic esterification reaction between monoglyceride and bis-MPA in the presence of PTSA as the catalyst and the desired HBPP was obtained. The use of catalyst in both the steps resulted in high yield (~98%) with less time (2 h). The hydroxyl value of HBPP is given in **Table 2C.1**. The acid value of HBPP was found 11.49 mg KOH/g. Higher acid value and hydroxyl value of the synthesized HBPP compared to the castor oil are due to the presence of polyester linkage and terminal bis-MPA moiety along with secondary -OH of ricinoleic acid moiety in the HBPP structure. HBPP was found to be soluble in most of the common organic solvents like MeOH, EtOH, acetone, THF, DMF, DMAc, DMSO, $CHCl_3$, toluene, xylene, ethyl acetate, etc. supporting the hyperbranched nature of the synthesized polyol. The solubility in hydrocarbon solvents like toluene and xylene confirmed the presence of hydrophobic fatty acid chain in the HBPP structure. The structure of HBPP was confirmed by FTIR and NMR studies. In FTIR spectrum of HBPP (**Figure 2C.4**), the following stretching frequencies (ν_{max}/cm^{-1}) were observed at 3471 (O-H), 2929 (C-H), 1728 (C=O) and 1460 (C-O).[22,40,42] The following structural features were found from ^{1}H NMR spectrum (**Figure 2C.5a**) of HBPP, (400 MHz, $CDCl_3$, Me_4Si) at δ_H (ppm): 4.8 (OH), 0.9-2.3 (fatty acid chain protons, terminal CH_3 and internal CH_2), 1.1 (CH_3 of bis-MPA unit), 3.6 (CH attached with OH), 3.7 (CH_2 attached with OH), 4.2 (CH_2 adjacent to the carbonyl group), 5.4 (central CH of monoglyceride) and 5.5 (CH=CH).[22,40,42] In ^{13}C NMR spectrum (**Figure 2C.5b**) δ_C, ppm were observed at 174 (carbonyl carbon), 14 (CH_3, bis-MPA unit), 18-36 (fatty acid chain carbons), 47-50 (mono-substituted, di-substituted and tri-substituted central carbon of bis-MPA unit), 64 (CH_2 attached with OH), 68 (CH_2 next to the carbonyl group), 72 (CH attached with OH), 74 (central carbon of monoglyceride), 125 and 133 (CH=CH).[22,40,42] From the ^{13}C NMR spectrum of HBPP the monosubstituted (T), disubstituted (L) and trisubstituted (D) central carbon of bis-MPA was observed at δ = 46.73, 48.67 and 49.90 ppm respectively. From the intensity values of these peaks the degree of branching (DB) value of the polyester polyol was calculated (according to the equation 2A.1) and found to be 0.63.



Scheme 2C.1: Synthesis of HBPP resin

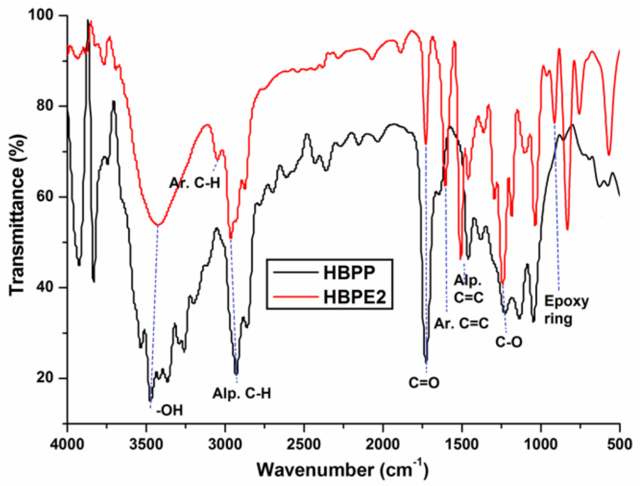


Figure 2C.4: FTIR spectra of HBPP and HBPE2 resins

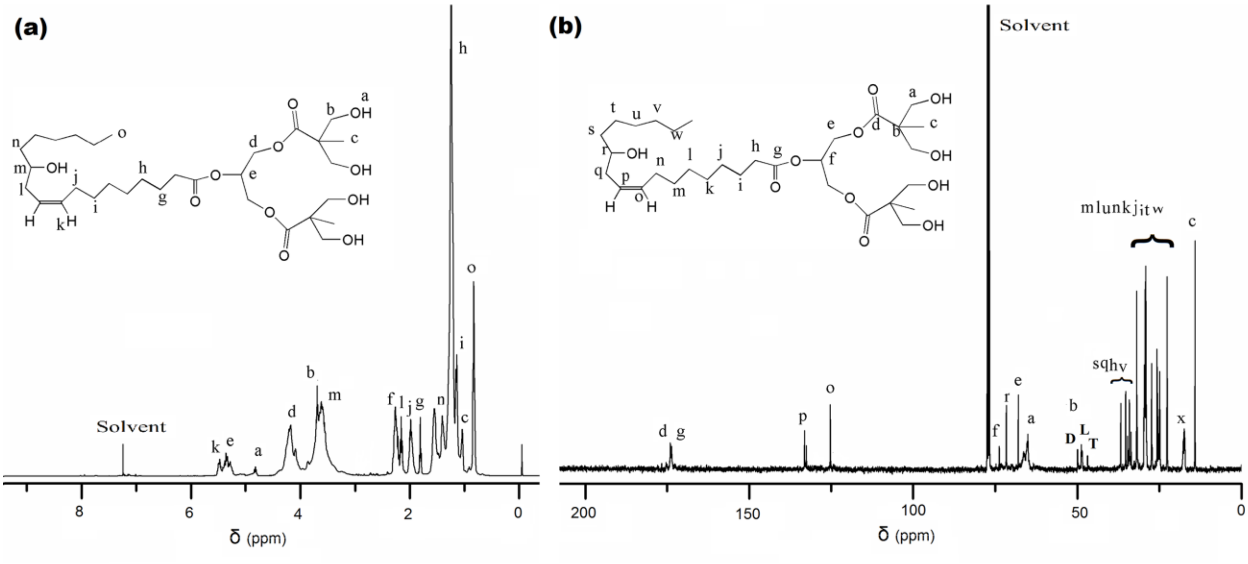
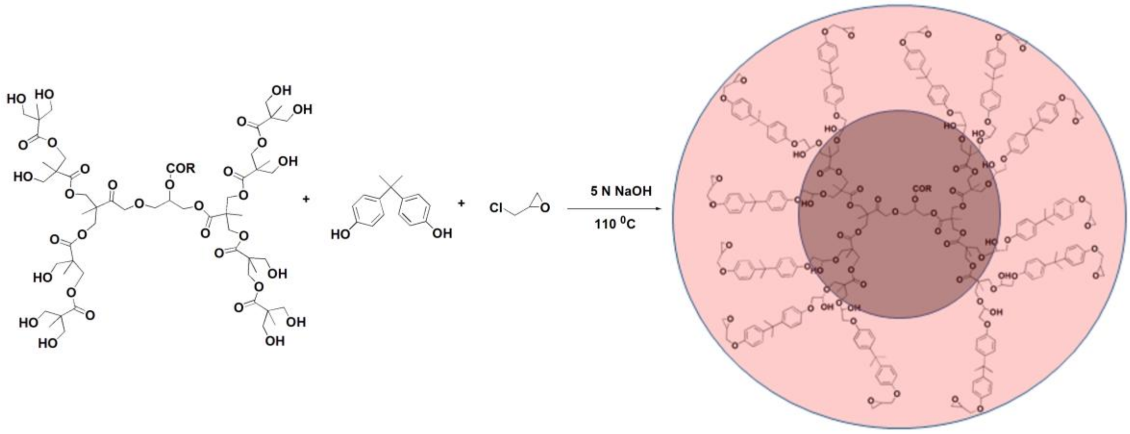


Figure 2C.5: (a) ^{1}H NMR and (b) ^{13}C NMR spectra of HBPP resin

2C.3.2. Synthesis and characterization of HBPE resins

HBPE resins were synthesized by the polycondensation reaction between *in-situ* prepared DGEBA and HBPP. First DGEBA was formed in the reaction mixture as the reactivity of

BPA with ECH was higher than HBPP due to higher acidity of phenolic proton as described in sub-chapter 2A and 2B. Then the hyperbranched epoxy resin was obtained by the reaction between DGEBA and HBPP as shown in **Scheme 2C.2**. The hyperbranched epoxy resin was also soluble in most of the common organic solvents like MeOH, EtOH, acetone, THF, DMF, DMAc, DMSO, $CHCl_3$, toluene, xylene, ethyl acetate, etc. The epoxy equivalent and hydroxyl value of HBPE1, HBPE2 and HBPE3 were given in **Table 2C.1**. The structure of the hyperbranched epoxy was confirmed by FTIR and NMR spectroscopic studies. In FTIR spectrum of representative resin, HBPE2 (**Figure 2C.4**), the following stretching frequencies were observed, ν_{max}/cm^{-1}: 3428 (O-H), 3049 (Ar. C-H), 2964 (Aliph. C-H), 1730 (C=O), 1605 (Ar. C=C), 1505 (Aliph. C=C of recinolic acid), 1459 (C-O of ester linkage), 1241 (C-O of ether linkage) and 914 (epoxy ring).[20-22,40,42] The following structural features for HBPE2 were found from ^1H NMR spectrum (**Figure 2C.6a**) (400 MHz, d_6-DMSO, Me_4Si) at δ_H, ppm: 3.3 (CH of oxirane ring), 2.6 and 2.8 (CH_2 of oxirane ring), 3.9 (CH_2 next to oxirane ring), 6.8 (aromatic protons of BPA), 7.1 (aromatic protons of BPA), 1.6 (CH_3 of BPA), 3.8 (CH_2 next to BPA), 4.3 (CH attached with OH), 4.9 (OH), 3.6 (CH_2 of polyester linkages attached with DGEBA moiety), 1.2 (CH_3 of bis-MPA), 4.1 (CH_2O attached with carbonyl group), 5.3 (CH attached with monoglyceride fatty ester), 5.5 (HC=CH of fatty ester), 3.5 (CH attached with OH of fatty ester) and 0.8-2.2 (monoglyceride fatty ester CH_2 and CH_3 protons).[20-22,40,42] In ^{13}C NMR spectrum (**Figure 2C.6b**) δ_C, ppm: 174 (carbonyl carbon), 14 (CH_3 of bis-MPA), 64 (CH_2O of bis-MPA), 46-48 (central carbon of bis-MPA), 71-72 (CH_2O and CHO of monoglyceride), 20-30 (chain carbons of fatty ester), 116 (HC=HC of fatty ester), 44 and 50 (oxirane ring carbons), 31, 42, 114, 128, 144 and 157 (aromatic BPA carbons) and 68-70 (carbon attached with -OH and ether linkages).[20-22,40,42]



Scheme 2C.2: Synthesis of hyperbranched epoxy from HBPP

Table 2C.1. Physical properties of HBPE1, HBPE2, HBPE3 and HBPP resins

Parameter	HBPE1	HBPE2	HBPE3	HBPP
Epoxy Eq. (g/Eq.)	352 ± 12	330 ± 9	286 ± 8	-
Hydroxyl value (mg KOH/g)	105 ± 4	87 ± 3	78 ± 5	420 ± 8

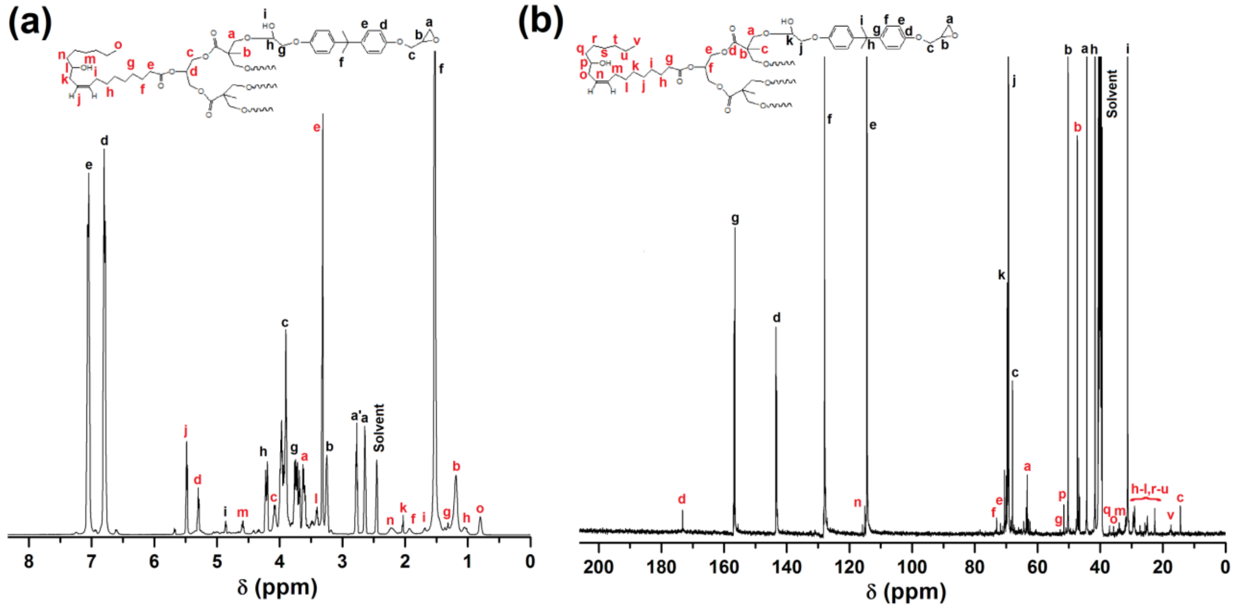


Figure 2C.6: (a) ^{1}H NMR and (b) ^{13}C NMR spectra of HBPE2 resin

2C.3.3. Curing of the resins

Curing time of HBPE resins with PAA hardener depends on the epoxy equivalent of the resins. The number of epoxy groups increases with the decrease of epoxy equivalent value of the resin and thus, curing time at 100 °C also decreases. The curing time for hard drying is the time required to attain the swelling value of the thermoset 20-30% (**Table 2C.2**). Thus, HBPE3 exhibited the lowest curing time as shown in **Table 2C.2**. The presence of aliphatic moieties and large amount of hydroxyl groups in HBPP, MSBE took the highest curing time due to the reaction of hydroxyl groups with epoxy rings requires higher curing time and temperature. The long chain hydrocarbon part of HBPP also decreases the reactivity of MSBE with hardener. Swelling value of MSBE was also slightly higher due to the high amount of free hydroxyl groups of HBPP.

2C.3.4. Mechanical properties of HBPE and MSBE thermosets

The mechanical properties like tensile strength, elongation at break, toughness, scratch hardness, impact resistance and bending values of the thermosets are given in **Table 2C.2**. The presence of aromatic rigid moiety of BPA in the hyperbranched epoxy resulted high tensile strength. On the other hand, the presence of aliphatic polyester moiety and ether linkage increases the elasticity (elongation at break) of the hyperbranched epoxy due to the plasticization effect. The hyperbranched epoxy thermosets exhibited very high toughness calculated from stress-strain curves in **Figure 2C.7**. This is due to the combination of aromatic and aliphatic moieties as well as the hyperbranched structure of the epoxy as described earlier. HBPE3 thermoset exhibited the highest tensile strength due to the presence of the highest amount of DGEBA moiety. On the other hand, due to presence of the lowest amount of BPA moiety HBPE1 thermoset showed the lowest tensile strength value (**Table 2C.2**). Due to the same reason, the highest elongation at break value for HBPE1 thermoset and the lowest elongation at break value for HBPE3 thermoset were observed. HBPE2 thermoset exhibited the best toughness as it possesses overall good tensile strength and elongation at break. The result of impact resistance and scratch hardness also reflects the toughness of a material. As the hyperbranched epoxy thermosets were exhibited very high toughness their impact resistance and scratch hardness value were also high. The thermosets exhibited the highest limit of impact resistance (100 cm, limit of the instrument) due to the presence of flexible moieties (namely aliphatic fatty ester of epoxy, aliphatic hydrocarbons of hardener and ether linkages of epoxy) which dissipate the impact energy by their segmental motions in their molecular chains as described in previous sub-chapters as well as reported in literature.[42] Thus, they also exhibited the highest limit of the bending test (1 mm dia. of the mandrel) and can be folded up to 180° without any damage or fracture as observed for PHE and TAHE thermosets. As the hyperbranched epoxy thermosets possessed both aromatic and aliphatic moieties in the structure, adequate crosslink density and unique structural architecture, they exhibited high scratch hardness also.

On the other hand, SBE thermoset exhibited very low toughness as it contains only aromatic rigid moiety in the structure as reported in sub-chapter 2A. It possessed adequate tensile strength but very low elongation at break. Thus, impact resistance and scratch hardness values were also very low for SBE (sub-chapter 2A, **Table 2A.3**). Again, when it was modified with 10 wt% HBPP by physical mixing (MSBE), the improvement of mechanical properties was not so high (**Table 2C.2**). This is due to the presence of more physical interactions rather than chemical between SBE and HBPP in the thermoset. Because of the plasticizing effect of HBPP the tensile strength of SBE was decreased and elongation at break was increased after this modification (**Figure 2C.7**). Thus, toughness, scratch hardness and impact resistance were slightly improved in MSBE (**Table 2C.2**).

Table 2C.2: Performance of HBPE and MSBE thermosets

Parameter	HBPE1	HBPE2	HBPE3	MSBE
Curing time at 100 °C (min)	70 ± 2	65 ± 3	50 ± 4	85 ± 5
Swelling value at 25 °C (%)	26 ± 0.4	24 ± 1	23 ± 0.7	28 ± 1
Tensile strength (MPa)	33 ± 2	42 ± 1.7	49 ± 3	34±1.2
Elongation at break (%)	94 ± 3	88 ± 1.5	50 ± 1.6	29 ± 5
Toughness (MPa)	2648 ± 15	3144 ± 8	2109 ± 7	762±18
Scratch hardness (kg)	9.5 ± 0.4	>10.0	>10.0	9.0±0.2
Impact resistance (cm)	>100	>100	>100	95 ± 3
Bending (mm)	<1	<1	<1	2
Adhesive strength, W-W (MPa)	>2881	>2927	>2958	1288±14
Adhesive strength, M-M (MPa)	1800±23	2646±28	2873±34	1012±11
Initial degradation temperature (°C)	280	308	312	260

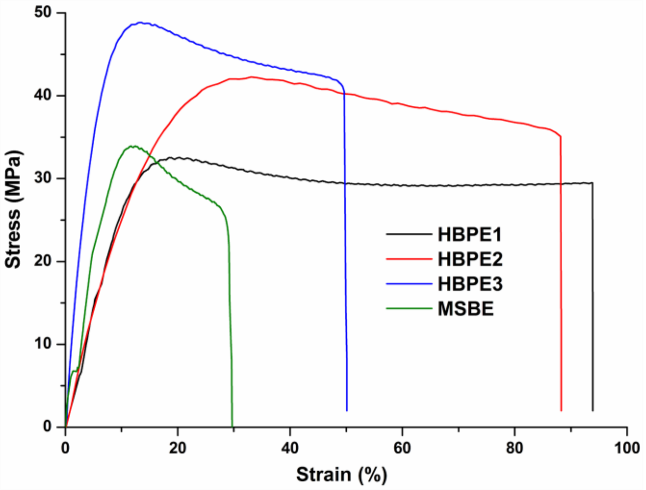


Figure 2C.7: Stress-strain profiles of HBPE and MSBE thermosets

2C.3.5. Adhesive strength of HBPE and MSBE thermosets

HBPE thermosets also exhibited high lap-shear tensile adhesive strength as shown in **Table 2C.2**. This is due to the strong interactions of polar -OH, ether and epoxy groups along with the unique branched structural architecture with terminal epoxide groups as well as the polar linkages of PAA hardener with the cellulosic wood substrates.[20,21] In case of metal substrates the high adhesive strength is due the strong physical interlocking as described in previous sub-chapters as well as in literature.[21] The variation of adhesive strength in HBPE1, HBPE2 and HBPE3 thermosets is due to the variation of load bearing capacity of the thermosets. In case of wood substrates a similar adhesive strength value for HBPE1, HBPE2 and HBPE3 thermosets was observed due to the substrate failure. Because of the linear structure and lower amount of polar groups (mainly hydroxyl and ether) SBE thermoset exhibited comparatively lower adhesive strength as reported in sub-chapter 2A. Again due to the hyperbranched architecture and high amount polar groups in HBPP, MSBE possessed slight higher adhesive strength (**Table 2C.2**) compared to SBE thermoset. But this improvement in MSBE thermoset is not so high because of the presence of more physical interactions rather than chemical between HBPP and SBE.

2C.3.6. Thermal stability of the thermosets

The initial degradation temperatures of the thermosets are given in **Table 2C.2**. HBPE2 and HBPE3 exhibited thermal stability above 300 °C. Due to the presence of more aliphatic moieties in HBPE1, it exhibited slight lower thermal stability (280 °C) and followed a two step degradation pattern (**Figure 2C.8**). First step (280 °C) is due to the degradation of aliphatic moieties of the HBPP and PAA hardener whereas the second step (400 °C) is due the degradation of BPA aromatic moiety.[20] However, HBPE2 and HBPE3 were degraded by single step (310 °C) pattern. This is due to the well combination of aliphatic and aromatic moieties in the structure. The aliphatic moieties are prohibited by aromatic moieties from thermal degradation. Thus, HBPE2 and HBPE3 exhibited higher thermal stability. In case of MSBE, due to the presence of more physical interactions rather than chemical between HBPP and SBE it exhibited 30 °C lower thermal stability than SBE (**Figure 2C.8**).

2C.3.7. Chemical resistance of the thermosets

The results of chemical resistance in aq. NaOH (2%), aq. HCl (10%), aq. EtOH (20%) and water are given in **Table 2C.3**. The thermosets exhibited excellent solvent resistance (aq. EtOH) and very good alkali and acid resistance. This is due to the compact structure with strong chemical linkages of the hyperbranched epoxy.[20,21] Though epoxy resin contains hydrolysable ester linkage in the structure, but the alkali resistance is very good for the thermosets. This is due to the presence of DGEBA as the terminal moieties, which protect the internal ester linkage from alkali attack. As HBPE2 and HBPE3 contain more DGEBA moiety than HBPE1, they exhibited more alkali resistance. However, the chemical resistance of these thermosets is poorer than PHE and TAHE thermosets. On the other hand MSBE exhibited poor alkali resistance due to the presence of hydrolysable free ester linkages of HBPP in MSBE as less chemical interactions are present between HBPP and SBE.

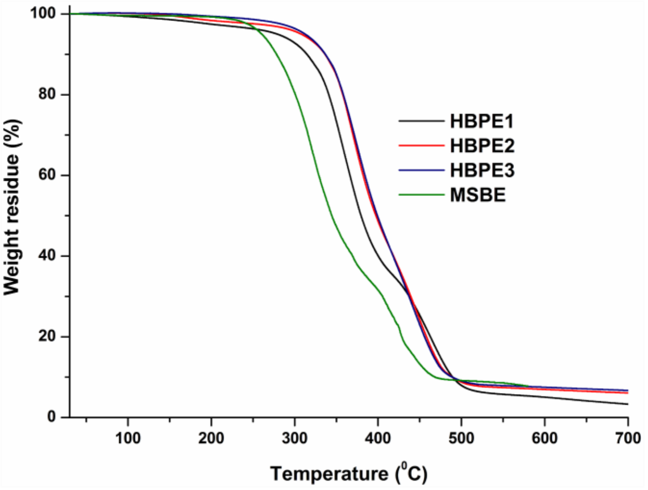


Figure 2C.8: TGA thermograms of HBPE and MSBE thermosets

Table 2C.3: Chemical resistance (weight loss %) of the thermosets in different chemical media

Chemical medium	HBPE1	HBPE2	HBPE3	MSBE
Aq. NaOH (2%)	2.59	1.42	0.63	4.12
Aq. HCl (10%)	2.76	2.33	2.0	3.54
Aq. EtOH (20%)	0	0	0	0.06
Water	0	0	0	0

2C.3.8. Biodegradation of the thermosets

From the biodegradation study (**Figure 2C.9**) it was found that HBPE thermoset films were degraded gradually with exposure time by the hydrocarbon degraded bacteria. This is due to the presence of the hydrolysable ester linkages of HBPP in the structure that are attacked by the bacteria.[44] As HBPE1 contains the highest amount of polyester in the structure, the growth of the bacteria was found to be the highest here (**Figure 2C.9a**) and also 30 wt% of weight loss was found after 60 days of exposure to the bacterial strain (**Figure 2C.9b**). HBPE3 contains the lowest amount of HBPP and thus, growth of the bacteria and weight loss was the lowest for it. On the other hand, SBE thermoset exhibited only a little amount of biodegradation, as it contains non biodegradable DGEBA moiety as the major constituent. The minor amount of biodegradation (**Figure 2C.9a and 2C.9b**) of SBE is due to the presence of only bio-based PAA hardener in the thermoset. The morphologies of the degraded surface of HBPE2 and SBE are also given in **Figure 2C.10**. In the figure, significant surface erosion (**Figure 2C.10b**) of the degraded film was found compared to the control (HBPE2 film without bacterial exposure, **Figure 2C.10a**). Slight erosion of the surface of SBE thermoset film (**Figure 2C.10d**) was also found compared to the control film of SBE (**Figure 2C.10c**). The biodegradation of MSBE thermoset was not studied due to its poor mechanical performance.

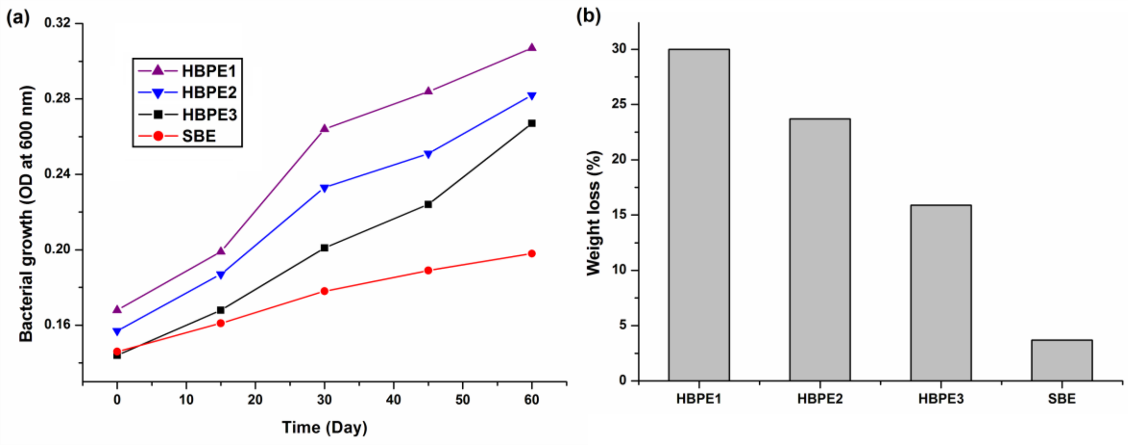


Figure 2C.9: (a) Variation of bacterial growth against exposure time for the thermosets and (b) weight loss of the thermosets after 60 days of exposure to the bacterial strain

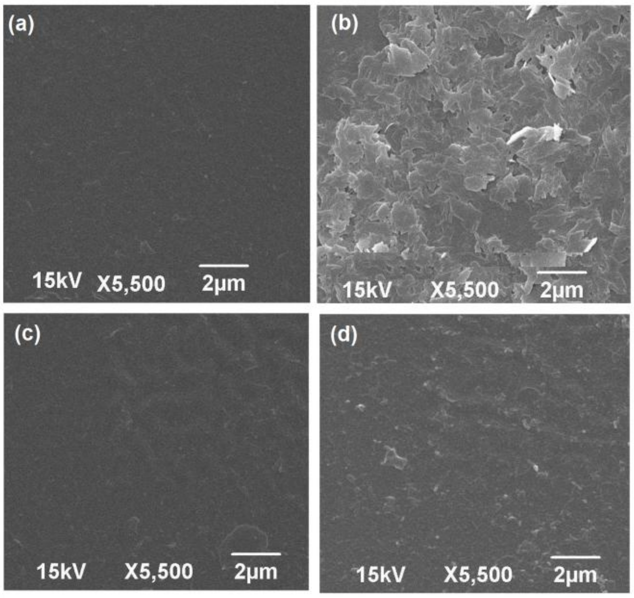


Figure 2C.10: SEM images of bio-degraded thermosets: HBPE2 (a) control and (b) degraded, and SBE (c) control and (d) degraded

2C.4. Conclusion

So in this study we demonstrated a hyperbranched BPA based epoxy with polyester backbone which exhibited outstanding toughness, flexibility and elasticity along with acceptable biodegradability and thermostability. Thus, the study solved the genuine problems like brittleness and non biodegradability nature of commercial epoxy thermosets. The high strength, toughness, flexibility and biodegradability of the thermosets may offer suitable advanced applications in the field of epoxy thermoset.

Thus, from this chapter it can be inferred that among the studied hyperbranched epoxy thermosets, triethanol amine branch generating unit based thermoset with 20 wt% triethanol amine exhibited overall the best performance by considering availability, cost, easy to synthesis and ultimate performance and hence it was used as the most potential matrix for fabrication of various nanocomposites in the present thesis.

References

1. Liu, F., et al. Curing of diglycidyl ether of bisphenol-A epoxy resin using a poly(aryl ether ketone) bearing pendant carboxyl groups as macromolecular curing agent, *Polym. Int.* **58**, 912--918, 2009.
2. Lee, H. & Neville, K. *Handbook of epoxy resins*, McGraw-Hill, New York, 1967.
3. Karak, N. *Fundamentals of Polymers*, PHI Learning Private Limited, New Delhi, 2010.
4. Chikhi, N., et al. Modification of epoxy resin using reactive liquid (ATBN) rubber, *Eur. Polym. J.* **38**, 251--264, 2002.
5. Ratna, D. & Banthia, A. K. Toughened epoxy adhesive modified with acrylate based liquid rubber, *Polym. Int.* **49**, 281--287, 2000.
6. Shin, S. M., et al. Toughening of epoxy resins with aromatic polyesters, *J. Appl. Polym. Sci.* **78**, 2464--2473, 2000.
7. Frigione, M. & Calo, E. Influence of an hyperbranched aliphatic polyester on the cure kinetic of a trifunctional epoxy resin, *J. Appl. Polym. Sci*. **107**, 1744--1758, 2008.
8. Voit, B. New developments in hyperbranched polymers, *J Polym. Sci. Part A: Polym. Chem.* **38**, 2505--2525, 2000.
9. Young, H. K. Hyperbranched polymers 10 years after, *J. Polym. Sci. Part A: Polym. Chem.* **36**, 1685--1698, 1998.
10. Jikei, M. & Kakimoto, M. Hyperbranched polymers: a promising new class of materials, *Prog. Polym. Sci.* **26**, 1233--1285, 2001.

11. Huang, P., et al. Synthesis of epoxy functionalized hyperbranched poly(phenylene oxide) and its modification of cyanate ester resin, *J. Appl. Polym. Sci.* **123**, 2351--2359, 2012.
12. Zhang, D., et al. Synthesis and characterization of low viscosity aromatic hyperbranched polyester epoxy resin, *Macromol. Res*. **17**, 289--295, 2009.
13. Fu, J. F., et al. Morphology, toughness mechanism, and thermal properties of hyperbranched epoxy modified diglycidyl ether of bisphenol A (DGEBA) interpenetrating polymer networks, *Polym. Adv. Technol*. **19**, 1597--1607, 2008.
14. Emrick, T., et al. An A_2 + B_3 approach to hyperbranched aliphatic polyethers containing chain end epoxy substituents, *Macromolecules* **32**, 6380--6382, 1999.
15. Lv, J. Y., et al. Synthesis of a hyperbranched polyether epoxy through one step proton transfer polymerization and its application as a toughener for epoxy resin DGEBA, *Chin. J. Polym. Sci*. **30** (4), 493--502, 2012.
16. Coessens, V., et al. Functionalization of polymers prepared by ATRP using radical addition reactions, *Macromol. Rapid Commun*. **21**, 103--109, 2000.
17. Yang, J. P., et al. Simultaneous improvements in the cryogenic tensile strength, ductility and impact strength of epoxy resins by a hyperbranched polymer, *Polymer* **49**, 3168--3175, 2008.
18. Constable, E. C., et al. Pentaerythritol-based metallodendrimers, *New J. Chem*. **22**, 193--200, 1998.
19. Kou, Y., et al. Preparation, characterization and modification of hyperbranched polyester-amide with core molecules, *React. Funct. Polym*. **67**, 955--965, 2007.
20. Roy, B. & Karak, N. Synthesis and characterization of thermostable hyperbranched epoxy resin for surface coating applications, *J. Mater. Res*. **27** (14), 1806--1814, 2012.
21. Barua, S., et al. Glycerol based tough hyperbranched epoxy: Synthesis, statistical optimization and property evaluation, *Chem. Eng. Sci.* **95**, 138--147, 2013.
22. Pavia, D. L., Lampman, G. M., Kriz, G. S. & Vyvyan, J. R. *Spectroscopy*, Cengage Learning India Private Limited, New Delhi, 2007.
23. Emrick, T., et al. The preparation of hyperbranched aromatic and aliphatic polyether epoxies by chloride-catalyzed proton transfer polymerization from AB_n and A_2 + B_3 monomers, *J. Polym. Sci., Part A: Polym. Chem*. **38**, 4850--4869, 2000.
24. Lan, T. & Pinnavaia, T. J. Clay-reinforced epoxy nanocomposites, *Chem. Mater*. **6**, 2216--2219, 1994.

25. Lin, C. H., et al. Low dielectric thermoset. II. Synthesis and properties of novel 2,6-dimethyl phenol-dipentene epoxy, *J. Polym. Sci., Part A: Polym. Chem*. **40**, 4084--4097, 2002.
26. Devaraju, S., et al. Hyperbranched polysiloxane-based diglycidyl ether of bisphenol a epoxy composite for low k dielectric application, *Polym. Compos*. **34**, 904--911, 2013.
27. Lv, J., et al. Synthesis of a hyperbranched polyether epoxy through one-step proton transfer polymerization and its application as a toughener for epoxy resin DGEBA, *Chin. J. Polym. Sci*. **30**, 493--502, 2012.
28. Pang, Y., et al. Design and synthesis of cationic drug carriers based on hyperbranched poly(amine-ester)s, *Biomacromolecules* **11**, 575--582, 2010.
29. Xu, F., et al. Multifunctional poly(amine-ester)-type hyperbranched polymers: lipase-catalyzed green synthesis, characterization, biocompatibility, drug loading and anticancer activity, *Polym. Chem*. **4**, 3480--3490, 2013.
30. Kalita, H. & Karak, N. Mesua ferrea L. seed oil-based hyperbranched shape memory polyurethanes: Effect of multifunctional component, *Polym. Eng. Sci*. **52**, 2454--2461, 2012.
31. Tomalia, D. A. and Dewald, J. R. Dense star polymers and dendrimers, **US Patent No.** 4568737, February 4, 1986.
32. Nalwa, H. S. *Handbook of low and high dielectric constant materials and their applications*, Academic Press, Boston, 1999.
33. Jin, F. L. & Park, S. J. Impact-strength improvement of epoxy resins reinforced with a biodegradable polymer, *Mater. Sci. Eng. A* **478**, 402--405, 2008.
34. Lukaszczyk, J. & Jaszcz, K. et al. Synthesis and characteristics of biodegradable epoxy-polyester resins cured with glutaric anhydride, *Macromol. Chem. Phys*. **203** (2), 301--308, 2002.
35. Wang, H. J. et al. Biodegradable foam plastics based on castor oil, *Biomacromolecules* **9**, 615--623, 2008.
36. Yeganeh, H. & Talemi, P. H. Preparation and properties of novel biodegradable polyurethane networks based on castor oil and poly(ethylene glycol), *Polym. Degrad. Stab*. **92**, 480--489, 2007.
37. Karak, N., et al. Synthesis and characterization of castor-oil-modified hyperbranched polyurethanes, *J. Appl. Polym. Sci*. **112**, 736--743, 2009.
38. Konwar, U. & Karak, N. Mesua ferrea L. seed oil-based highly branched polyester resins, *Polym. Plastics Technol. Eng*. **48**, 970--975, 2009.

39. Dutta, N., et al. Synthesis and characterization of polyester resins based on nahar seed oil, *Prog. Org. Coat*. **49**, 146--152, 2004.
40. Das, G. & Karak, N. Epoxidised mesua ferrea L. seed oil-based reactive diluent for epoxy resin and their green nanocomposites, *Prog. Org. Coat*. **66**, 59--64, 2009.
41. Thakur, S. & Karak, N. Castor oil-based hyperbranched polyurethanes as advanced surface coating materials, *Prog. Org. Coat*. **76**, 157--164, 2013.
42. Pathan, S. & Ahmad, S. s-Triazine ring-modified waterborne alkyd: synthesis, characterization, antibacterial, and electrochemical corrosion studies, *ACS Sustainable Chem. Eng*. **1**, 1246--1257, 2013.
43. Roy, B., et al. Silver-embedded modified hyperbranched epoxy/clay nanocomposites as antibacterial materials, *Bioresour. Technol.* **127**, 175--180, 2013.
44. Lukaszczyk, J. & Jaszcz, K. et al. Synthesis and characteristics of biodegradable epoxy-polyester resins cured with glutaric anhydride, *Macromol. Chem. Phys*. **203** (2), 301--308, 2002.