

Novel high performance tough hyperbranched epoxy
by an $A_2 + B_3$ polycondensation reactionCite this: *J. Mater. Chem. A*, 2013, **1**,
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High performance tough epoxy thermoset with excellent adhesive strength is one of the most in demand materials for advanced engineering applications. In the present investigation three hyperbranched epoxy resins with varying compositions were synthesized by a single step controlled polycondensation reaction using an $A_2 + B_3$ approach for the first time. The physical properties like epoxy equivalent, hydroxyl value, viscosity, etc. of the synthesized epoxy resins were determined by different analytical techniques. The hyperbranched structure of the resins was characterized by spectroscopic techniques. The degrees of branching were found to be 0.60, 0.79 and 0.51 for the resins with 10, 20 and 30 wt% of the B_3 moiety respectively, as obtained from the ^{13}C NMR study. The poly(amidoamine) cured hyperbranched epoxy thermosets exhibited high thermostability (up to 293, 298 and 296 °C), tensile strength (38, 47 and 26 MPa), elongation at break (43, 21 and 52%), strain energy or toughness (1277, 758 and 1056 MPa), exceptionally high adhesive strength (1987, 2662, 1638 MPa), impact resistance (>100 cm) and scratch hardness (8.5, 9.0, 8.0 kg). The results showed the prominent role of the amount of the B_3 moiety in the performance of the thermosets. The study, therefore, revealed that the unison of the aliphatic–aromatic moiety in the hyperbranched structure can offer a high performance tough epoxy thermoset without any processing difficulty.

Received 21st August 2012

Accepted 25th September 2012

DOI: 10.1039/c2ta00011c

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Introduction

Attributes of high mechanical properties, excellent weather and chemical resistance, low shrinkage, excellent adhesion and others endow a unique position to epoxy resins in the domain of engineering materials. Thus epoxy thermosets have a broad range of applications. They are mainly used as binders for surface coatings and paints along with flexible resins, binders for fiber reinforced plastic (FRP) composites, adhesives, electrical insulating materials, water-proofing materials, flooring materials, etc.^{1–3} However, their many advanced applications are restrained due to their inherent brittleness and low toughness as well as very low (1–5%) elongation at break. Hence, the modification of epoxy resins to impart the desired toughness has been the subject of intense investigation throughout the world.

Epoxy resins are toughened by blending them with different flexible polymers like rubbers,^{4–7} hyperbranched polyesters,^{8–10} hyperbranched epoxy resins,^{11–13} etc. However, they suffer from processing difficulty. For example, compatibility of rubber with epoxy is low and also needs a large amount of solvent or high temperatures for their processing. Modification with polyester resin demands high curing temperatures and long time scales. So, designing an epoxy resin with unique architectural features

such as a hyperbranched structure with a combination of aliphatic–aromatic moieties may result in toughened epoxy without any processing difficulty, as no extra polymer or modifying agent will be required in such cases.

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.¹ It is pertinent to mention that low solution and melt viscosity, high reactivity and solubility amongst other properties attest the advantages of hyperbranched polymers over their conventional linear analogs with equivalent molecular weight.^{14–17} In order to develop high performance epoxy resins for engineering applications, the mechanical properties of these resins have been extensively investigated. The reports reveal that the control of the chemical and physical structures is very important to optimize their performance for such applications.¹⁸ Hyperbranched epoxy resins are of special interest because of their easy synthetic accessibility, low viscosity, high solubility and large number of end functional groups for their industrial scale productions and applications. Various synthetic approaches including end group modification of suitable hyperbranched polymers,¹⁹ proton transfer polymerization,^{20,21} functionalization of poly(methyl acrylate) using atom transfer radical polymerization (ATRP),²² etc. have been reported for hyperbranched epoxy resins. However, all these products are either solid or highly viscous liquids and would thus need dilution with organic solvents, which is detrimental to the

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environment (high VOC). In most of the cases the mechanical strength was also found to be low and thus they are mainly used as toughening agents for commercial epoxies.¹¹ Hyperbranched epoxy resins with the desired performance, are therefore very limited. In addition, synthesis of such hyperbranched epoxy resins by a single step $A_2 + B_3$ polycondensation reaction would be a good proposition from an industrial point of view. In the present investigation, therefore, an attempt has been made to obtain industrially suitable hyperbranched epoxy thermosets with high tensile strength and elongation at break (*i.e.* high toughness), exceptional adhesive strength, *etc.* by combining an aliphatic–aromatic moiety in the hyperbranched structure of the resin with an aliphatic poly(amido-amine) as a hardener.

Experimental

Materials

Triethanol amine (Merck, India) was used after vacuum drying. Bisphenol-A and epichlorohydrin were purchased from G. S. Chemical, Mumbai. Bisphenol-A was re-crystallized from toluene before use. Sodium hydroxide (Rankem, New Delhi) and poly(amidoamine) hardener (HY840, Ciba Geigy, Mumbai, amido-amine type) were used as received without any further purification. All other reagents used in the present investigation were of reagent grade.

Preparation of the hyperbranched epoxy resin

The hyperbranched epoxy resin was synthesized by the polycondensation reaction of bisphenol-A and triethanol amine (10, 20 and 30 wt% with respect to bisphenol-A) with epichlorohydrin (2 moles per hydroxyl group) at 110 °C with continuous stirring. Bisphenol-A (5 g, 21.90 mmol), triethanol amine (0.5 g, 3.35 mmol) and epichlorohydrin (9.97 g, 107.70 mmol) were taken in a two neck 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 (2.15 g, 53.85 mmol) (equivalent to the hydroxyl group) was slowly added from a dropping funnel (45–60 min). 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 with 15% aqueous sodium chloride solution followed by distilled water 2–3 times. Finally the epoxy resin was dried at 80 °C under vacuum to get a viscous sticky transparent mass. The epoxy resins for three different wt% of triethanol amine *viz.* 10, 20 and 30 were synthesized similarly and coded as TAHE10, TAHE20 and TAHE30 (yield: 8.12 g, 8.26 g and 8.34 g, ~95%) respectively. The structure of the hyperbranched epoxy resin was confirmed by NMR (Fig. 1 and 2) studies. ^1H NMR δ_{H} : (400 MHz, CDCl_3 , Me_4Si) 3.33 (1H, t, CH of the oxirane ring), 2.73 and 2.89 (2H, d, CH_2 of the oxirane ring), 3.72–3.74 (2H, m, $\text{NCH}_2\text{CH}_2\text{OH}$), 2.61 (2H, t, NCH_2), 1.62 (3H, s, CH_3), 6.82 (4H, d, Ph), 7.11 (4H, d, Ph), 2.19 (1H, d, OH), 4.04 and 4.06 (2H, d, OCH_2) 4.18 (1H, m, CHOH). ^{13}C NMR δ_{C} : (400 MHz, CDCl_3 , Me_4Si) 45.95 (CH_2 of the oxirane ring), 50.21 (CH of the oxirane ring), 113.94, 127.83, 143.90 and 156.30 (4C, Ph), 30.99 (CH_3),

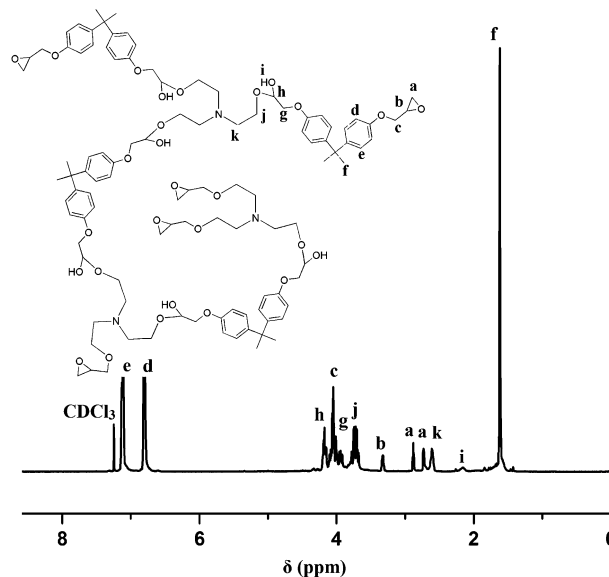


Fig. 1 ^1H NMR spectrum of the hyperbranched epoxy.

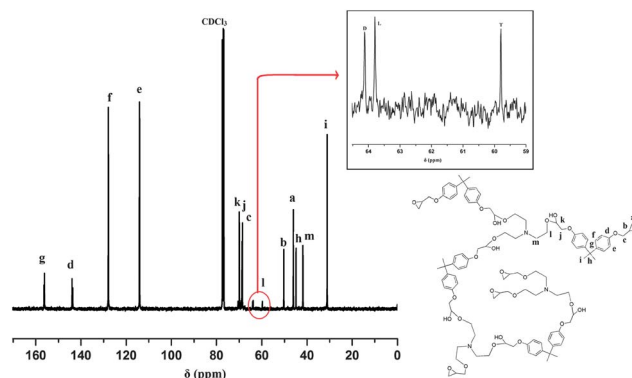


Fig. 2 ^{13}C NMR spectrum of the hyperbranched epoxy.

44.77 ($\text{Ph}_2\text{C}(\text{CH}_3)_2$, bisphenol-A unit), 68.42 and 68.71 (OCH_2) 69.87 (CHOH), 41.73 (NCH_2), 59.68 ($\text{NCH}_2\text{CH}_2\text{OH}$ of mono-substituted triethanol amine), 63.69 ($\text{NCH}_2\text{CH}_2\text{OH}$ of disubstituted triethanol amine), 64.01 ($\text{NCH}_2\text{CH}_2\text{OH}$ of trisubstituted triethanol amine).

Curing of the resins

The TAHE10, TAHE20 and TAHE30 resins were cured by hand mixing 50 phr (parts per hundred of resin) of the poly(amido-amine) hardener with the hyperbranched resin in a glass beaker at room temperature in the presence of a small amount of THF (0.5 mL per g of resin) as the solvent. Then the mixtures were uniformly coated on mild glass plates (75 mm \times 25 mm \times 1.3 mm) for scratch hardness and tensile tests and steel plates (150 mm \times 50 mm \times 1.6 mm) for the impact strength test. The solvent was removed under vacuum and then the plates were cured at 100 °C for 65 min, 45 min and 75 min and post-cured at 130 °C for 35 min, 20 min and 45 min for TAHE10, TAHE20 and TAHE30. The extent of the curing reaction was determined from their respective swelling values.

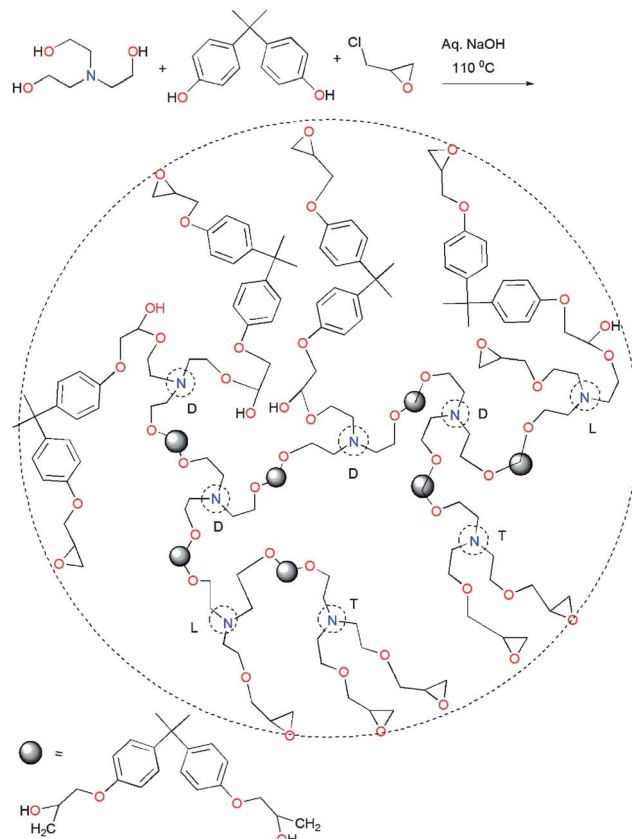
Characterization

The ^1H NMR and ^{13}C NMR spectra of the resins were recorded with a 400 MHz, JEOL FTNMR spectrometer by using CDCl_3 as the solvent and TMS as the internal standard. The physical properties such as epoxy equivalent, hydroxyl value, specific gravity, solubility and swelling value of the resins were measured by the standard test methods.^{23,24} The mechanical properties such as scratch hardness were determined using a scratch hardness tester (Sheen instrument Ltd., UK) and impact strength using an impact tester (S. C. Dey Co., Kolkata) as per the standard falling weight (ball) method (standard ASTM D 1037). In this test a weight of 850 g was allowed to fall on the film coated on a mild steel plate from minimum to maximum falling heights. The maximum height was taken as the impact resistance up to which the film was not damaged. The tensile and adhesion tests of the cured films were carried out using a Universal Testing Machine (UTM, WDW10, Jinan, China) with a 10 kN load cell and a crosshead speed of 50 mm min^{-1} . The adhesion test was carried out on two interfaces of adherents, viz. metal–metal (M–M) and plywood–plywood (W–W), by the lap-shear test where the area of the overlapping zone was $25 \times 25\text{ mm}^2$ and the thickness of the zone was 0.02–0.03 mm. The lap-shear tensile strength (MPa) was calculated as the maximum load per unit bond area, obtained directly from the UTM. The thermal stability of the samples was studied by thermogravimetric analysis (TGA) in a Shimadzu TG 50 using a nitrogen flow rate of 30 mL min^{-1} at a heat rate of $10\text{ }^\circ\text{C min}^{-1}$ from room temperature to $600\text{ }^\circ\text{C}$. The chemical resistance test was carried out in various chemical environments such as aqueous HCl (10%), aqueous NaOH (5%), aqueous NaCl (15%), aqueous ethanol (20%) and fresh water to investigate the effect of these chemicals on the cured epoxy films. The cured films were cut into small pieces and kept in 100 mL amber bottles containing aforesaid media at an ambient temperature ($30\text{ }^\circ\text{C}$). The percentage of weight loss was measured after 30 days of test.

Results and discussion

Synthesis and characterization of hyperbranched epoxy

The hyperbranched epoxy resins were synthesized by an $\text{A}_2 + \text{B}_3$ approach. First the A_2 monomer i.e., a diglycidyl ether of bisphenol-A was formed 'in situ' from the reaction mixture as the reactivity of bisphenol-A with epichlorohydrin was higher than triethanol amine due to higher acidity of phenolic protons. Then the hyperbranched epoxy resins were obtained by the reaction between diglycidyl ether of bisphenol-A (A_2) and triethanol amine (B_3) as shown in Scheme 1. So the process is almost similar to the conventional epoxy resin and hence there should not be any difficulty for their industrial production. Furthermore, in the formulation of epoxy only triethanol amine is used as an additional component, which is available as an industrial chemical with acceptable price. So the overall cost would not be affected, particularly with respect to its cost to performance ratio. The hyperbranched structures of the resins were confirmed by the NMR study (Fig. 1 and 2). NMR



Scheme 1 Synthesis of the hyperbranched epoxy.

spectroscopy is an important tool for the characterization of hyperbranched polymers since detailed analysis of the spectrum permits extraction of information about the degree of branching (DB). According to the polymerization mechanism of the hyperbranched polymer and the definition of DB, the resulting polymer should contain a dendritic unit (D), linear unit (L) and terminal unit (T). The DB is the ratio of the sum of integration of dendritic and terminal units to the sum of integration of dendritic, linear and terminal units, i.e., $\text{DB} = (\text{D} + \text{T}) / (\text{D} + \text{L} + \text{T})$.¹ From the ^{13}C NMR spectrum (Fig. 2, for TAHE10) of the resin the monosubstituted (T), disubstituted (L) and trisubstituted (D) CH_2 carbon of triethanol amine were observed at $\delta = 59.68\text{ ppm}$, 63.69 ppm and 64.01 ppm , respectively. From these peaks the calculated DBs of TAHE10, TAHE20 and TAHE30 were 0.60, 0.79 and 0.51 respectively. The DB and the physical properties like the epoxy equivalent, hydroxyl value,

Table 1 Physical properties of the resins

Properties	TAHE10	TAHE20	TAHE30
Epoxy equivalent (g per equiv.)	424	358	599
Hydroxyl value (mg KOH per g)	119	102	144
Viscosity (Pas) at $40\text{ }^\circ\text{C}$	25.61	22.80	30.61
Degree of branching (DB)	0.60	0.79	0.51
Curing time at $100\text{ }^\circ\text{C}$ (min)	65	45	75
Post curing time at $130\text{ }^\circ\text{C}$ (min)	35	20	45
Swelling value (%)	20	16	22

solubility, viscosity, *etc.* of the resin obtained at three different wt% of the B₃ moiety (TAHE10, TAHE20 and TAHE30) are given in Table 1. From this table it can be seen that the epoxy equivalent, hydroxyl value and viscosity of the resin were the lowest in TAHE20. This is due to the presence of an appropriate mole ratio (3 : 1) of A₂ : B₃ 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 A₂ : B₃ 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 B₃ monomer.^{20,21} The viscosities of the resins were slightly higher than general hyperbranched polymers, this 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 hyperbranched epoxy resins were soluble in most of the common organic solvents like methanol, ethanol, acetone, THF, DMF, DMAC, DMSO, CHCl₃, CH₂Cl₂, toluene, xylene, ethyl acetate, *etc.* 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.

Curing study of hyperbranched epoxy

The curing of the hyperbranched epoxy resin was carried out at 100 °C with poly(amidoamine) as the hardener, followed by post-curing at 130 °C for specified time to obtain the desired swelling values (Table 1). From this table, it is found that TAHE20 has the lowest curing and post-curing times as it has the highest number of epoxide groups. The possible reactions occurred during the curing process are the reactions between amine groups of the hardener with the strained epoxy oxirane ring, and secondary hydroxyl groups with the amine groups of the hardener and the oxirane ring of the epoxy resin. On the other hand TAHE30 has the highest curing time as it has the highest epoxy equivalent and also contains the highest amount of the triethanol amine moiety, which decreases the reactivity of the resin due to the presence of electronegative nitrogen atom.

Performance of thermosets

The stress–strain profiles with toughness of TAHE10, TAHE20 and TAHE30 are shown in Fig. 3. The toughness of the hyperbranched epoxy is defined by the integrated area under the stress–strain curve *i.e.*, strain energy. The values obtained for all the three thermosets were more than for commercially available epoxies. Commercially available epoxies possess adequate strength but they are generally brittle in nature as their elongation at break values are very low (1–5%).²⁵ Whereas these hyperbranched epoxy thermosets possess both high tensile strength, as well as comparatively higher elongation at break so these are tough materials. This is due to the presence of both

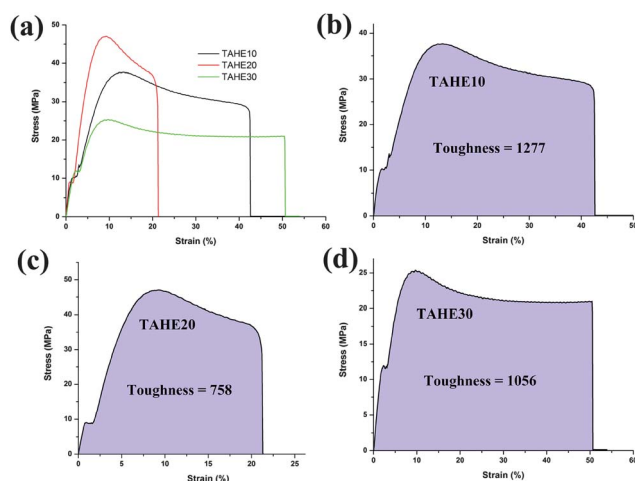


Fig. 3 (a) Stress–strain profiles and (b–d) toughness (calculated by integrating stress–strain curves) of the thermosets.

aromatic and aliphatic moieties in the structure as well as the 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).¹⁸ Thus the stress–strain curves for these thermosets are like those of ductile materials. The most reported of the epoxy thermosets possess much lower toughness than the thermosets of the present study.^{26,27} 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 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.

Both the tests of scratch hardness and impact resistance determine the toughness of the materials. Higher impact strength and scratch hardness resulted in higher toughness. As the hyperbranched epoxy thermosets possess both aromatic

Table 2 Performance of the thermosets

Properties	TAHE10	TAHE20	TAHE30
Tensile strength (MPa)	38	47	26
Elongation at break (%)	43	21	52
Toughness	1277	758	1056
Scratch hardness (kg)	8.5	9.0	8.0
Impact strength ^a (cm)	>100	>100	>100
Bending dia. ^b (mm)	<1	<1	<1
Adhesion strength (M–M) (MPa)	1987	2662	1638
Adhesion strength ^c (W–W) (MPa)	1109	1319	1000
Initial degradation temperature (°C)	293	298	296
Mid-point degradation temperature (°C)	373	377	375
Weight residue (%) at 600 °C	11	12	23

^a The limit of the impact strength was 100 cm (highest). ^b The limit of the mandrel diameter was 1 mm (lowest). ^c In all the thermosets the plywood substrate failed.

and aliphatic moieties, adequate crosslink density (swelling values, Table 1) and unique structural architecture, they exhibited high toughness, scratch hardness and impact resistance (Table 2). The thermosets absorbed the highest limit of impact energy (100 cm, limit of the instrument) because of the flexible moieties (namely aliphatic moieties of epoxy as well as the hardener and flexible ether linkages) which dissipate the impact energy by their segmental motions in their molecular chains.¹⁸

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 the hardener, poly(amidoamine), that contains flexible aliphatic hydrocarbon which offers the plasticizing effect to the thermosets.

The thermosets exhibited very high adhesive strength (Table 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 poly(amidoamine) hardener with the substrates. 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. In the case of the plywood substrate all the thermosets showed almost equal adhesive strength because of the failure of the substrate. Here the adhesive strength of the thermosets was higher than the plywood's 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.

Thermal stability

The TGA thermograms (Fig. 4) of hyperbranched epoxy thermosets showed that the thermal stabilities of TAHE10, TAHE20 and TAHE30 were adequately high, as the initial decomposition temperatures were ~ 300 °C. From the TGA thermograms, the

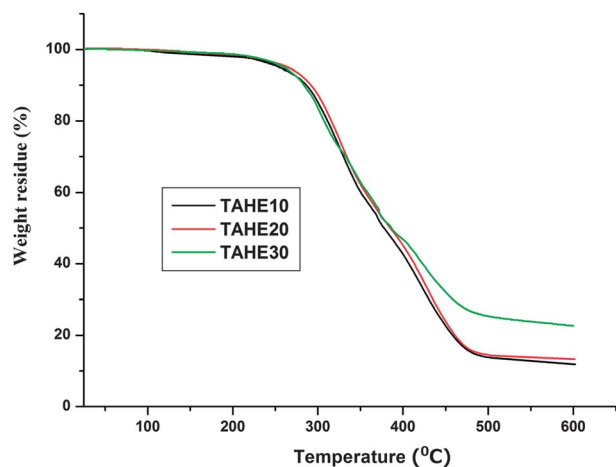


Fig. 4 TGA thermograms of the thermosets.

Table 3 Weight loss (%) of the thermosets in different chemical environments after 30 days

Chemical environments	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%)	NC ^a	NC	NC
Water	NC	NC	NC

^a NC = no weight change.

initial decomposition temperature (5% weight loss), mid-point of degradation (50% weight loss) and the weight residue at 600 °C were determined and are tabulated in Table 2. 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 followed by the second stage to the degradation of the aromatic moieties (~ 400 °C). As all the thermosets have almost same structural units, their degradation patterns and the degradation temperatures were almost the same. The weight residue of TAHE30 at 600 °C was found to be the highest. However, the reason for such behavior is difficult to explain at this moment, though the presence of the highest amount of nitrogen in the structure may be one of the reasons.

Chemical resistance

The results of chemical resistance of the thermosets in different chemical environments are given in Table 3. 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. With the decrease of compactness in TAHE10 and TAHE30, the alkali and acid resistance decreased, though the decrements are marginal.

Conclusions

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.

Acknowledgements

The authors express their gratitude to the NRB for financial assistance through the grant no. DNRD/05/4003/NRB/251 dated

29.02.12, SAP (UGC), India through grant no. F.3-30/2009(SAP-II) and the FIST program-2009 (DST), India through the grant no. SR/FST/CSI-203/209/1 dated 06.05.2010.

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