Environmental benign synthesis of low-viscous triethanolamine based hyper- branched epoxy thermoset

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A room temperature curable, low viscosity hyper-branched (HPBs) epoxy resin has been synthesised by a single step $A_2 + B_3$ polycondensation reaction which would be a good proposition from an industrial point of view. An attempt has been made to obtain industrially suitable hyperbranched epoxy thermosets which exhibit high thermostability, high tensile strength and elongation at break (i.e. high toughness), where an aromatic (Bisphenol A, A_2) and aliphatic (Triethanolamine, B_3) moiety is combined in the hyperbranched structure of the resin with an aliphatic poly (amido-amine) as a hardener. The prepared resin show surprisingly low viscosity when the ratio of Bisphenol A: Epichlorohydrine (ECH) is maintained at a ratio of 1:3 i.e. a high amount of ECH is added and the remaining ECH is washed off by azeotropic distillation process. Prepared HPBs resins have been studied using ^{1}H NMR, ^{13}C NMR, IR, and TGA analysis. The hyperbranched epoxy resin with 20 wt% triethanolamine (TELA) show high performance and might be utilized in advanced thin film application.

Keywords: Epoxy resin**,** Hyper-branched polymer, Low viscosity, Coating

Tiethanolamine based hyperbranched epoxy resin is one of the most important alternative for the industrial coating. Low volatile organic content and low viscosity are the excellent properties of the resin as a coating binder. Easier one pot solvent free synthetic route with low cycle time makes the resin a better raw material for paint and surface coating industries. Due to their highly branched structure and the large number of functional groups hyperbranched polymers possess unique properties that make them interesting for uses in a wide variety of applications. Hyperbranched polymers are often more soluble and possess a lower viscosity than linear polymers. So the hyperbranched epoxy has the potential as a thermoplastic tougheners for thermosets.

Epoxy resins are widely used in industry as a protective coating and for structural applications, such as coating, laminates, composites, and adhesives. However, in terms of structural applications, epoxy resins are usually brittle. As a result, tremendous efforts have been focused on the improvement of toughness during the past three decades. Modification by reactive liquid rubbers is one of the most common and widely used approaches to improve the toughness of epoxy networks[1-3]. The resulting products have good impact behaviour but inferior strength, and unsuitable for high-performance engineering applications[4]. The epoxy resins are toughned by blending them with different polymers, such as hyperbranched epoxy resin[5,6], hyperbranched polyesters[7-13]. Hyperbranched epoxies have been used in blends with conventional bisphenol A- based liquid epoxy resin as a toughner for epoxy hardner system intended for marine and sports application[14]. The materials used to toughen epoxies, such as rubbers and thermoplastics, are linear polymers. These materials behave as a classical chain entangled polymers and often have high viscosities, and reduces processibility of the resin. The use of hyperbranched polymers (HBPs) has been proposed in order to overcome the limitations of traditional modifiers, such as linear thermoplastics and rubber particles.

Various methods have been adopted for the synthesis of hyperbranched epoxy resin, such as SMM-polycondensation of AB2 monomers, SMM-self-condensing vinyl polymerization, SMM-self-condensing ring-opening and proton-transfer polymerizations, DMM (A_2+B_3) polycondensation of A_2 and B_3 monomers, AB2 + AB copolymerisation, etc[15-19]. However, all the products obtained are either solid or highly viscous and requires dilution with organic solvents, which is harmful to the environment (high VOC's). There has been a considerable effort to decrease the amount of volatile organic compounds

(VOCs) present in organic coatings. The risks to human health, and environmental hazards associated with VOCs, governmental directives, and economic factors are the main driving forces behind this effort. One way of achieving less or no VOC containing coating systems is to produce low viscosity resins.

The viscosity aspects, reduction in the viscosity, and limits to the reduction depends on the mehtods of preparation of the thermoset. Generally, the viscosity of the thermoset obtianed in the indsutrial process was high and requires solvent for dilution. The resin obtained was also not cured at room temperature. Therefreo, the method of preparation of thermoset is very much improtant in the industrial process. Hyperbranched resins owing to their globular structure have low viscosities and are promising materials for decreasing the VOCs. Thus, in this work, authors tried to synthesise a very low viscous hyperbranched epoxy resin, where, a sufficiently high volume of epichlorohydrine was added by changing the molar ratio of monomer units. As a result, an easily processable low viscosity epoxy resin was obtained, which don't require any solvent for dilution. It is an one pot synthetic route, and the prepared resins have high solid content (98%) which is possible to get at a low cycle time. The prepared resin/thermoset is cured at room temperature with poly(amidoamine) as a hardener, and therefore, might be utilized in thin film application.

Experimental Section

Material

Poly (amidoamine), sodium hydroxide (HY840, Ciba-Geigy, Mumbai, India) and epichlorohydrine (EPC, Merck, India) were used as received. Bisphenol-A (Merck, India) was used after recrystallization from toluene. Tri-ethanol amine (Merck, India) was used after drying in vacuum.

Synthesis

Hyper-branched epoxy resin was prepared by one pot synthetic method by polycondensation reaction of bisphenol A and tri-ethanol amine with epichlorohydrine at 90°C at a very low rpm under continuous stirring. In a three necked round bottom flask, 80 g of bisphenol A, 312 g of epichlorohydrine (2 moles per hydroxyl group) (sufficiently high) and 20 g of trietanolamine were mixed. The round bottom flask was equipped with a spiral water condenser, a mechanical stirrer and a dropping funnel through which 5 (N) of sodium hydroxide (equivalent to the hydroxyl group) was slowly added to the reaction mixture. The reaction

mixture was heated for 20 min to get a clear solution. The drop wise addition of NaOH was completed in the first one hour of the reaction and continued up to 4 h. The mechanical stirrer was stopped and checked the neutral pH (7-7.5) of the mixture. The upper part i.e. the epoxy part was decanted into a round bottom flask and stirred the resin by mechanical stirrer with high rpm by adding distilled water and repeated for several times. Finally the lump was put into a rotary evaporator for azeotropic distillation (at 90°C, 105 rpm and with full vacuum) for 20 min. Finally a highly low viscous and transparent sticky product was obtained. Three different wt% of tri-ethanol amine (10, 20 and 30 wt.%) containing hyper-branched epoxy were synthesised and the viscosity of hyper-branched epoxy containing 20% of tri-ethanol amine was found to be of lowest amongst them.

Curing of the resin

Poly (amido amine) was used as the curing agent to harden the hyper-branched epoxy resin. An amount of 30 phr (parts per hundred of resin) (calculated from epoxy value of the prepared resin) was added by hand mixing without any solvent (as the prepared resins were of low viscosities). Then the mixture was cast onto glass slides and mild steel plates, and cured at room temperature.

Characterisation

The ^{1}H NMR and ^{13}C NMR spectra of the resins were recorded with a 400 MHz, JEOL FTNMR spectrometer using CDC1$_3$ as the solvent and TMS as the internal standard. The FTIR spectra of the resins were recorded on a Nicolet (Ramsey, MN) Impact 410 FTIR spectrometer using KBr pallet. The thermogravimetric analysis was conducted by Diamond TG/DTA analyser, Perkin Elmer (USA) from room temperature to 600°C at a heating rate of 10°C /min. Chromatographic study for the removal of excess epichlorohydrine was studied by Varian CP3800 Gas Chromatography. The chemical resistance test was carried out in various chemical environments, such as conc. and aqueous (10%) HCl, aqueous NaOH (5%), conc. and aqueous H$_2$SO$_4$, 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 the bottles containing different media at a temperature of 30°C. The percentage of weight loss was measured after 24 days of test. The tensile test of the cured films were carried out using a Universal Testing Machine (UTM, WDW10, Jinan, China) with a 10 kN load cell and a cross head speed of 50 mm min^{-1}.

Results and Discussion

Synthesis and characterisation of hyperbranched epoxy

Industrially suitable methodology was adopted for the synthesis of triethanolamine based hyperbranched epoxy resin with very less cycle time, and easier separation technique of the unreacted epichlorohydrine, and water from the reaction mixture. Azeotropic distillation was applied for the removal of unreacted epichlorohydrine along with water in a very short time to get 100% solid content of the final resin. Synthesis was carried out in the conventional $A_2 + B_3$ polycondensation reaction between bisphenol A and epichlorohydrine in presence of a base catalyst. The diglycidyl ether intermediate was reacted in situ with triethanolamine (TELA) which is a trifunctional molecule based on the preferential reactivity of bisphenol A than triethanolamine, both of which are polyhydroxy compound. The amount of epichlorohydrin is taken three times higher than the actual mole balance for the polycondensation reaction process suitable for industrial scale production. The requirement of organic solvent and the brine washing for the extraction of epoxy resin was completely skipped and therefore, established an easier way for synthesis. The exceptional reduction in cycle time was possible due to azeotropic distillation under reduced pressure with N_2 blasting in the single batch reactor to remove excess epichlorohydrine. The cost of the preparation of thermosets depends on the cost of the chemicals involved in the synthesis. However, as the sample is cured at room temperature, the cost involved in the curing is eliminated here. The requirement of organic solvent for dilution and the brine washing for the extraction of epoxy resin was completely skipped. Hence the cost involved for solvent and brine washing is completely eliminated. These are some of the advantages in terms of cost from industrial application point of view. Furthermore, the simple water washing for removal of sodium salt and other water soluble impurities, makes the process a suitable option for the synthesis of hyperbranched epoxy resin within 8 h cycle time in the industrial scale. The formation, structure and degree of branching of the hyperbranched epoxy were confirmed by NMR spectroscopy. The ^{1}H NMR spectrum of the hyperbranched epoxy resin showed chemical shift values at δ 1.63 indicates the presence of methylol (-CH_2-OH) group proton of the hyperbranched epoxy resin. Triethanolamine unreacted –OH and the epoxy

ring protons are indicated by the presence of peaks at δ 2.16 and δ 2.74, respectively. The ethylene proton peaks are observed at δ 3.34-4.04. Phenyl protons are observed at δ 6.80 and 7.12. The integration value corresponding to the peak area in the HB20 sample is the lowest for the peak at δ 2.16 and indicates the highest degree of branching in the 20% TELA based hyperbranched epoxy resin.

From the ^{13}C NMR spectrum, the -CH_2 carbon of triethanolamine linked with ether linkage between triethanolamine and diglycidyl show peaks at δ 59, 62 and 64. These indicates the terminal unit (monosubstituted with glycidyl ether), linear unit (disubstituted with glycidyl ether) and dendritic unit (trisubstituted with glycidyl ether), respectively and provides the degree of branching in the hyperbranched epoxy resin. The degree of branching for 20% TELA based hyperbranched epoxy was 0.80 and found to be highest among 10, 20, 30% TELA based hyperbranched epoxy resin.

The ^{13}C NMR indicates that the peak height of mono substituted and trisubstituted peaks are comparitively higher than disubstituted peaks which indicate higher degree of branching in 20% TELA based epoxy. The number of dentritic and terminal unit are higher than the linear unit in case of 20% TELA.

The chemical linkages predicted in the hyperbranched epoxy were identified by Infra Red spectroscopy as shown in Fig. 1. The bands for asymmetric vibrations for epoxy ring appeared at 914-834 cm^{-1}(s). The absorption band at 1040 cm^{-1}(s) confirms the presence of aryl alkyl ether linkage. Also the aryl ether linkage present between the glycidyl ether and the trietanolamine is indicated by the peak
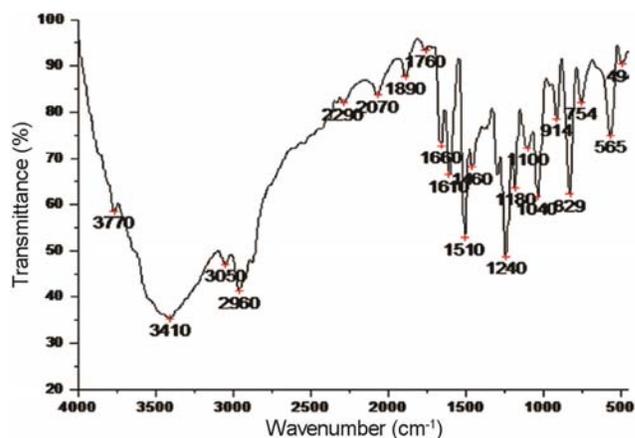

Fig. 1 — FT-IR spectrum of hyperbranched epoxy resin containing 20% TELA

at 1460 cm^{-1}(s). The peak at 1610 cm^{-1} is assigned for the –C=C- in the aryl group. The peak at 2960 cm^{-1} is the stretching vibration frequency observed for the aryl and alkyl -CH group. The peak at 3410 cm^{-1} is obtained for the –OH groups present in the resin which are formed by epoxy ring opening. The –C-N linkage in the triethanolamine is confirmed by the stretching peak at 1240 cm^{-1}. The comparative study of the FTIR spectra between neat epoxy resin, epichlorohydrine and the hyperbranched epoxy resin indicates the absence of traces of epichlorohydrine in the hyperbranched resin. This was because of the absence of the peak at 742 cm^{-1} in the epoxy resin and heperbranched epoxy resin. The complete removal of epichlorohydrine by azeotropic distillation was evidenced from FTIR spectra. The physical property, such as epoxy equivalent weight, viscocity, hydroxyl value, curing time post curing time, and swelling value were lowest in case of HB20 formulation. The 3:1, A_2:B_3 ratio is maintained in 20% TELA based hyperbranched epoxy due to which higher degree of branching was obtained. As proper approach of the monomers are possible or facilitate polycondensation, unlike 2:1 and 6:1 ratio which are maintained in the 30% and 10% TELA based hyperbranched epoxy,respectively. The excessive epichlorohydrine used facilitate the polycondensation reaction in a manner so that diglycidyl ether molecule cannot grow up with high molecular weight. Three parts by moles of epichlorohydrine required in the actual mole balancing reduces the viscosity more enough and the aquous part of the reaction mixture from the resin was separated easily without using nonpolar solvent.

From the Gas chromatography the purity of the prepared hyper-branched epoxy resin was determined. The sizes of the peaks in the chromatogram provides useful information. The ratio of the sizes of the peaks indicates the ratio of the relative amounts of substances in the sample. In this test a standard epichlorohydrine sample with prepared resin was compared. It was observed that the epoxy resin showed a small peak and for standard epichlorohydrine resin a large peak was obtained. This indicates that the prepared resin is free from epichlorohydrin. Comparative result of various physical properties of the prepared thermoset is shown in Table 1. The viscosity of the the prepared thermosets was found to be 261, 222, and 272 cps for HB 10, HB 20, and HB 30, respectivley. The above

Table 1 — Physical properties of hyperbranched resin

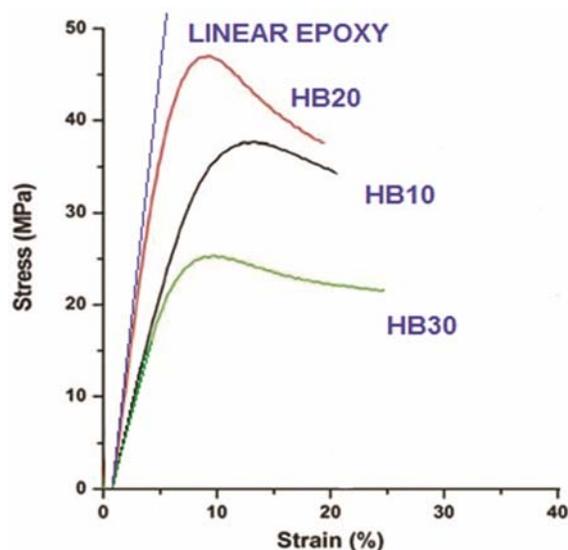| Properties	HB10	HB20	HB30
State	High viscous	Low viscous	High viscous
Tnasperency	Transperent	Transperent	Transperent
Colour	Light yellow	Light yellow	Light yellow
Epoxy equivalent (gm per eqvt.)	401	350	570
Hydroxyl value (mg KOH per gm)	122	87	150
Viscosity (cps)	261	222	272
Curing time at room temperature	3 hr	1hr	4hr
Swelling value (%)	20	10	30

Fig. 2 — Stress-strain profiles of the thermosets HB10, HB20, HB30 AND LINEAR EPOXY

data indicates that the HB 20 thermosets possess lowere viscosity than that of HB 20 and HB 30. Similaryl, the curing time and sweeling time were also found to be lower in case of HB 20 thermoset.

Performance of thermosets

The prepared hyper-branched epoxy thermosets possess both high tensile strength and comparatively higher elongation at break indicating the tough materials. This is due to the presence of both aromatic and aliphatic moieties. The stress-strain profiles showed that the tensile strength of the 20% TELA based hyperbranced epoxy is having the highest value of tensile strength (Fig. 2). However, the other two compositions, HB10 and HB30 are having the more flexibility as they are having low degree of brancing which makes them linear enough with sufficient brancing, showing decreased toughness. Table 2 shows that the elongation at break is lowest in case of the linear epoxy resin and it is highest for the 30%

TELA based hyperbranced epoxy resin. This is because the hyper-branched molecules are having more free volume inside the polymer matrix due to the non linear structure. The tests of scratch hardness determine the toughness of the materials. Higher scratch hardness resulted in higher toughness, as the hyper-branched epoxy thermosets possess both aromatic aliphatic moieties. Similarly the adhesive strength is also highest in case of the 20% TELA based hyper branched formulation as these have the highest degree of branching and no pealing off takes place easily. Because of the combination of the linear units and the partial branching in the 30% TELA based hyperbranced epoxy resin we get sufficient cushioning effect in the polymer matrix after curing.

Curing study of hyperbranched epoxy

The curing of the hyper-branched epoxy resin was carried out at room temperature with poly (amidoamine) as the hardener (Table 1). Hyper-branched resin reacts with the curing agent, epoxide rings are opened and forms new chemical chains with amine molecules, and thus, a cross-linked polymer network can be formed. The cross linking reaction is possible with enough epoxide group functionalities. The reactions between amine groups of the hardener with the strained epoxy oxirane ring occurred during the curing process and form covalent linkages between resin and hardener chain. In case of HB20 resin, the curing time was decreased. This may be explained by the fact that because of much lower viscosity of HB20 than HB10, and HB30, the dispersion and diffusion of the hardener is much better for crosslinking reactions.

Themal stability

The TGA thermograms of hyperbranched epoxy thermosets showed that the thermal stabilities of HB10, HB20 and HB30 were very high, as the initial decomposition temperatures were about 300°C. The thermosets were degraded mainly by two stages, where the first step is related to the degradation of the aliphatic moieties (300°C) and followed by the second stage due to the degradation of the aromatic moieties (470°C). As all the thermosets have almost same structural units, their degradation patterns and the degradation temperatures were almost the same. The high thermostability is because of the presence of thermostable rigid aromatic moiety and better crosslinking of the resin.

Table 2 — Mechanical performance tests

Properties	HB10	HB20	HB30	Linear epoxy
Tensile strength(Mpa)	6.8	8.21	4.2	2.67
Elongation(%)	38	44	51	3.57
Young's Modulus (Mpa)	370	253	450	972
Pendulum hardness(Mpa)	31	34	26	153
Scratch hardness(Kg)	8	9	7	5
Pull off adhesion(Mpa)	2.23	2.61	2.45	2.01

Table 3 — Chemical Resistance–twenty-four hour spot tests

Chemical environment	HB 10	HB 20	HB30
NaOH(5%)	8	8	8
NaOH(50%)	6	6	6
H_2O	10	10	10
HCl (10%)	8	8	8
H_2SO_4, conc	8	8	8
H_2SO_4 (10%)	8	8	8
Ethyl alcohol, 95%	10	10	10

10= no change
8=slight change
6= major change

Chemical resistance

The results of chemical resistance of the thermosets in different chemical environments are given in Table 3. From the table, it was found that the prepared resin showed excellent aqueous alcohol resistance. The resin has very good aqueous alkali, hydrochloric, and sulphuric acid resistance. This may be explained by the fact that the prepared thermoset resin possessed tougher chemical linkages and also showed higher condensed configuration. The chemical resistance was observed to be almost same for all the studied thermoset resin and suggest that all the prepared resin have higher comparable compact and crosslinked configuration.

Conclusion

A low viscous, room temperature curable, and high performance hyperbranched tough epoxy thermosets with good thermostability were obtained. The industrially important hyperbranched epoxy resins were synthesized by a single step, one pot $A_2 + B_3$ polycondensation reaction. The amount of epichlorohydrin used was three times higher than the actual mole balance of the polycondensation reaction and make the process suitable for industrial scale production. The requirement of organic solvent and the brine washing for the extraction of epoxy resin was completely skipped off and established an easier way for the synthesis of hyperbranched epoxy with zero VOCs. The synthesised epoxy resin was useful

for coating application and greener to the environment. Moreover, the exceptional reduction in cycle time was possible due to the azeotropic distillation to remove excess epichlorohydrine. This is the most advantageous findings for industrial manufacturing process development.

Acknowledgement

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