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ORIGINAL PAPER

Modification of hyperbranched epoxy by vegetable oil-based highly branched polyester resin

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Abstract Modification of existing polymers by physico-chemical technique is not only interesting and useful to the academic community but the resulted product is attractive to industrial application too. In this investigation, hyperbranched epoxy was modified by vegetable oil-based highly branched polyester resin at different weight percentages and properties of the cured systems were evaluated in order to justify them as advanced thin film materials with high adhesive strength. Modified systems were studied using FTIR, XRD, TGA and SEM analyses. Curing reaction was confirmed by FTIR study and swelling test. Performance characteristics like tensile strength, impact strength, adhesive strength, flexibility, scratch hardness, gloss and chemical resistance of cured films have also been studied. Modified systems showed improved properties over pristine epoxy. Comparison study of modified systems showed that hyperbranched epoxy with 30 wt% polyester content is the best composition w.r.t performance and might be utilized in advanced thin film application.

Keywords Hyperbranched epoxy · Vegetable oil-based polyester · Adhesive · Performance

Introduction

Epoxy resins are one of the most important industrially used thermosets because of their high strength, low creep, very low cure shrinkage excellent resistance to corrosion, good adhesion to many substrates and appropriate electrical insulating properties. These features make epoxy resins as one of the choices for various fields of application such as in fibre-reinforced composites, adhesives, coatings,

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electronics, building materials, food packaging etc. However, their brittleness character inhibits further proliferation into various advanced industrial applications [1]. Hence, the modification of epoxy resins to impart adequate flexibility and good toughness has been the subject of growing interest for many researchers in industrial as well as academic levels. There have been several attempts to improve the flexibility and toughness of the epoxy resins both via chemical and physical modifications [2–5].

Epoxy resins are successfully toughened by modifying them with plasticizer, low molecular weight toughening agent, thermoplastic resins, core shell particles, liquid rubber and nanosized particles. However, they suffer from leaching, phase separation, decrease in tensile and flexural strength in most of the cases. Moreover, the modifying agents used are commercial petrochemical-based products. There are a few reports also on toughening of epoxy resins by hyperbranched polymers, polyesters etc. [6–9]. Flexible polymeric materials such as amine-terminated acrylonitrile-butadiene (ATBN), carboxyl-terminated acrylonitrile-butadiene (CTBN), hydroxyl-terminated acrylonitrile-butadiene (HTBN), nitrile rubber and polyacrylates have also been found to be used as impact modifiers for epoxy resins [10–12]. The resulting products have good impact behaviour but inferior strength properties, and are unsuitable for high-performance engineering applications. Although, epoxy resin modified with these materials can be used in application areas connected with structural adhesives, corrosion and weather resistant coatings. All these results led to the researchers to find some newer, improved and efficient techniques to modify the epoxy resins to suit the high-performance applications.

In this context, author attempted a simple solution technique to modify the hyperbranched epoxy resin (HBE) with improved properties with a highly branched vegetable oil-based polyester resin. Moreover, hyperbranched epoxy resin used in this study has some unusual properties like high solubility, large number of functional groups, low cures time etc. In addition to these, strong interaction with the vegetable oil-based highly branched flexible polyester resin may result improvement in the performance and hence fulfil the demands of advanced applications.

Authors, therefore, wish to report here the performance of the modified hyperbranched epoxy resin by a vegetable oil-based polyester resin at different dose levels. The characterization of the modified systems by FTIR, XRD, TGA and SEM analyses were also reported here. The performance of the modified epoxy resins was evaluated by the measurements of tensile strength, impact strength, adhesive strength, flexibility, scratch hardness, gloss etc. to justify them as advanced thin film materials.

Experimental

Materials

Toluene, tetrahydrofuran (THF), petroleum ether, acetone (Merck, India) were used after distillation and stored with molecular sieves. Epichlorohydrin (EPC, Aldrich, Germany) and poly(amido amine) (Hindustan Ciba-Geigy Ltd., India) were used as received. Bisphenol-A (BPA, m.p. 159 °C, G.S. Chemical, India) was used after

re-crystallization from toluene. Vegetable oil-based highly branched polyester was prepared as reported earlier [13] and used in this study as modifier. Other chemicals like sodium hydroxide, sodium chloride and methanol etc. were obtained from Merck India Ltd. and used as received.

Instrumentation techniques and methods

IR spectra were recorded on a Nicolet (USA) Impact 410 FTIR spectrophotometer using KBr pellets. The viscosities of hyperbranched epoxy and its modified systems without curing agent were measured using Rheometer (Model CVO100, Malvern, UK). The variation of viscosity against time at constant stress and single shear, viscosity against shear stress and viscosity against temperature at constant stress of these systems were also studied by using the above instrument. Thermal study was conducted by thermogravimetric analysis, TGA (Shimadzu TG50, Japan) at a heating rate of 10 °C/min under nitrogen flow rate of 30 mL/min. Gloss of the cured films were measured by gloss meter (Sheen Instrument Ltd., Model No. 160, UK) at an angle of 60°. X-Ray diffraction study was carried out on Rigaku X-diffractometer (Miniflex, UK) at room temperature over the range of $2\theta = 2°–60°$. The surface morphology of the samples was done by a JEOL scanning electron microscope of model JSM-6390LV SEM after platinum coating on the surface. The adhesion test was performed by measuring lap shear strength on surface-treated plywood substrates as per the standard ASTM D2339-98 method [14]. The overlapping zone was 1×1 inch^2 for each case, the thickness of the adhesive within the overlapping area was ca. 0.03–0.04 mm. Scratch hardness test was done by scratch hardness tester (Sheen instrument Ltd., Model No. 705/1, UK) as per ASTM D5178 at a cross-head speed of 6 mm/s. The chemical resistance test was carried out by immersing the samples in different chemical media and by observing visible physical changes of the films and by measuring gloss (Table 2). The swelling was carried out by immersing the weighted amount (W_d) of cured film in DMF. After attaining equilibrium (48 h) the weight of the swollen film (W_s) was also measured. Then the swelling value was calculated by using the following formulae:

$$\text{Swelling } (\%) = (W_s - W_d)/W_d \times 100. \quad (1)$$

Preparation of hyperbranched epoxy and vegetable oil-based polyester resin

Preparation of hyperbranched epoxy resin

The hyperbranched epoxy resin was prepared by the following method. The hyperbranched polyether polyol (HBP, 20 wt% of total mass of hydroxyl compound, obtained as reported earlier) [15] and bisphenol-A were taken in a three necked round-bottom flask fitted with a condenser and thermometer. Calculated amount of epichlorohydrin (1:1.5 mol ratio of hydroxyl group to epichlorohydrin) was mixed with above mixture at room temperature under stirring. On complete dissolution of HBP and bisphenol-A, the system was placed on a preheated oil bath at (54 ± 1) °C. To this reaction mixture 5N aqueous solution of

sodium hydroxide was added drop wise for 1 h under stirring condition at constant temperature. After complete addition of sodium hydroxide solution, the reaction mixture was continued for 3 h at the aforementioned conditions. On completion of the reaction, the product obtained was dissolved in chloroform and filtered to remove the salt formed. The filtrate was then washed with 15% brine solution followed by washing with distilled water for 3–4 times. The washed product was dried under reduced pressure at 40 °C to complete dryness to get the sticky mass. The yield was about 60%. FTIR, ^{1}H NMR and ^{13}C NMR confirmed the formation of hyperbranched epoxy resin as described elsewhere.

Synthesis of highly branched vegetable oil-based polyester resin

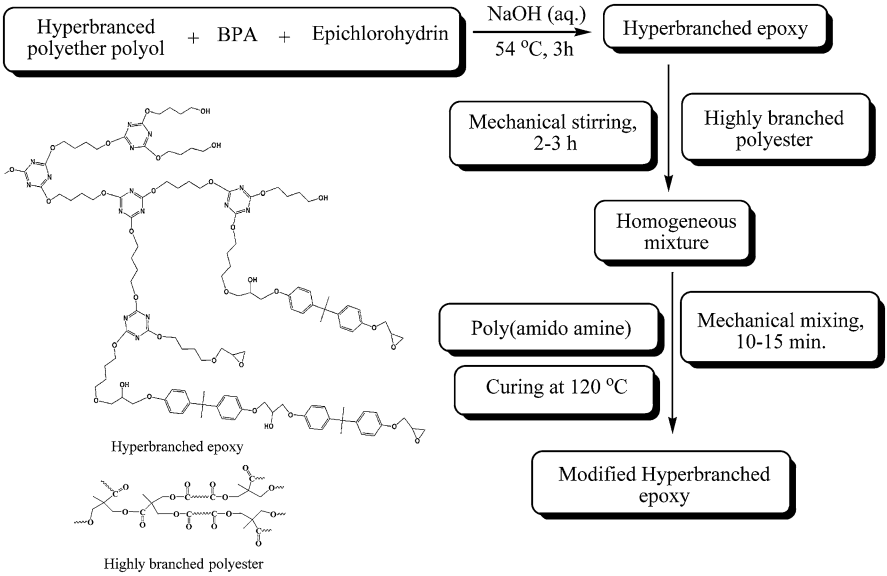
The polyester resin used was prepared as reported earlier [13], by reacting 0.12 mol (42.09 g) of monoglyceride of *Mesua ferrea* L. seed oil with 0.064 mol (6.27 g) of maleic anhydride and 0.096 mol (14.22 g) of phthalic anhydride at 150–220 °C to form the carboxyl-terminated pre-polymer. 20 g of this pre-polymer was then reacted with 3.32 g (0.016 mol) of 2, 2-bis(hydroxymethyl) propionic acid (bis-MPA) at 220 °C to obtain the desired resin. The prepared resin has the similar characteristics as reported earlier.

Modification of hyperbranched epoxy

The hyperbranched epoxy was modified by mixing of different weight percentages of highly branched polyester resin (10, 20, 30 and 50 wt% coded as MHBE10, MHBE20, MHBE30 and MHBE50, respectively) at room temperature. A little amount of THF was used to facilitate mixing. To this mixture 50 phr of poly(amido amine) with respect to epoxy resin was added in each case followed by stirring for about 10–15 min at room temperature to get a homogeneous mixture. The modification process has been diagrammatically shown in Scheme 1.

Preparation of thin films for curing and performance study

Films of the above homogeneous mixture were prepared by drawing them on glass plates of 120 × 100 × 2 mm^3 under ambient conditions. Similarly, coatings of the above mixtures on different substrates such as commercially available mild steel strips, 150 × 50 × 1.6 mm^3 for impact test and tin strips, 150 × 50 × 0.4 mm^3 for bending test were also prepared. After removal of sufficient amount of solvent under atmospheric conditions, the coated strips were degassed under vacuum to remove the last trace of entrapped solvent and volatiles. Then the coated mixtures were cured by heating at 120 °C in an oven for a specified period of time. The modified hyperbranched epoxy was kept under ambient conditions for 24 h before further investigations. The dried films from the glass plates were then peeled off by immersing the plates in warm water, followed by drying in a desiccator under vacuum and stored for 7 days before testing. The average dry coating thickness of the blends was measured by pen tester (Sheen Instrument Ltd., UK) and found to be 35–40 μm.



Scheme 1 Flow sheet diagram of the modification of hyperbranched epoxy by vegetable oil-based highly branched polyester resin

Results and discussions

Curing study of the modified systems

The crosslinking of epoxy–polyester mixture with poly(amido amine) hardener is a nucleophilic reaction. The possible reactions occurred in the curing process are the reaction between the amine group of the hardener with the strained oxirane ring of the epoxy resin and the hydroxyl groups present in the epoxy resin preformed or generated during crosslinking, hydroxyl groups of highly branched polyester resin with the amine hardener and oxirane ring of the other epoxy chains in the presence of a base poly(amido amine) to generate the ether linkages. Thus, the role of poly(amido amine) is multifold, which acts as a crosslinker as well as a base to facilitate the curing process in the curing reactions. Furthermore, there is a possibility of the formation of intermolecular hydrogen bonding between C=O of the polyester resins with –OH of the epoxy resin present in the system. The formation of a network structure is confirmed by the decrease in intensity of the hydroxyl band at 3,410 cm^{-1} and by vanishing of epoxy band at 916 cm^{-1} (Fig. 1). The epoxy resin and polyester also interact through intermolecular hydrogen bonding between the carbonyl group on the polyester and the epoxide ring [16]. These explained the high rate of curing of the epoxy resin by the amine hardener. An increase in the curing time (both touch free time and hard dry time) with respect to the increase in the polyester resin content in the modified system may be explained by the decrease in the active oxirane ring content of the mixtures (Table 2).

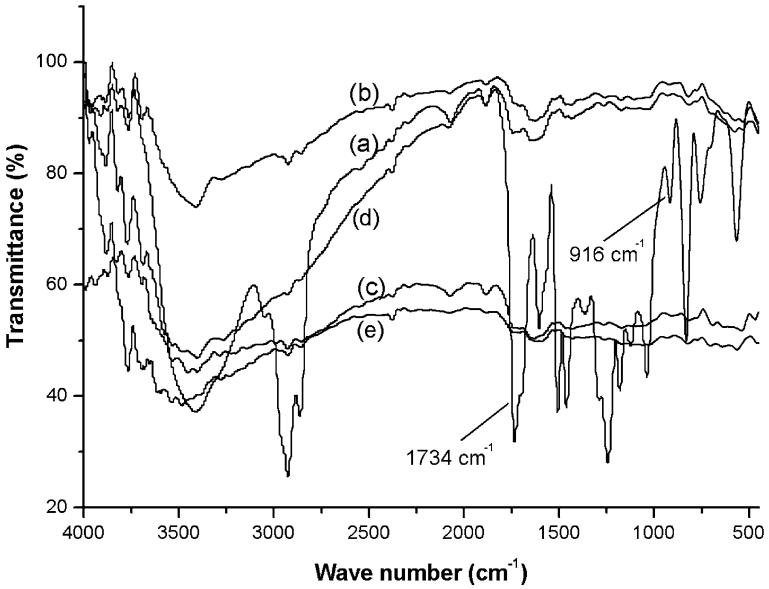


Fig. 1 FTIR spectra of uncured mixture of HBE and highly branched polyester (*a*), and its modified systems viz. MHBE10 (*b*), MHBE20 (*c*), MHBE30 (*d*) and MHBE50 (*e*)

Morphology of the hyperbranched epoxy and its modified systems

The properties of a modified system largely depend on the morphology. The modification with improved combination of properties of the individual component depends mainly upon the degree of compatibility of the systems. Epoxy resin, in general, showed to have good compatibility with polyester resin as evidenced by earlier studies [17].

The SEM micrographs (Fig. 2) of pristine hyperbranched epoxy and modified systems show a single phasic system. There is no observable phase separation encountered in the modified systems. This may be explained as the miscibility or interaction of the modifier with the pristine system. This is because of the domain size of the disperse phase which is governed by the level of polymer miscibility, physical and chemical nature of the modifier and pristine systems. The reduction of the domain size and relatively good interfacial adhesion of highly branched polyester resin and hyperbranched epoxy (Fig. 2) may be explained by better compatibility of the hyperbranched epoxy by virtue of its hyperbranched architecture as well as polar–polar interaction between both the resins [18]. In addition to that the higher compatibility may be due to better interpenetrating network formation through the reaction of amine groups of hardener with ester groups of polyester resin along with normal crosslinking of hydroxyl or epoxy groups by amine hardener. Along with this, there is the possibility of H-bonding between C=O of polyester groups with the –OH of hyperbranched epoxy resin present in the systems. Thus, the amine hardener acts both as a crosslinking and

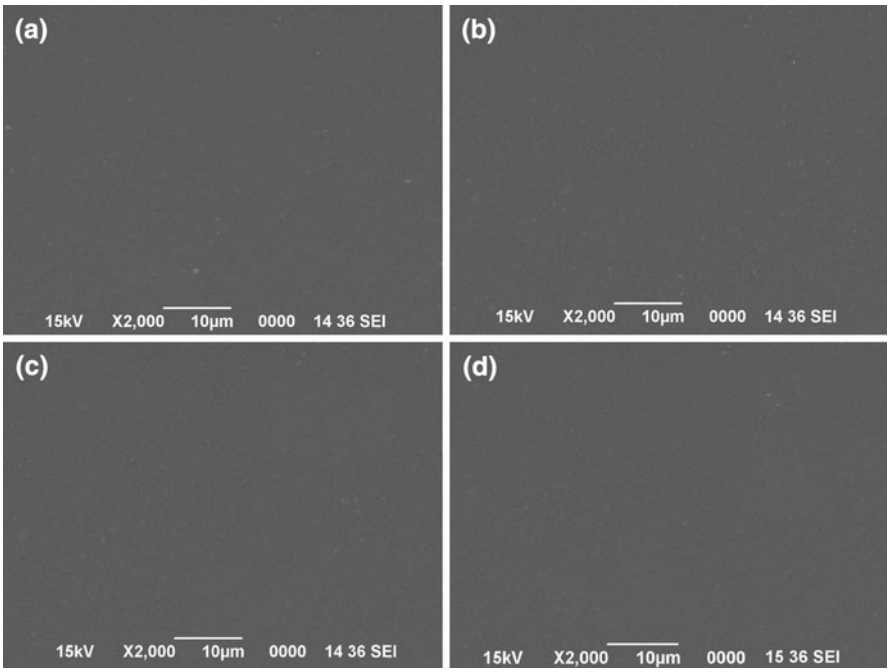


Fig. 2 SEM micrographs of modified HBE systems viz. MHBE10 (**a**), MHBE20 (**b**), MHBE30 (**c**) and MHBE50 (**d**)

compatibilising agent for these modified systems. This is reflected in the performance of the modified systems.

The X-ray diffraction patterns (Fig. 3) of both pristine HBE and modified systems do not show any sharp peak in the XRD plot indicating that there is little compactness in the systems and are found to be amorphous in nature.

Performance study of the modified systems

From Table 2, it has been found that the flexibility of the modified systems increases with the increase of polyester content in the systems which is also evidenced by the increase in the impact strength. This is due to decrease in cross-linking density and the presence of flexible hydrocarbon chain of the vegetable oil-based highly branched polyester resin, which results an increase in the molecular mobility and hence the flexibility. The decrease in cross-linking density is supported by swelling test in DMF (Table 2). The values of tensile strength of unmodified hyperbranched epoxy resin and modified systems are presented in Table 1. From the data, it is clearly observed that the incorporation of highly branched polyester has a specific influence on the value of tensile strength. Incorporation of 10, 20 and 30 wt% highly branched polyester into hyperbranched epoxy resin increases the tensile strength when compared with unmodified epoxy system. This may be explained as being due to the better interpenetrating network formation through the

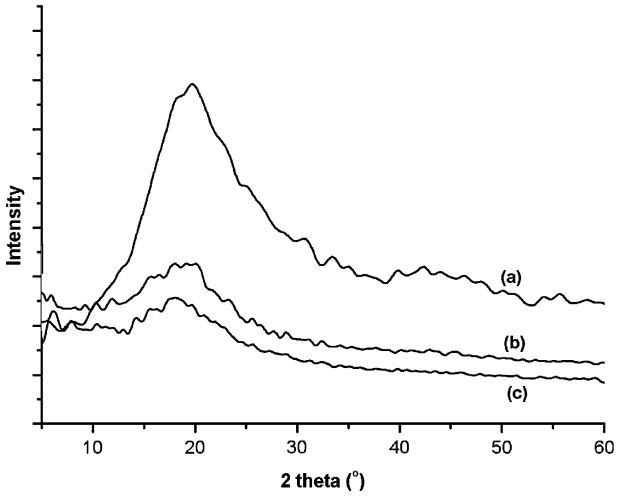


Fig. 3 XRD plot of HBE (*a*) and its modified system, MHBE20 (*b*) and MHBE50 (*c*)

Table 1 Compositions of HBE and its modified systems

Sample code[a]	Hyperbranched epoxy (wt, g)	Highly branched polyester (wt, g)	Poly(amido amine) (wt, g)
HBE	100	0	50
MHBE10	100	10	50
MHBE20	100	20	50
MHBE30	100	30	50
MHBE50	100	50	50

[a] The digits of the sample code indicate the polyester content with respect to hyperbranched epoxy

reaction of amine groups of hardener with ester groups of polyester resin along with normal crosslinking of hydroxyl or epoxy groups by amine hardener. On the other hand with 50 wt% of highly branched polyester content a slight decrease in the tensile strength was observed (Table 1), which may be due to the increase in the free volume that affect the close packing of chain molecules and thus decrease in the tensile properties [19]. The optimum tensile strength value for the modified system was found with 30 wt% of highly branched polyester content may be due to better compatibility and optimum level of cross-linking density.

Adhesive strength as measured by lap shear test increases with the increase of the highly branched polyester content in the modified systems due to increase of number of polar functional groups in the systems, which may chemically react with the hydroxyl groups of the plywood substrate. This increase of polarity also enhances the secondary interactions such as H-bonding, dipole–dipole, dipole-induce dipole, etc. which in turn increases the adhesive strength [20].

The variation of impact strength of the modified systems with highly branched polyester content may be explained from the angle of toughness of the films, which is the ability to absorb the applied external energy. The increase in the impact strength of the modified systems with the increase of highly branched polyester

Table 2 Curing study and performances of HBE and its modified systems

Property	HBE	MHBE10	MHBE20	MHBE30	MHBE50
Touch free time (min)	10	3	4	6	8
Drying time (min)	30	20	23	28	85
Swelling (%)	27	26.5	30.9	31.5	35
Bending test (mm)	>5	>3	<3	<3	<3
Impact strength[a] (cm)	60	65	100	100	100
Scratch hardness[a] (kg)	5.5	5	5.7	7	6
Gloss (60°)	82	85	90	93	95
Tensile strength[a] (MPa)	8.25	8.3	10	11.5	9.17
Adhesive strength[a] (N/m) $\times 10^{10}$	0.98	0.99	1.14	1.35	1.34

[a] All measurements are the mean value of three readings

content may be due to the presence of free volume and flexible hydrocarbon chain present in the systems. The presence of free volumes and flexible hydrocarbon chain in the systems impart flexibility and easy transfer and distribution of high impact energy to its adjacent molecular chains and thus improvement in impact strength. Gloss found to be increased with the increase of highly branched polyester content in the modified systems. This may be due to the increase in amount of highly branched polyester resin, which has higher gloss than epoxy resin. Scratch hardness test measures the ability of a coating film to resist the formation of any scratch at a specified load under dynamic condition. Thus, it measures the overall flexibility and hardness of the film. This is reflected in this study also as the scratch hardness was low initially and increased with increase in the highly branched polyester content (Table 2). The optimum scratch hardness was found with 30 wt% of polyester content in the modified hyperbranched epoxy systems. Thus, with 30 wt% polyester loading an optimum of both the hardness and flexibility was achieved and thus improvement in the properties.

Rheological studies of the hyperbranched epoxy and its modified systems

The rheological characteristics like variation of viscosity against time, shear stress and temperature were studied for hyperbranched epoxy resin and its modified systems. Both the resin and modified hyperbranched epoxy show Newtonian-like behaviour (Fig. 4). A decrease in the viscosity was observed after modification with highly branched polyester up to 30 wt% polyester content but increased at 50 wt% polyester content. This may be due to the highly branching nature of the polyester resin providing free space for the epoxy resin chains to move freely and thus reduction in the viscosity. While at higher polyester content the number of functional groups in the modified system increases leading to the increase in interaction with hyperbranched epoxy resin, which results a net increase in the viscosity. Figure 5 indicates no change in shear viscosity with increase in the shear stress (50–150 Pa) both for hyperbranched epoxy resin and its modified systems except for MHBE50, which shows pseudoplastic behaviour. The effect of temperature on the viscosity of

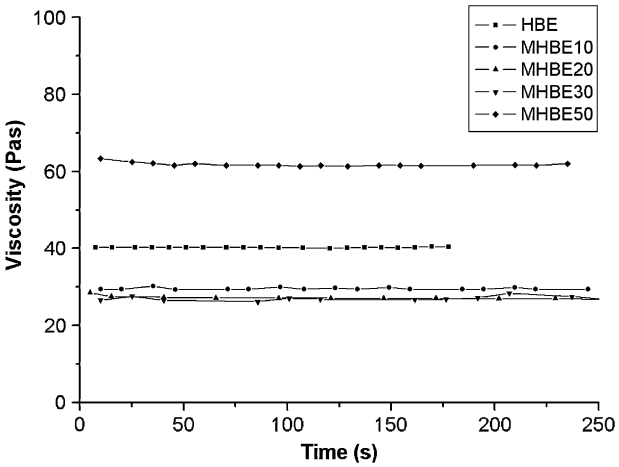


Fig. 4 Variation of viscosity at constant stress (100 Pa) under isothermal condition (25 °C) of HBE and its modified systems

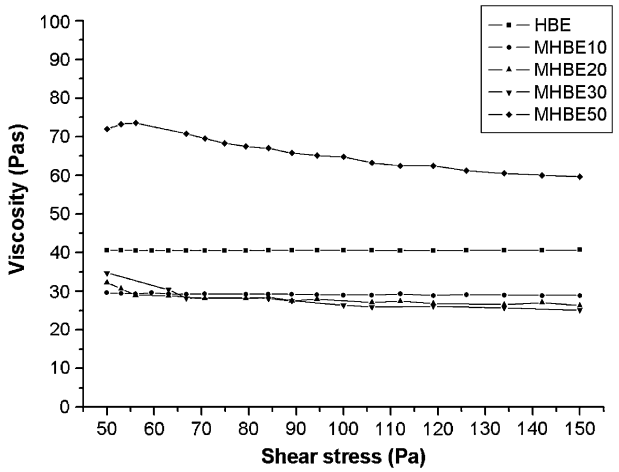


Fig. 5 Variation of viscosity against shear stress under isothermal condition (25 °C) of HBE and its modified systems

polymers is important as the polymers may undergo considerable changes in input heat energy during their processing. Generally, the viscosity decreases with temperature. The dependence of flow properties of the hyperbranched epoxy resin and its modified systems with respect to temperature is shown in Fig. 6. Shear viscosities of pristine hyperbranched epoxy resin and its modified systems decreases with the increase of temperature in the range of 25–75 °C at shear stress of 100 Pa (Fig. 6), which indicates improvement in flow behaviour of the systems at higher temperature. This is due to the accelerated molecular motion at higher temperature due to the availability of greater free volume and also due to the decreasing entanglement density and weaker intermolecular interactions at higher temperature.

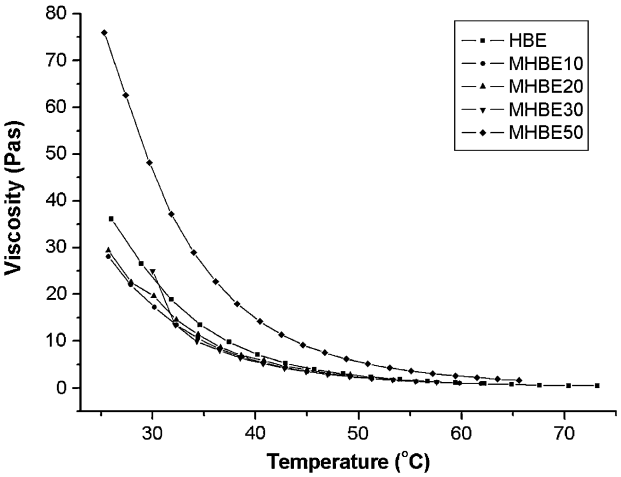


Fig. 6 Variation of viscosity against temperature under constant stress (100 Pa) of HBE and its modified systems

Thermal properties

The thermal stability of the modified systems was found to be almost remained constant except at very high percentage of polyester (50 wt%) (Fig. 7). The initial decomposition of the modified systems occurred in the temperature range of 220 °C and a multistep pattern of thermal degradation was observed in TGA curves. The thermal stability of the modified systems mainly depends on the extent of crosslinking, thermostable moieties and free volumes present in the systems. As in this case, the nature of moieties present in all the systems is the same, which varies in quantities, so the final thermostability of the modified systems depend only on the extent of crosslinking, free volumes and the amount of thermostable or thermolabile moieties present in the systems. This is evidenced from the TGA thermograms of the systems as shown in Fig. 7. This is due to the fact that with the increase of loading of highly branched vegetable oil-based polyester resin into the hyper-branched epoxy the amount of thermolabile linear hydrocarbon part of the highly branched polyester resin and free volumes in the system increases [19], which in turn may decrease the thermostability of the systems as observed with 50 wt% of polyester content (Fig. 7). However, this effect is not very significant at lower percentages of polyester because of the balance between cross-linking density and free volume at lower polyester content, so the thermostability was not affected to a large extent. The marginal increase in thermostability can be explained in terms of extent of crosslinking as with the increase in the highly branched polyester the cross-linking density of the modified systems increases resulting increase in the molecular restriction and hence net increase in the thermostability (Fig. 7). The combination of above two effects resulted the observed thermostability of the systems. The char residue of the all the modified systems was very low (3–4 wt%) indicating that the materials are almost fully combustible. The weight loss in the

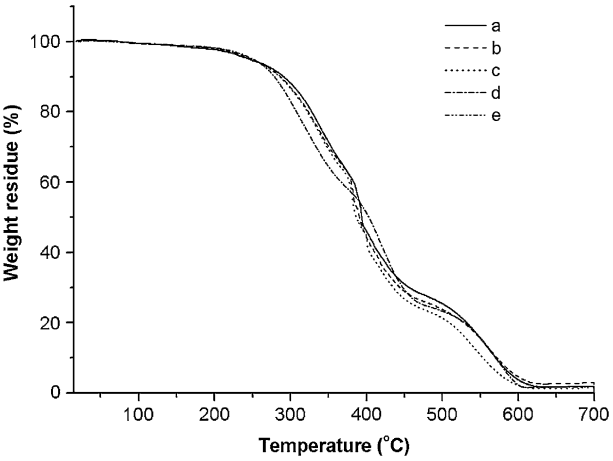


Fig. 7 TGA thermograms of pristine HBE (*e*) and its modified systems viz. MHBE10 (*a*), MHBE20 (*b*), MHBE30 (*c*) and MHBE50 (*d*)

first stage is most probably due to the decomposition of aliphatic hydrocarbon parts of the oil, epoxy moiety and ether linkages. The final stage of degradation is mainly due to the decomposition of rigid aromatic and hetero aromatic moiety present in the systems.

Chemical resistance

The chemical resistance test of the modified systems was performed in various chemical media (Table 3) for 10 days and the changes in appearance and gloss of the films were measured in each case after the aforementioned test time. Almost all the films showed good chemical resistance in most of the test media as no physical change in the appearance of the films was observed. The gloss values of different system showed excellent in distilled water and 10 % NaCl solution, whereas a little reduction was observed in acidic and alkaline medium. This may be due to the presence of hydrolyzable ester linkages in the systems. However, the reduction in the gloss was significant in alkaline medium with the increase in the polyester content in the modified system. This is due to the presence of a maximum amount of alkali hydrolysable ester linkages in that system. The overall good chemical

Table 3 Chemical resistance of HBE and its polyester modified systems

Sample code	At pH ~7.4	At pH ~6.8	NaCl solution (10%)	Distilled water
HBE	Good	Good	Excellent	Excellent
MHBE10	Good	Good	Excellent	Excellent
MHBE20	Good	Good	Excellent	Excellent
MHBE30	Good	Good	Excellent	Excellent
MHBE50	Good[a]	Good[b]	Excellent	Excellent

[a] Loss in gloss

[b] Slight loss in gloss

resistance of all the modified systems may be due to the presence of strong intra- and inter-molecular secondary interactions such as polar–polar and H-bonding, mutual crosslinking, the presence of aromatic moiety, etc. [18].

Conclusions

From this study, therefore, it can be concluded that relatively brittle hyperbranched epoxy thermoset is modified to a tough and flexible thermoset with the help of a highly branched vegetable oil-based polyester resin. The performances like bending, gloss, impact strength, tensile strength, adhesive strength, scratch resistance etc. are improved whereas chemical resistance, thermal stability etc. remained almost constant for the modified system from the unmodified one. However, it is found that 30 wt% of polyester is the optimum level of modification to obtained the best performance among the studied systems. Thus, 30 wt% highly branched vegetable oil-based polyester modified hyperbranched epoxy thermoset can be used as an advanced thin film material.

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