Renewable resource based thermostable tough hyperbranched epoxy thermosets as sustainable materials

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Renewable resource based thermostable tough hyperbranched epoxy thermosets as sustainable materials

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Abstract

The present study is focused on developing an environmentally benign bio–based epoxy thermoset that can be used as a sustainable material for various engineering applications. So, renewable resources like sorbitol and castor oil are used to synthesize novel hyperbranched epoxy resins. Three hyperbranched epoxy resins of castor oil with varying ratios of sorbitol along with conventional reactants are reported here. The chemical structure of them is confirmed by FTIR and NMR studies. The epoxy thermosets cured by fatty acid derived poly (amido amine) showed excellent mechanical properties such as high impact resistance (upto 34.5 kJ/m); good tensile strength (upto 31 MPa); good elongation at break (upto 37%) and moderate scratch hardness (upto 5 kg); high thermal stability (upto 293 °C); high tensile adhesive strength (upto 2152 MPa); good chemical resistance in different chemical environments and acceptable biodegradability. Thus, the sorbitol modified castor oil based hyperbranched epoxy thermosets are found to be superior in toughness, biodegradability, elongation etc. compared to a linear epoxy resin without sorbitol as well as previously reported thermosets derived from bio–based materials like vegetable oil, starch and glycerol. Therefore, these thermosets possess great potential to be used as sustainable materials for various advanced applications.

Keywords Bio–based hyperbranched epoxy, Castor oil, Sorbitol, Biodegradation, Eco–friendly

1. Introduction

Epoxies are one of the most widely used engineering thermosets because of their advantages like high stiffness, superior tensile strength, easy to process, excellent electrical strength, exceptional solvent resistance, good chemical as well as thermal resistance and compositional versatility [1,2]. However, these epoxy thermosets possess some serious disadvantages like low toughness, high brittleness and relatively high cost [3–5]. So, to address such limitations branch generating moiety has been introduced to the epoxy matrix which has achieved noteworthy interest to the researchers. These hyperbranched epoxy resins are of unique nature due to their simple as well as single–step preparative technique, high solubility, low viscosity and existence of large numbers of reactive end functional groups that provides strength and toughness to the epoxy thermosets [3]. Numerous synthetic protocols and their relevant applications have been reported by several research groups [6–9]. Although substantial work has been done on hyperbranched epoxy resins but they are mostly synthesized from petroleum based feedstocks which are non–biodegradable and also causes detrimental effect to health and environment. The depleting petroleum resources and societal issues across the globe have urged the researchers and chemical industries towards the sustainable development by adopting renewable bio–based chemicals and products. Therefore, to deal with such issues epoxy resins modified with bio–based feed stocks such as cardanol, tannin, lignin, glucose, vegetable oil etc. have been of extensive research interest as they offer biodegradability to the thermosets [10].

Vegetable oils have achieved considerable attention due to their advantages like non–toxicity, biodegradability, renewability, easy modification and environment friendly nature [11–16]. They can be chemically crosslinked in the open atmosphere which causes the reaction between the atmospheric oxygen to form polymeric materials with three dimensional network structures [17,18]. Das and Karak synthesized epoxy resin by using *Mesua ferera* seed oil to provide flexibility to the prepared epoxy thermoset [19]. However, the prepared epoxy resins showed poor mechanical properties compared to the commercial epoxy. Among the different types of vegetable oils, castor oil has been widely used in industries because of its easy availability in large quantity and unique chemical composition. So, De et al. reported a biodegradable hyperbranched epoxy from the polyester polyol of the monoglyceride of castor oil which showed excellent adhesive strength, good impact strength, scratch hardness, chemical resistance as well as biodegradability.[3] However, they have used costly bis(hydroxyl methyl) propionic acid modified polyol as branching unit as well as the biodegradability rate is very slow. Thus, in the present study bio–derived sorbitol is used directly as branch generating unit and monoglyceride of castor oil as another bio–based reactant for synthesizing the desired hyperbranched epoxy. Sorbitol is a naturally available sugar alcohol that has got good plasticizing ability, oxygen permeability and environmentally friendly substance [16–18]. It is also used as a substitute of sugar for food, starting material for synthesis of vitamin 12, plasticizer in ionomer and also in the manufacture of bio composites [20–25]. Thomzaine et al. studied the effect of sorbitol and glycerol blends on the physical properties of gelatin films [21]. On the contrary, it has been observed that with the increase in the amount of sorbitol the flexibility of the films increases but its barrier properties decreases [22]. As a result, adopting a dual strategy by incorporating sorbitol as a branch generating moiety in castor oil based epoxy resin might fulfill the objective of conveying flexibility and biodegradability to the resulting thermoset and thereby addressing almost all the shortcomings like high brittleness, low toughness, high cost, non renewability and biodegradability.

In the present study, therefore, an attempt has been made to overcome the existing drawbacks of commercially available epoxy thermosets by using bio–based components, combination of aromatic and aliphatic moieties and hyperbranched structure. Thus, three hyperbranched epoxy resins were synthesized by the polycondensation of monoglyceride of castor oil and bisphenol A with epichlorohydrin in presence of sorbitol at different weight percentages. The sustainable thermosets of these hyperbranched epoxy resins were obtained by curing with poly(amido amine). The performance characteristics such as mechanical, thermal, chemical properties and bacterial biodegradation were studied and the same were compared with a linear epoxy without sorbitol as well as previously reported thermosets derived from bio–based materials like starch, vegetable oil and glycerol.

2. Experimental

2.1. Materials

Castor oil (*Ricinus communis*) (Sigma Aldrich, Germany), sorbitol (HiMedia Laboratories Pvt. Ltd., India) and glycerol (Rankem, India) were dried under vacuum before use. Bisphenol A (Sisco Research Laboratories Pvt. Ltd., India) was recrystallized from toluene prior to use. Epichlorohydrin (Sisco Research Laboratories Pvt. Ltd., India), sodium chloride (Rankem, India), sodium hydroxide (HiMedia Laboratories Pvt. Ltd., India), sodium sulphate anhydrous (Merck Specialities Pvt. Ltd., India), poly(amido amine) hardener (Asian Paints, India, as gift sample with amine value 5-7 equiv/kg) were used as received.

2.2. Preparation of monoglyceride of castor oil

Monoglyceride from castor oil was prepared by the previously reported standard procedure. In brief, castor oil, glycerol (1:2 ratio) and calcium oxide (0.05 wt.% with respect to the oil) were taken together in a three–neck round bottom flask equipped with a mechanical stirrer, a thermometer and a nitrogen gas inlet. Nitrogen gas was purged inside the flask through the inlet. After that the mixture was continuously stirred and heated upto 225±5 °C for 2 h. The formation of the preferred monoglyceride was confirmed by checking its solubility in methanol (monoglyceride:methanol = 1:3, v/v) at room temperature [26].

2.3. Preparation of hyperbranched epoxy

The hyperbranched epoxy resin was synthesized by an A_x+B_y ($x,y \geq 2$) polycondensation reaction of monoglyceride of castor oil and bisphenol A with epichlorohydrin in presence of sorbitol. Bisphenol A, monoglyceride of the oil (10 wt.% of bisphenol A), sorbitol (10 wt% of bisphenol A) and epichlorohydrin (taken as 1 : 3 mol ratio with respect to the total hydroxyl groups) were taken together in a three necked round bottom flask, fitted with a condenser and a pressure equalizing funnel and stirred by a magnetic stirrer. A 5 N aqueous solution of NaOH (equivalent amount to hydroxyl groups) was slowly added to the reaction mixture at 80 °C through the pressure equalizing funnel under continuous heating. The reaction temperature was allowed to attain 110 °C. The addition took about 45–60 min to complete. After the completion of addition, the reaction was continued for another 3 h. The reaction was then stopped, allowed to cool down to room temperature with continuous stirring. The cooled, white viscous mass obtained was transferred to a separating funnel, washed with brine solution, followed by distilled water for 2−3 times and the aqueous layer was separated out to obtain the desired organic layer after absorbing the remaining water using anhydrous sodium sulphate. Then, the resin was dried at 75 °C in a rotary evaporator under vacuum to remove the excess of epichlorohydrin, THF and entrapped water. Finally, a viscous sticky transparent light yellowish mass was obtained which was coded as SMD 10. The yield obtained was 96%. Similarly, MGE, SMD 05 and SMD 15 were synthesized by following the same method with 0, 5 and 15 wt% of sorbitol (with respect to bisphenol A) respectively. The amount of all other reagents remained same for all the cases. The yield obtained for MGE, SMD 05 and SMD 15 were 88.8%, 93% and 91% respectively.

The physical properties of the resins such as solubility, viscosity, degree of branching (DB), epoxy equivalent and hydroxyl equivalent were evaluated as per standard protocols.

2.4. Curing study of the resins

The thermosets of the synthesized resins were obtained by curing the homogenous mixture of them with poly(amido amine) hardener. For this purpose, the required amount of hardener was mixed with each of the epoxy resins (1:1 equivalent ratio of epoxy to amine), separately taken in glass beakers, at room temperature. Further, the mixing was facilitated by adding few drops of THF to the mixture and then thoroughly stirred for about 15 min until a homogenous mixture was obtained. The mixture was then uniformly coated on cleaned glass slide of dimension 75 mm × 25 mm × 1.3 mm. This coated glass slide was then degassed in vacuum desiccator and kept under room temperature for 24 h to remove the volatiles present in it. Finally, the clean, bubble free slide was cured at 100 °C followed by post curing at 120 °C temperature in an oven for specified period of times. The degree of curing of the thermoset was verified by determining the swelling value as per the following formula,

$$\text{Swelling (\%)} = [(W_s - W_d)/W_d] \times 100$$

where W_s and W_d are the weights of the swelled and dried films respectively. The thermosets of SMD 05, SMD 10, SMD 15 and MGE are coded as SMDT 05, SMDT 10, SMDT 15 and MGET respectively.

2.5. Instrumentation

The FTIR spectra of the prepared resins were recorded by using KBR pellets in the FTIR spectrophotometer Nicolet (Madison, USA) FT-IR Impact 410. The ^1H and ^{13}C NMR spectra of the resins were recorded by 500 MHz AV500 Avance-III FT-NMR (Bruker, Switzerland), spectrometer by using $CDCl_3$ as the solvent. The viscosity of the resins was evaluated by using rheometer (Bohlin Instruments, Rheometer CVO, Malvern, UK). The mechanical properties like tensile strength and elongation percentage of the cured thermosets were evaluated by using the Universal Testing Machine (UTM), (WDW10, Jinan, China) with a load cell of 500 N at crosshead speed of 20 mm min^{-1} (ASTM D 638). The scratch hardness was tested by the scratch hardness tester (Sheen Instruments Ltd., UK). The adhesive strengths of the thermosets were also evaluated by UTM machine using lap shear test on metal–metal (78 mm × 25 mm × 0.50 mm) substrates with a load of 10 kN at a crosshead speed of 50 mm min^{-1} as per ASTM D 897. The impact tester (S. C. Dey Co. Ltd., India) was used to check the impact resistance of the thermosets on coated galvanized iron plates (150 mm × 50 mm × 1.50 mm) by using the standard (ASTM D 1709) falling ball method. The thermal stability of the thermosets were calculated by a thermogravimetric analyzer (TGA) (Shimadzu TG 50) with a nitrogen flow rate of 30 mL min^{-1}, at a heat rate of 10 °C min^{-1}, in a temperature range of 30 to 600 °C. The chemical resistance test of the thermosets was studied in different chemical environments for instance aqueous NaOH (5%), aqueous NaCl (15%), aqueous HCl (10%), aqueous ethanol (20%) as well as fresh water. For this study the cured thermosets were cut into small pieces and kept in abovementioned media at room temperature (30 °C) for a period of 30 days. After completing the experiment, weight loss percent of these thermosets was measured.

2.6. Biodegradation study

The biodegradation of the films were studied by following the McFarland turbidity method on the cured films using the bacterial strains of *P. aeruginosa* and *B. subtilus*.[27] These bacteria were isolated from the crude oil–contaminated soil of Assam, India. A nutrient medium containing 3.61 g of KH_2PO_4, 1.75 g of $MgSO_4.7H_2O$, 2.0 g $(NH_4)_2SO_4$,0.2 g of $CaCl_2.2H_2O$, 2.0 g of Na_2HPO_4, 0.5 g of $FeSO_4.7H_2O$, 0.01 g of $CuSO_4.7H_2O$, 0.5 g of $MnSO_4$, 0. 7 g of $ZnSO_4.7H_2O$, 0.1g of $H_3BO_3.5H_2O$ and 0.1 g of MoO_3 was prepared in 1.0 L in distilled water. Then, in a 100 mL conical flask 10 mL of this nutrient medium was transferred and sterilized by using an autoclave at a temperature of 121 °C and pressure of 15 lb for 15 min. The bacterial strains to be used for this study were cultured in this nutrient medium at 37 °C inside an incubator shaker for a time period of 48 h. The thermosets to be used for this study were incubated inside the medium under sterile condition at 37 °C. The growth of bacteria of the medium was signified by the increasing turbidity of the medium. A medium without the cured films was taken as the control. The extent of degradation was measured by taking absorbance of the medium at 600 nm to check the optical density (OD) of the microorganism with regard to the control for a time gap of 15 days. This study was performed as per the standard ASTM D 5332-98. The experiment was carried out for 8 weeks and the amount of degradation of the films was analyzed by SEM [3, 27,28].

3. Results and Discussion

3.1. Synthesis and characterization of the resins

The hyperbranched epoxy resins with three different weight percentages of sorbitol (viz. 5, 10 and 15 wt%) were synthesized by polycondensation reaction using an A_x+B_y ($x,y \geq 2$) approach. In this approach, bisphenol A reacts with epichlorohydrin and forms diglycidyl ether of bisphenol A (DGEBA) in situ due to higher reactivity of aromatic hydroxyl of bisphenol A compared to aliphatic hydroxyl of monoglyceride of castor oil and sorbitol, in presence of a base. The monoglyceride is used in this synthesis as an aliphatic diol which helps in the improvement of flexibility of the thermoset. This is due to the fact that the presence of flexible hydrocarbon chain as a pendent moiety attached with the fatty acid provides plasticization effect. The hyperbranched epoxy containing only sorbitol moiety may result into the formation of a rigid and brittle thermoset. Hence, the existence of this flexible moiety within the non entangled highly branched structure results in superior flexibility and high impact resistance compared to the commercially available epoxy as well as the linear epoxy prepared without the hyperbranched moiety.

The formation of diglycidyl ether of bisphenol A (DGEBA) in the first step was proved by taking a ^{1}H NMR after complete addition of NaOH in order to have a more clear understanding about the reaction pathway of the hyperbranched epoxy resin. The in situ generated DGEBA also contains a little amount of entrapped sorbitol and monoglyceride of castor oil even after normal purification. The ^{1}H NMR spectrum (Figure 1), [500 MHz, $CDCl_3$ (S), Me_4Si, δ (ppm)] indicates the presence of peaks for DGEBA at 1.62 (3H, CH_3 groups of bisphenol A), 2.73 and 2.87 (2H, CH_2 protons of oxirane ring), 3.3 (1H, CH of oxirane ring), 3.9 (2H, CH_2 present next to oxirane ring), 6.8 (4H, protons present in aromatic bisphenol A) and 7.15 (4H, aromatic protons of bisphenol A). The peaks at 3.67–3.78 (5H, C_1,C_4 and C_6 of sorbitol), 3.89– 3.96 (2H, C_6 protons of sorbitol), 4.02–4.12 (C_1, C_3 and OH of sorbitol), 4.15–

4.20 (3H, C_2 and C_5 of sorbitol), 0.88 (terminal methyl protons of fatty acid chain) and 1.25–1.47 (CH_2 protons of fatty acid chain) [3,28-32] were also found in the spectrum due to the existence of entrapped un-reacted sorbitol and monoglyceride of castor oil. The presence of unsubstituted aliphatic hydroxyl groups clearly indicates the fact. Again, with due course of reaction the epoxy group of DGEBA reacts with hydroxyl groups of monoglyceride of castor oil and sorbitol for chain extension. However, the primary hydroxyl groups react faster than the secondary ones due to their difference in reactivity. Furthermore, the remaining hydroxyl groups may react with epichlorohydrin directly [28]. All such polycondensation reactions resulted to the desired hyperbranched epoxy resin as shown in Scheme 1.

3.2. Structural characterization

The presence of different chemical linkages in the structure of epoxy resin was confirmed by the FTIR spectroscopic studies (Figure 2). The band around 3444 cm^{-1} is due to –OH stretching vibration and the bands around 915 – 831 cm^{-1} are assigned for asymmetric vibrations of oxirane ring.[29] The presence of a sharp absorption band at 1244 cm^{-1} reveals the existence of aryl–ether linkage in the structure. This blue shift in absorption value is associated with the electron withdrawing aryl group attached with the ether linkages. Similarly, the band observed at 1035 cm^{-1} is due to the presence of alkyl–ether linkage in the resin. The aliphatic and aromatic –C–H groups present in the epoxy matrix showed bands of stretching frequencies at 2966–2929 cm^{-1} and 3057 cm^{-1} respectively. The stretching vibrations at 1732 cm^{-1} and 1608 cm^{-1} correspond to –C=O and aromatic –C=C– groups respectively. Also, the band at 1505 cm^{-1} refers to the aliphatic –C=C– stretching frequency of the ricinoleic acid group [3,4,29,30].

The structure of SMD 10 was confirmed by ^{1}H NMR spectral analysis (Figure 3 (a)) δ_H, ppm (500 MHz, $CDCl_3$, Me4Si): peaks at 3.36 (1H, CH of oxirane ring), 2.74 and 2.88 (2H, CH_2 of oxirane ring), 3.94 (2H, CH_2 next to oxirane ring), 6.86 (4H, aromatic protons of bisphenol A), 7.17 (4H, aromatic protons of bisphenol A), 1.69 (3H, CH_3 of bisphenol A), 4.22 (1H, CH attached with OH), 3.71–3.77 (protons attached to $C_{1,}$ C_4 and C_6 of sorbitol), 3.93–3.95 (protons attached to C_1 and C_3 of sorbitol), 4.07 and 4.08 (1H, protons attached to C_1 and C_5 of sorbitol), (C_1, $C_{2,}$ C_3, C_4 and C_5 are named according to IUPAC format and are designated in the structure as l, m, n, o, p and q respectively), [31] 0.91 (terminal methyl protons of fatty acid chain), 4.9–5.5 (CH=CH of aliphatic chain) and 1.35–1.50 (CH_2 protons of ricinoleic acid chain) . The ^{13}C NMR spectral analysis was also conducted to study the presence of carbon in different chemical environments (Figure 3 (b)),δ_C, ppm ($CDCl_3$, S): peaks at 31.0 (CH_3 of bisphenol A), 44.5 and 50 (ring carbons of oxirane ring), 113, 127.7, 143.4 and 156.2 (carbons belonging to aromatic moiety of bisphenol A), 68.4, 68.7 and 69.8 for linear (L), dendritic (D) and terminal (T) substituted sorbitol moiety, 14.5–36.8 (carbons of fatty acid chain) and 113 ($CH_2=CH_2$ of fatty acid chain). The degree of branching (DB) of the hyperbranched structure was calculated from Fréchet equation: DB = (D + T)/(D + L + T) where D, L and T are the integration values of dendritic, linear and terminal units. The DB for the SMD 10 was found to be 0.82. The values of DB for SMD 05 and SMD 15 were found to be 0.80 and 0.83 respectively (Figure 4).

3.3. Physical properties of the resins and thermosets

The prepared epoxy resins are odorless and light yellowish sticky mass. The physical properties such as hydroxyl value, epoxy equivalent, viscosity etc. of the resins was evaluated and presented in Table 1. The epoxy equivalent decreases with the increase in sorbitol content of the resin which implies that the number of epoxy groups in a molecule is more, indicating faster curing rate as supported by the curing time (discussed later). Based on the proposed structure of the hyperbranched resin the epoxy equivalent should be 425 g/eq, however, experimentally it was found to be 389 g/eq which indicates the presence of some amount of DGEBA as shown in Scheme 1. The hyperbranched resins were found to be soluble in most of the common organic solvents like dichloromethane, chloroform, acetone, ethanol, DMAc, DMF, DMSO etc. The solubility of hyperbranched resin was found to be more compared to its linear analog in a particular tested solvent. This is due to the presence of large number of flexible moieties and polar functional groups along with the unique structural attribute of the former compared to the later.[5] The gloss characteristic of the cured thermosets was good because of appropriate crosslinking density, structural stability and the smooth surface. The specific gravity of the thermosets varies from 1.13 to 1.18 as presented in Table 1 which is also due to the compact globular structure of the resins. The molecular weight (Mw), number average molecular weight (Mn) and poly dispersity index (PDI) of the resin (SMD 10) were found to be 1437 g/mol, 1393 g/mol and 1.03 respectively. These results are for the parts that are soluble in THF. However, the actual molecular weight is higher than this as the standard used is linear polystyrene, which is also reflected by the molecular weight (4257 g/mol) of the proposed structure (Scheme 1).

3.4. Curing study

The curing of the synthesized resins was carried out to evaluate the mechanical, thermal and chemical resistance properties of their respective thermosets. For this purpose, the synthesized resins were cured with poly(amido amine) hardener at 1:1 equivalent ratio of epoxy to amine. Thus, the amount of hardener added to each of the resin was different as they have different epoxy equivalent values. On curing at elevated temperature with poly(amido amine) hardener the highly strained oxirane ring of epoxy resin open up due to its reaction with labile protons of amine group of hardener and hence, the resinous substance was transformed to a solid form of three dimensional crosslinked structure [22]. The plausible crosslinking reaction pathway is shown in Scheme 2. This is also evident from the FTIR study, where the band for oxirane ring in the region of 914-835 cm^{-1}, was completely disappeared [32]. The curing time decreases with the decreasing epoxy equivalent value because the number of epoxy groups increases (Table 1). Thus, SMD 10 took the lowest time to cure due to its lowest value of epoxy equivalent compared to SMD 05 and SMD 15. The optimum curing time is taken as the time at which the swelling value of the thermoset in a suitable solvent lies in between 20–30% as shown in Table 2. The linear resin MGE took higher time to cure than the hyperbranched resins because hyperbranched resins possesses greater number of epoxy functionality and hence, higher crosslinking density compared to linear one [28].

3.5. Performance

The evaluation of mechanical properties like tensile strength, elongation, scratch hardness, impact strength and adhesive strength for three different hyperbranched thermosets and the linear analog were evaluated and the data are given in Table 3. SMDT 15 displayed the highest tensile strength and toughness but lower percent of elongation. However, the overall percentage of elongation is superior than the glycerol based hyperbranched epoxy thermosets reported by Barua et al.[4] Better elongation at break of the thermoset may be due to the combined effect of relatively high molecular weight of the hyperbranched epoxy as a result of higher functionality of the branch generating moiety and the plasticizing effects of the hardener, sorbitol and monoglyceride of the oil. The presence of sorbitol in the hyperbranched moiety also affects the tensile strength of the thermoset. The value increases with the increasing proportion of sorbitol due to the higher functionality of it [21]. Again, as sorbitol is used here as a branching moiety so the formation of non entangled globular structure of the resin offers best possible level of crosslinking in the structure which results into fairly good tensile strength and toughness (Figure 5).

The evaluation of impact resistance showed that the hyperbranched epoxy thermosets exhibited higher impact resistance compared to its linear analog. This is because of the presence of unique combination of aromatic and aliphatic linkages in appropriate proportions. The scratch resistance of the thermosets was also studied and found to be good because of the above mentioned reasons. The adhesive strength of the prepared thermosets for metal substrates was found to be better than the linear thermoset and it increases with the increasing percentage of sorbitol content in the epoxy matrix. This is due to the good physical interactions of the polar epoxy, ether and hydroxyl groups of the hyperbranched structure and the poly(amido amine) hardener with the substrates as well as better mechanical interlocking. The structure of sorbitol leads to globular like hyperbranched structure which possesses low viscosity that results into higher rate of diffusion and hence the mechanical interlocking with the pore structure of the metal substrate [33].

3.6. Thermal properties

The thermal stabilities of the hyperbranched as well as linear thermosets were studied (Figure 6) and their degradation temperatures were recorded (Table 4). The thermograms showed that the hyperbranched epoxy thermosets exhibited a two–step degradation pattern. The initial degradation temperature varies from 261 to 293 °C which were found to be better than the starch based epoxy resins reported by Duarah and Karak [22]. The peak temperatures of the different thermosets were found to be in the range from 340 to 353 °C which is due to the degradation of the aliphatic thermolabile moieties of the monoglyceride and sorbitol present in the matrix of the thermosets. This variation is also in accordance with the epoxy equivalent values of the respective resins, (as shown in Table 1), which signifies adequate degree of crosslinking of the thermosets. The peak temperature for second step of degradation varies from 432 to 449 °C which is attributed to the thermostable aromatic moiety of diglycidyl ether of bisphenol A linkage as well as the amide linkages present in the epoxy thermosets [4,33]. However, the peak temperature for second step of degradation is much higher for the starch based epoxy thermosets because starch is made up of closed chain of aliphatic linkages which offer high stability to the thermoset under high temperature. On the other hand, sorbitol is made up of only flexible straight chain aliphatic linkages and hence its peak temperature for the second degradation step is low. An initial reduction of 2–5 wt% is due to the loss of volatiles including moisture associated with the polar functional groups present in the thermoset [28,34]. The thermosets also possess weight residues of 3.49 - 8.66 % at 600 °C which is due to the presence of carbonaceous substances. The glass transition temperatures (Tg) of the thermosets showed an increasing trend along with the proportion of sorbitol in the epoxy matrix because of the increase of secondary interactions such as the polar-polar interaction and hydrogen bonding as a result of hyperbranched structure [28,35]. The percentage of rigid aromatic moiety present in MGET is more compared to any of these sorbitol based hyperbranched structure and thus, the rigidity of the former is higher so the glass transition temperature.

3.7. Biodegradation study

The biodegradation study of the hyperbranched and linear thermosets revealed the gradual degradation of the thermosets upon exposure of *P. aeruginosa* bacterial strain with time (Figures 7 and 8). The degradation was also studied by *B.subtilis* but the degradation was found to be low compared to *P. aeruginosa* bacterial strain and hence the results are not presented. *P. aeruginosa* is a hydrocarbon degrading bacteria extracted from crude petroleum oil field. Biodegradability is achieved by the increase of amorphous nature, flexibility as well as polarity of the linkages and the hydrophilic character of the polymer [36]. Further, the presence of hydrolysable ester linkages of the monoglyceride resulted in biodegradation of the thermosets. However, the rate of biodegradation increases with the increasing amount of sorbitol content in the epoxy matrix. Sorbitol is a sugar alcohol which is naturally available and biodegradable. SMDT 15 with the highest amount of sorbitol content and hyperbranched structure offers better surface for bacterial growth. The SEM micrographs further revealed the adherence and growth of bacteria on the surface of the hyperbranched epoxy thermoset (SMDT 15).

3.8. Chemical resistance

The chemical resistance of the thermosets was studied in different chemical media such as 10% HCL, 5% NaOH, 15% NaCL, 20% EtOH and water and the results are given in Table 5. The hyperbranched thermosets showed good chemical resistance against the acid and alkali medium compared to its linear analog which is due to its unique structural attribute and presence of polar moieties. Also, the good crosslinking density contributed to the good chemical resistance of the thermosets [4].

4. Conclusion

From this study, it can be concluded that a sustainable and biodegradable hyperbranched epoxy thermoset of castor oil and sorbitol with high performance was obtained. The degree of branching of the synthesized resin was increased with sorbitol content. The cured thermosets was also found to exhibit sorbitol content dependent good toughness, biodegradability, thermostability and excellent adhesive strength compared to the linear as well as previously reported bio–based epoxy thermoset. The thermal resistance, biodegradability and chemical resistance were also found to be much better than the linear analog. Thus, these bio–based epoxy thermosets have potential to be used as tough biodegradable advanced sustainable materials.

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References

(1) May C. A. Epoxy Resins Chemistry and Technology; 2nd ed.; Marcel Dekker, Inc.; New York, 1988.

(2) Ray D, Ghorui S, Bandyopadhyay NR, Sengupta S, Kar T. New materials from maleated castor oil/epoxy resin blend reinforced with fly ash. Ind Eng Chem Res 2012; 51(6): 2603-2608.

(3) De B, Gupta K, Mandal M, Karak, N. Biodegradable hyperbranched epoxy from castor oil-based hyperbranched polyester polyol. ACS Sustainable Chem Eng 2014; 2(3): 445-453.

(4) Barua S, Dutta G, Karak N. Glycerol based tough hyperbranched epoxy: synthesis, statistical optimization and property evaluation. Chem Eng Sci 2013; 95: 138-147.

(5) Karak N. Fundamentals of polymers: raw materials to applications. PHI Learning Pvt. Ltd., New Delhi, 2009.

(6) Mezzenga R, Boogh L, Manson JE. A review of dendritic hyperbranched polymer as modifiers in epoxy composites. Compos Sci Technol 2001; 61(5): 787-795.

(7) Zhang D, Jia D. Synthesis of novel low-viscosity liquid epoxidized aromatic hyperbranched polymers. Eur Polym J 2006; 42(3): 711-714.

(8) Samuelsson J, Sundell, PE, Johansson, M. Synthesis and polymerization of a radiation curable hyperbranched resin based on epoxy functional fatty acids. Prog Org Coat 2004; 50(3): 193-198.

(9) Ratna D, Varley R, Simon GP. Toughening of trifunctional epoxy using an epoxy–functionalized hyperbranched polymer. J Appl Polym Sci 2003; 89(9): 2339-2345.

(10) Auvergne R, Caillol S, David G, Boutevin B, Pascault JP. Biobased thermosetting epoxy: present and future. Chem Rev 2014; 114(2): 1082-1115.

(11) Gupta AP, Dev A, Ahmad S. Modification of novel bio–based resin–epoxidized soybean oil by conventional epoxy resin, Polym. Eng. Sci. 2011; 51(6): 1087-1091.

(12) Gupta AP, Dev A, Ahmad S. Development of novel bio–based soybean oil epoxy resins as a function of hardener stoichiometry. Polym Plast Technol Eng 2010; 49(7): 657-661.

(13) Ahmed S, Ashraf SM, Naqvi FS, Hasnat A. A polyesteramide from *Pongamia glabra* oil for biologically safe anticorrosive coating. Prog Org Coat 2003; 47(2): 95-102.

(14) Samarth NB, Mahanwar PA. Modified vegetable oil based additives as a future polymeric material – review. Open J Org Polym Mater 2015; 5(1): 1-22.

(15) Lu Y, Larock RC. Novel polymeric materials from vegetable oils and vinyl monomers: preparation, properties, and applications. Chem Sus Chem 2009; 2(2): 136-147.

(16) Xia Y, Larock RC. Vegetable oil–based polymeric materials: synthesis, properties, and applications, Green Chem 2010; 12: 1893-1909.

(17) Meier AR, Metzgerb JO, Schubert US. Plant oil renewable resources as green alternatives in polymer science. Chem Soc Rev 2007; 36: 1788-1802.

(18) Williams CK, Hillmyer A. Polymers from renewable resources: A perspective for a special issue of polymer reviews. Polym Rev 2008; 48(1): 1-10.

(19) Das G, Karak N. Epoxidized *Mesua ferrea L.* seed oil–based reactive diluent for BPA epoxy resin and their green nanocomposites. Prog Org Coat 2009; 66(1): 59-64.

(20) McHught TH, Krochta JM. Sorbitol vs glycerol–plasticized whey protein edible films: integrated oxygen permeability and tensile property evaluation. J Agric Food Chem. 1994; 42(4)**:** 841-845.

(21) Thomazine M, Rosemary AC, Sobral PJA. Physical properties of gelatin films plasticized by blends of glycerol and sorbitol. J Food Sci 2005, 70(3), 172-176.

(22) Pasupuleti S, Madras G. Synthesis and degradation of sorbitol–based polymers. J Appl Polym Sci 2011; 121(5): 2861-2869.

(23) Shibata M, Nakai K. Preparation and properties of biocomposites composed of bio–based epoxy resin, tannic acid, and microfibrillated cellulose. J Polym Sci Part B: Polym Phys 2010; 48(4): 425-433.

(24) Krogars K, Heinämäki J, Karjalainen M, Niskanen A, Leskelä M, Yliruusi J. Enhanced stability of rubbery amylose–rich maize starch films plasticized with a combination of sorbitol and glycerol. Int J Pharm 2003; 251(1-2): 205-208.

(25) Shimasaki T, Yoshihara S, Shibata M. Preparation and properties of biocomposites composed of sorbitol-based epoxy resin, pyrogallol–vanillin calixarene and wood flour. Polym Compos 2012; 33(10): 1840-1847.

(26) Thakur S, Karak N. Castor oil-based hyperbranched polyurethanes as advanced surface coating materials. Prog Org Coat 2013; 76(1): 157-164.

(27) Gogoi S, Karak N. Biobased biodegradable waterborne hyperbranched polyurethane as an ecofriendly sustainable material. ACS Sustainable Chem Eng 2014; 2(12), 2730-2738.

(28) Duarah R, Karak N. A starch based sustainable tough hyperbranched epoxy thermoset. RSC Adv 2015; 5(79): 64456-64465.

(29) Das G, Karak N. *Mesua ferrea L.* seed oil-based epoxy resins. J Appl Polym Sci 2010; 118(1): 128-134.

(30) Delor-Jestin F, Drouin D, Cheval PY, Lacoste J. Thermal and photochemical ageing of epoxy resin – influence of curing agents. Polym Degrad Stab 2006; 91(6): 1247-1255.

(31) Wishart DS, Knox C, Guo AC, Eisner R, Young N, Gautam B, Hau DD, Psychogios N, Dong E, Bouatra S, Mandal R, Sinelnikov I, Xia J, Jia L, Cruz JA, Lim E, Sobsey CA, Shrivastava S, Huang P, Liu P, Fang L, Peng J, Fradette R, Cheng D, Tzur D, Clements M, Lewis A, Souza AD, Zuniga A, Dawe M, Xiong Y, Clive D, Greiner R, Nazyrova, A, Shaykhutdinov R, Li L, Vogel HJ, Forsythe I. HMDB: a knowledgebase for the human metabolome. Nucleic Acids Res 2009; 37(1): W603-610.

(32) Sangermano M, El-Sayed H, Voit B. Ethoxysilyl-modified hyperbranched polyesters as mulitfunctional coupling agents for epoxy–silica hybrid coatings. Polymer 2011; 52(10): 2103-2109.

(33) Roy B, Karak N. Synthesis and characterization of thermostable hyperbranched epoxy resin for surface coating applications. J Mater Res 2012; 27(14): 1806-1814.

(34) De B, Karak N. A room temperature cured low dielectric hyperbranched epoxy adhesive with high mechanical strength. J Chem Sci 2014; 126: 587-595.

(35) Allauddin S, Narayan R, Raju KVSN. Synthesis and properties of alkoxysilane castor oil and their polyurethane/urea-silica hybrid coating films. ACS Sustainable Chem Eng 2013; 1(8): 910-918.

(36) Baruah P, Karak N. Bio-based tough hyperbranched epoxy/graphene oxide nanocomposite with enhanced biodegradability attribute. Polym Degrad Stab 2016; 129: 26-33.

Scheme Captions

Scheme 1. Reaction pathway for the synthesis of hyperbranched epoxy resin.

Scheme 2. Crosslinking reaction between hyperbranched epoxy and poly(amido amine) hardener.

Figure Captions

Fig. 1. ^{1}H NMR spectrum of DGEBA resin.

Fig. 2. FTIR spectra of SMD 10 and its thermoset.

Fig. 4. Linear (L), dendritic (D)and terminal (T) units of (a) SMD 05, (b) SMD 10 and (c) SMD 15.

Fig. 5. Stress–strain profiles of MGET, SMDT 05, SMDT 10 and SMDT 15.

Fig. 6. (a) TGA thermograms, (b) DTG curves and (c) glass transition temperatures of epoxy thermosets.

Fig. 7. Bacterial growth profiles of *P.aeruginosa* against exposure time for the thermosets.

Fig. 8. SEM micrographs along with surface plots of (a) MGET before degradation, (b) MGET after degradation, (c) SMDT 15 before degradation and (d) SMDT 15 after degradation.

Table Captions

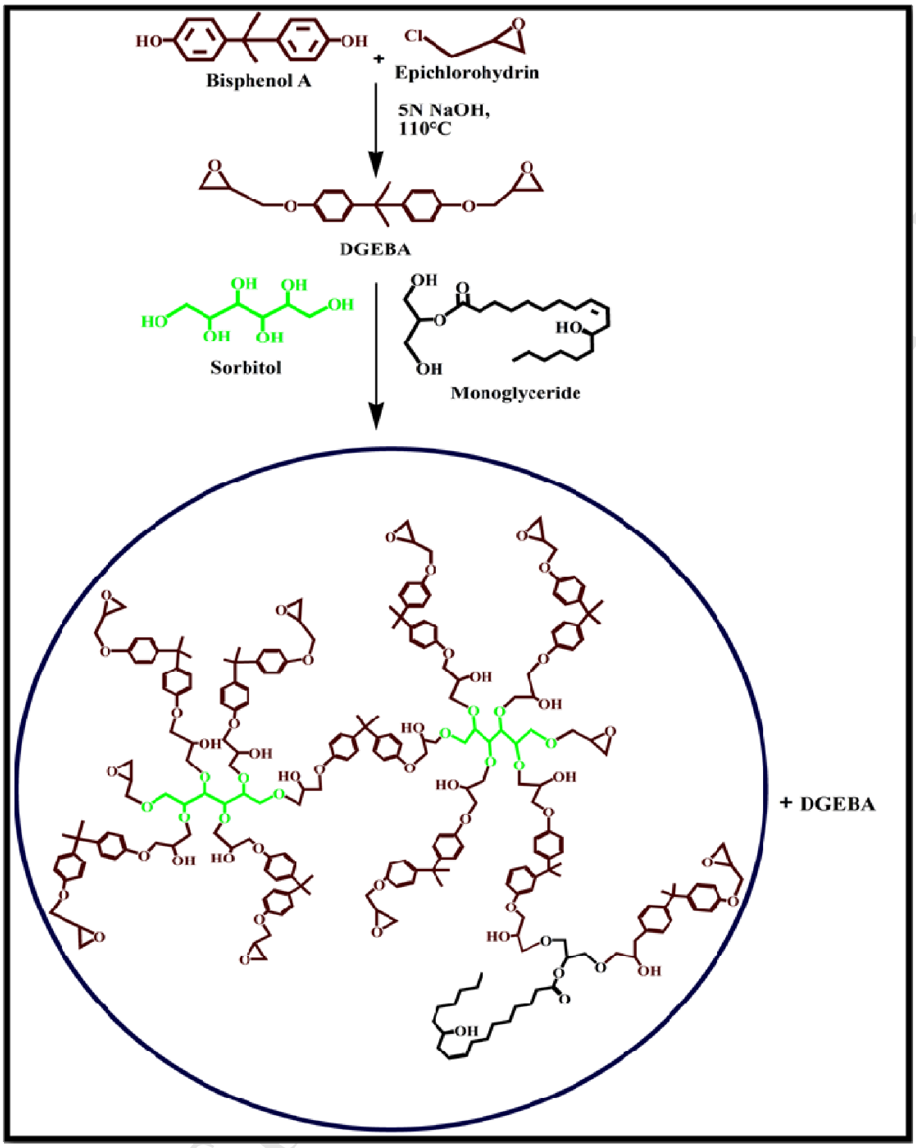
Table 1. Physical properties of the resins and thermosets

Table 2. Curing parameters of the resins

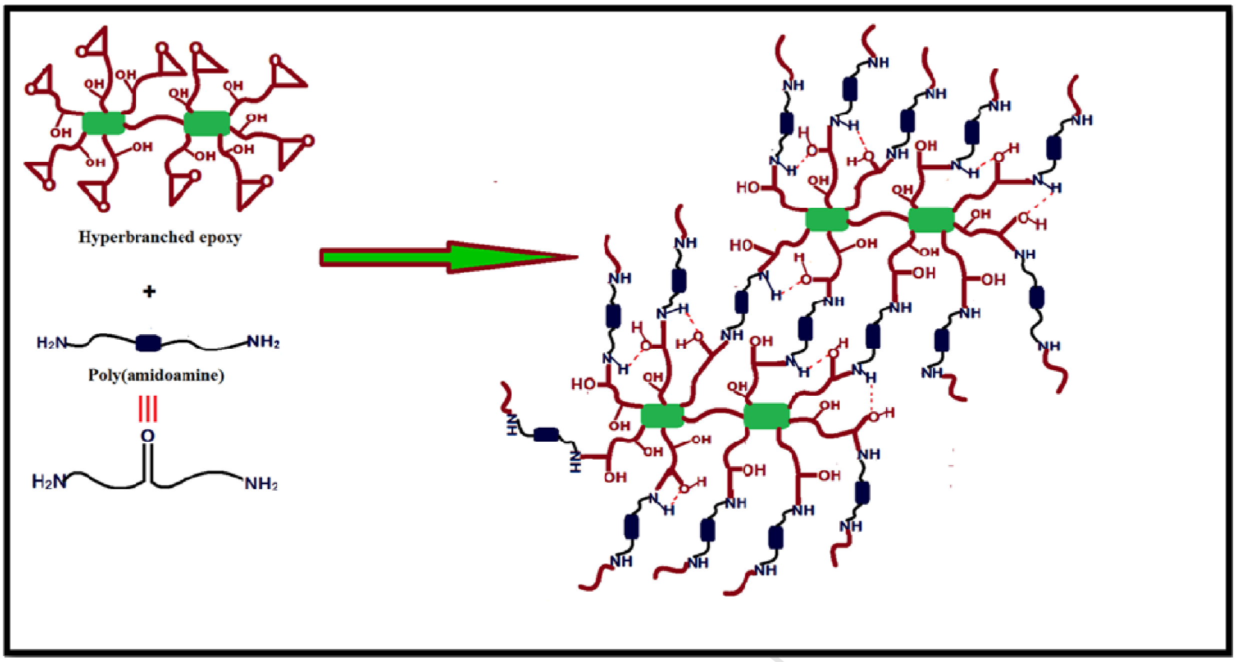
Table 3. Mechanical properties and adhesive strength of the thermosets

Table 4. Thermal parameters of the epoxy thermosets

Table 5. Weight changes (%) of the thermosets in different chemical media



Scheme 1. Reaction pathway for the synthesis of hyperbranched epoxy resin.



Scheme 2. Crosslinking reaction between hyperbranched epoxy and poly(amido amine) hardener.

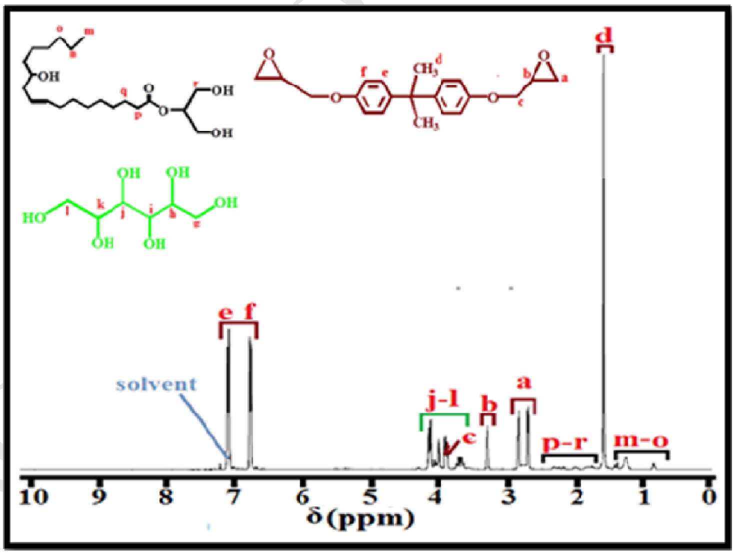
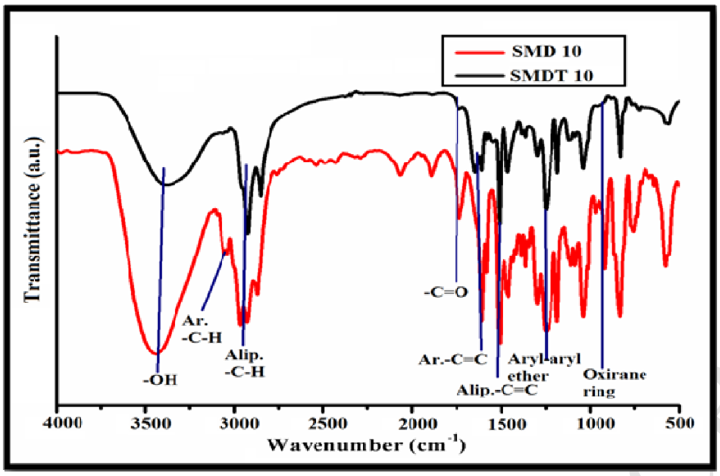


Fig. 1. ^{1}H NMR spectrum of DGEBA resin.



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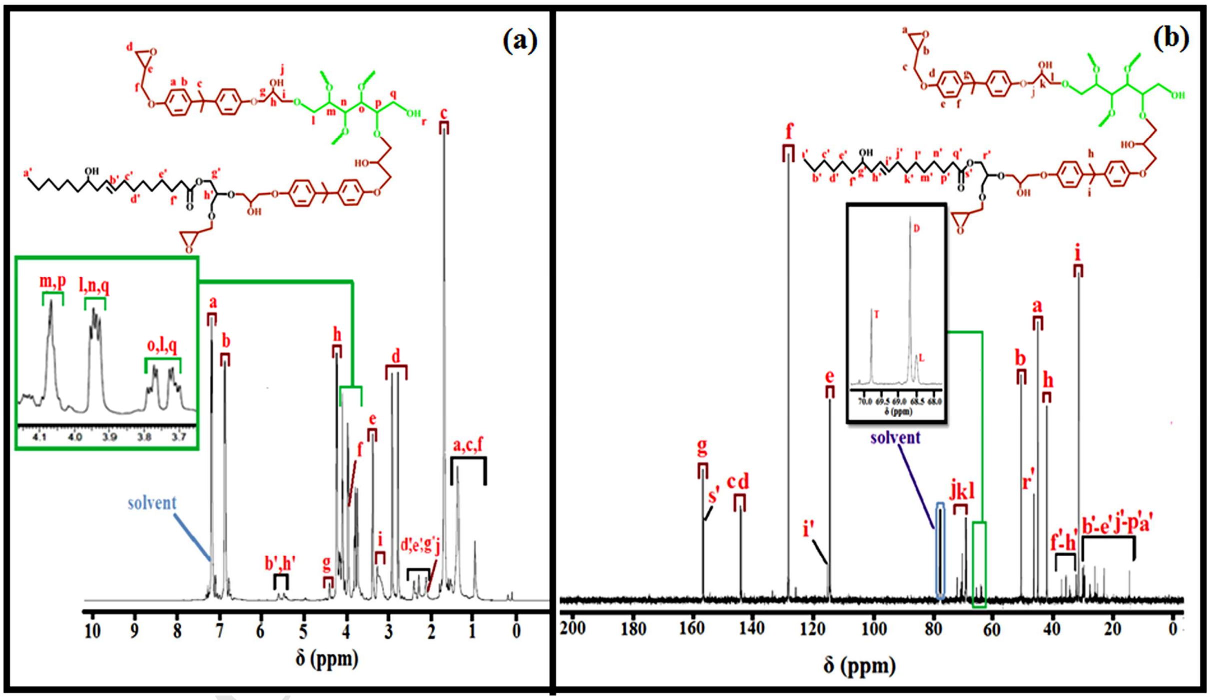


Fig. 3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of SMD 10.

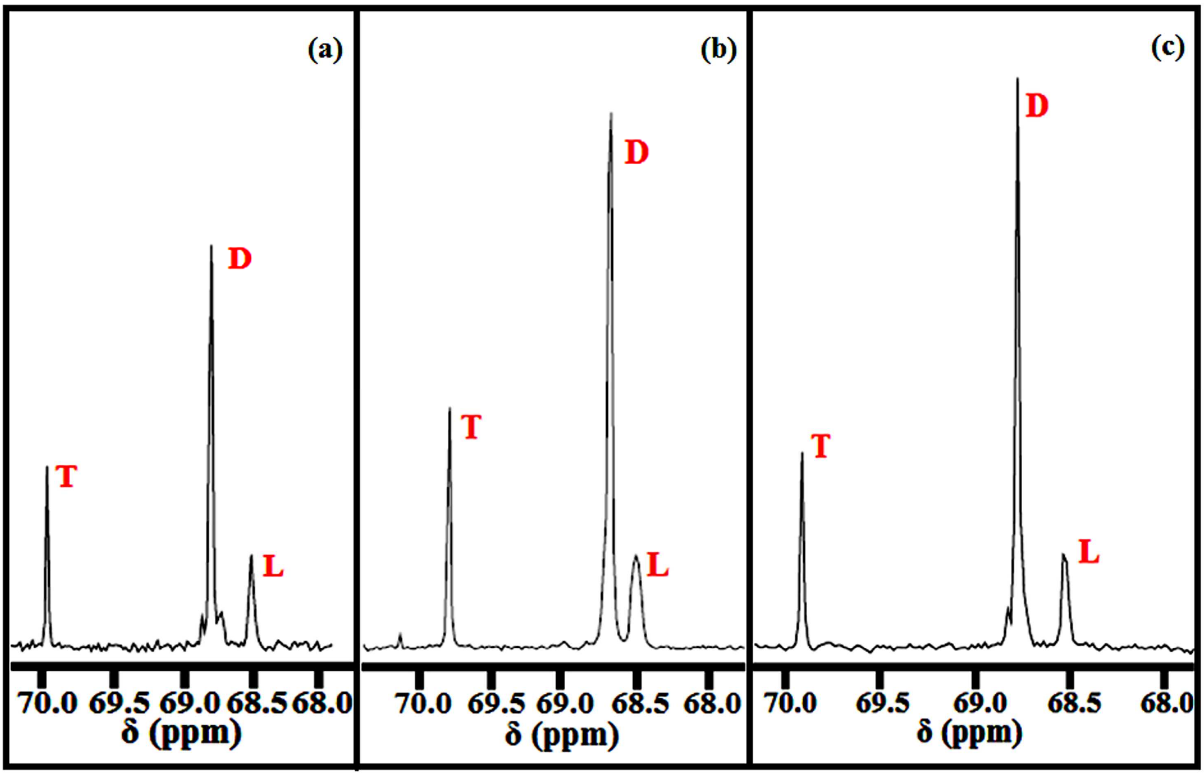
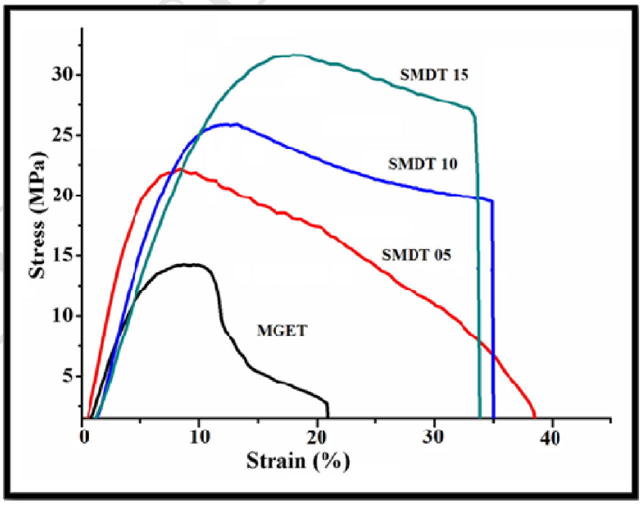


Fig. 4. Linear (L), dendritic (D)and terminal (T) units of (a) SMD 05, (b) SMD 10 and (c) SMD 15.



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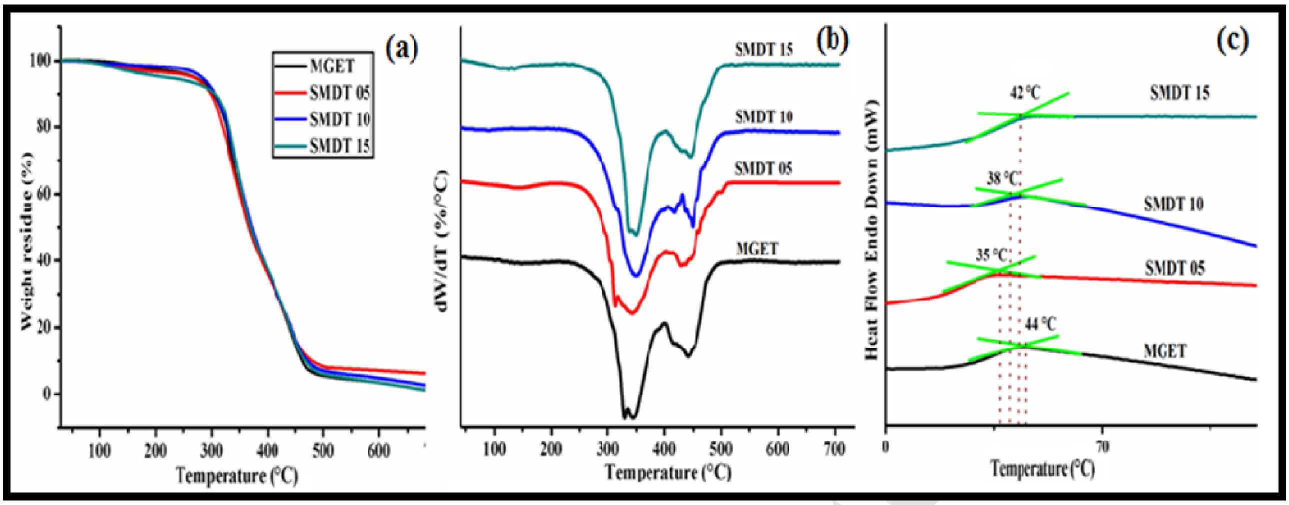

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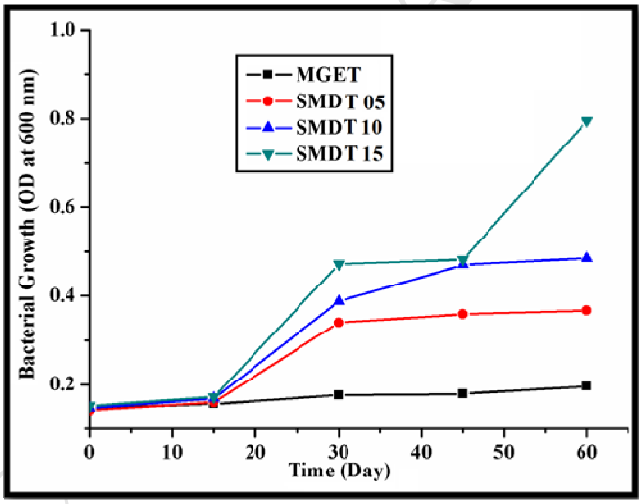

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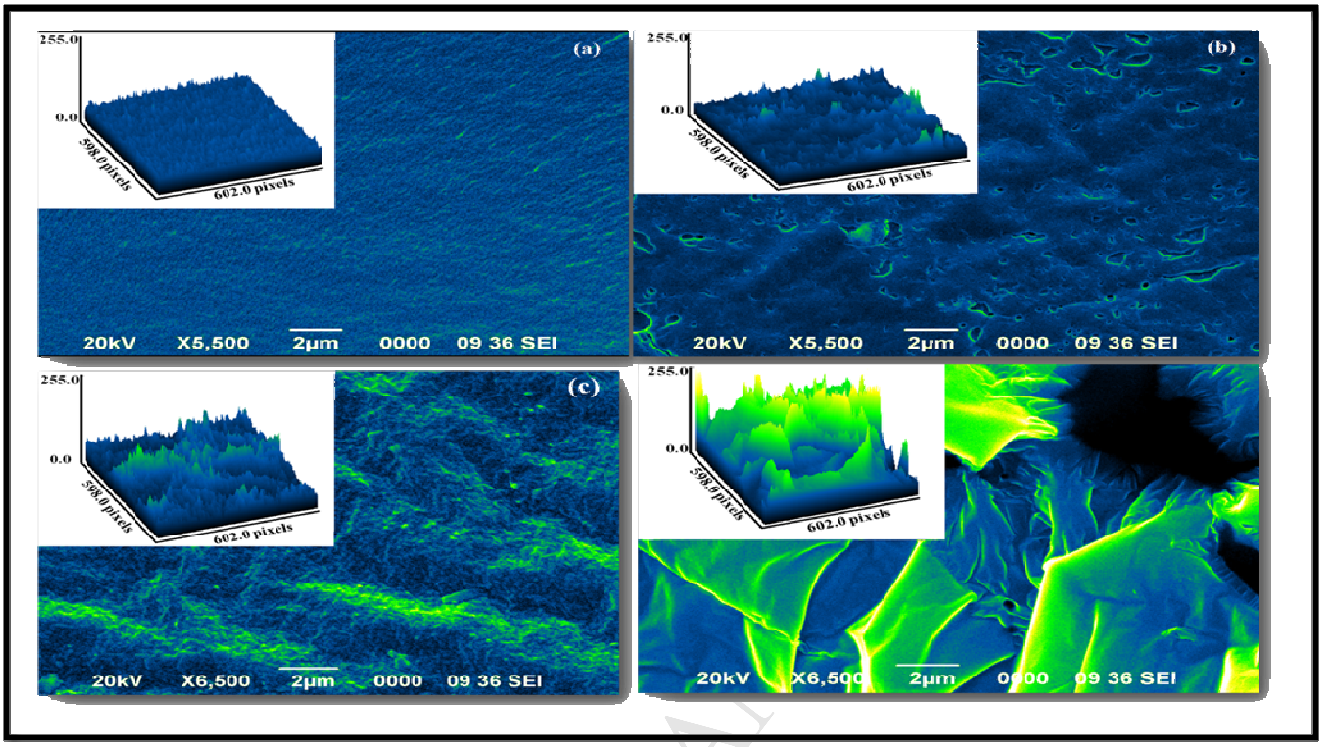

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Table 1. Physical properties of the resins and thermosets

	Resin					Thermoset	
Sample code	**Hydroxyl equivalent (g/eq)**	**Epoxy equivalent (mg KOH/g)**	**Degree of branching (DB)**	**Viscosity (Pa.s)**	**Sample Code**	**Gloss (°C)**	**Specific gravity**
SMD 05	172.06	482	0.80	20.82	**SMDT 05**	74.3±1	1.13±0.01
SMD 10	122.25	389	0.82	3.16	**SMDT 10**	74.6±4	1.11±0.03
SMD 15	178.16	403	0.83	9.18	**SMDT 15**	81.8±1	1.07±0..01
MGE	147.80	352	_	57.01	**MGET**	78.7±7	1.18±0.01

Table 2. Curing parameters of the resins

Properties	SMD 05	SMD 10	SMD 15	MGE
Time for curing at 100 °C (min)	40	20	25	60
Time for post curing at 120 °C (min)	20	10	15	30
Swelling value at 25 °C (%)	28	22	25	28

Table 3. Mechanical properties and adhesive strength of the thermosets

Properties	SMDT 05	SMDT 10	SMDT 15	MGE
Tensile strength (MPa)	22 ± 0.6	25±0.4	31±0.5	20±1
Elongation at break (%)	37±1	35±2	33±0.5	14±1
Toughness (MJ m^{-3})	5.56±0.5	7.33±1.0	8.11±2	1.73±0.5
Scratch hardness (kg)	2±0.5	4±0.6	5±1	3
Impact strength (kJ/m)	17±3	34.5	31.9	16.8
Adhesive strength (MPa)	1680±3	1989±5	2152±1	1402±6

Table 4. Thermal parameters of the epoxy thermosets

Parameter	MGET	SMDT 05	SMDT 10	SMDT 15
Initial degradation temperature (°C)	272	261	274	293
Peak temperature for first step of degradation (°C)	342	340	346	353
Peak temperature for second step of degradation (°C)	432	436	445	449
Weight residue (%)	8.66	7.01	4.90	3.49
Glass transition temperature (°C)	44	35	38	42

Table 5. Weight changes (%) of the thermosets in different chemical media

Chemical medium	SMDT 05	SMDT 10	SMDT 15	MGET
Aq. HCl (10%)	0.006	0.005	0.006	0.012
Aq. NaOH (5%)	0.005	0.009	0.005	0.010
Aq. NaCl (15%)	0.004	0.006	0.003	0.011
Aq. EtOH (20%)	0.006	0.001	0.004	0.009
Water	0	0	0	0