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Biodegradable Hyperbranched Epoxy from Castor Oil-Based Hyperbranched Polyester Polyol

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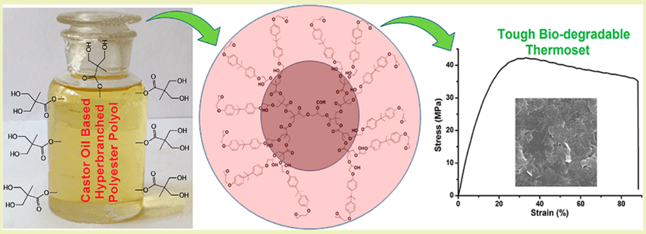

ABSTRACT: An outstanding tough, highly elastic, biodegradable, and thermostable hyperbranched epoxy was synthesized by a simple polycondensation reaction between a castor oil-based hyperbranched polyester polyol (HBPP) of monoglyceride of oil and bis(hydroxy methyl)propionic acid (Bis-MPA) and in situ-generated diglycidal ether of bisphenol A (DGEBA). The structure of HBPP was confirmed from FTIR, NMR, and different analytical studies. The formation of hyperbranched epoxy along with its structure was analyzed by different spectroscopic and analytical techniques. The poly(amido amine)-cured hyperbranched epoxy exhibited high tensile strength (42 MPa), extensibility (88% elongation), toughness (3144), scratch hardness (>10.0 kg), impact resistance (>100 cm), flexibility (bent up to 180° without damage), and biodegradation. The results indicate the strong influence of the amount of polyester polyol and bisphenol A on the performance of the thermosets. The study showed the superiority of the studied hyperbranched epoxy over the standard commercial bisphenol A-based epoxy (SBE) as well as the physically modified SBE with 10 wt % of HBPP. This biodegradable, elastic, and tough epoxy thermoset can be used as a sustainable advanced material.

KEYWORDS: *Castor oil, Polyester, Hyperbranched epoxy, Biodegradable, Toughness*

INTRODUCTION

It is now essential in many areas to tailor-fit polymeric materials for their specific applications where high performance and novel functions are needed. The commercial linear epoxy thermoset exhibits good mechanical strength, chemical resistance, adhesive strength, and dimensional stability.[1−4] However, their low toughness and high brittleness restrict their many advance applications. Hence, researchers are trying to improve their toughness by incorporating a flexible phase, like blending rubbers or polyesters into them.[5−10] However, due to processing difficulties and insignificant improvements, the modified systems cannot address the demands, and therefore, commercial exploration is limited. Also, control of the chemical and physical structures of epoxy resins is very important for optimizing their desired performance. In this endeavor, recently hyperbranched epoxy achieved significant attention to the researchers. The epoxy resins of that kind are of special interest due to their easy synthetic protocol, low viscosity, high solubility, and presence of large numbers of end functional groups.[11−14] In addition to those, a single-step synthetic protocol helps their mass scale production and, hence, are attractive to industry. Different synthetic approaches have been reported for hyperbranched epoxy resins, which include end group modification of hyperbranched polymers,[15,16] proton transfer polymerization,[17,18] and functionalization of poly(methyl acrylate) using ATRP.[19] All of these products were either solid or highly viscous liquid and hence needed dilution with organic solvents, which is detrimental to the environment due to the production of large amounts of VOCs. In most of the cases, the mechanical strength is also found to be low, which attributed to low cross-link density. Thus, hyperbranched epoxy with desired performance that is also synthesized by the single-step polycondensation process is very limited. Therefore, we report a simple strategy to achieve the desired tensile strength, high elongation at break, high toughness, and ductile hyperbranched epoxy from a castor oil-modified hyperbranched polyester polyol and in situ-prepared bisphenol A-based epoxy by a polycondensation reaction. Fu et al. synthesized a highly branched aromatic polyester-based hyperbranched epoxy resin via the reaction between epichlorohydrin and carboxy-terminated hyperbranched polyester of trimellitic anhydride and triethylene glycol using tetrabutyl ammonium bromide catalyst.[20] Zhang et al. reported a low-viscosity, liquid-epoxidized, aromatic, hyperbranched polymer synthesis by the reaction between epichlorohydrin and carboxy-terminated hyperbranched polyester prepared from trimellitic anhydride and dihydroxy alcohols.[11] Wang et al. synthesized an epoxy-terminated, hyperbranched, aromatic polyester from 5-acetoxyisophthaloyl chloride and glycidol.[16] All the synthesized resins possess low viscosity, and the corresponding thermosets are highly flexible. However, in all the above cases, the mechanical properties as well as alkali resistance were found to be very

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poor. This is because of the presence of a soft and alkali hydrolyzable polyester backbone. Thus, they were mainly used as toughners for commercial bisphenol A-based epoxy. However, in our case, polyester moieties are combined with glycidyl ether epoxy of bisphenol A in the same molecular structure. The use of castor oil in hyperbranched polyester polyol synthesis adds a positive component to this study. This is due to the fact that castor oil is a renewable, low cost, and abundant material, and it may impart biodegradability to the final product in contrast to commercial bisphenol A-based epoxy thermosets.[21−23] Presently, the biodegradability of a polymer is important to addressing global pollution and solid waste management issues. Thus, the use of vegetable oil-based polymers, mainly polyesters polyol, might serve the double goal of imparting flexibility and biodegradability to the resultant epoxy thermosets.

In the present study, to overcome the existing genuine limitations of epoxy thermoset like brittleness or low toughness and nonbiodegradability, an attempt has been made to synthesize a hyperbranched epoxy from castor oil-modified hyperbranched polyester polyol and in situ-generated glycidyl ether epoxy of bisphenol A. Its performance, including biodegradation of poly(amido amine)-cured hyperbranched epoxy thermosets at different compositions, was investigated.

■ EXPERIMENTAL SECTION

Materials. Castor oil (*Ricinus communis*) (BD Pharmaceutical Works Pvt. Ltd., Kolkata, India, acid value 3.7 mg KOH/g, hydroxyl value 157 mg KOH/g) and glycerol (Rankem, New Delhi, India) were used after vacuum drying. Bisphenol A and epichlorohydrin were purchased from GS Chemical, Mumbai, India. Bisphenol A was recrystallized from toluene prior to use. 2,2-Bis(hydroxyl methyl)-propionic acid (bis-MPA) (Alfa Aesar, Lancaster, U.K.), sodium hydroxide (Rankem, New Delhi, India), poly(amido amine) hardener (HY840, Ciba Geigy, Mumbai, India, amine value 5−7 equiv/kg), and commercial diglycidyl ether of bisphenol A-based epoxy (Araldite GY250, Ciba Geigy, Mumbai, India, epoxy equivalent 190 g/equiv) were used as received without any further purification. All other reagents used in the present investigation were of reagent grade.

Synthesis of Hyperbranched Polyester Polyol (HBPP) from Castor Oil. Hyperbranched polyester polyol (HBPP) was synthesized by a two-step method from castor oil. The first step was the alcoholysis process in which monoglyceride of castor oil was prepared by reaction of castor oil with glycerol in a 1:2 mol ratio at 220 °C using sodium methoxide as the catalyst (0.05 wt % with respect to oil). The reaction was carried out for 1.5 h, and the formation of the product was confirmed by checking the solubility in methanol at a regular interval of time. The reaction was stopped when the reaction product was completely soluble in methanol at room temperature.[24,25]

In the second step, the esterification reaction was carried out between monoglyceride and 2,2-bis(hydroxyl methyl) propionic acid in 1:2 mol ratio at 140 °C using p-toluene sulfonic acid as the catalyst (0.1 wt % with respect to monoglyceride). Briefly, an amount of 12 g of monoglyceride was taken in a three-necked round-bottomed flask equipped with a mechanical stirrer, thermometer, and nitrogen gas inlet. To the monoglyceride, 8.64 g of 2,2-bis(hydroxy methyl) propionic acid and 0.012 g of p-toluene sulfonic acid were added and stirred for about 2 h at 140 °C. Formation of the product was confirmed by determination of the acid value of the reaction mixture, which was found to be decreased with time as the reaction proceeded.[25,26] The reaction was stopped when the acid value was found to be below 15. The synthesized resin was washed with 15% aqueous sodium chloride solution followed by distilled water 2−3 times and dried under vacuum at 70 °C. The yield of the final product was about 98% (19.12 g).

Synthesis of Hyperbranched Epoxy. The hyperbranched epoxy was synthesized by the polycondensation reaction of polyester polyol with bisphenol A and epichlorohydrin at 110 °C for 4 h using aqueous NaOH as the catalyst. In a typical procedure, HBPP (2.35 g, hydroxyl value 420 mg KOH/g), bisphenol A (8.03 g, 0.035 mol), and epichlorohydrin (13.02 g, 0.14 mol) were taken in a two-necked round-bottomed flask equipped with a water condenser and a dropping funnel. The reaction mixture was stirred with a magnetic stirrer. To this reaction mixture, a 5 N aqueous solution of NaOH (3.52 g, 0.088 mol) was added very slowly from a dropping funnel (1−1.5 h). After 4 h, the reaction was stopped and allowed to settle in a separating funnel, and the aqueous layer was separated out from the desired organic layer. Then the organic layer was washed with 15% aqueous sodium chloride solution followed by distilled water 2−3 times. Finally the epoxy resin was dried at 70 °C under vacuum to remove excess epichlorohydrin and entrapped water. The final product was a viscous sticky transparent light yellow mass with a yield of 13.26 g (98%). The synthesized resin was coded as HBPE2 (2.0 mol bisphenol A per hydroxyl group of HBPP). Similarly HBPE1 and HBPE3 (1.0 and 3.0 mol bisphenol A per hydroxyl group of HBPP, respectively) were synthesized and found approximately same yield. The amount of polyester (HBPP) was taken at 30%, 20%, and 10% (approx.) in weight with respect to the synthesized resin of HBPE1, HBPE2, and HBPE3, respectively.

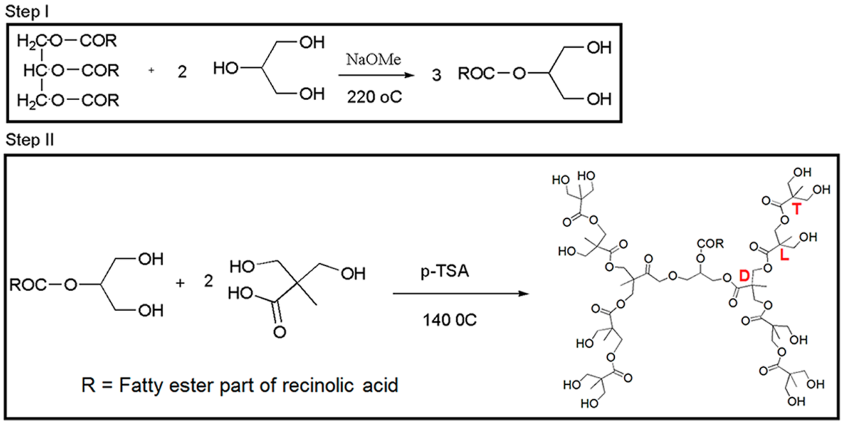
Physical Modification of Commercial Epoxy Resin by HBPP (MSBE). For the modification of diglycidyl ether of bisphenol A-based epoxy, 10 wt % of HBPP (with respect to epoxy resin) was mixed with the commercial epoxy resin in the presence of little amount of THF (to facilitate mixing) under stirring at room temperature. After homogenization of the mixture, 50 phr of poly(amido amine) hardener was mixed with the above mixture, which was then cast onto glass plates to determine the curing time as described below. This was used just for comparison purposes.

Curing of the Resins. The resins were cured by mixing with 50 phr of poly(amido amine) hardener with respect to resin in a glass beaker at room temperature. Then the mixtures were uniformly coated on mild glass plates (75 mm × 25 mm × 1.3 mm) for measurement of scratch hardness and tensile strength and steel plates (150 mm × 50 mm ×1.6 mm) for impact strength. The casting plates were degassed by vacuum and then were cured at 100 °C for specific time intervals and optimized with a curing reaction by determining the swelling values. Commercial epoxy thermoset (SBE) and modified commercial epoxy thermoset (MSBE) samples were also prepared by the same method to compare with the resulted thermosets.

Biodegradation Study. The biodegradation study was done with the help of the McFarland turbidity method using *P. aeruginosa* as the bacterial strain.[26−28] The crude oil-contaminated soil of Assam, India, was used to isolate the bacterial species. The used salt medium consisted of the following main constituents (g/L): $(NH_4)_2SO4$ (1.0), KH_2PO_4 (13.3), $MgSO_4$ (1.3), citric acid (1.7); trace element of 10 mL of (g/L): $FeSO_4 \cdot 7H_2O$ (10), $ZnSO_4 \cdot 7H_2O$ (2.25), $CuSO_4 \cdot 5H_2O$ (1), $MnSO_4 \cdot 5H_2O$ (0.5), $CaCl_2 \cdot 2H_2O$ (2.0), $Na_2B_4O_7 \cdot 10H_2O$ (0.23), $(NH_4)_6MO_7O_{24}$ (0.1), HCl (0.1 N, to adjust the pH 7), and dextrose (10 g). A total of 50 mL aliquots of the mineral salt medium was dispensed in 100 mL conical flasks, each inoculated with polymer films with a dimension of 2 cm × 2 cm × 0.03 cm, and the flasks were incubated at 37 °C for 60 days. One flask containing mineral salt medium and with no bacteria was used as the control. Increase in turbidity of the culture medium indicates the growth of bacteria in the medium. The optical density (OD) of the bacterial growth was calculated at an interval of every 15 days at λ max of 600 nm. The weight loss (%) of degraded films was measured after 60 days of exposure to the bacterial strain. The experiment was performed in triplicate.

Characterization. FTIR spectra of the resins were recorded by a Nicolet FTIR spectrophotometer (Impact-410, Madison, WI) using KBr pellet. A 400 MHz Jeol FT-NMR spectrometer was used to record the ^1H NMR and ^{13}C NMR spectra of the resins by using TMS as the internal standard and $CDC1_3$ as the solvent . The physical properties such as epoxy equivalent, hydroxyl value, acid value, solubility, and swelling value of the oil and resins were measured by the standard test methods.[26,29] A scratch hardness test was carried out

Scheme 1. Synthesis of HBPP from Castor Oil



on the cured films by a scratch hardness tester (Sheen instrument Ltd., U.K.). Impact strength of the thermosets was tested by an impact tester (S. C. Dey Co., Kolkata) as per the standard falling weight (ball) method (ASTM D 1709). The bending test of the thermosets was performed by the standard ASTM D 522, using a mandrel with of a diameter from 1 to 100 mm. The tensile (standard ASTM D 638) and adhesion tests of the cured films were carried out with a universal testing machine (UTM, WDW10, Jinan, China) with a 10 kN load cell and crosshead speed of 50 mm/min. The adhesion test was performed on metal−metal (M−M) and wood−wood (W−W) joints by a lap-shear test with an overlapping area of 25 mm × 25 mm and thickness of 0.02−0.03 mm. The lap-shear tensile strength (MPa) as maximum load per unit bond area was obtained directly from the UTM. The thermal stability of the thermosets was studied by thermogravimetric analysis (PerkinElmer TG 4000) using a nitrogen flow rate of 30 mL/min at the heat rate of 10 °C/min from 30 to 700 °C. The chemical resistance test was done in different chemical environments, such as aqueous NaOH (2%), aqueous HCl (10%), aqueous ethanol (20%), and water was used to study the effect of those chemicals on the thermosets. The small pieces of cured films were kept in 100 mL amber glass bottles containing the aforesaid media at 30 °C. The percent of weight loss was measured after 21 days of test. The surface morphologies of the biodegradation films and control films (without bacterial strain) were done with the help of a scanning electron microscope, SEM (JEOL, JSM-6390 LV).

■ RESULTS AND DISCUSSION

Synthesis and Characterization of HBPP. The HBPP was synthesized by a two-step reaction viz. glycerolysis of the oil followed by polycondensation with bis-MPA as shown in Scheme 1. In the first step, castor oil undergoes a catalytic alcoholysis reaction with glycerol at elevated temperature using sodium methoxide as a catalyst to obtain monoglyceride. While the second step was also a catalytic esterification reaction of monoglyceride with bis-MPA in the presence of p-TSA as the catalyst, the desired HBPP was obtained. The use of catalyst in both steps resulted in high yield (~98%) with less time (2 h). The hydroxyl value of HBPP is given in Table 1. The acid value of the HBPP was found as 11.49 mg of KOH/g. A higher acid value and hydroxyl value of the synthesized HBPP compared to the castor oil are due to the presence of ester linkages and terminal bis-MPA moiety along with secondary −OH of a ricinoleic acid moiety in the HBPP structure. The hyperbranched polyester polyol was found to be soluble in most of the common organic solvents, like methanol, ethanol, acetone, THF, DMF, DMAc, DMSO, $CHCl_3$, toluene, xylene, ethyl acetate, etc., supporting the hyperbranched nature of the synthesized polyol. The solubility in hydrocarbon solvents like toluene and xylene confirmed the presence of a hydrophobic fatty acid chain in the HBPP structure.

Table 1. Physical Properties of Resins of HBPE1, HBPE2, HBPE3, SBE, and HBPP

Properties	HBPE1	HBPE2	HBPE3	SBE	HBPP
epoxy eqiuv (g/equiv)	352 ± 12	330 ± 9	286 ± 8	190 ± 9	–
hydroxyl value (mg KOH/g)	105 ± 4	87 ± 3	78 ± 5	50 ± 7	420 ± 8

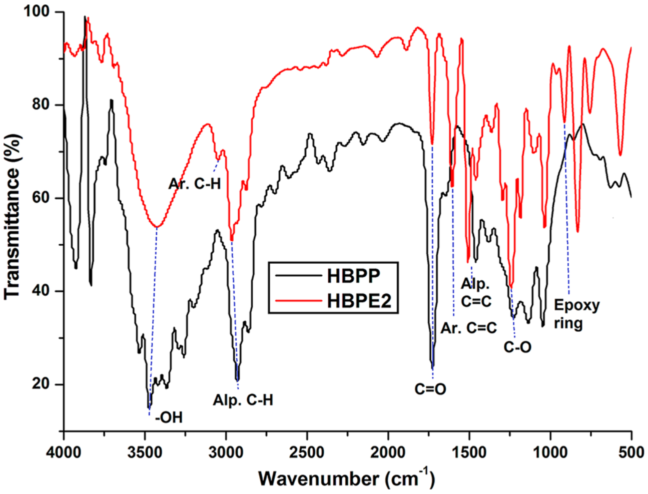


Figure 1. FTIR spectra of HBPP and HBPE2.

The structure of the HBPP was confirmed by FTIR (Figure 1) and NMR (Figure 2) studies: ν max/cm^{-1} in FTIR 3471 (O−H), 2929 (C−H), 1728 (C=O), 1460 (C−O).[25,29,30] ^{1}H NMR (Figure 2a) δH, ppm (400 MHz, $CDCl_3$, Me4Si): 4.8 (1H, t, OH), 0.9−2.3 (fatty acid chain protons, terminal CH_3 and internal CH_2), 1.1 (3H, s, CH_3 bis MPA unit), 3.6 (1H, m, CH attached with OH), 3.7 (2H, d, CH_2 attached with OH), 4.2 (2H, d, CH_2 adjacent to the carbonyl group), 5.4 (1H, m, central CH of monoglyceride), 5.5 (2H, t, CH=CH).[25,29,30] ^{13}C NMR (Figure 2b) δC, ppm: 174 (carbonyl carbon), 14 (CH_3, bis-MPA unit), 18−36 (fatty acid chain carbons), 47−50 (monosubstituted, disubstituted and trisubstituted central carbon of bis-MPA unit), 64 (CH_2 attached with OH), 68 (CH_2 next to the carbonyl group), 72 (CH attached with OH),

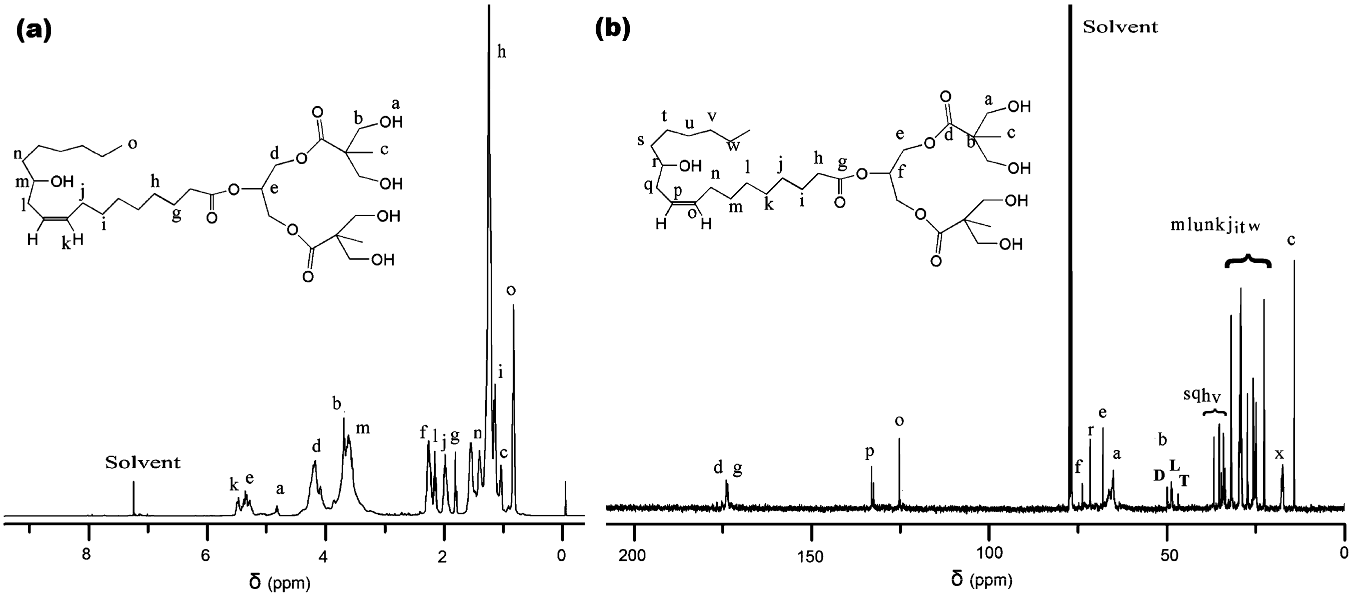
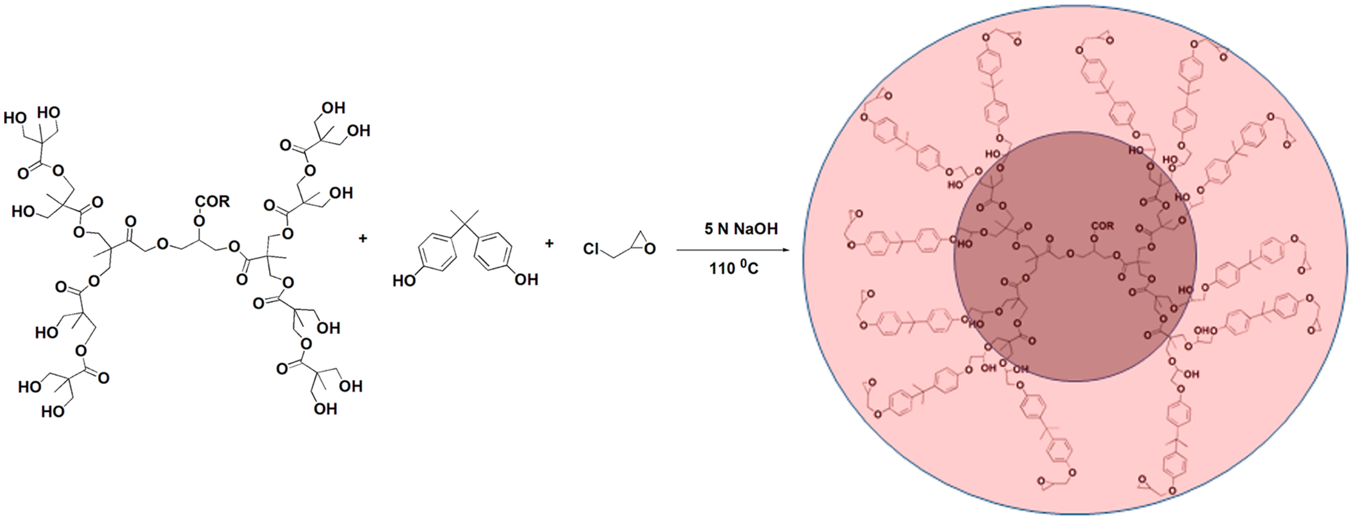


Figure 2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of HBPP.

Scheme 2. Synthesis of Hyperbranched Epoxy from HBPP



74 (central carbon of monoglyceride), 125 and 133 (CH=CH).[25,29,30] The NMR spectroscopy is an important tool for the characterization degree of branching (DB) of a hyperbranched polymer. According to the polymerization mechanism of the hyperbranched polymer, the resulting polymer should contain a dendritic unit (D), linear unit (L), and terminal unit (T). The DB is the ratio of the sum of integration of dendritic and terminal units to the sum of integration of dendritic, linear, and terminal units, i.e., DB = (D + T)/(D + L + T).[1,2,31] From the ^{13}C NMR spectrum of HBPP (Figure 2b), the monosubstituted (T), disubstituted (L), and trisubstituted (D) central carbon of bis-MPA was observed at δ = 46.73, 48.67, and 49.90 ppm, respectively. From the intensity values of these peaks, the degree of branching (DB) of the polyester polyol was calculated and found to be 0.63.

Synthesis and Characterization of Hyperbranched Epoxy. The hyperbranched epoxy resin was synthesized by the polycondensation reaction between in situ prepared diglycidyl ether of bisphenol A and HBPP. First, diglycidyl ether of bisphenol A was formed in the reaction mixture as the reactivity of bisphenol A with epichlorohydrin was higher than HBPP due to the higher acidity of phenolic proton. Then, the hyperbranched epoxy resin was obtained by the reaction between diglycidyl ether of bisphenol A and HBPP as shown in the Scheme 2. The hyperbranched epoxy resin was also soluble in most of the common organic solvents like methanol, ethanol, acetone, THF, DMF, DMAc, DMSO, $CHCl_3$, toluene, xylene, ethyl acetate, etc. The epoxy equivalent and hydroxyl value of HBPE1, HBPE2, and HBPE3 are given in Table 1.

The structure of the hyperbranched epoxy was confirmed by FTIR (Figure 1) and NMR (Figure 3) spectroscopy: νmax/cm^{-1} in FTIR 3428 (O−H), 3049 (Ar. C−H), 2964 (Aliph. C−H), 1730 (C=O), 1605 (Ar. C=C), 1505 (Aliph. C=C of recinolic acid), 1459 (C−O of ester linkage), 1241 (C−O of ether linkage), and 914 (epoxy ring).[4,25,29−33] ^{1}H NMR (Figure 3a) δH, ppm (400 MHz, d_6-DMSO, Me4Si): 3.3 (1H, CH of oxirane ring), 2.6 and 2.8 (2H, CH_2 of oxirane ring), 3.9 (2H, CH_2 next to oxirane ring), 6.8 (4H, aromatic protons of bisphenol A), 7.1 (4H, aromatic protons of bisphenol A), 1.6 (3H, CH_3 of bisphenol A), 3.8 (2H, CH_2 next to bisphenol A),

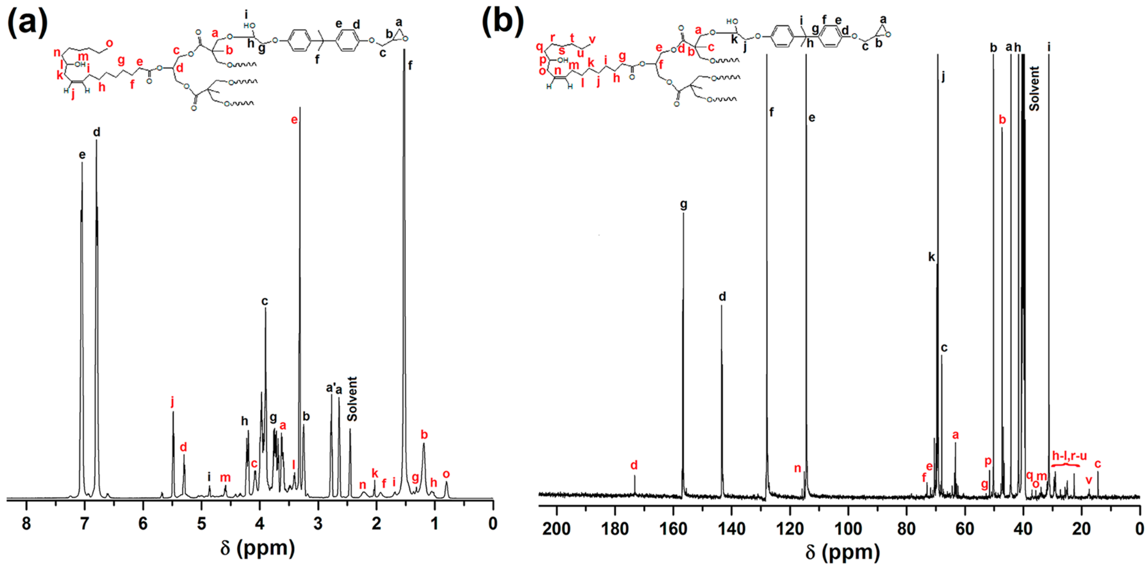


Figure 3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of HBPE2.

Table 2. Performance of Thermosets of HBPE1, HBPE2, HBPE3, SBE, and MSBE

properties	HBPE1	HBPE2	HBPE3	SBE[f]	MSBE
curing time at 100 °C (min)	70 ± 2	65 ± 3	50 ± 4	75 ± 2	85 ± 5
swelling value at 25 °C (%)	26 ± 0.4	24 ± 1	23 ± 0.7	21 ± 0.5	28 ± 1
tensile strength (MPa)	33 ± 2	42 ± 1.7	49 ± 3	38 ± 1.5	34 ± 1.2
elongation at break (%)	94 ± 3	88 ± 1.5	50 ± 1.6	5 ± 2	29 ± 5
toughness[a]	2648 ± 15	3144 ± 8	2109 ± 7	143 ± 12	762 ± 18
scratch hardness (kg)[b]	9.5 ± 0.4	>10.0	>10.0	7.0 ± 0.5	9.0 ± 0.2
impact resistance (cm)[c]	>100	>100	>100	65 ± 5	95 ± 3
bending (mm)[d]	<1	<1	<1	4	2
adhesive strength, W−W (MPa)[e]	>2881	>2927	>2958	1202 ± 22	1288 ± 14
adhesive strength, M−M (MPa)	1800 ± 23	2646 ± 28	2873 ± 34	988 ± 8	1012 ± 11
initial degradation temperature (°C)	290	318	320	324	268

[a] Calculated by integrating the area under stress−strain curves. [b] Limit of the instrument for impact strength was 100 cm (highest). [c] Limit of the instrument for scratch hardness was 10.0 kg (highest). [d] Limit of the mandrel diameter was 1 mm (lowest). [e] In the case of HBPE1, HBPE2 and HBPE3 wood substrates failed. [f] The data for standard bisphenol A based epoxy are reproduced from our earlier work (coded as DEBA)[34] just for comparison purpose for better understanding.

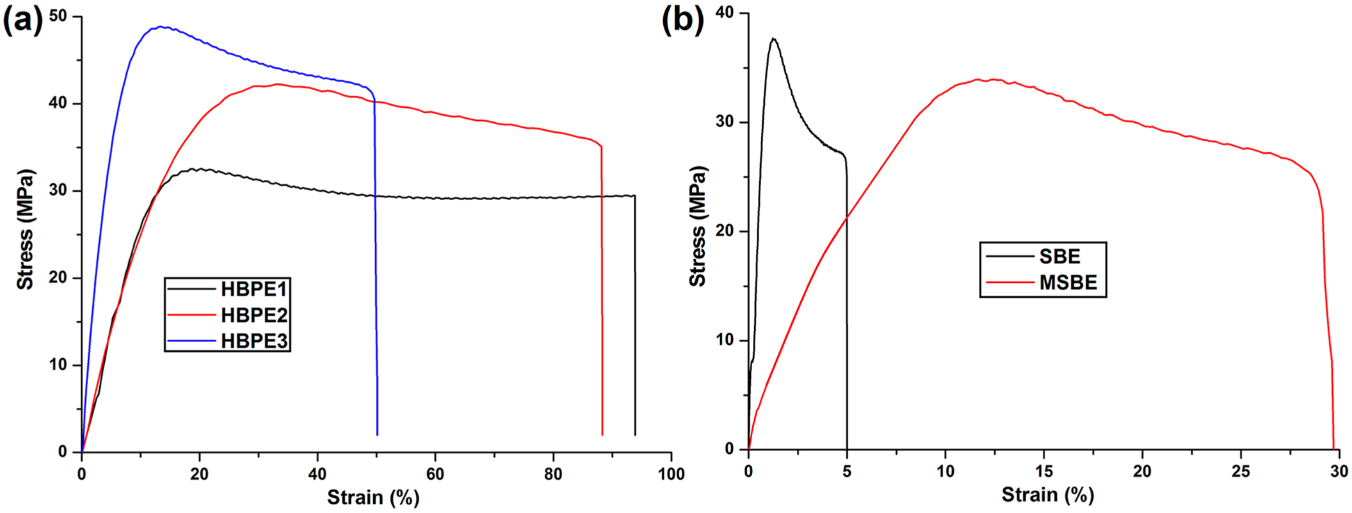


Figure 4. Stress−strain profiles of the thermosets.

4.3 (1H, CH attached with OH), 4.9 (1H, OH), 3.6 (2H, CH$_2$ of polyester attached with diglycidyl ether of bisphenol A moiety), 1.2 (3H, CH$_3$ of bis-MPA), 4.1 (2H, CH$_2$O attached with carbonyl group), 5.3 (1H, CH of attached with

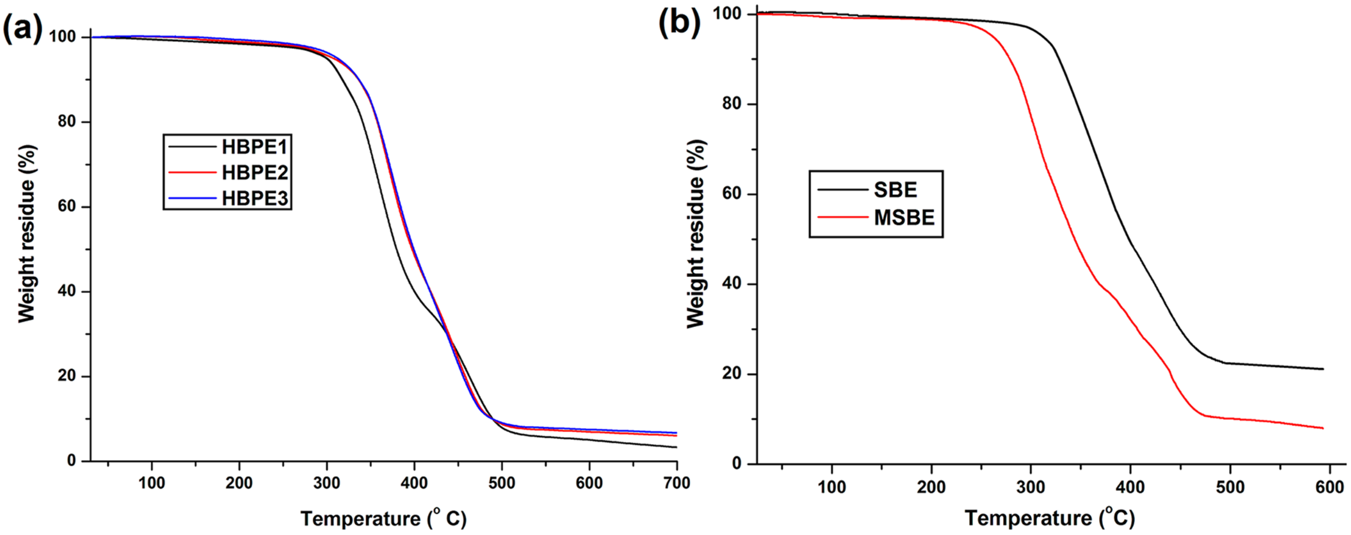


Figure 5. TGA thermograms of the thermosets.

Table 3. Chemical Resistance (weight loss %) of Thermosets in Different Chemical Environments

chemical environments	HBPE1	HBPE2	HBPE3	SBE	MSBE
aq. NaOH (2%)	2.59	1.42	0.63	0.34	4.12
aq. HCl (10%)	2.76	2.33	2.0	1.33	3.54
aq. EtOH (20%)	0	0	0	0	0.06
water	0	0	0	0	0

monoglyceride fatty ester), 5.5 (2H, HC═CH of fatty ester), 3.5 (1H, CH attached with OH of fatty ester), 0.8–2.2 (monoglyceride fatty ester CH_2 and CH_3 protons).[1,4,29−32] ^{13}C NMR (Figure 3b) δC, ppm: 174 (carbonyl carbon), 14 (CH_3, bis-MPA), 64 (CH_2O, bis-MPA), 46–48 (central carbon bis-MPA), 71–72 (CH_2O and CHO of monoglyceride), 20–30 (chain carbons of fatty ester), 116 (HC═HC, fatty ester), 44 and 50 (oxirane ring carbons), 31, 42, 114, 128, 144, and 157 (bisphenol A carbons), 68–70 (carbon attached with −OH and ether linkages).[1,4,29−31]

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

Mechanical Properties of the Thermosets. Mechanical properties like tensile strength, elongation at break, toughness, scratch hardness, impact resistance, and bending are given in Table 2. The presence of aromatic rigid moiety of bisphenol A in the hyperbranched epoxy resulted high tensile strength. On

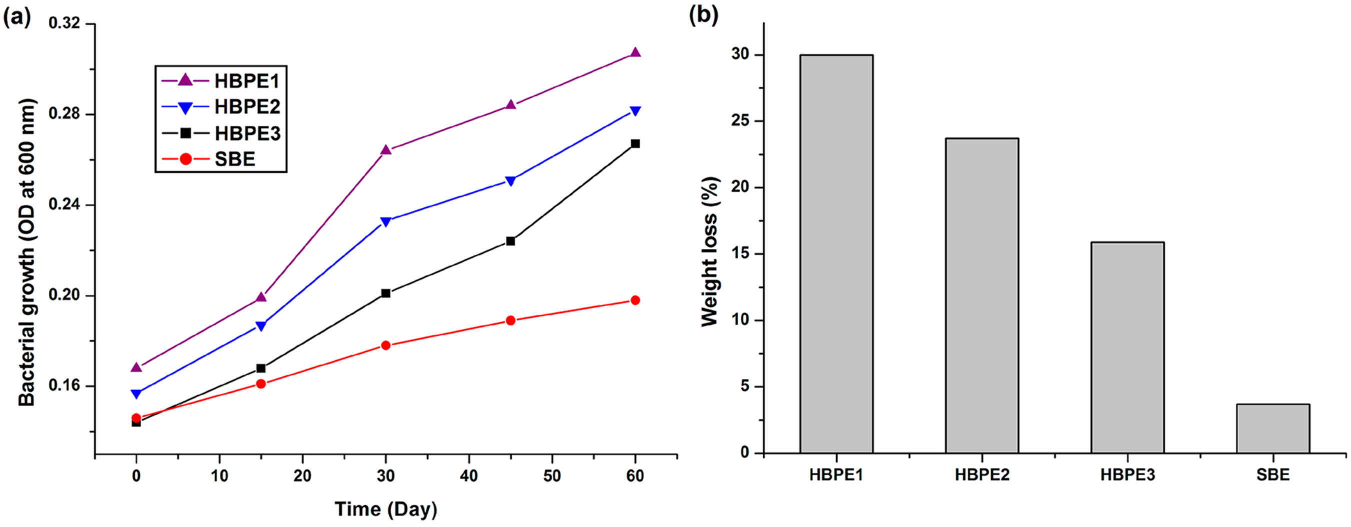


Figure 6. (a) Variation of bacterial growth against exposure time for the thermosets. (b) Weight loss of the thermosets after 60 days of exposure to the bacterial strain.

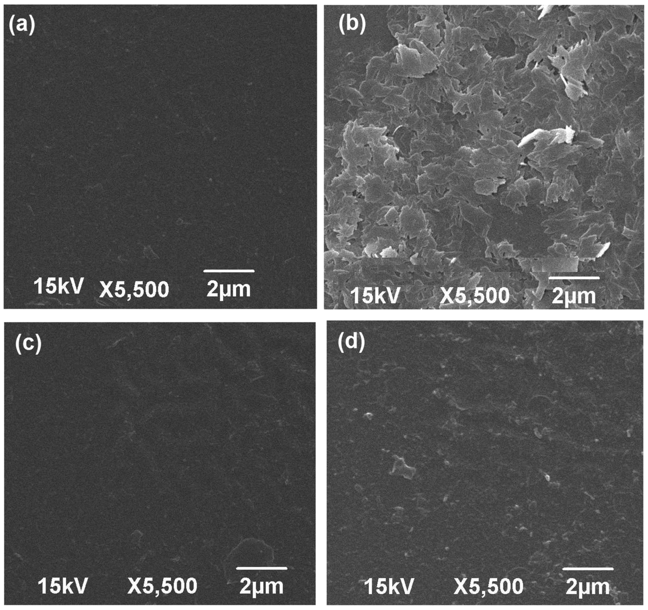


Figure 7. SEM images of biodegraded thermosets: HBPE2 (a) control and (b) degraded, and SBE (c) control and (d) degraded.

the other hand, the presence of the aliphatic polyester moiety and ether linkage increases the elasticity (elongation at break) of the hyperbranched epoxy due to the plasticization effect. The hyperbranched epoxy thermoset exhibited very high toughness calculated from the stress−strain curves in Figure 4a. This is due to the combination of aromatic and aliphatic moieties as well as the hyperbranched structure of the epoxy, which increases the free volume between the molecules (due to steric effect) in the three-dimensional network. HBPE3 exhibited the highest tensile strength due to the presence of the highest amount of diglycidyl ether of the bisphenol A moiety. On the other hand, due to the presence of the lowest amount of bisphenol A moiety, HBPE1 showed the lowest tensile strength value (Table 2). Because of the same reason, the highest elongation at the break value for HBPE1 and the lowest elongation at the break value for HBPE3 were observed. HBPE2 exhibited the best toughness as it possesses overall good tensile strength and elongation at break. The result of impact resistance and scratch hardness determines the toughness of a material. As the hyperbranched epoxy thermosets exhibited very high toughness, their impact resistance and scratch hardness values were also high. The thermosets exhibited the highest limit of impact resistance (100 cm, limit of the instrument) due to the presence of flexible moieties (namely, aliphatic fatty ester of epoxy, aliphatic hydrocarbons of hardener, and ether linkages of epoxy), which dissipate the impact energy by their segmental motions in their molecular chains. Thus, they also exhibited the highest limit of the bending test (1 mm diameter of the mandrel) and can be folded up to 180° without any damage or fracture. As the hyperbranched epoxy thermoset possessed both aromatic and aliphatic moieties in the structure, adequate cross-link density and unique structural architecture, it exhibited high scratch hardness also.

On the other hand the standard bisphenol A-based epoxy (SBE) exhibited very low toughness as it contains only an aromatic rigid moiety in the structure. It possessed adequate tensile strength but very low elongation at break. Thus, impact resistance and scratch hardness values were also very low for the SBE (Table 2). Again, when it was modified with 10 wt % HBPP by physical mixing (MSBE), the improvement of mechanical properties was not so high (Table 2). This is due to the presence of more physical interactions rather than chemical between SBE and HBPP in the thermoset. Because of the plasticizing effect of HBPP, the tensile strength of SBE was decreased and elongation at break was increased after this modification (Figure 4b). Thus, toughness, scratch hardness, and impact resistance were slightly improved in MSBE (Table 2).

Lap-Shear Tensile Adhesive Strength. Hyperbranched epoxy also exhibited high lap-shear tensile adhesive strength as shown in Table 2. This is due to the strong interactions of polar −OH, ether, and epoxy groups, along with the unique branched structural architecture with terminal epoxide groups as well as the polar linkages of the poly(amido amine) hardener with the cellulosic wood substrates. In the case of metal substrates, the high adhesive strength is due to the strong physical interlocking. The variation of tensile adhesive strength in HBPE1, HBPE2, and HBPE3 is due to the variation of load-bearing capacity of the thermosets. In the case of wood substrates, a similar adhesive strength value for HBPE1, HBPE2, and HBPE3 was observed due to substrate failure. Because of the linear structure and lower amount of polar groups (mainly hydroxyl and ether), SBE exhibited comparatively lower adhesive strength. Again, due to the hyperbranched architecture and high amount of polar groups in HBPP, MSBE possessed a slight higher adhesive strength (Table 2). However, this improvement in MSBE is not so high because of the presence of more physical interactions rather than chemical between HBPP and SBE.

Thermal Stability of the Thermosets. The initial degradation temperature of the thermosets is given in Table 2. HBPE2 and HBPE3 exhibited thermal stability above 300 °C. Because of the presence of more aliphatic moieties in HBPE1, it exhibited slightly lower thermal stability (290 °C) and followed a two-step degradation pattern (Figure 5a). The first step (290 °C) is due to the degradation of aliphatic moieties of the HBPP and the poly(amido amine) hardener, whereas the second step (400 °C) is due the degradation of bisphenol A aromatic moiety. However, HBPE2 and HBPE3 were degraded by a single-step (320 °C) pattern. This is due to the good combination of aliphatic and aromatic moieties in the structure. The aliphatic moieties are prohibited by aromatic moieties from thermal degradation. Thus, HBPE2 and HBPE3 exhibited higher thermal stability. In the case of MSBE, due to the presence of more physical interactions rather than chemical between HBPP and SBE, it exhibited a lower thermal stability than SBE (Figure 5b).

Chemical Resistance. The results of chemical resistance in aq. NaOH (2%), aq. HCl (10%), aq. EtOH (20%), and water are given in Table 3. The thermosets exhibited excellent solvent resistance (aq. EtOH) and very good alkali and acid resistance. This is due to the compact structure with strong chemical linkages of the hyperbranched epoxy. Though epoxy resin contains hydrolyzable ester linkage in the structure, the alkali resistance is very good for the thermosets. This is due to the presence of diglycidyl ether of bisphenol A as the terminal moieties, which protects the internal ester linkage from alkali attract. As HBPE2 and HBPE3 contain more diglycidyl ether of the bisphenol A moiety than HBPE1, they exhibited more alkali resistance. On the other hand, MSBE exhibited poor alkali resistance due to the presence of hydrolyzable free ester linkages of HBPP in MSBE as less chemical interactions are present between HBPP and SBE.

Biodegradation of the Thermosets. From the biodegradation study (Figure 6), it was found that the hyperbranched epoxy films were degraded regularly with exposure time by the hydrocarbon-degraded bacteria. This is due to the presence of the hydrolyzable ester linkages of HBPP in the structure that are attacked by the bacteria. As HBPE1 contains the highest amount of polyester in the structure, the growth of the bacteria was found to be the highest for it (Figure 6a), and also, 30 wt % of weight loss was found after 60 days of exposure to the bacterial strain (Figure 6b). HBPE3 contains the lowest amount of HBPP, and thus, growth of the bacteria and weight loss was the lowest for it. On the other hand, standard bisphenol A-based epoxy thermoset (SBE) exhibited only a little amount of biodegradation, as it contains nonbiodegradable diglycidyl ether of the bisphenol A moiety as the major constituent. The minor amount of biodegradation (Figure 6a and 6b) of SBE is due to the presence of the poly(amido-amine) hardener in the thermoset. The morphologies of the degraded surface of HBPE2 and SBE are also given in Figure 7. In the figure, significant surface erosion (Figure 7b) of the degraded film is found compared to the control (HBPE2 film without bacterial exposure, Figure 7a). Slight erosion of the surface of SBE thermoset film (Figure 7d) was also found compared to the control film of SBE (Figure 7c). The biodegradation of MSBE was not studied due to its poor mechanical performance.

■ CONCLUSIONS

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

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. B. De and N. Karak designed and performed the work except the biodegradation, which was contributed equally by K. Gupta and M. Mandal.

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Notes

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