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Waterborne Sustainable Tough Hyperbranched Aliphatic Polyester Thermosets

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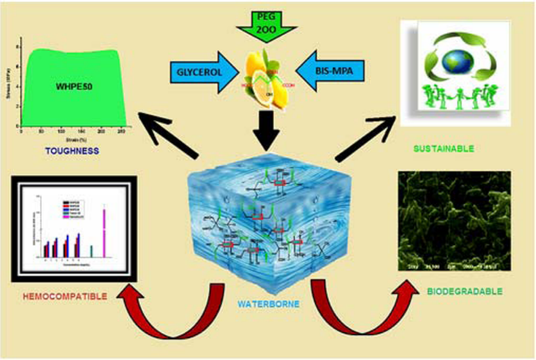
ABSTRACT: A waterborne polymer is a greener alternative than a solvent borne one because of its nontoxicity and nonflammability nature as well as it does not need any organic solvent. Thus, three biodegradable waterborne hyperbranched aliphatic polyesters were synthesized from citric acid, poly(ethylene glycol), glycerol and 2,2-bis(hydroxyl methyl) propionic acid, by a polycondensation reaction without using any additional catalyst or neutralizing agent. The structures of these polyesters were elucidated from spectroscopic analyses. Degrees of branching of the polymers were evaluated from ^{13}C NMR spectra and found to vary from 0.59 to 0.70. Thermoset of these polyesters was obtained by curing of a formulation composed of waterborne hyperbranched polyester (57.1%), hyperbranched epoxy (28.87%) and poly(amidoamine) (14.28%) using water as a solvent with a little amount of THF as a cosolvent. The performance characteristics such as tensile strength (4.0–7.8 MPa), elongation at break (175–245%), toughness (655–1742 MPa), impact resistance (>1 m), gloss (89–96), scratch resistance (3–4 kg) and chemical resistance (good) of the thermosets were evaluated. The results clearly revealed the profound influence of citric acid content on performance of such polyester thermosets. These polyester thermosets were found to be highly biodegradable by *Pseudomonas aeruginosa* and *Bacillus subtilis* bacterial strains and also exhibited hemocompatibilty. Therefore, the citric acid based sustainable tough hyperbranched polyester thermosets with acceptable performance were obtained through a facile and environmentally benign route.



KEYWORDS: *Waterborne, Citric acid, Hyperbranched aliphatic polyester, Synthesis, Biodegradation*

■ INTRODUCTION

Polyesters have attracted renewed interest in industries because of their inherent advantages over other industrially used polymers, over long time. Again, in recent time researchers and industrialists have been more concerned about the environmental protection because pollution caused by petroleum based products results in severe damage to human health and the environment. Thus, efforts have been made to substitute the petroleum raw materials by renewable ones to address the problems related to exhaustion of petroleum resources and production of hazardous volatile organic compounds (VOCs).[1−4] Among these, biobased resources are considered to be the best alternative because of their low cost, chemical and physical stability, easily availability, biodegradability, environmentally and eco-friendly nature.[5−7] Use of catalyst and organic solvent can also produce VOCs that are responsible for such environmental pollution and harming human health. So, the use of an organic solvent should be avoided wherever possible and in accordance to green chemistry, a green solvent like water can be used. Therefore, the waterborne polymers draw greater attention than the solvent borne. This is mainly due to the fact that such a system possesses favorable attributes like low or no VOCs, no odor, nontoxicity, nonflammalibility, environmentally friendly and easy to clean up.[8−10] The general way to solubilize or disperse an organic polymer into water is to introduce some highly hydrophilic polar functional groups like hydroxyl, sulfonic, carboxylic, etc. into its structure. Some of the biobased raw materials with similar polar functionalities such as citric acid, tannic acid, etc. are valuable starting materials to produce waterborne polyester.[1,6,11] Citric acid, an aliphatic polyfunctional biobased raw material, has been evaluated as an attractive functionality enhancing monomer in aliphatic polyester because it contains two reactive primary carboxylic groups, one sterically hindered hydroxyl group and one less reactive tertiary carboxylic group. It is a metabolic product of the Krebs (or citric acid) cycle and a versatile monomer that participates in prepolymer formation as well as in postpolymerization to produce a cross-linked polyester network with degradable ester bonds.[12−14] Therefore, an attempt would be made to use a greener approach for the synthesis of citric acid based waterborne aliphatic polyester without using any type of neutralizing agent and catalyst. It is expected that such polyesters would be sustainable because of their biodegrad-

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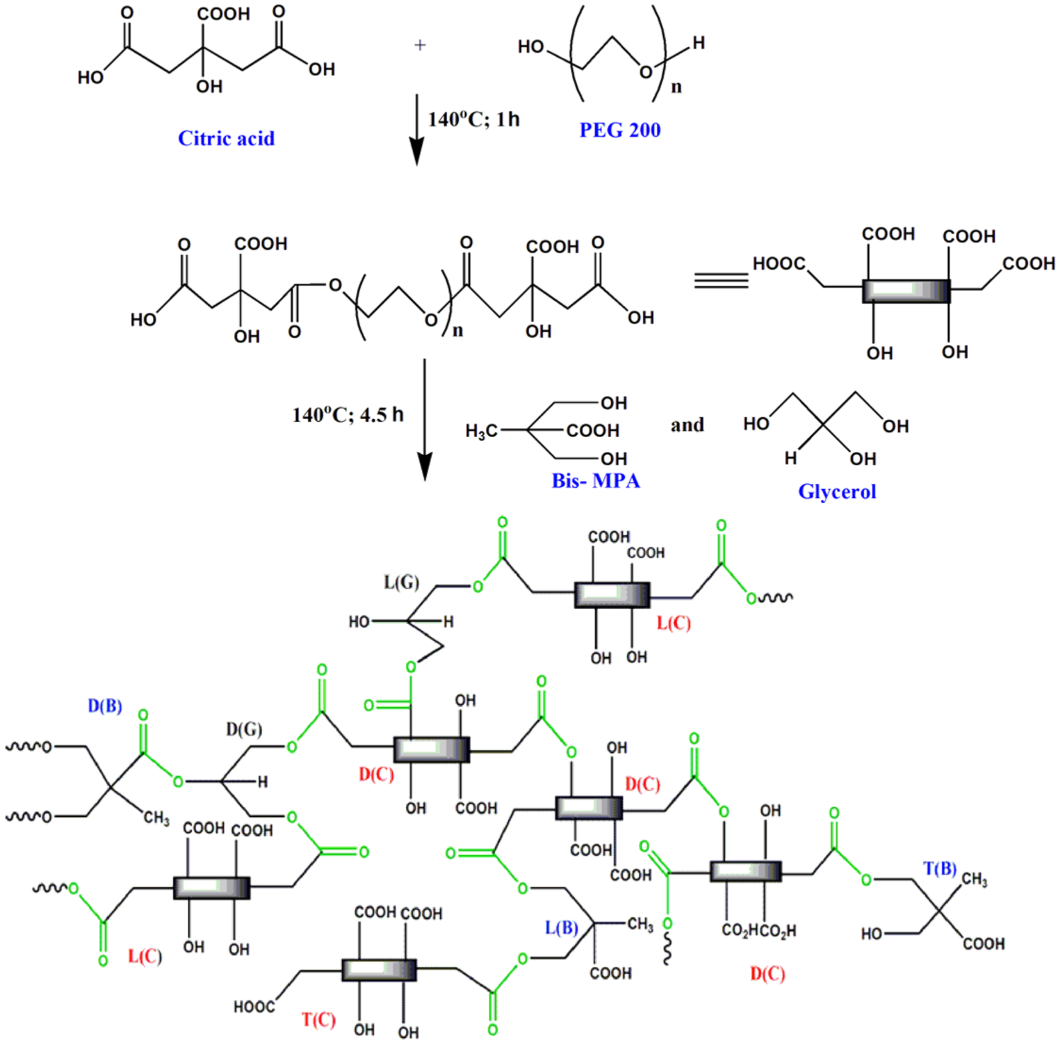
Scheme 1. Synthesis of Waterborne Hyperbranched Aliphatic Polyester



ability and use of a facile approach using renewable resources (biobased raw materials). Biodegradable polyesters are of significant interest both in academic and industrial research for their favorable attributes like biocompatibility, good mechanical and chemical properties and thus find applications in pharmaceutical and biomedical fields. One of the most representative examples of environmentally relevant a polymeric material is the aliphatic polyester, which plays an important role as a biodegradable polymer due to hydrolyzable ester bonds and presence of relatively short aliphatic chains in the macromolecule.[15,16] Again, the hyperbranched architecture of such a polyester is gaining significant attention due to its unique structural features and useful properties like three-dimensional architecture, low viscosity, high solubility, high reactivity, large number of surface functionality, etc. along with single step preparative protocol.[17−19] A few reports on biobased linear and hyperbranched polyesters have been found in the literature. Jasinska et al. synthesized biobased water-soluble polyesters using "green" biomass like isosorbide with maleic anhydride and poly(ethylene glycol) in the presence of titanium(IV) *n*-butoxide as the catalyst.[9] Pathan et al. reported waterborne soya alkyd (oil modified polyester), obtained by the reaction of soya monoglyceride with phthalic anhydride.[4] Malar et al. also synthesized citric acid based solvent borne polyester elastomer by the reaction of citric acid along with 1,6-hexane diol and 1,3-propane diol with sunflower oil based polyol. However, the reported polyester was not a hyperbranched one.[20] Asif et al. reported the synthesis of a waterborne hyperbranched polyester consisting of a multihydroxy functional aliphatic polyester core (BoltornTM H20). But they used a neutralizing agent (triethylamine) to make it waterborne and were not able to calculate the degree of branching for this hyperbranched polyester.[21] The use of additional neutralizing agent not only increases the cost due to the cost of the material as well as extra step involved in it but it is also toxic and health hazardous as mainly organic amine compounds are used for this purpose.[21] Jung et al. synthesized waterborne polyester using the reactions of three different polyols such as ethylene glycol, diethylene glycol and propylene glycol with three different dibasic acids like tetrahydrophthalic anhydride, terephthalic acid and trimellic anhydride.[22] Saravari et al. reported the synthesis of water-reducible acrylic−alkyd resins by esterification of monoglycerides, i.e., prepared from modified palm oil and carboxy-functional acrylic copolymer followed by neutralization of carboxyl groups with diethanolamine.[1] However, none of these reports elaborated the details of properties evaluation and characterization, in addition they have used some additional neutralizing agents. Thus, the synthesis of citric acid based waterborne biodegradable hyperbranched aliphatic polyester in absence of any catalyst without using neutralizing agent was not reported, so far.

In the present study, therefore, a sustainable waterborne hyperbranched aliphatic polyester was synthesized by a facile polycondensation reaction using biobased reactants such as citric acid and glycerol with PEG200 and bis-MPA without using any additional catalyst or neutralizing agent. The synthesized polyesters with varying percentages of citric acid were characterized by different spectroscopic and analytical tools. Thermosets of the polyesters were prepared by curing of a formulation composed of waterborne hyperbranched polyester, hyperbranched epoxy and hardener, poly(amidoamine). The performance characteristics of these thermosets along with biodegradation and hemocompatibility were delved into to investigate the effect of citric acid on such attributes.

■ EXPERIMENTAL SECTION

Materials. Citric acid (Merck, Germany), glycerol (Merck, Germany), poly(ethylene glycol) with Mn = 200 (PEG-200, Merck, India) and 2,2-bis(hydroxymethyl) propionic acid (bis-MPA, Aldrich, Germany) and epichlorohydrin (Merck, India) were used after drying in a vacuum oven. Bisphenol A (GS Chemical, India) was recrystallized from toluene and then used. Sodium hydroxide (Rankem, India) was used as received. Poly(amido amine) hardener (HY840, Ciba Geigy, India) with amine value 5 equiv/kg), viscosity at 25 °C (20 000 mPa·s) and density at 25 °C (0.98 g/cm^3) was used as received. The bacterial strains of *Pseudomonas aeruginosa* and *Bacillus subtilis* were obtained from Molecular Biology and Biotechnology Department of Tezpur University. All other chemicals used in this study were of reagent grade and used without further purification.

Synthesis of Waterborne Hyperbranched Polyesters. The synthesis of waterborne hyperbranched polyester was a two stage single pot process (Scheme 1). In the first step, a required amount of citric acid and PEG-200 was placed in a three neck round-bottomed flask equipped with a nitrogen inlet, a thermometer and a mechanical stirrer. The reaction was carried out at 140 °C for 1 h under nitrogen atmosphere with constant mechanical stirring. The obtained reaction mixture was cooled to room temperature. In the second step, required amounts of glycerol and bis-MPA were added to the above reaction mixture. The reaction was carried out at 140 °C for another 4.5 h. The change of acid value was monitored during the course of the reaction and reaction was stopped before any gel formation but viscosity was sufficiently high. The gel point was determined from Carothers eq (Table 1). The addition of water with vigorous agitation yielded the desired hyperbranched waterborne polyester. By following the same procedure, three different weight percentages (31.6, 40.6 and 50.26%) of citric acid containing hyperbranched polyesters were synthesized and coded as WHBPE30, WHBPE40 and WHBPE50, respectively. The actual compositions of the reactants for all these three resins are given in Table 1.

Table 1. Composition of Reactants for the Synthesis of Polyesters

reactant (mol) and functionality	WHBPE50	WHBPE40	WHBPE30
citric acid	0.02	0.01	0.01
PEG-200	0.01	0.005	0.005
glycerol	0.005	0.005	0.005
bis-MPA	0.01	0.01	0.02
total equivalent OH	0.075	0.055	0.075
total equivalent COOH	0.07	0.04	0.05
equivalent ratio of OH/COOH	1.07	1.37	1.5
gel point (%)	62	63.1	64

Preparation of Glycerol Based Hyperbranched Epoxy. The glycerol based hyperbranched epoxy was prepared by the same method as reported earlier.[23] It was prepared by reacting glycerol (4.56 g, 0.02 mol) and bisphenol A (0.912g, 0.01 mol) with epichlorohydrin (012.86 g. 0.14 mol). They were placed in a two neck round-bottomed flask equipped with a dropping funnel, a stirrer and a water condenser. The temperature of the reaction was maintained at 110 °C. 5 N aqueous solution of NaOH (2.78 g, 0.0695 mol) was added very slowly to the above reaction mixture from a dropping funnel. The reaction was stopped after 3 h, and the obtained viscous mass was separated by the help of a separating funnel. The organic layer was washed with brine solution followed by distilled water for 3−4 times. Finally, the resin was dried at 70 °C under vacuum to remove entrapped water and excess epichlorohydrin. The molecular weight, hydroxyl value and epoxy equivalent of the prepared resin was found to be (2400 g/mol), (150 mg KOH/g) and (289 g/eq), respectively. The shear viscosity and density of the resin at 25 °C was found to be 35 Pa·s and 1.1 g/cm^3. This epoxy was used to modify the synthesized waterborne hyperbranched polyester.

Characterization. Fourier transform infrared (FTIR) spectra of polyesters were recorded on Nicolet (Impact-410, Madison, USA) using KBr pellets. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz FT NMR (JEOL, Japan) using trimethyl silane as the internal standard and d_6-DMSO as the solvent. UV spectra were recorded using an Evolution-300 UV−visible spectrophotometer (UV-300, ThermoFisher USA). The shear viscosity of the resin was measured at constant stress (100 Pa) under single shear using a rheometer (CVO100, Malvern, UK). The physicochemical properties of the resins such as acid value, hydroxyl value, saponification value and specific gravity were measured using the standard methods. Thermal properties of polyester thermosets were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies. Thermogravimetric study was done by using a PerkinElmer TGA 4000 thermal instrument, at a scanning rate of 10 °C/min, maintaining an inert atmosphere of nitrogen at a gas flow rate of 30 mL/min in the temperature range 25−700 °C. The differential scanning calorimetric study was carried out by a PerkinElmer DSC 6000, USA instrument following a cycle of heating−cooling−heating under an atmosphere of nitrogen and at a scanning rate of 5 °C/min for heating and 10 °C/min for cooling in the temperature range −70 to +160 °C. Mechanical properties, such as tensile strength and elongation at break, were measured by a Universal Testing Machine (UTM, WDW10, Jinan, China) equipped with a 500 N load cell operated at a crosshead speed of 50 mm/min. The scratch hardness of the cured films was measured by using a scratch hardness tester, Model No. 705 (Sheen instrument limited, UK). The impact strength of the polyester thermosets was tested with the help of an impact tester (S. C. Dey Co., Kolkata) as per the standard falling weight (ball) method. The chemical resistance test was done in different chemical media such as aqueous NaOH (0.5%), aqueous HCl (10%), aqueous NaCl (15%), aqueous ethanol (20%) and distilled water 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 aforementioned media at room temperature. After 20 days of test, the percentage of weight loss was measured.

Curing of Polyesters. The formulation used for curing process comprises hyperbranched polyester (57.1%) as the base polymer, hyperbranched epoxy (28.87%) as the modifier and fatty acid based poly(amidoamine) (14.28%) as the hardener. Poly(amidoamine) was used 50 wt % of epoxy resin. A homogeneous mixture of the components was made with minimum amount (1 mL for 5g resin) of THF in a glass beaker at room temperature by hand string for 15 min. The solvent was only used to facilitate the mixing of the components during the film casting. Then the mixture was uniformly coated on 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 plates were kept in a desiccator under vacuum for 3 days to remove the solvent and other volatiles present in it. Then the films were cured in an oven at a specified temperature for a desired period of time. The optimization curing time was determined

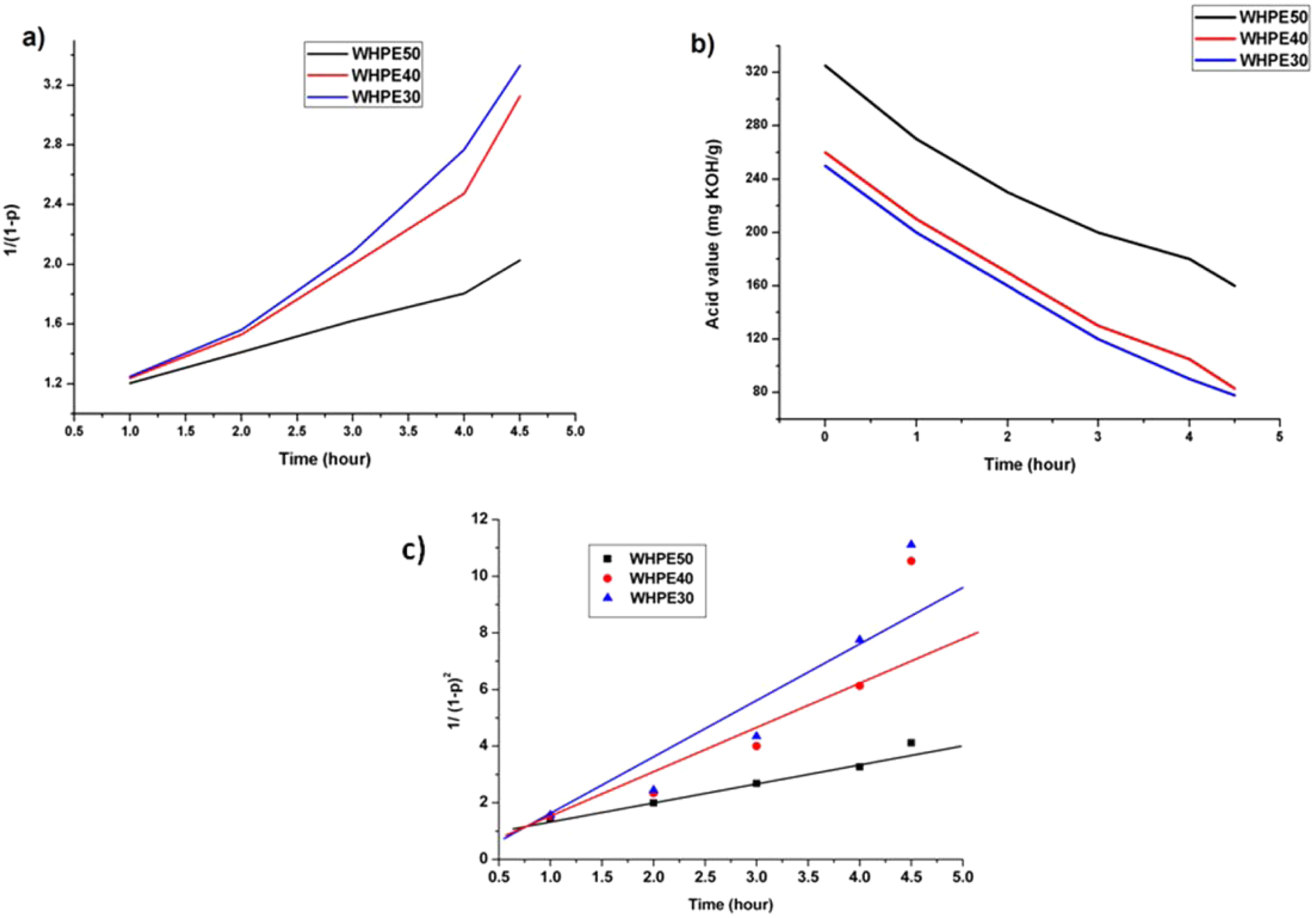


Figure 1. (a) Plot of $(1 - p)^{-1}$ vs time (b) variation of acid value with time and (c) plot of $1/(1 - p)^2$ vs time for polyesters.

by measurement of swelling value of the cured film (thermoset) by immersing in THF for 48 h. The process is followed for all the polyester thermosets.

Swelling Test. Swelling test was done by immersing the weighted amount of the dried films in THF. After 48 h, the swelled films were taken out from the solvent, excess solvent was removed with the help of blotting paper and the weight of the swollen films was taken. This procedure was repeated until a constant weight was obtained. The swelling value (%) was determined by difference in weight between dried film and swelled film as follows:

$$\text{swelling (\%)} = (W_s - W_d)/W_d \times 100 \qquad (1)$$

where W_s and W_d are the weight of the swelled film and dried film, respectively.

Biodegradation Study. Biodegradation study was done by McFarland turbidity method using *Pseudomonas aeruginosa* and *Bacillus subtilis* as the bacterial strain.[15] A medium of mineral salts such as 2.0 g of $(NH_4)_2SO_4$, 2.0 g of Na_2HPO_4, 4.75 g of KH_2PO_4, 1.2 g of $MgSO_4 \cdot 7H_2O$, 0.5 mg of $CaCl_2 \cdot 2H_2O$, 100 mg of $MnSO_4 \cdot 5H_2O$, 70 mg of $ZnSO_4 \cdot 7H_2O$, 10 mg of $H_3BO_3 \cdot 5H_2O$, 100 mg of $CuSO_4 \cdot 7H_2O$, 1 mg of $FeSO_4 \cdot 7H_2O$ and 10 mg of MoO_3, all in 1.0 L of demineralized water, was prepared. It was sterilized for 15 min at 120 °C under a pressure of 15 lb and then allowed to cool to room temperature. Bacterial strains of *Pseudomonas aeruginosa* and *Bacillus subtilis* were cultured in the medium inside an incubator shaker at 37 °C for 48 h. 100 μL (10^8 microbes/mL, as calculated by McFarland turbidity method) of the cultured medium was placed in a conical flask containing 10 mL of the prepared salt medium. The polymeric films of average thickness 0.25 mm were sterilized by exposing them to UV light of wavelength 254 nm for 20 min inside a laminar hood. The sterilized films were incubated inside the medium under sterile condition at 37 °C. Medium without polymeric films was used as the negative control. The increase in turbidity of the cultural medium with time indicates bacterial growth in that medium. The optical density (OD) of the bacterial growth was monitored by measuring the absorbance of the medium at 600 nm with respect to the control at an interval of every 7 days.[15] The experiment was conducted in triplicate for an experimental period of 4 weeks.

Hemolytic Assay. Hemolytic assay was performed to investigate lysis of the red blood cell (RBC) membrane by the tested macromolecule and know about the cytocompatibility of waterborne hyperbranched polyester. Goat's blood collected in a heparinized tube containing 4% sodium citrate was centrifuged for 20 min at 3000 rpm (503*g*). The erythrocytes were washed thrice with phosphate buffer saline. To obtain 5% hematocrit, the packed erythrocytes were resuspended in PBS (10 mM at pH of 7.4) after washing. Thermoset films with varying concentrations of 0.5, 2.00, 4.00 and 6.00 mg mL^{-1} were prepared. Then 100 mL of each medium containing film was placed in a microfuge tube along with 1900 mL of the hematocrit and the solutions were incubated at 37 °C for 30 min. After completion of the incubation period, cells were placed in an ice bath for 1 min followed by centrifugation at 3000 rpm (503*g*) for 5 min. Then hemoglobin concentration was determined by the help of UV absorbance at 540 nm as a measure of hemolysis. The experiment was performed in triplicate and average result was reported.

■ RESULTS AND DISCUSSION

Synthesis of the Polyesters. In the first step, a prepolyester was formed by the polycondensation reaction of citric acid and PEG-200. The above prepolyester was also further esterified in the second step with bis-MPA and glycerol which results the desired hyperbranched polyester. In this esterification reaction, glycerol, citric acid and bis-MPA act as branch generating units. The obtained polyester became water-soluble without using any neutralizing unit due to the presence of large number hydrophilic hydroxyl and carboxylic acid groups along with globular hyperbranched architecture. During the reaction, after every hour, reaction mixture was taken out from the reaction to determine the acid value. The extent of reaction, *p*, and average degree of polymerization, DP, with respect to the acid value were calculated using the following equation.[24]

$$p = C_o - C_t/C_t \tag{2}$$

where C_0 is the acid value at zero reaction time and C_t is the acid value after time *t*. The average degree of polymerization, DP, is given by

$$\mathrm{DP} = 1/(1-p) \tag{3}$$

It is observed from Figure 1 that with the increase of reaction time, the acid value decreases for all the three polyesters. During the early stage of esterification, the decrease in acid value is more rapid though at the later stage of reaction, the rate of decrease of acid value became slow. This is due to the fact that in the early stage, the more reactive primary hydroxyl and carboxylic groups were reacted, whereas in the later stage the reactions are mainly due to less reactive secondary such groups. Further, with the passage of reaction the viscosity of the medium increases which hindered the effective collisions among the reactants.

From Figure 1, it is clear that the initial variation of $(1-p)^{-2}$ versus time is linear for the polycondensation reaction, but after a certain point it deviates from linearity and deviation is maximum at the final stage. The nonlinearity at higher conversion of reaction is due to large decrease in polarity of the reaction system as the polar acid and hydroxylic groups are replaced by less polar ester group with the simultaneous removal of water molecule. The nonlinear portion may also represent onset period of branching that is formation of three-dimensional architecture of the polyester.[2] Because this polyesterification reaction is autocatalytic (acid catalyzed), it nearly follows third-order kinetics. After low conversion, the reaction medium became less polar and unionized carboxylic is the major catalyst in the reaction system. From Figure 1, it is clear that the degree of polymerization decreases with the increase of citric acid content. This may be due to the fact that the total functionality of both OH and COOH increases with the same and thus the results as the polycondensation reaction was stopped before gelation. Here it is worthy to mention that the polyester without citric acid was not possible to synthesize as only one carboxylic acid group is present in bis-MPA and other two reactants do not possess any such group. The waterborne hyperbranched polyesters were found to be soluble in most of the organic solvents like methanol, ethanol, THF, acetone, DMSO, DMAc, DMF etc. and insoluble in toluene, xylene, hexane, ethyl acetate etc. This is due to the presence of large numbers of functionality and globular like structure of the hyperbranched polyesters.

Physical Properties of the Polyesters. The physical properties of the polyesters are shown in Table 2. The acid and hydroxyl values of the synthesized polyesters are found to be increased with the amount of citric acid in the polymer. This is due to decrease in extent of reaction and hence more number of such groups remained unreacted. The saponification value also increases as the content of citric acid increases. This is due to the fact that with the increase of citric acid content more number of ester linkages is formed. The density of the hyperbranched polyesters increases with the decrease of citric acid content may be due to increase of degree of polymerization, which result more intra- and intermolecular interactions among the chain molecules. The variation of viscosity with increase of temperature and addition of water was studied by help of a rheometer for representative polyester. The shear viscosity of WHPE50 was found to be 20 140 Pa·s at 25 °C. The viscosity drops to 79 Pa·s by increasing the temperature to 60 °C. The decrease in viscosity with increasing temperature is due to decrease in intermolecular hydrogen bonding in the resin. Further the viscosity was drastically reduces to 20.610, 0.588 and 0.128 Pa·s on addition of 5, 10 and 15 wt % water at room temperature. The increase of gloss value with weight percentage of citric acid is due to the formation of highly branched three-dimensional rigid network structure which enhances the dimensional stability of the thermosets.

Table 2. Physical Properties of Polyesters

property	WHBPE30	WHBPE40	WHBPE50
acid value (mg KOH/g)	75 ± 8	83 ± 5	160 ± 3
hydroxyl value (mg KOH/g)	400 ± 2	443 ± 3	450 ± 5
saponification value (mg KOH/g)	630 ± 4	650 ± 3	696 ± 2
density at 25 °C (g/cm^3)	1.18	1.0	0.97
gloss at 60° (thermosets)	87 ± 4	92 ± 4	96 ± 3

FTIR Study. FTIR spectroscopy was used to confirm the presence of important linkages in the structures of the synthesized hyperbranched polyesters. The representative FTIR spectrum of WHPE50 is shown in Figure 2. The characteristic absorbance band at 1732 cm^{-1} is due to the stretching vibration of aliphatic ester C═O, which is the confirmation of ester bond formation by the polycondensation reaction between hydroxyl and carboxylic groups of the reactants. The absorption band at 3466 cm^{-1} is due to stretching vibration of O—H, and bands at 3000−2600 cm^{-1} are due to aliphatic symmetric and asymmetric C—H stretching vibrations. The same characteristic absorbance bands for other two polyesters were found at 3460 cm^{-1} (O—H stretching), 1736 cm^{-1} (C═O stretching of ester) and 3000−2600 cm^{-1} (C—H symmetric and asymmetric stretching) for WHPE40 and 3464 cm^{-1} (O—H stretching), 1734 cm^{-1} (esters, aliphatic C═O stretching) and 3000−2600

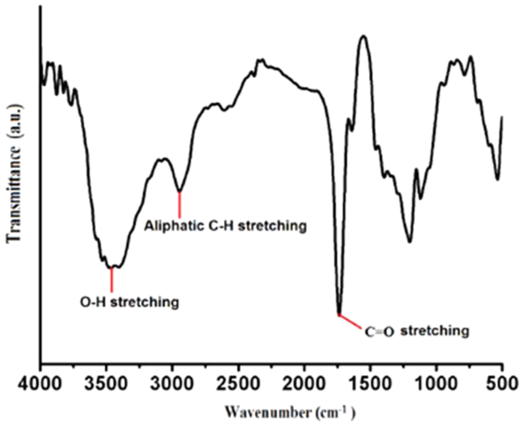


Figure 2. FTIR spectrum of WHPE50.

cm^{-1} (C—H symmetric and asymmetric stretching) for WHPE30.[2,4,6]

^{1}H NMR Study. Protons present at different chemical environments in the structure of hyperbranched polyesters were confirmed from ^{1}H NMR spectral study. A representative ^{1}H NMR spectrum of WHPE50 is shown in Figure 3 that shows the correlation between various structural units and observed NMR peaks. The chemical shift values at δ = 0.98−1.14 ppm are due to the methyl protons of bis-MPA moieties present in different neighboring chemical environments in branching units of the hyperbranched polyester. The methylene protons attached with substituted hydroxyl groups of glycerol and bis-MPA moieties were observed at δ = 3.30−4.0 ppm due to different chemical environments of the neighboring structures. The methylene protons of citric acid showed a chemical shift value at δ = 2.7−2.95 ppm. The variation is again due to the difference in neighboring chemical structures. The signals at δ = 2.04, δ = 3.65 and δ = 4.2 ppm are due to unsubstituted hydroxyl proton associated with glycerol moiety, methylene protons of PEG 200 and unsubstituted OH of citric acid, respectively. The chemical shift values for other two synthesized polyesters are as follows δH, ppm: 0.95−1.13 (3H, CH_3 of bis-MPA), 2.05 (1H, OH attached to CH of glycerol), 3.68 (2H, CH_2 of PEG), 4.3 (1H, OH attached to central carbon of citric acid), 2.6−2.98 (2H, CH_2 of citric acid) and 3.30−3.90 (2H, CH_2 of glycerol and bis-MPA) for WHPE40 and 0.97−1.13 (3H, CH_3 of bis-MPA), 3.65 (2H, CH_2 of PEG), 4.20−4.23 (1H, OH attached to central carbon of citric acid), 2.65−3.0 (2H, CH_2 of citric acid), 3.65 (2H, CH_2 of PEG) and 3.28−3.97 (2H, CH_2 of glycerol and bis-MPA) for WHPE30.[25−30]

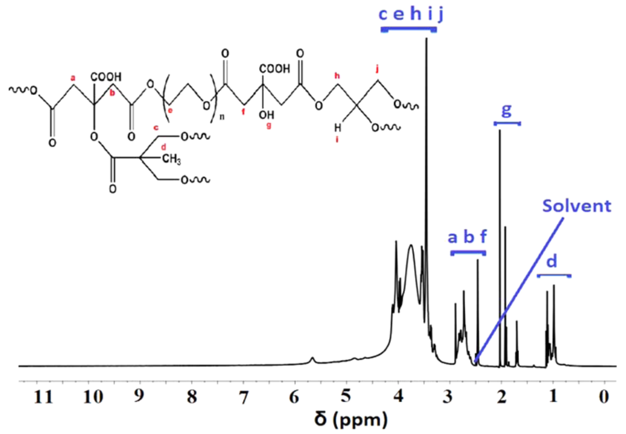


Figure 3. ^{1}H NMR spectrum of WHPE50.

^{13}C NMR Study. Similarly, different chemical environments for carbon atoms present in the structure of hyperbranched polyesters were confirmed by the ^{13}C NMR spectral study. Signals at δ = 15−20 ppm are due to carbon atom of $-CH_3$ of bis-MPA unit. The different values are due to different chemical environments of it as substitutions are different. Carbon of $-CH_2$ of citric acid showed chemical shift value at δ = 42−43 ppm. The signals for carbonyl carbon of acid groups and ester groups were observed at δ = 170−180 ppm. The monosubstituted, disubstituted and trisubstituted central carbon of bis-MPA unit as the terminal (T), linear (L) and dendritic (D) units were found at δ = 47.8, 47.9 and 48.5 ppm, respectively. Similarly, the monosubstitued, disubstituted and trisubstituted glycerol units as T, L and D units were observed at δ = 67.5, 68.5, and 69.6 ppm, respectively. The citric acid based T, L and D units appeared at δ = 72.7, 72.9 and 73.4 ppm, respectively. These peak values of WHPE30 are shown in Figure 4. Thus, the resulting hyperbranched polyesters in all three cases possess three dendritic, three linear and three terminal units. 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 = $(D + T)/(D + L + T)$. Here degree of branching is calculated from three dendritic, three linear and three terminal units. Hence DB = $(D_1 + D_2 + D_3) + (T_1 + T_2 + T_3)/\ (D_1 + D_2 + D_3) + (T_1 + T_2 + T_3) + (L_1 + L_2 + L_3)$. From the intensity values of three dendritic, linear and terminal units, DB values of the polyesters were found to be 0.70, 0.63 and 0.59 for WHPE30, WHPE40 and WHPE50 respectively. Thus, DB decreases with the increase of citric acid content due to the decrease in extent of reaction or degree of polymerization. The other two polyesters showed chemical shift value at δC, ppm: 16−18 (CH_3, bis-MPA unit), 46−50 (monosubstituted, disubstituted and trisubstituted central carbon of bis-MPA unit), 72−74 (terminal, linear and dendritic unit of citric acid), 68−70 (mono, di and tri substituted glycerol moiety) and 42−45 (CH_2, citric acid unit) 170−180 (carbonyl carbon) for WHPE40, and 15−18 (CH_3, bis-MPA unit), 43−45 (CH_2, citric acid unit), 46−50 (terminal, linear and dendritic units of bis-MPA), 68−70 (terminal, linear and dendritic units of glycerol moiety), 72−74 (terminal, linear and dendritic unit of citric acid) and 170−180 (carbonyl carbon) for WHPE50.[25−31] The terminal, linear and dendritic units for WHPE40 and WHPE50 are shown separately in Figure 5.

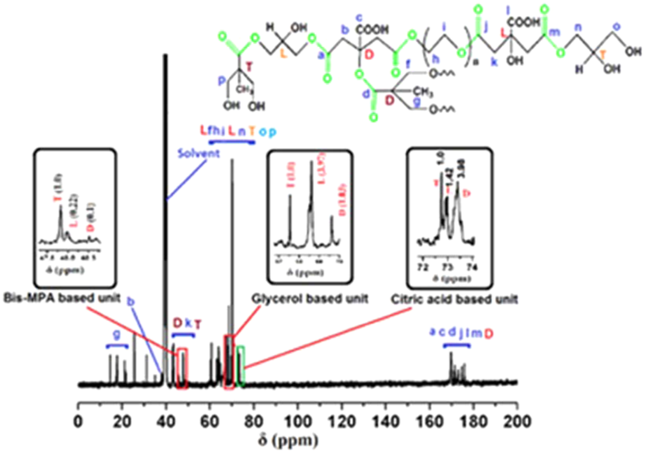


Figure 4. ^{13}C NMR spectrum of WHPE30.

Curing of the Polyesters. During cross-linking reactions of polyester with glycerol based hyperbranched epoxy in the presence of poly(amidoamine) hardener, the hydroxyl groups of polyester and amino groups of hardener react with the epoxide groups of epoxy resin. The reactions among carboxyl and hydroxyl groups of the hyperbranched polyester, epoxide groups of hyperbranched epoxy and amino groups of the hardener would also be occurred (unless they are strongly hindered). The transesterification reactions between hydroxyl and ester groups can also take place, as well as hydroxyl-epoxy etherification (at high temperature and in the presence of basic catalyst) reaction may also occur. Further, hydrogen bonding between C═O of polyester with −OH of the epoxy resin was formed. All the possible physicochemical interactions taken

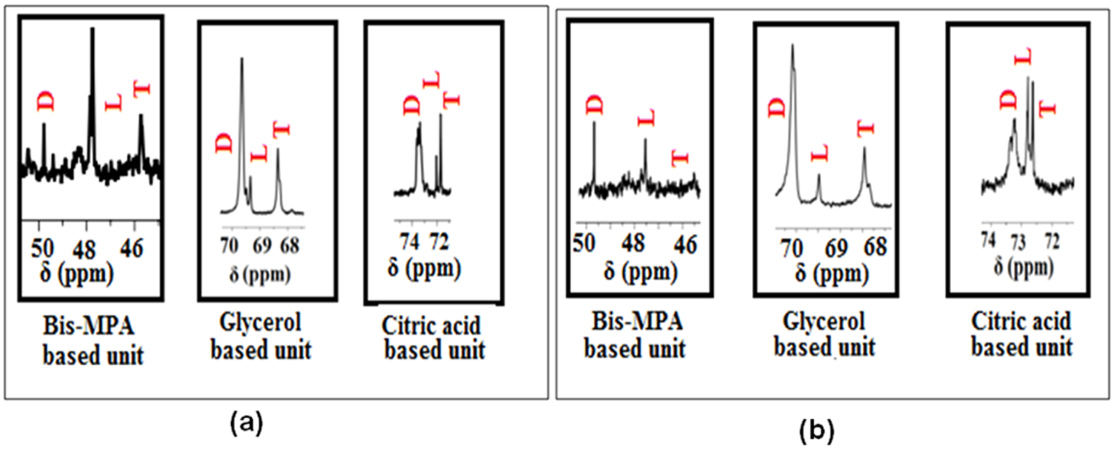
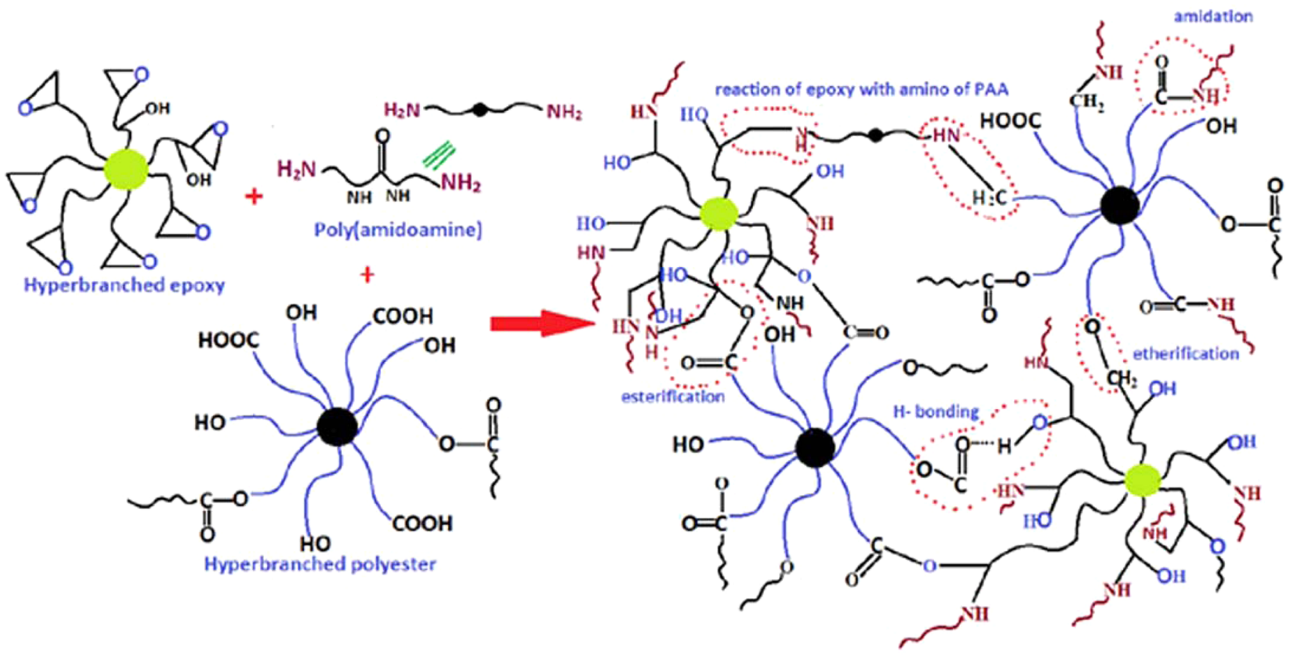


Figure 5. Terminal, linear and dendritic units of (a) WHPE50 and (b) WHPE40.

Scheme 2. Possible Crosslinking Reaction of Hyperbranched Polyester with Hyperbranched Epoxy and Poly(amidoamine) Hardener



place during curing process are shown in Scheme 2. In this curing reaction, poly(amidoamine) hardener acts as cross-linking agent as well as increases the basicity of the medium and thereby improving the curing efficiency of polyester.[15,32] The curing time is the time required to attain the swelling value of 20−30% for the thermosets (Table 3). From this table, it is found that the curing time decreases with the increase of citric acid content in the polyesters due to increase in number of cross-linkable hydroxyl, acid and ester groups.

Table 3. Performance Characterestics of WHPE30, WHPE40 and WHPE50

properties	WHPE 30	WHPE40	WHBPE50
curing time at 150 °C (min)	360 ± 5	330 ± 8	300 ± 12
swelling value	25 ± 0.5	24 ± 0.7	21 ± 0.4
tensile strength (MPa)	4 ± 1	5.3 ± 1.5	7.8 ± 2
elongation at break (%)	175 ± 3	224 ± 1.5	245 ± 2
toughness (MPa)	655 ± 6	895 ± 7	1782 ± 10
scratch hardness (kg)	2.5 ± 0.3	3 ± 0.5	4 ± 0.7
impact resistance (m)	>1	>1	>1

Mechanical Properties. Different mechanical properties such as tensile strength, elongation at break, toughness, impact resistance and scratch hardness of the synthesized waterborne hyperbranched polyester thermosets are given in Table 3. The tensile strength and elongation at break increase with the increase in weight percentage of citric acid. As the content of citric acid increases, ester linkages and different intermolecular interactions like hydrogen bonding, polar−polar interaction increase as well as the presence of epoxy and poly(amidoamine) hardener resulted in a cross-linked network structure. This cross-linked network structure formed a highly strained structure that causes steric hindrance to free rotation of shorter polyester linkage and introduced rigidity to the structure. These factors strengthened the polymeric chains. High intermolecular attraction forces also help in full extension of the polymer chains and thereby increasing the elongation break with the same. Thus, the tensile strength and elongation at break values were increased in the order of WHPE30 < WHPE40 < WHPE50 (Table 3). It is pertinent to mention that these thermosets showed better tensile strength compared to earlier reported waterborne polyesters, reported by Jung et al. (20−60 kgf/cm^2 = 1.96−5.8 MPa as 1 kgf/cm^2 = 0.098 MPa) and Malar et al. (1.56−1.77 MPa).[20,22] Further, the toughness of the waterborne hyperbranched polyester thermosets as calculated from stress−strain curves (Figure 6) of them was found to be followed the same order. WHPE50 exhibited the highest toughness, as it possesses the highest tensile strength and elongation at break. As it showed the highest toughness, the impact resistance and scratch hardness values were also found to be the highest. The scratch hardness also increases with the content of citric acid are due to increase of branching and rigidity in the structure. These scratch hardness values are better than the earlier reported trimellitic anhydride based highly branched polyester thermosets where vegetable oil was used as the biobased resource in spite of the presence of aromatic rigid trimellitic anhydride moiety.[2] The studied polyester thermosets also showed the highest limit of impact resistance (1 m is the limit of the instrument), which clearly demonstrated their high toughness character.

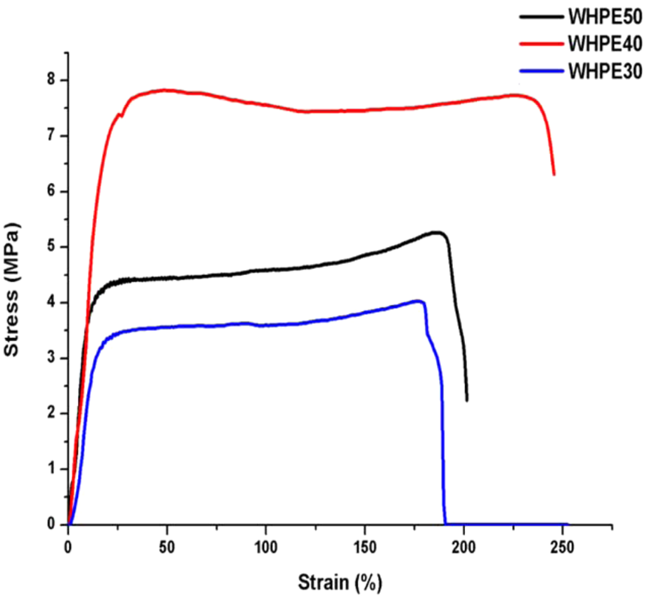


Figure 6. Stress−strain profiles of thermosets.

Thermal Properties. The thermal degradation behaviors of waterborne hyperbranched aliphatic polyester thermosets are shown in Figure 7. All the three thermosets exhibited similar thermostability, as they possess equivalent thermostable aromatic moieties and almost equal cross-link density. The polyester thermosets degraded by multi step process, first step degradation (225−232 °C) is attributed to the aliphatic moieties and ester, ether linkages and later step degradation (281−428 °C) is due to the aromatic moieties generated during the cross-linking reaction between the polyester, glycerol based epoxy and poly(amidoamine) hardener or may be due to the process of aromatization or cyclization of citric acid moiety.[25,33] The weight residues increased with the increase of citric acid content in the polyester and the values were found to be 7.7, 10 and 11.9% at 700 °C for WHPE30, WHPE40 and WHPE50, respectively.

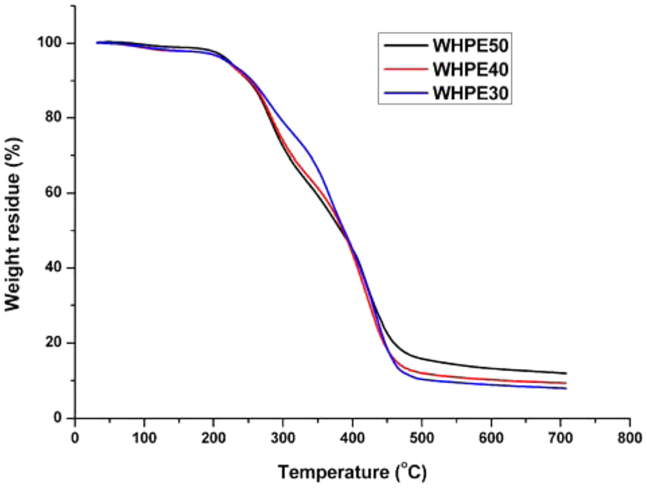


Figure 7. TG thermograms of thermosets.

Glass Transition Behavior. The DSC curves for waterborne hyperbranched polyester thermosets are given in Figure 8. The glass transition temperature (T_g) of the polyester thermosets was calculated from the cooling curves and found to be in the range of 42−49 °C. The T_g value increases with the content of citric acid. This is due to the fact that with the increase of citric acid content ester bond formation increases and also inter- and intramolecular force of attraction increases resulting in reduced molecular segmental dynamics. WHPE50 showed the highest T_g value (49 °C), as it contains the highest amount of citric acid and the T_g values for WHPE30 and WHPE40 thermosets were 42 and 46 °C, respectively.

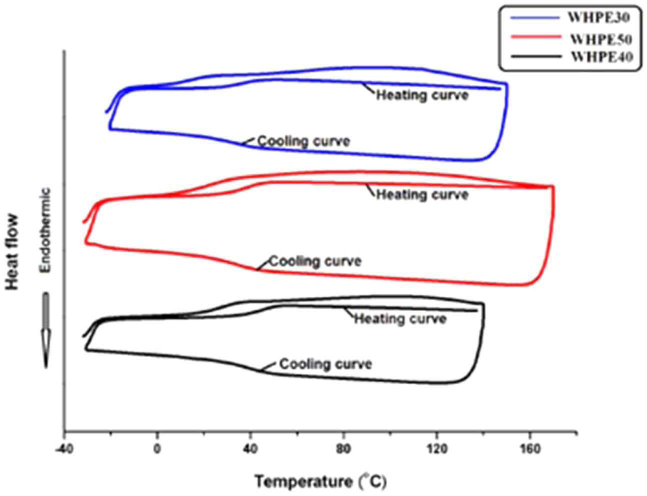


Figure 8. DSC curves of WHPE50, WHPE40 and WHPE30.

Biodegradation Study. Biodegradation of waterborne hyperbranched polyester was studied with Gram-negative (*Pseudomonas aeruginosa*) and Gram-positive (*Bacillus subtilis*) bacterial strains and it was found that the hyperbranched polyester films were degraded gradually with time during the experiment. The results of biodegradation clearly indicated the difference in bacterial growth for Gram-positive and Gram-negative bacteria. Higher growth rate in the case of Gram-negative bacteria compared to the Gram-positive bacteria is due

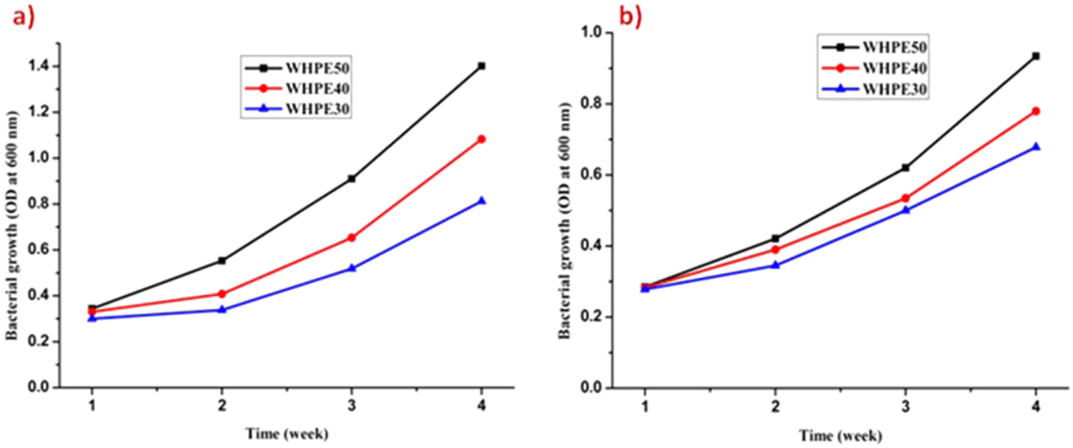


Figure 9. Growth curves of (a) *Pseudomonas aeruginosa* and (b) *Bacillus subtilis* on WHPE30, WHPE40 and WHPE50.

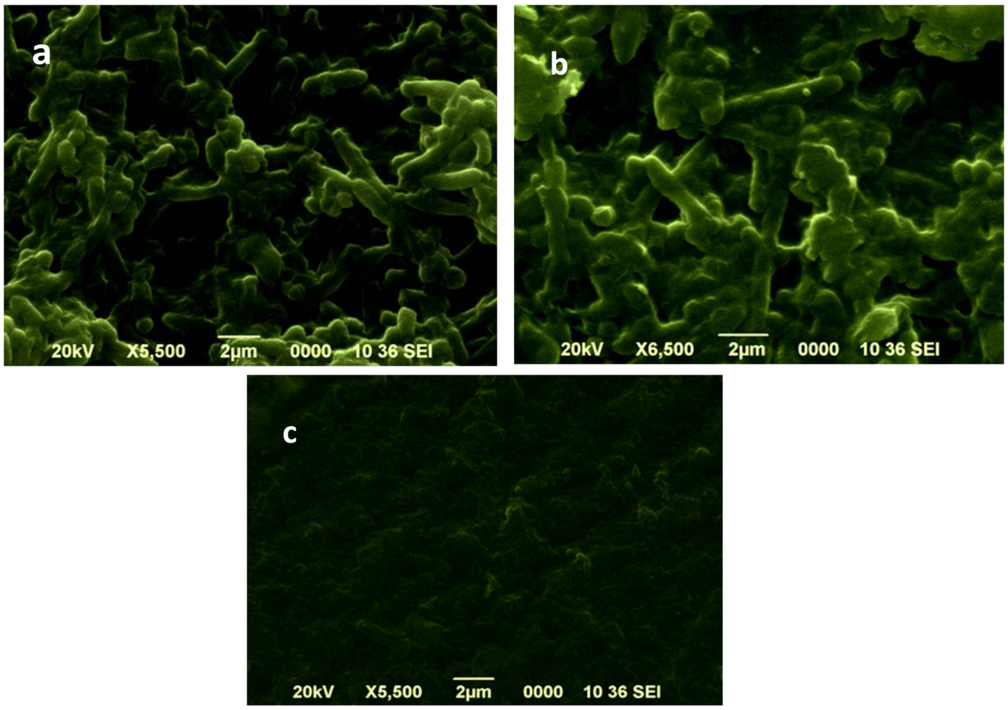


Figure 10. SEM images of WHPE50 after biodegradation by (a) *Pseudomonas aeruginosa*, (b) *Bacillus subtilis* and (c) Control.

to the difference in their cell structures. Because of the presence of hydrolyzable ester linkages in the polymeric chain of polyester, they are prone to microbial attack. Generally, biodegradation takes place through breaking of main chain or side chains of the macromolecules. It is a complex process that involves four phenomenons: absorption of water; cleavage of ester linkages and formation of oligomeric fragments such as monomeric carboxylic acids and diols; solubilization of these segments and diffusion of soluble oligomers by bacteria to produce water, carbon dioxide and humus.[16] Therefore, the factors that increase hydrolysis tendency of polyester also control the biodegradation. The bacterial growth curves as measured by OD of degraded films with time are shown in Figure 9. The bacterial growth shows an increasing order with the content of citric acid. This is due to the fact that as the amount of citric acid increases the number of ester linkages in their structure also increased, which is supported by saponification value (Table 2). These polyesters are aliphatic in nature and hence the thermosets of them exhibited high biodegradability. Among them, the WHPE50 thermoset showed the highest biodegradation as it contains the highest number of ester linkage in its structure, which is supported by its saponification value. These ester linkages are mainly responsible for biodegradation. However, cross-link density retards the biodegradation process. The difference in cross-link density is not very high, further ester linkages are also forming through cross-linking reaction. The bacterial growth was the lowest for WHPE30 as the citric acid content was the lowest for it. The extent of bacterial growth as well as biodegradation of polyester thermosets can be seen from SEM images taken after 4 weeks of exposure of bacterial strain. Representatives SEM images of degraded WHPE50 by *Pseudomonas aeruginosa* and *Bacillus subtilis* bacteria and control (WHPE50 film without bacterial medium) are shown in Figure 10. These images were used to compare the erosion of surface and bacterial adherence of the degraded film with respect to the control. This biodegradable polyesters are important because they are eco-compatible and environmentally degradable. These thermosets can be used as top coat for decorative and protective coatings as after their useful service they can be degraded by the environment due to their biodegradation nature. Further, this type of biodegradable and biocompatible polyester could be used for biomedical applications. The biodegradability provides waterborne hyperbranched polyester with green credits in the area of surface coating applications.

Hemolytic Assay. The hemocompatibility of the polyester thermosets was investigated by RBC hemolytic protection assay (Figure 11), which is a one type of acute toxicity assay. By detecting hemolyzation of erythrocytes, it evaluates the hemocompatibility of the material. The measure of toxicity is the extent of disruption of erythrocyte membrane, which is obtained by the direct interaction of material with the erythrocyte membrane. The RBC hemolysis protection assay showed that all the thermosets exhibited good compatibility with the erythrocyte. Among these thermosets, WHPE50 showed the excellent compatibility with the erythrocyte as it contains the highest amount of citric acid, which is confirmed by absorbance of hemoglobin almost parallel to hematocrit. The compatibility of polyester thermosets increases with the content of citric acid due to increase in the amount of biocompatible moieties in their structure. This was observed from the value of hemoglobin absorbance. The positive control (hematocrit) showed low absorbance value and the negative control, Tween 20 showed high absorbance of hemoglobin which indicates multifold destruction of RBC membrane. Thus, hemolysis assay confirmed the biocompatibility of polyester thermosets with mammalian RBC.

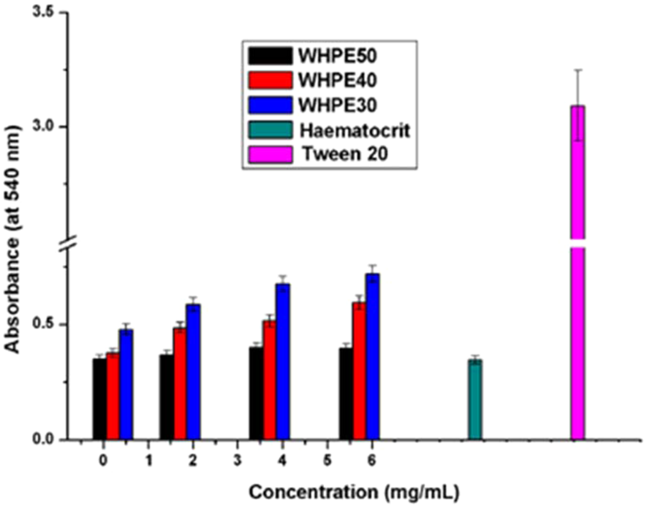


Figure 11. Bar diagrams of absorbance against concentration of thermosets for antihemolylic activity assessment.

Chemical Resistance. The chemical resistance of polyester thermosets was tested by exposing them in different chemical environments for 20 days at room temperature and results as the weight losses are given in Table 4. All the thermosets showed good resistance toward HCl, NaCl and water. But the alkali resistance of these thermosets was poor due to the presence of hydrolyzable ester bonds.[15] Among these three polyester thermosets, WHPE50 showed the best resistance toward HCl, NaCl and water due to the highest cross-linked density but the alkali resistance is the poorest due to the presence of the highest degree of ester bonds in its structure. The alkali resistance of this material can be improved by increasing the amount of hyperbranched epoxy during the cross-linking reaction of WHPE50 with hyperbranched epoxy and poly(amidoamine). Though WHPE50 contains the highest number of ester bonds, due to the highest degree of cross-linking reactions with hyperbranched epoxy, the cross-link density increased along with the increase of alkali resistance ether and amide linkages.

Table 4. Chemical Resistance (weight loss %) of Polyester Thermosets in Different Chemical Media

chemical media	weight loss (%)		
	WHPE30	WHPE40	WHPE50
0.5 wt % aqueous NaOH	4.5	4.6	4.9
10 wt % aqueous HCl	0.8	0.7	0.5
15 wt % aqueous NaCl	0.05	0.04	0.03
20 wt % aqueous EtOH	2	2.3	2.5
distilled water	0.03	0.02	0.01

■ CONCLUSION

In this study, citric acid based biodegradable, biocompatible waterborne hyperbranched aliphatic polyester was synthesized by a catalyst free polycondensation reaction without using any neutralizing agent along with other readily available relatively low expensive reactants such as PEG 200 and glycerol. The mechanical properties and degradation rate of polyester thermosets can be tuned by varying the weight percentage of citric acid. It showed good mechanical strength, high toughness, flexibility, biodegradability and biocompatibility as well as good chemical resistance. Thus, the synthesized polyester thermosets may be used as high performance material for various applications such as biomedical, anticorrosive surface coating, etc.

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The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

Notes

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