
Synthesis, characterization and evaluation of properties of waterborne hyperbranched polyesters

Highlights

The synthesis, characterization and evaluation of physical, mechanical, thermal as well as chemical properties of water dispersible and completely water soluble hyperbranched polyesters are highlighted in this chapter to address the drawbacks of solvent borne polyesters. In accordance to branch generating moieties, this chapter was divided into two sub-chapters. First sub chapter deals with synthesis, characterization and property evaluation of water dispersible polyester synthesized using aliphatic and aromatic moieties containing glycerol-based hyperbranched polyol as branch generating moiety along with citric acid and 2,2 bis-(hydroxymethyl) propionic acid (bis-MPA). Second sub chapter deals with synthesis of completely water soluble polyester using bio-based raw material (glycerol) as branch generating moiety along with citric acid and bis-MPA. Further, the probable chemical structures of synthesized polyesters were confirmed by characterizing both the polymers with the help of various analytical and spectroscopic techniques. Both types of polyesters were synthesized through a facile polycondensation reaction without using any solvent, catalyst and neutralizing agent. The developed waterborne polyesters exhibited good mechanical, thermal and chemical properties as well as showed excellent biodegradability behavior.

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2A. Hyperbranched polyol-based water dispersible polyester

2A.1. Introduction

It is noticed from **Chapter 1** that polyester is a versatile polymeric material with a wide range of applicability in different fields including surface coating, adhesive, laminates, biomedical, etc. [1, 2]. However, considerable importance was paid to reduce the amount of volatile organic compounds (VOC) released into the atmosphere by solvent borne polyesters which cause environmental legislation and health awareness. In this milieu, synthesis of waterborne polyester may most probably be able to address the above problems as it possesses some unique features as mentioned in **Chapter 1** [3, 4]. Further, use of catalyst and organic solvent can also produce VOC which are responsible for such environmental pollution and harming the human health. So use of organic solvent should be avoided wherever possible and accordance with respect to the principles of green chemistry, green solvent like water can be used. Designing of such polymer from renewable resource-based raw materials with unique structural architecture may lead to a high performing environmentally friendly material [5]. In this context, the establishment of structure-property relationship has tremendous technological and scientific importance to meet the demand of industry [1, 6]. Keeping this in mind, high performing water dispersible hyperbranched polyester (WHBP) is attempted to synthesize in absence of solvent and catalyst using hyperbranched polyol containing both aromatic and aliphatic moieties along with bio-based raw materials to address the issues of modern applications. The reactants selected for the synthesis of polyester based on the following parameters (a) multi-functional to form randomly cross-linked networks, (b) inexpensive, nontoxic, readily available from renewable feedstocks and (c) allow to form ester linkages through polycondensation reactions which are easily hydrolysable [7, 8]. Thus, a hyperbranched polyether polyol containing both aromatic and aliphatic moieties with large number of hydroxyl functionality is attempted to introduce as a branch generating unit in the proposed hyperbranched polyesters along with other branch generating bio-based precursors to achieve such attributes. So, it is expected that this moiety could not only influence the mechanical properties but also enhance the thermal stability and chemical resistance. It can be produced by hydrolyzing glycerol-based hyperbranched epoxy (HBGE) obtained by a conventional polycondensation approach [9]. Other bio-based and easily available reactants such as citric acid, poly(ethylene glycol) (PEG) and bis-MPA are also chosen as precursors for synthesis of WHBP. Further, citric acid can react with

alcohols or polyols to form esters without any catalysts [10, 11]. As these precursors have more number of polar functionalities and hence water solubility may be achieved without any neutralizing agent. Thus, this approach offers many advantages such as one pot synthesis, high conversion, no need of any catalyst, solvent and neutralizing agent, no need of purification, low or no VOC, environmentally friendliness, good applicability, etc. [12]. Further, introduction of highly branched structure and the large number of functional groups offer unique properties as mentioned in **Chapter 1**. The single step preparative protocol of such hyperbranched polyester makes them interesting for different advanced industrial applications [13]. Again, biodegradable polyesters suffer from wide applicability because of their poor mechanical property. While aromatic polyesters like poly(ethylene terephthalate) exhibit excellent physical and mechanical properties but proved to be almost resistant to bacterial or fungal attack. Similarly, aliphatic polyesters turned out to be biodegradable but lack in properties [14]. Therefore, the desired polyester should possess acceptable biodegradability and high mechanical properties. This kind of desired high performing WHBP as well as synthesis of such polyester in absence of solvent, catalyst and neutralizing agent is very limited in literature. Thus, the development of such a high performance material with unique architectural features by the combination of aliphatic-aromatic moieties, is important.

Aiming at this target, we have synthesized WHBP containing unique combination of structural units using hyperbranched polyol along with bio-based raw materials through an eco-friendly and facile approach. The performance characteristics of this polyester after curing with HBGE and poly(amidoamine) (PAA) were investigated with respect to dose level of hyperbranched polyol.

2A.2. Experimental section

2A.2.1. Materials

Glycerol (**Table 1.2, Chapter 1**) was obtained from Merck, India which is odorless and colorless viscous liquid with 99% purity. Its molecular weight, boiling point, melting point and density are 92.09 g mol^{-1} , 1.26 g cm^{-3} , $290 \text{ }^\circ\text{C}$ and $17.8 \text{ }^\circ\text{C}$, respectively. It was used for synthesis of epoxy resin as well as a branch generating moiety in the synthesis of WHBP after drying under vacuum for 12-14 h at $60 \text{ }^\circ\text{C}$.

4,4'-(Propane-2, 2-diyl) diphenol or Bisphenol-A (BPA) was purchased from

SRL, India and used for synthesis of epoxy resin. It offers high mechanical and thermal properties as well as good chemical resistance to the thermosets of epoxy. In this study, it was used as a reactant for the preparation of epoxy resin after recrystallization from toluene. The molecular weight and melting point of the purified BPA was $228.29 \text{ g mol}^{-1}$ and $159 \text{ }^\circ\text{C}$ respectively.

Epichlorohydrin (ECH) is another important chemical used for synthesis of epoxy resin and received from SRL, India. It is a colorless liquid and molar mass, boiling point, and density of it are 92.52 g mol^{-1} , $117.9 \text{ }^\circ\text{C}$ and 1.18 g cm^{-3} respectively.

Sodium hydroxide (NaOH) was used for preparation of epoxy resin, which takes a role of base catalyst. It was purchased from Merck, India with density 2.13 g cm^{-3} and molar mass 40 g mol^{-1} . It was further used for determination of epoxy equivalent of prepared epoxy resin as well as chemical resistance test for the thermosets of epoxy and WHBP.

Sodium chloride (NaCl) with $\geq 99\%$ purity was purchased from Merck, India and used for washing of organic layer of epoxy resin. The melting point, molar mass and density of epoxy resin are $80.1 \text{ }^\circ\text{C}$, 58.44 g mol^{-1} and 2.16 g cm^{-3} , respectively. Further, it was also used for chemical resistance test of epoxy and WHBP thermosets.

Hydrochloric acid (HCl) was used for preparation of hyperbranched polyol. Further, it was used to determine the epoxy equivalent values of the epoxy resins and saponification value of WHBP as well as in chemical resistance test for the thermosets. It was obtained from Merck, India with 37% weight by volume in water. The molecular weight of HCl is 36.5 g mol^{-1} .

Citric acid (**Table 1.1, Chapter 1**) with 99.9 % purity was received from Merck, Germany. Its molecular weight, density, melting point and boiling point are $192.12 \text{ g mol}^{-1}$, 1.66 g cm^{-3} , $156 \text{ }^\circ\text{C}$ and $310 \text{ }^\circ\text{C}$, respectively. It was used as a branch generating moiety of WHBP after drying under vacuum at $60 \text{ }^\circ\text{C}$ for 12 h.

bis-MPA (**Table 1.1, Chapter 1**) was purchased from Sigma Aldrich, Germany with 99% purity. It has a hydroxyl value of 810-860 mg KOH/g and acid value of 405-425 mg KOH/g. Its molecular weight and melting point are $134.13 \text{ g mol}^{-1}$ and $180 \text{ }^\circ\text{C}$ respectively.

PEG (**Table 1.2, Chapter 1**) with weight average molecular weight 200 g mol^{-1} was purchased from Merck, India and used for synthesis of WHBP.

Potassium hydroxide (KOH) purchased from Merck, India was used for the

determination of acid value, hydroxyl value and saponification value. The molecular weight, density and melting point of KOH are 56.11 g mol^{-1} , 2.12 g cm^{-3} and $406 \text{ }^\circ\text{C}$.

Oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) is a white crystalline solid achieved from Merck, India and used in this study as the primary standard for standardization of KOH and NaOH solutions. The molar mass, density and melting point of 90.03 g mol^{-1} , 1.9 g cm^{-3} and $102 \text{ }^\circ\text{C}$ respectively.

Maleic anhydride (**Table 1.3, Chapter 1**) purchased from Merck, India was used as a reactant for the determination of hydroxyl value. It is a white solid with molar mass and melting point of 98.06 g mol^{-1} and $52.8 \text{ }^\circ\text{C}$ respectively.

Triethylamine (Et_3N) is a colorless liquid and is commonly used as a base for the organic synthesis. Here it was used as a nucleophilic catalyst with maleic anhydride to determine hydroxyl value. It was obtained from Merck, India. The molar mass, density and boiling point of it are $101.19 \text{ g mol}^{-1}$, 0.725 g mL^{-1} and $88 \text{ }^\circ\text{C}$ respectively.

PAA was received as a gift from Asian Paints, India. It is non-volatile resinous hardener and a polycondensation product of diethylene triamine and vegetable oil-based dimmer acid. In this study, it was used as a hardener for preparing the thermosets of WHBP. The measured viscosity and amine value of the hardener are 10-14 Pas and 5-7 eq. kg^{-1} .

Toluene used for recrystallization of BPA was received from Merck, India. The density, boiling point and molar mass of it are 0.86 g cm^{-3} , $110.6 \text{ }^\circ\text{C}$ and 92.14 g mol^{-1} respectively. Tetrahydrofuran (THF) purchased from Merck, India was used as a processing solvent during the preparation of epoxy resin and polyol as well as for solubility test of WHBP. Ethanol (EtOH) was used in solubility and chemical resistance test and acquired from Merck, India. Methanol (CH_3OH) with molecular weight 58.0 g mol^{-1} , purity $\geq 99.5\%$, density 0.971 g mL^{-1} and boiling point $56\text{-}57 \text{ }^\circ\text{C}$ was obtained from Merck, India and used to check the solubility of WHBP. *N, N'*-Dimethylformamide (DMF) molecular weight 73.09 g mol^{-1} , purity $\geq 98.0\%$, density 0.94 g cm^{-3} and boiling point $153 \text{ }^\circ\text{C}$ was purchased from Merck, India and used for solubility test. *N, N'*-Dimethylacetamide (DMAc) used in solubility test was purchased from Merck, India with 99.5% . Acetone with purity $\geq 99\%$ obtained from Merck, India was also used for solubility test of WHBP. The molecular weight, density and boiling point of it are 32.05 g mol^{-1} , $0.8\text{-}0.9 \text{ g cm}^{-3}$ and $64\text{-}65 \text{ }^\circ\text{C}$ respectively.

2A.2.2. Characterization

Fourier transform infrared (FTIR) spectra (resolution 4 cm^{-1}) were recorded by a Nicolet (Impact-410, Madison, USA) spectrophotometer using KBr pellets. ^1H NMR and ^{13}C NMR spectra were documented on a 400 MHz FT NMR (JEOL, Japan) spectroscopy using tetramethyl silane as the internal standard and $\text{d}_6\text{-DMSO}$ as the solvent. The shear viscosity of the polyesters was measured using a parallel plate with the help of a rheometer (CVO100, Malvern, UK). The viscosity was measured under three different conditions: shear viscosity against (a) time at constant stress (100 Pa) and temperature ($25\text{ }^\circ\text{C}$), (b) temperature at constant time and constant stress (100 Pa) and (c) shear stress at constant time and temperature ($25\text{ }^\circ\text{C}$). Acid value, hydroxyl value, saponification value and density of the polyesters were measured using the standard methods. The molecular weight of HBGE was carried out in THF in gel permeation chromatography (Empower 2, USA) using refractive index detector 2414. Thermal behaviors of the thermosets were evaluated by thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC). TG study was done by using a PerkinElmer TGA 4000, USA thermal instrument at a scanning rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere at a flow rate of $30\text{ mL}/\text{min}$ in the range of $25\text{--}700\text{ }^\circ\text{C}$. DSC study was carried out by a PerkinElmer DSC 6000, USA instrument following a heating-cooling-heating cycle under an atmosphere of nitrogen and at a scanning rate of $5\text{ }^\circ\text{C}/\text{min}$ for heating and $10\text{ }^\circ\text{C}/\text{min}$ for cooling in the range from -70 to $+160\text{ }^\circ\text{C}$. Mechanical properties such as tensile strength and elongation at break were measured by a Universal Testing Machine (UTM, WDW10, Jinan, China) by the standard ASTM D 3039 method. The scratch hardness of the thermosets was measured with the help of a scratch hardness tester (Model No. 705, Sheen instrument limited, UK) by using standard ASTM G171-03 method. The impact strength of the polyester thermosets was tested by the help of an impact tester (S. C. Dey & Co., Kolkata) as per the standard falling weight (ball) method (ASTM D4272-08). The surface morphologies of the degraded polymeric films were obtained by scanning electron microscopy (JEOL, model JSM- 6390LV, Japan) using voltage of 20 keV after platinum coating on the surface. The chemical resistance test of the thermosets was done using standard ASTM D543-95 method in different chemical media such as aqueous NaOH (0.5%), aqueous HCl (10%), aqueous NaCl (15%), aqueous ethanol (20%) and water. The small pieces of cured films were kept in 100 mL glass bottles containing the aforementioned media under ambient conditions. After 20 days of test, the percentage of weight loss was measured.

2A.2.3. Method**2A.2.3.1. Preparation of hyperbranched polyol**

For this, first HBGE was prepared by earlier reported method [15]. In brief; it was prepared by reacting glycerol and BPA with epichlorohydrin by maintaining the temperature of the reaction at 110 °C. 5M aqueous solution of NaOH was added from a dropping funnel slowly to the above reaction mixture. The reaction was stopped after 4h and obtained viscous product was separated using a separating funnel. The resin was obtained after separation from aqueous phase, washing with brine solution followed by water and finally drying at 70 °C under vacuum.

Hyperbranched polyol was prepared by hydrolysis of HBGE with dilute HCl (equivalent amount to epoxy equivalent of the resin) at 70 °C. The hydrolysis reaction was carried out for about 5 h and the product was washed with distilled water for several times to remove any trace of HCl. This was confirmed by AgNO₃ test. The hydrolyzed product was dried under vacuum at 70 °C for 24 h and encoded as HBGP.

2A.2.3.2. Synthesis of WHBP

It was synthesized by following polycondensation reactions without using any solvent, catalyst and neutralizing agents. In the first step, citric acid and PEG-200 were taken in a three neck round bottomed flask fitted with a nitrogen gas inlet, a thermometer, a mechanical stirrer and a glass rod with a teflon blade. The reaction was carried out at 140 °C for 1 h under the nitrogen atmosphere with constant stirring (240-300 rpm speed). The obtained reaction mixture was then cooled to room temperature. In the second step, HBGP and bis-MPA were added to the above reaction mixture by maintaining the stoichiometry and the reaction was carried out at 140 °C for another 3 h to obtain the desired polyester. By following the same procedure, three different hyperbranched polyesters with 7, 12 and 16 wt% (calculated with respect to total weight of the reaction mixture) HBGP were synthesized and encoded as WHBP7, WHBP12 and WHBP16 respectively. Hyperbranched polyester in absence of HBGP was also synthesized for comparison purposes and coded as WHBP0. The actual compositions of the reactants are given in **Table 2A.1**.

2A.2.3.3. Preparation of the thermosets

WHBP was cured with HBGE and PAA hardener at 1:0.5:0.25 wt ratio. A homogeneous mixture of the components was made with minimum amount of aqueous ethanol in a glass beaker at room temperature by hand stirring for 20 min. Then the mixture was

uniformly coated on glass plates for measurement of scratch hardness and tensile strength and steel plates for impact strength. The plates were kept in a desiccator under vacuum for 2 days to remove the volatiles. Then the films were cured in an oven at a specified temperature for a desired period of time. The optimization curing time was determined by measurement of swelling value of the cured thermosets by immersing the cured films in THF for 48 h.

Table 2A.1: Composition of WHBP

Reactant	WHBP0	WHBP7	WHBP12	WHBP16
Citric acid (mol)	0.02	0.02	0.02	0.02
PEG-200 (mol)	0.01	0.01	0.01	0.01
HBGP (wt%)	0	7	12.2	16.04
bis-MPA (mol)	0.01	0.01	0.01	0.01

2A.2.3.4. Swelling test

Swelling test was done by immersing the weighed amount of the dried films in THF. After 48 h of exposure, the swelled films were taken out from the solvent 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 measuring the difference in weight of dried film from swelled film as given in equation [15].

$$\text{Swelling (\%)} = (W_s - W_d)/W_d \times 100 \dots\dots\dots(\mathbf{Eq. 2A.1})$$

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

2A.2.3.5. Biodegradation study

A biodegradation study was conducted using the McFarland turbidity method [16] using *Pseudomonas aeruginosa* and *Bacillusq subtilis* as the bacterial strains. A medium of mineral salts containing 10 mg of $H_3BO_3 \cdot 5H_2O$, 0.5 mg of $CaCl_2 \cdot 2H_2O$, 70 mg of $ZnSO_4 \cdot 7H_2O$, 2.0 g of $(NH_4)_2SO_4$, 4.75 g of KH_2PO_4 , 1.2 g of $MgSO_4 \cdot 7H_2O$, 100 mg of $MnSO_4 \cdot 5H_2O$, 100 mg of $CuSO_4 \cdot 7H_2O$, 2.0 g of Na_2HPO_4 , 1 mg of $FeSO_4 \cdot 7H_2O$, and 10 mg of MoO_3 was prepared by mixing all together in 1.0 L of demineralized water. It was sterilized for 15 min at 120 °C under a pressure of 0.103 MPa and then allowed to cool to room temperature. The bacterial strains were cultured in the medium inside an incubator shaker at 37 °C for 48 h. An amount of 100 mL (10^8 microbes per mL, as calculated

using the McFarland turbidity method) of the cultured medium was taken in a conical flask containing 10 mL of the prepared salt medium. The polymer films were sterilized by autoclaving and were incubated inside the medium under sterile conditions at 37 °C. The flasks containing mineral salt medium but without any bacterial strain were used as the control. The bacterial growth is indicated by the increase in turbidity of the medium with time. The optical density (OD) of the microorganism at 600 nm with respect to the control was measured by an Evolution-300 UV–visible spectrophotometer (UV-300, ThermoFisher USA). The experiment was performed in triplicate. Scanning electron microscope was used to record the images of the degraded films after 5 weeks of bacterial degradation in order to study their surface morphology. The test was performed as per ASTM D 5338-98 standard procedure.

2A.3. Results and discussion

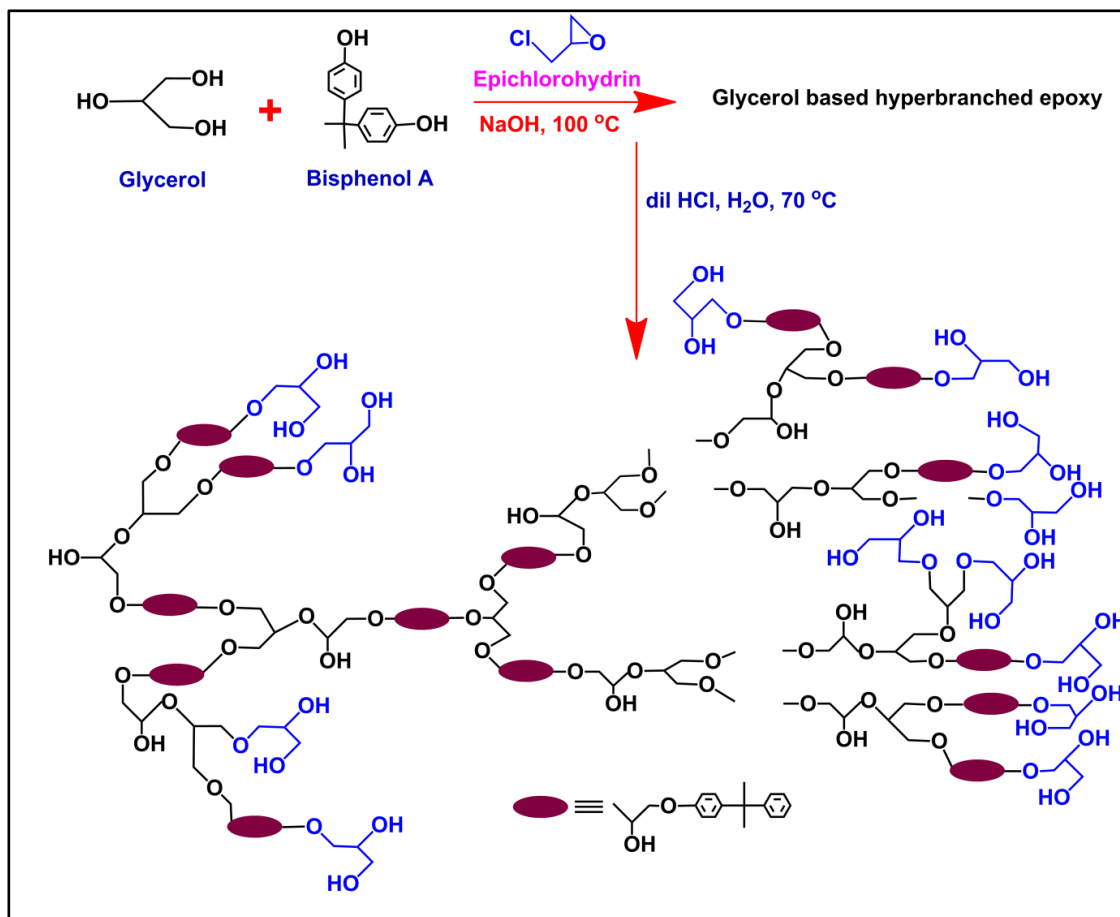
2A.3.1. Preparation of HBGP

HBGP was obtained from HBGE by a hydrolytic process. HBGE is a hyperbranched epoxy resin formed by polycondensation reaction of BPA and glycerol with epichlorohydrin by an $AA' + B_2 + B'_4$ polycondensation reaction. Further, the hydrolysis of HBGE by dilute HCl resulted HBGP by the ring opening reaction of oxirane rings. The preparative protocol of HBGP is shown in **Scheme 2A.1**.

2A.3.2. Characterization and physical properties of HBGP

The viscosity, hydroxyl value, and degree of branching (DB) of HBGP and HBGE resins are given in **Table 2A.2**. The hydroxyl value of HBGP is higher than HBGE. This is due to formation of more hydroxyl groups by ring opening of oxirane rings upon hydrolysis. The density of both HBGP and HBGE was almost equal and the values are similar to other reported HBGE and polyol. DB values of HBGP and HBGE are exactly same as there is only difference in hydroxyl groups. HBGP was found to be soluble in most of the organic solvents owing to the existence of a large number of polar functionalities along with hyperbranched structure. This also supports the presence of hyperbranched architecture in the synthesized polyol. The presence of different chemical functional groups in HBGP was supported by FTIR spectroscopic analysis (**Figure 2A.1**). The bands (ν max/cm⁻¹) at 3427 cm⁻¹ (-OH stretching), 2969-2861 cm⁻¹ (symmetric and asymmetric -CH stretching), 1606 cm⁻¹ (-C=C stretching), 1029 cm⁻¹ (alkyl ether) and

1242 cm^{-1} (aryl ether) were found in the spectrum [9, 17, 18]. The sharp band near 912 cm^{-1} (asymmetric vibration of the oxirane ring) was absent in FTIR spectrum of HBGP, while the same was present in the FTIR spectrum of HBGE. This confirmed the oxirane rings of epoxy are completely opened up upon hydrolysis of HBGE by dilute HCl.



Scheme 2A.1: Preparation of HBGP

Table 2A.2: Physical properties of HBGP and HBGE

Properties	HBGP	HBGE
Hydroxyl value (mg KOH/g)	339.3	157
DB	0.89	0.89
Viscosity (g/cc)	0.90	0.89

The structure of HBGP was further confirmed from NMR spectral studies. **Figure 2A.2a** shows the peaks (δH ppm, 500 MHz, d₆-DMSO, Me₄Si) at 3.78 (a, -CH₂ protons of the primary hydroxyl group), 3.7 (b, -CH proton of the secondary hydroxyl

group), 3.58 (c, $-\text{CH}_2$ protons adjacent to secondary hydroxyl group), 6.82 and 7.21 (d and e, aromatic protons of BPA), 1.4 (f, $-\text{CH}_3$ protons of BPA), 3.28-3.89 (g and h, protons attached with the substituted glycerol unit), 2.12 (i, $-\text{OH}$ proton of glycerol moiety), 3.3 (j, $-\text{CH}$ proton of glycerol unit) were found in ^1H NMR spectrum [4, 15, 19].

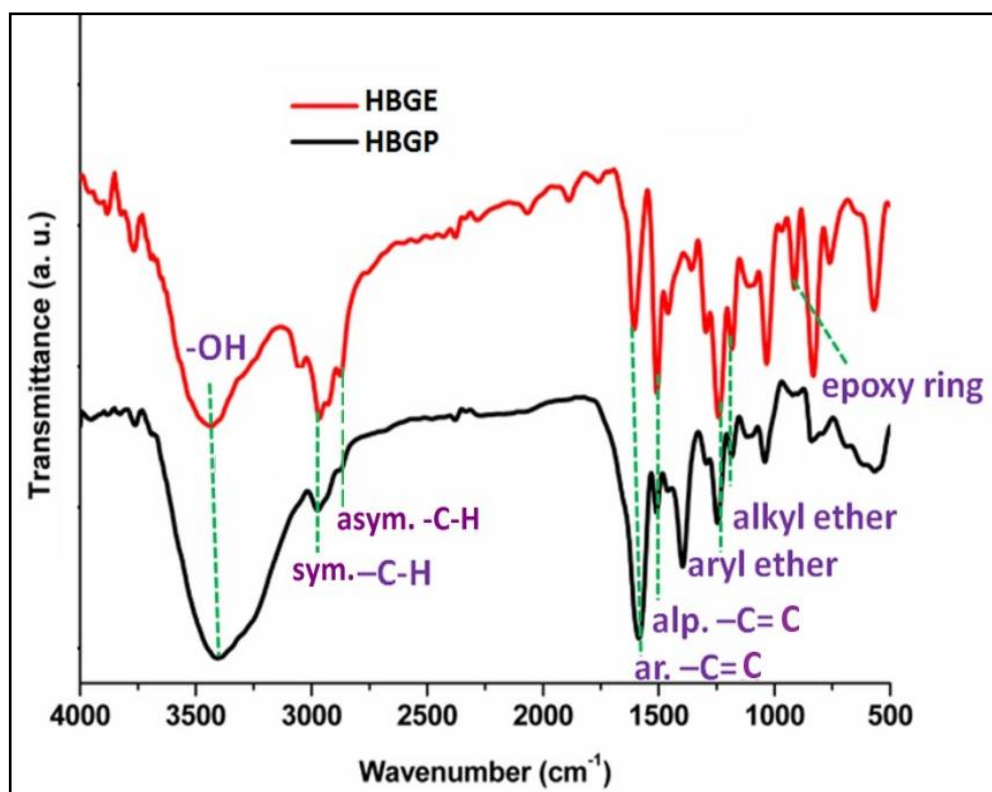


Figure 2A.1: FTIR spectra of HBGE and HBGP

Similarly, carbons present in different chemical environments in the structure of HBGP were confirmed from the ^{13}C NMR spectrum, as shown in **Figure 2A.2b**. The peaks (δC , ppm, d_6 -DMSO) at 66.6 (a, carbon attached with the primary hydroxyl group), 71.5 (b, carbon attached with secondary hydroxyl group), 69.7 (c, carbon adjacent to secondary hydroxyl group), 113.92 and 127.81 (d and e, different carbons of the BPA moiety), 30.98 (f, CH_3 carbon of BPA), and 62-68 (g and h, carbon attached with substituted hydroxyl of glycerol unit), 41.66 (i, quaternary carbon of BPA), 67 (j, $-\text{CH}$ proton of glycerol unit), and 141 and 156.3 (k and l, different carbons of BPA moiety) were found in ^{13}C NMR spectrum [9, 20]. Further, the chemical shift values at 68.9 (dendritic, D), 68.8 (linear, L) and 69.4 (terminal, T) are associated with the carbons of trisubstituted, disubstituted and monosubstituted glycerol units. These were utilized to determine the DB.

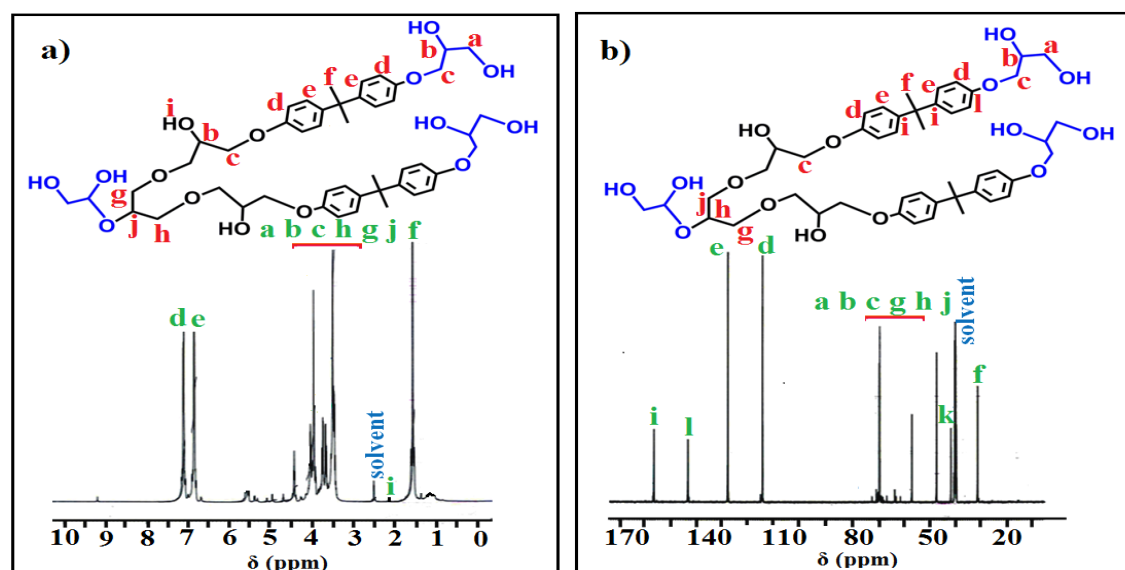


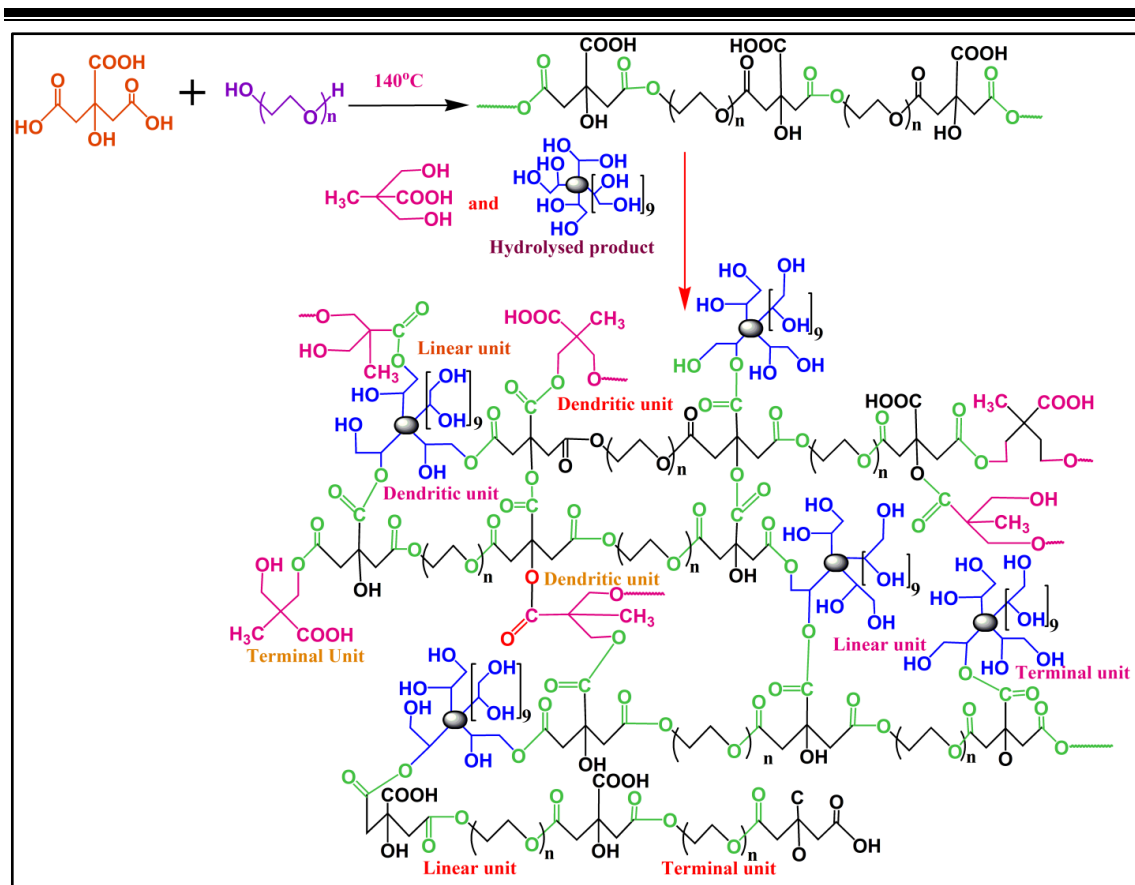
Figure 2A.2: (a) ^1H and (b) ^{13}C NMR spectra of HBGP

2A.3.3. Synthesis of WHBP

The synthesis was a two stage single pot process. In the first step, required amount of citric acid and PEG-200 were taken in a three neck round bottom flask. 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 amount of HBGP and bis-MPA were added to the above reaction mixture. In this polyester, hyperbranched polyol, citric acid and glycerol act as branch generating units. The resulted polyester became water dispersible without using any neutralizing moiety because of the presence of large number polar groups and globular hyperbranched architecture. The proposed reaction routes and structure of WHBP are shown in **Scheme 2A.2**. The synthesized polyester contains unique combination of aliphatic (80-75 wt%) and aromatic (20-25 wt%) moieties. The polyester was soluble in MeOH, EtOH, THF, acetone, DMSO, DMAc, DMF, etc. but insoluble in toluene, xylene, hexane, ethyl acetate, etc. This is due to the same reason as stated above. Further, due to high solubility in common industrial organic solvents and reactivity of freely exposed end groups, they can be easily process and cross-linked.

2A.3.4. Characterization of polyesters

A representative FTIR spectrum of WHBP16 is shown in **Figure 2A.3**. The formation of ester linkages is confirmed by the presence of carbonyl band at 1734 cm^{-1} .



Scheme 2A.2: Synthesis of WHBP

The bands at 2940 cm^{-1} and 2858 cm^{-1} are attributed to $-\text{CH}$ symmetric and asymmetric stretching vibrations. The absorption band at 3464 cm^{-1} is due to stretching vibration of $-\text{OH}$. The FTIR spectrum of WHBP0 is also shown in **Figure 2A.3**. The characteristic absorption peak at 1730 cm^{-1} confirmed the formation of ester linkages [12, 17].

A representative ^1H NMR spectrum of WHBP16 is shown in **Figure 2A.4a**. The peaks (δH ppm, 500 MHz, $\text{d}_6\text{-DMSO}$, Me_4Si) at 3.82 (a, $-\text{CH}_2$ protons of the primary hydroxyl group), 3.7 (b, $-\text{CH}$ proton of secondary hydroxyl group), 3.58 (c, $-\text{CH}_2$ protons of the primary hydroxyl group due to different chemical environment), 6.81 and 7.23 (d and e, aromatic protons of BPA), 1.4 (f, $-\text{CH}_3$ protons of BPA), 2.0 (g, unsubstituted $-\text{OH}$ proton of glycerol unit), 3.48 (h, $-\text{CH}_2$ protons attached with the substituted glycerol unit), 4.1 (i, unsubstituted $-\text{OH}$ proton of citric acid), 2.5-2.9 (j and k, $-\text{CH}_2$ protons of citric acid due to different chemical environment), 3.69 (l, $-\text{CH}_2$ protons of PEG 200), 3.28-3.7 (m, protons of $-\text{CH}_2$ of bis-MPA due to different chemical environment), 0.94-1.12 (n, $-\text{CH}_3$ protons of bis-MPA due to different neighboring chemical structure), 3.1 (o, $-\text{CH}$ proton of glycerol unit) were found in ^1H NMR spectrum [15, 19, 21].

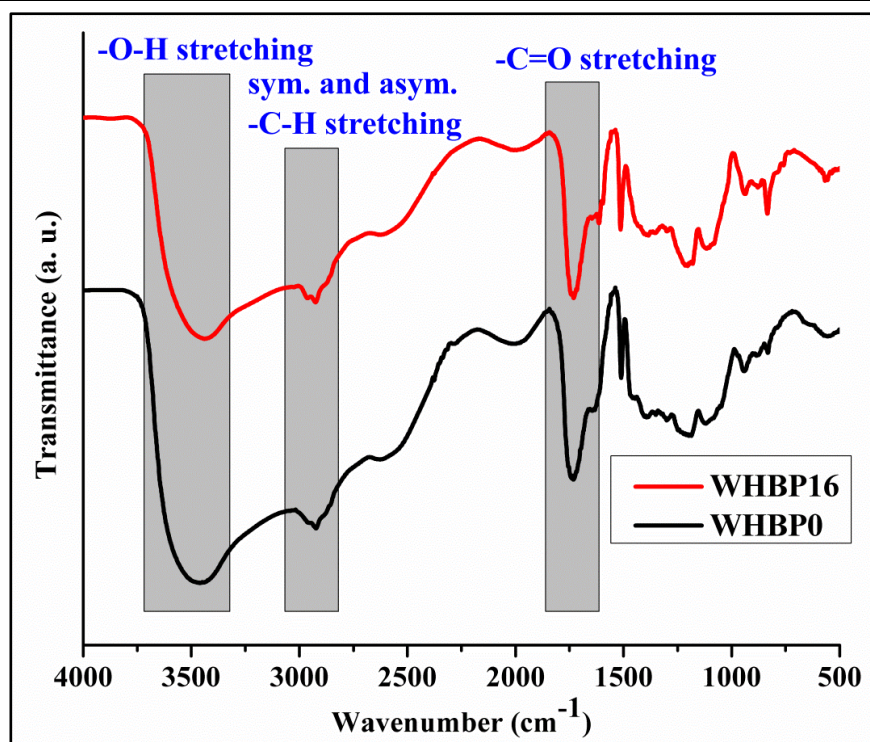


Figure 2A.3: FTIR spectra of WHBP0 and WHBP16

Similarly, ^{13}C NMR spectral study confirmed the presence of different carbon atoms present in the structure of WHBP. The peaks (Figure 2A.4b, δC , ppm, d_6 -DMSO) at 68.2 (a, carbon of $-\text{CH}_2$ attached with primary substituted OH), 73.1 (b, carbon of $-\text{CH}$ attached with substituted secondary $-\text{OH}$), 69.1 (c, carbon adjacent to secondary hydroxyl group), 113.92, 127.81 (d and e, carbons of the BPA moiety), 31.1 and 41.5 (f and g, $-\text{CH}_3$ carbon and quaternary carbon of BPA), 68-70 (h and I, carbon of substituted glycerol moiety), 170-173 (j and j', carbonyl carbon of ester groups owing to difference in adjacent chemical structure), 43-44 (k, carbon of $-\text{CH}_2$ of citric acid), 175-179 (l and l', carbonyl carbon of acid groups due to different chemical environment of neighboring structure), 62-66 (m, $-\text{CH}_2$ carbon of PEG-200), 70.2 (n, carbon of $-\text{CH}_2$ attached to substituted $-\text{OH}$ of bis-MPA), 17-21 (o, carbon atom of $-\text{CH}_3$ of bis-MPA unit due to different chemical environment); 45.7, 47.5 and 48.7 (monosubstituted, disubstituted and trisubstituted central carbon of bis-MPA unit as T, L and D units), and 72.8, 73 and 73.7 (T, L and D units of citric acid), were found in ^{13}C NMR spectrum [9, 15, 22]. DB of a polymer is the ratio of the sum of integration of D and T units to the sum of integration of D, L, and T units, i.e., $\text{DB} = (\text{D} + \text{T}) / (\text{D} + \text{L} + \text{T})$. Here DB is calculated as $\text{DB} = (\text{D1} + \text{D2}) + (\text{T1} + \text{T2}) / (\text{D1} + \text{D2}) + (\text{T1} + \text{T2}) + (\text{L1} + \text{L2})$ [15, 19]. DB was calculated considering values of intensity of D, L and T units of bis-MPA and citric acid, and the

value was found to be 0.83 for WHBP16. However, as it is difficult to determine the D, L and T units of hyperbranched polyol as it is a very large moiety with large number of functional groups, so DB is calculated from the ratio of integrated value of substituted methylene proton to the unsubstituted proton of WHBP16. The value was found to be 0.86.

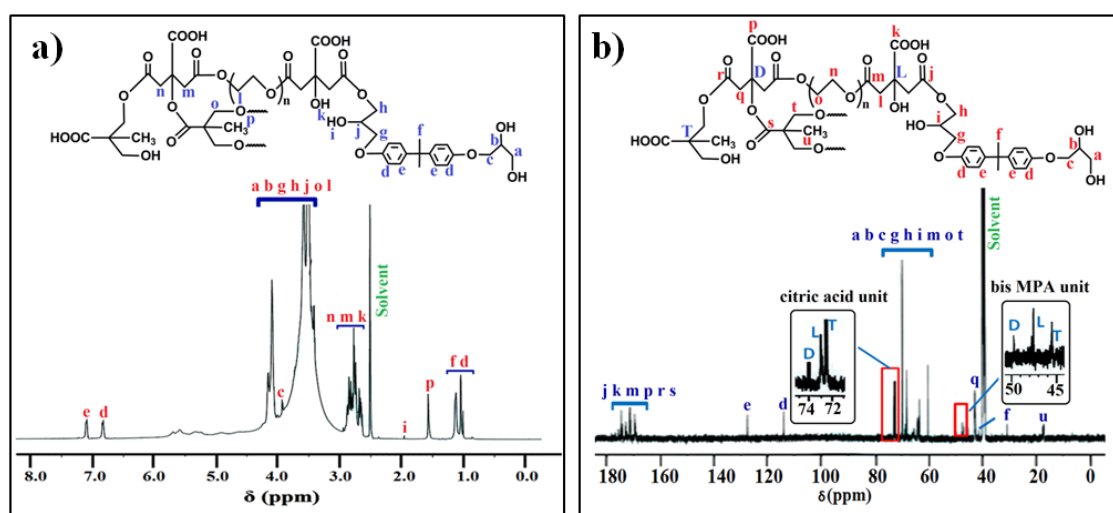


Figure 2A.4: (a) A representative ^1H NMR and (b) ^{13}C NMR spectra of WHBP16

2A.3.5. Physical properties

The physical properties of the synthesized polyesters are tabulated in **Table 2A.3**. The acid values were decreased, while hydroxyl values were increased with increasing wt% of HBGP. The decrease in acid value is due to the esterification reactions, while the increase in hydroxyl value is due to increase of HBGP amount, which contains large number of hydroxyl groups. This result also confirmed the presence of large number free hydroxyl groups in the polymer chains. The saponification values also increases as the amount of HBGP increased. This is owing to the fact that more number of ester linkages is formed with the increase of HBGP content. The density of the hyperbranched polyesters increased with the content of HBGP may be due to increase of degree of polymerization, which result more intra- and inter- molecular interactions among the chain molecules and also increase in the content of aromatic moieties. The increase in gloss value with the wt% of HBGP is due to the formation of highly branched three-dimensional rigid network structure which enhances the dimensional stability of the thermosets. Good cross-linking of the cured thermosets results in a smooth surface which leads to enhancement of gloss characteristic [23]. In this case, gloss refers to specular

reflection or the light reflected as the angle of incidence at the same angle from viewer. The obtained values (80-105°) were found to be better than already reported butylated melamine formaldehyde (BMF) cured waterborne castor oil-based alkyd which showed gloss value from 52 to 59° with increasing BMF loading [23].

Table 2A.3: Physical properties of hyperbranched polyester resins

Property	WHBP0	WHBP7	WHBP12	WHBP16
Acid value (mg KOH/g)	70	60	49	35
Density (g/cc)	1	0.7	0.9	1.15
Gloss (°)	80	88	96	105
Hydroxyl value (mg KOH/g)	350	400	440	490
Saponification value (mg KOH/g)	460	511	539	580

2A.3.6. Rheological study

Rheological study was carried out by a rheometer equipped with parallel plate geometry. The viscosity arises from the interaction among the components of polymers. Several factors such as molecular weight, solid content, free volume, molecular architecture, molecular interactions, etc. affect the rheology of the polymeric material. Furthermore, the viscosity of a formulation is associated to the segmental density, which depends on the inter-molecular chain entanglement and volume of a molecule [24]. However, entanglements among molecular chains will be absent in this hyperbranched polyester. The viscous flow behavior signifies the absence of chain entanglement which is the characteristic of hyperbranched polymers. Actually highly compact chain topology and surface congestion prevent chain entanglement [25]. The variation of viscosity as a function of time at controlled stress and single shear value is shown in **Figure 2A.5a**. The shear viscosity was found to be remained almost constant with time. However, with the increase in the content of HBGP the shear viscosity of all the polyesters was increased. The increased viscosity may be attributed to higher interaction level that results in higher effective polyol content and less number of polymer segments participating in the bulk flow process. The melt flow behavior of polyesters was determined by the variation of shear viscosities as a function of temperature in the range

of 25–75 °C, at shear stress of 100 Pa (**Figure 2A.5b**). It is seen that the viscosity sharply decreased with the increase in temperature for all the polyesters. This is due to decrease in inter-molecular hydrogen bonding, lack of inter-molecular chain entanglements and increase free volume as well as increased kinetic energy of the molecules present in the system. As the viscosity of polyester decrease with temperature, it suggests that the temperature dependence of shear viscosity may follow an Arrhenius type of equation, $\eta = A \times e^{E_a/RT}$ where A, R, E_a and T represents frequency factor, gas constant, Arrhenius energy and absolute temperature respectively. The plot $\ln\eta$ against $1/T$ of polyesters showed a linear relationship (**Figure 2A.5c**) and confirmed the Arrhenius type of function. Further, the effect of shear stress on the shear viscosity of WHBP is shown in **Figure 2A.5d**.

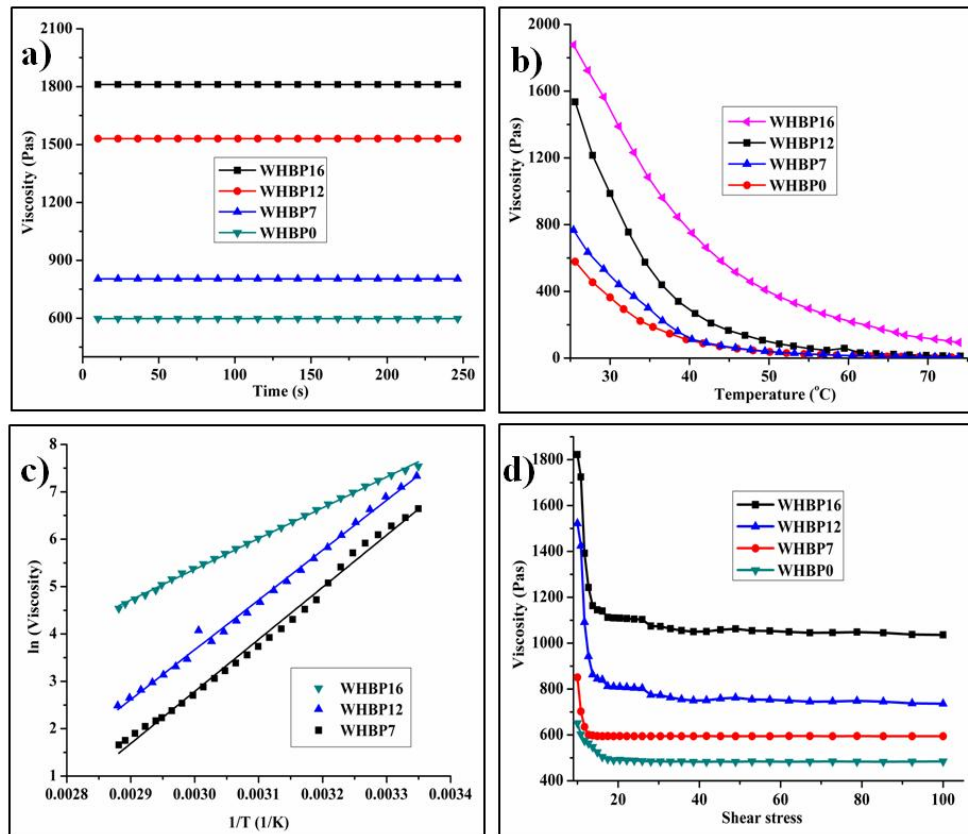


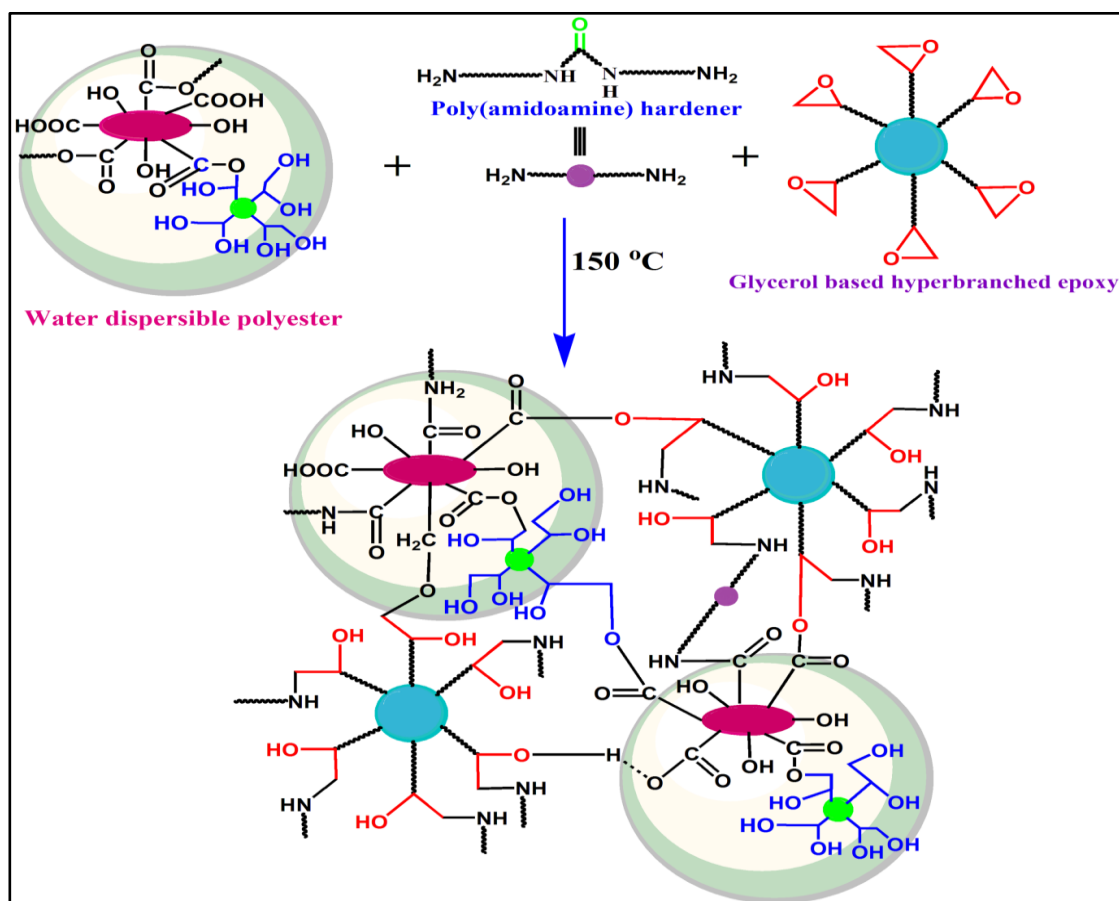
Figure 2A.5: Variations of shear viscosity of WHBP against (a) time, (b) temperature, (c) plot of $\ln\eta$ vs $1/T$ (1/K) and (d) variations of shear viscosity vs shear stress

The viscosity of all WHBP decreased with the increase of shear stress. However, the shear viscosity increased significantly with the content of HBGP over a broad range of shear stress. The physical cross-links are broken down with increase in shear stress

which resulted in decrease in viscosity. This is ascribed to shear thinning or pseudo-plastic behavior, which is usually observed in common polymer dispersions.

2A.3.7. Curing of WHBP

The formation of possible three-dimensional network and the presence of different interactions by curing of hyperbranched polyester with HBGE and PAA hardener are shown in **Scheme 2A.3**. The possible reactions occurred during the curing process are the reactions of the epoxide and hydroxyl groups of the epoxy resin as well as hydroxyl groups of highly branched polyester resin with the amine group of the hardener. PAA hardener used in this curing process acts as cross-linking agent as well as increases the basicity of the medium and thus improving the curing efficiency of the process.



Scheme 2A.3: Possible cross-linking reactions of polyester with HBGE and PAA

The reactions among carboxyl and hydroxyl groups of the hyperbranched polyester, epoxide groups of HBGE and amino groups of the hardener also occurred. The carbonyl group of polyester could also interact with free hydroxyl groups of epoxy resin through

inter-molecular hydrogen bonding. Further, the etherification and transesterification reactions may also occur [16, 19]. The optimum curing time is taken as the time required to attain the swelling value of 20-30% for the thermosets (**Table 2A.4**). The overall curing time was the sum of both first stage and second stage curing time. It is noticed from the table that the overall curing time decreased with increase in the content of HBGP due to increase in number of cross-linkable acid, ester and hydroxyl groups. Further, the total bio-based content of the resulted thermosets lies in the range of 41-55%.

2A.3.8. Mechanical properties

The mechanical properties of polymers usually depend on numerous factors including the presence of hydrogen bonding, existence of inter- and intra-molecular interactions, entanglement of molecular chains, molecular weight, compositions and nature of reactants, rigidity, etc. [9, 26]. The tensile strength of the polyester thermosets increased after incorporation of glycerol modified polyol as observed from stress-strain profiles of them (**Figure 2A.6**). The addition of HBGP owing to its rigidity and highly branched structure with polar functional groups can impart the above mentioned factors on which the mechanical properties are dependent. Further, the values increased with the increase in wt% of HBGP, may be due to increase in amount of aromatic content (3.25-8.61%), present in the hyperbranched polyol. In addition, the percentage of aromatic content increases (19.44-23.04%) in the thermosets with the increase of HBGP content, as 26.12% aromatic moiety is present in HBGE. The cross-link density also increases with the increase of HBGP content, which restricts the motion of the chains and increases the strength of the polyester. Thus, all of the above mentioned factors led to excellent tensile strength of the polyester thermosets [9]. Among all the thermosets, WHBP16 showed the highest tensile strength as it contains the highest content of aromatic moieties. It is pertinent to mention that these thermosets showed better tensile strength compared to earlier reported thermosets of solvent borne castor oil-based polyester (0.34 to 0.81 MPa), soybean oil-based aliphatic polyester thermosets (2.9-16.5 MPa) and ricinoleic acid-based aliphatic polyester (0.7-12.7 MPa) [7, 17, 27]. The results are also superior to waterborne polyester thermosets reported by Jung *et al.* [28] ($20-60 \text{ kgf/cm}^2 = 1.96-5.8 \text{ MPa}$). Further, these values are also better than those of already reported thermoplastic polyester elastomer (16.81 MPa). After blending with poly(butylenes terephthalate) with 5:5, 7:3, 9:1, 8:2, they showed tensile strength of 23.38, 20.28, 18.25 and 18.72 MPa

respectively [29], which are found to be lower than the strength of our WHBP system. Further, WHBP showed yield point in the stress-strain profiles, while it is absent in WHBP0. The reason is that all WHBP contain certain amounts of rigid aromatic moiety in addition to different aliphatic components. This rigid moiety imparts chain stiffening, while aliphatic moieties provide chain flexibility. Thus, a transition from elastic to plastic deformation is resulted and hence a yield point was found, while WHBP0 does not contain any such rigid aromatic moiety containing stiffening component.

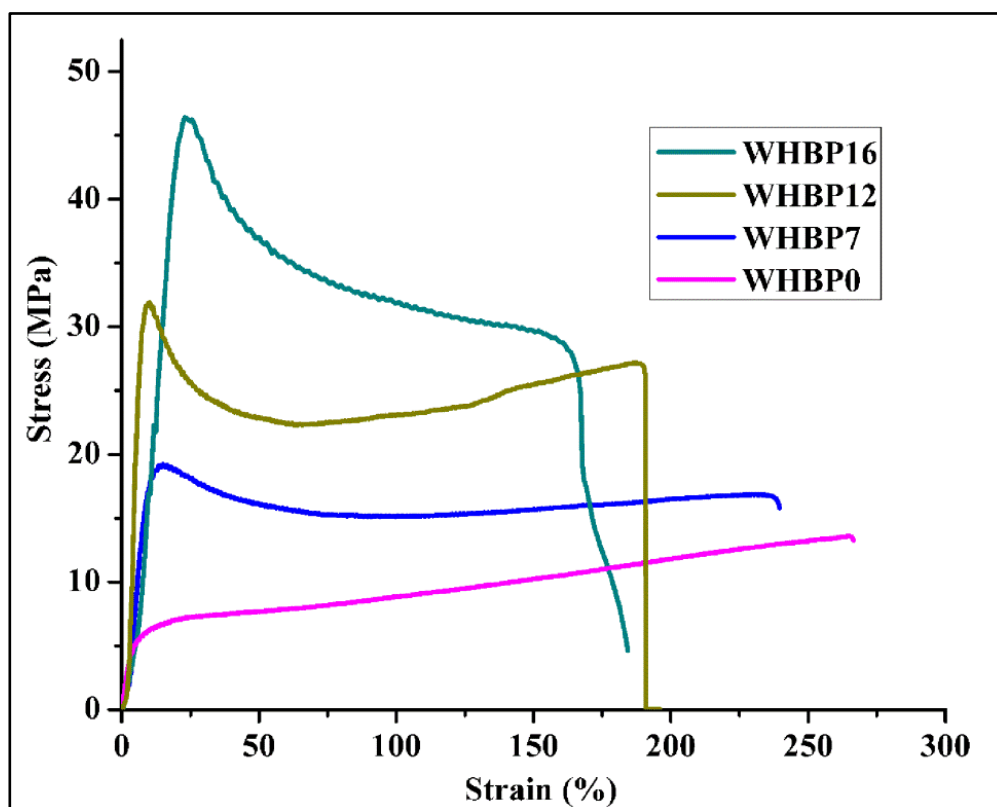


Figure 2A.6: Stress-strain profiles of the thermosets

Hence, there is no yield point. Compared to WHBP0, other polyesters also contain more flexible links in the polymer chain, thus showed clear yield points on their stress-strain curves and moderate elongation at break, indicative of high toughness. Further, barring WHBP0, in all the other cases stress is high and the strain deviates from being proportional to the stress and resulted a yield point in stress-strain curve [30]. However, elongation at break decreased with the increase of wt% of HBGP though the extent of decrease is only marginal. The values may be further decreased if the aromatic content in the thermoset is very high. The flexibility of the thermosets was retained due to the presence of the aliphatic moieties, ether and ester linkages in the structures of polyester

as well as PAA hardener which contains flexible aliphatic hydrocarbon that offers the plasticizing effect to them [19]. These values are found to be higher than those of castor oil-based polyester (38-62%) [12]. The other mechanical properties such as toughness, impact resistance and scratch hardness of WHBP are tabulated in **Table 2A.4**.

Table 2A.4: Curing characteristics and mechanical properties of the WHBP thermosets

Property	WHBP0	WHBP7	WHBP12	WHBP16
Swelling value (%)	23 ± 2	22 ± 1	21 ± 1.5	21 ± 1
First stage curing (100 °C, 240 min)	240	240	240	240
Second stage curing (150°C, 150 min)	150	90	60	30
Tensile strength (MPa)	13.6 ± 2	19.1 ± 2	32.5 ± 4	46 ± 2
Elongation at break (%)	266 ± 3	239 ± 2	190 ± 4	179 ± 3
Scratch hardness (kg)	4 ± 0.5	6 ± 1	7.5 ± 0.5	9 ± 1
Impact resistance (kJm ⁻¹)*	>8.3	>8.3	>8.3	>8.3
Toughness (MJm ⁻³)	26.18 ± 1.5	37.86 ± 2	50.63 ± 2	55.38 ± 3
Young's modulus (MPa)	220 ± 2	250 ± 4	263 ± 2	280 ± 3

*Upper limit of the instrument

Toughness is measured as the area under stress-strain curves and it reflects the resistance to fracture. Both the tensile strength and the elongation at break contributed to the toughness [19]. The toughness of the thermosets (**Figure 2A.6**) increased with the increase in amount of HBGP. This is due to the increase in the percentage of aromatic moieties (3.24-8.6 %) with the increase in amount of HBGP and unique combination of aliphatic and aromatic moieties in the hyperbranched structure of the polyester. Though elongation at break of WHBP16 was relatively low compared to other two, it exhibited the highest toughness as the value of tensile strength is very high. As the hyperbranched polyester thermosets possess an unique combination of aromatic and aliphatic moieties, adequate cross-link density (swelling value, **Table 2A.4**) and hyperbranched structural architecture, they exhibited high toughness, scratch hardness and impact resistance. All the thermosets absorbed the impact energy up to the highest limit of the instrument (>8.3 kJ m⁻¹) because of the presence of flexible moieties (namely aliphatic moieties of epoxy

as well as aliphatic chain of the hardener and flexible ether linkages) in the structure, which can dissipate the impact energy by segmental motion of the molecular chains. The scratch hardness also increases with the content of HBGP may be due to increase of branching and rigidity in the structure [9, 23]. The scratch hardness value of WHBP16 is superior to butylated melamine formaldehyde cured waterborne castor oil-based alkyd (7.5 kg) [23].

2A.3.9. Thermal properties

The glass transition temperature (T_g) of a polymer depends on the rigidity/flexibility of its structure and the value was obtained from the DSC cooling curve (**Figure 2A.7a**). It is governed by inter-molecular forces of attractions, presence of thermostable moieties, stiffening groups and cross-link density [23, 31]. T_g of the thermoset in absence of HBGP was found to be 37 °C. After incorporation of HBGP, the T_g value increased from 46 to 52 °C with an increase in wt% of HBGP due to increase in the content of aromatic moieties (19.44-23.01%) in their hyperbranched structure. This resulted in difficulty of chain relaxation, thus leading to higher T_g of the thermosets. Further cross-links between chains restrict the chain motion and thus increase T_g . The presence of bulky pendant groups like benzene ring can also restrict the rotational freedom leading to higher T_g , [31, 32] so with the increase in wt% of HBGP, T_g value increases.

The thermal degradation behaviors of WHBP thermosets are shown in **Figure 2A.7b** and **7c**. The polyester thermosets were degraded by a multi-step process as seen from dTG curves (**Figure 2A.7c**), where the first step of degradation (233-290 °C) is attributed to the degradation of aliphatic moieties of hyperbranched polyester, epoxy, PAA hardener and aliphatic chain scission of the cross-linked structure as well as moderately thermostable linkages present in the chains. While the second steps of degradation (300-450 °C) is due to the random chain scission of the free linear chains formed during the first step degradation as well as degradation of aromatic moieties (BPA) belonging to HBGP and moiety generated during the cross-linking with HBGE [15, 19]. It is evident from the thermograms that increased in the content of HBGP in the polyester can enhance the thermal stability. Thus, globular and confined geometry of hyperbranched structure, aromatic content, cross-link density, enhanced secondary interactions like hydrogen bonding, stronger intra- and inter-molecular interactions contributed towards such high thermal stability and T_g value [19, 31, 32].

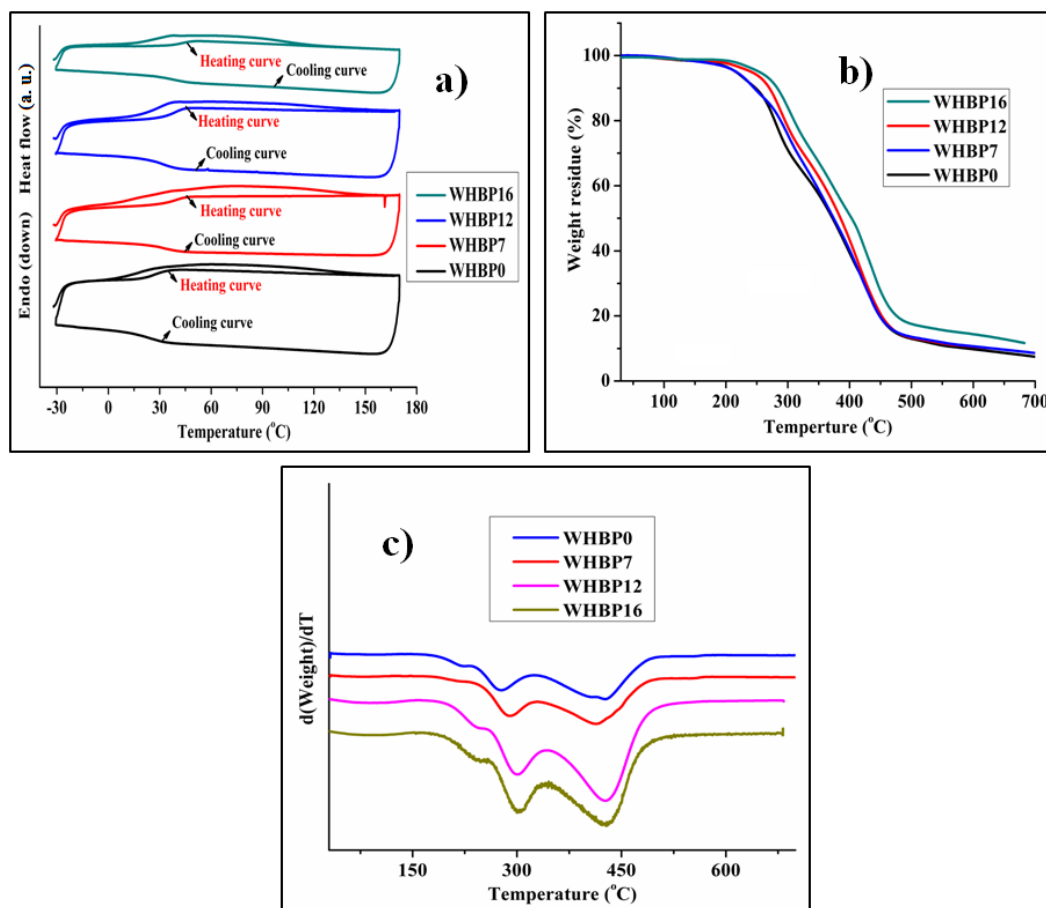


Figure 2A.7: (a) DSC, (b) TG thermograms and (c) dTG curves of the WHBP thermosets

2A.3.10. Chemical resistance

The results of chemical resistance of polyester thermosets in different chemical media such as aqueous NaOH (0.5%), aqueous HCl (10%), aqueous NaCl (15%), aqueous EtOH (20%) and tap water for 30 days are given in **Table 2A.5**.

Table 2A.5: Chemical resistance (weight loss %) of hyperbranched polyester thermosets in different chemical media

Chemical media	WHBP0	WHBP7	WHBP12	WHBP16
0.5 wt% NaOH	3	2.5	1.8	1.2
10 wt% HCl	0.9	0.5	0.4	0.3
15 wt% NaCl	0.04	0.03	0.02	0.02
20 wt% EtOH	2.2	1.7	1.1	0.8
Distilled water	0.02	0.01	0.00	0.00

All the thermosets showed excellent resistance toward HCl, NaCl and water owing to the presence of compact cross-linked hyperbranched architecture and strong chemical linkages. The alkali resistance of these thermosets was relatively poor due to the presence of hydrolyzable ester bonds. However, compared to aliphatic polyester they showed better resistance to alkali because of the presence of aromatic moieties in the hyperbranched structure of this polyester [16]. Among these thermosets, WHBP16 showed the best chemical resistance toward aqueous HCl, NaCl, NaOH solution and water as it contains the highest percentage of HBGP, thus possessing the highest cross-linked density and the highest aromatic moiety. However, polyester without HBGP exhibited poor alkali resistance owing to the presence of free hydrolysable ester linkages and less number of chemical interactions.

2A.3.11. Biodegradation study

The thermosets of WHBP were found to be degraded gradually with time under exposure of *Pseudomonas aeruginosa* (gram-negative) and *Bacillus subtilis* (gram-positive) bacterial strains. *Pseudomonas aeruginosa* strain has been reported to degrade the aromatic moiety [32, 33]. The results of biodegradation study clearly distinguished higher growth rate of gram-negative bacterial strain compared to the gram-positive one. This is owing to the fact that the former possesses higher biosurfactant activity and cell surface hydrophobicity (CSH) than the later. Hence, a faster colonization and growth of the former bacterial strain on the polymeric surface was observed than the later bacterial strain [34]. The presence of hydrolyzable ester linkages in the polymeric chain of these polyesters, makes them prone to microbial attack. The factors which increase hydrolyzable tendency of polyester also increase biodegradation [9, 35]. The bacterial growth curves as measured by OD of degraded thermosets with exposure time are shown in **Figure 2A.8**. The bacterial growth for the thermoset in absence of HBGP is the highest as it contains high amount of aliphatic moieties. The bacterial growth increases with the increase in amount of HBGP in the thermosets. This is due to increase in number of ester linkages in the structure with increase in amount of polyol, as supported by saponification value (**Table 2A.3**). Further, increased in number of ester linkages and water solubility nature of this polyester resulted excellent biodegradability though the aromatic content increased with the content of polyol. Thus, the degree of ester linkages is mainly responsible for such biodegradation.

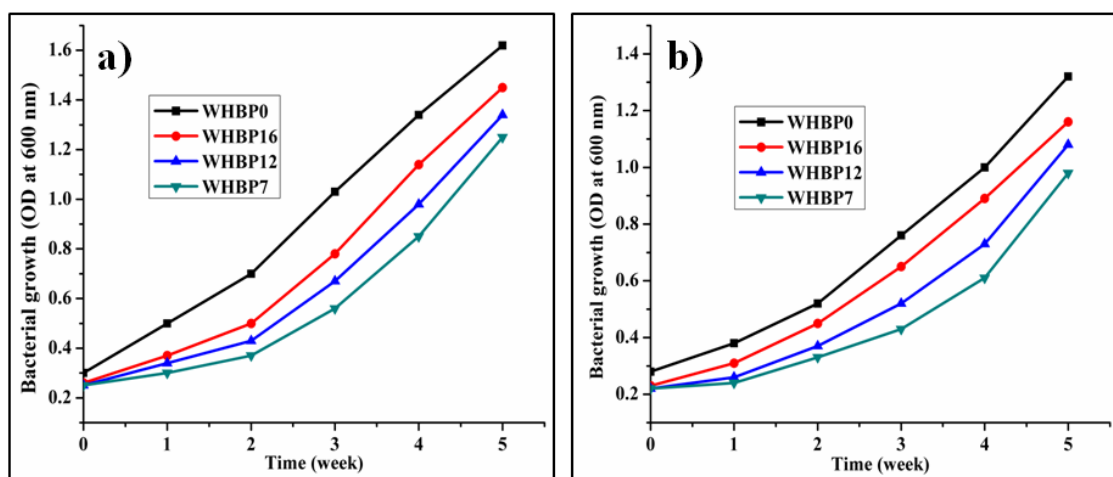


Figure 2A.8: Growth curves of (a) *Pseudomonas aeruginosa* and (b) *Bacillus subtilis* on WHBP thermosets

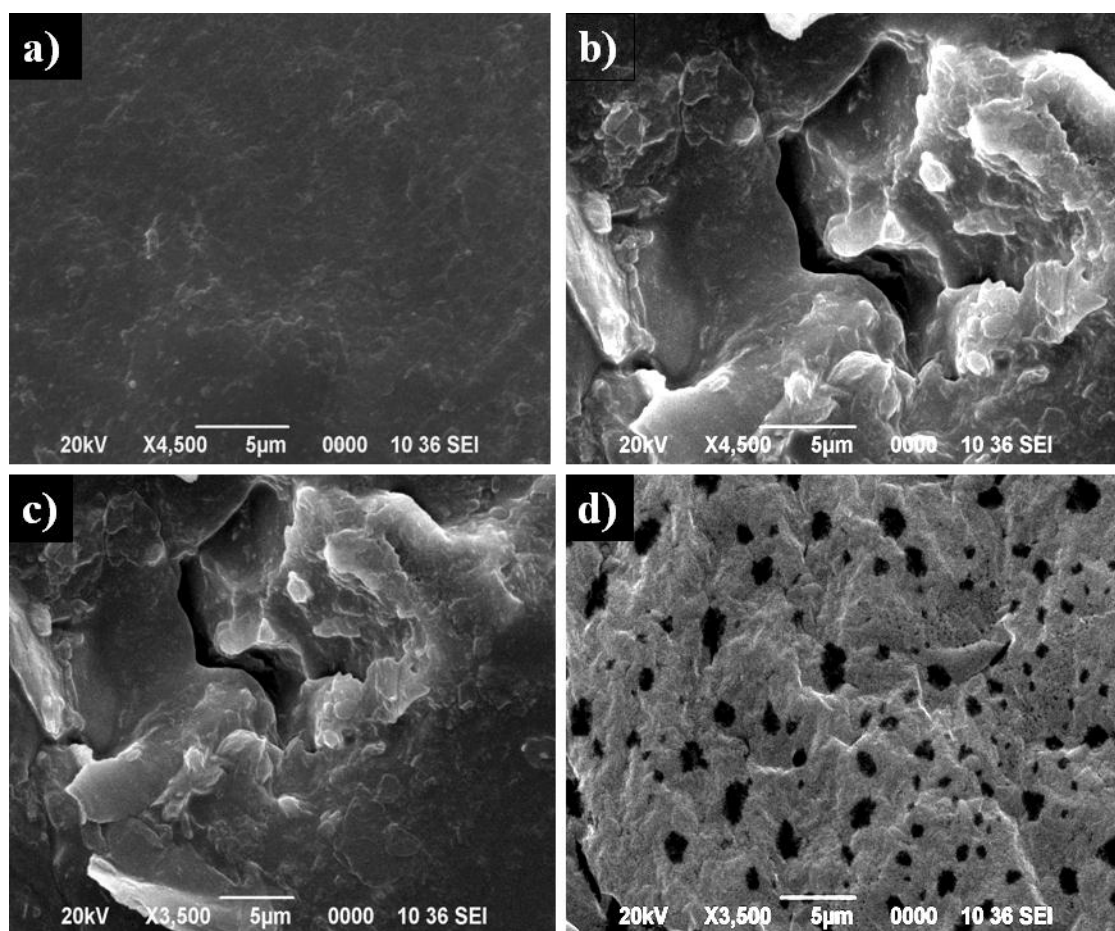


Figure 2A.9: Representative SEM images of (a) control (without bacterial strain), degraded thermosets of (b) WHBP16 and (c) WHBP7 against *Pseudomonas aeruginosa* and (d) WHBP16 against *Bacillus subtilis*

The extent of biodegradation of polyester thermosets as well as bacterial surface growth can be seen from SEM images of the biodegraded films (after 5 weeks of exposure of bacterial strain) (**Figure 2A.9**). These images were used to compare the erosion of exposure and bacterial adherence of the degraded film with respect to the control and clearly indicate the biodegradation of the thermosets.

2A.4. Conclusion

In the present study, WHBP thermosets were fabricated using hyperbranched polyol along with other bio-based precursors through a facile approach. These novel polyester thermosets exhibited excellent mechanical and thermal properties along with good chemical resistance comparable to those of many commercial petroleum-based polyesters. Thus, the study clearly demonstrated that appropriate structural combination results in high performing sustainable tough polymeric materials. The overall results suggest promising potential of these environmentally friendly polymeric materials in different advanced fields like coating, biomedical, tissue engineering, etc.

2B. Citric acid-based waterborne hyperbranched polyester

2B.1. Introduction

It is mentioned in the first chapter that waterborne polyesters with hyperbranched architecture are still not explored widely and thus to enhance the field of such polyester, different branch generating units are tried to explore in this study. Again in **sub-chapter 2A** it is noticed that WHBP addresses the shortcomings of solvent borne polyester and proper combination of aliphatic-aromatic moieties and unique hyperbranched structure showed good performance. However, the synthesis of this WHBP involved two extra steps: one is preparation of HBGE and second one is preparation of HBGP. In addition, the bio-based content of the polyester is not up to the expectation to fulfill the desired requirement as well as it is not completely water soluble. Thus, in this chapter, branch generating moiety namely glycerol is used due to low cost and easy availability in place of HBGP along with citric acid and 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) in order to develop bio-based completely water soluble hyperbranched aliphatic polyesters (WHPE) which possess many attractive attributes. One of the most significant attributes is that they are highly biodegradable materials which have a low environmental impact upon disposal and have broad potential applications in different fields such as fibers, agricultural implements, packing materials, drug delivery systems and tissue engineering scaffolds. Further, key feature for citric acid-derived materials is that it provides precious pendant functionality participating in the ester bond cross-link formation, balancing the hydrophilicity of the polymer network, enhancing hemocompatibility and providing hydrogen bonding [10, 17] .

In the present study, therefore, a sustainable WHPE with aliphatic structure was synthesized by a facile polycondensation reaction using bio-based reactants such as citric acid and glycerol with PEG200 and bis-MPA without using any additional catalyst or neutralizing agent. The performance characteristics of these thermosets along with biodegradation and hemocompatibility were delved into to investigate the effect of citric acid on such attributes.

2B.2. Experimental

2B.2.1. Materials

Chemicals such as citric acid, glycerol, bis-MPA and PEG-200 were utilized for synthesis of WHPE. Other chemicals such as oxalic acid, BPA, PAA hardener, maleic

anhydride, ECH, KOH, NaOH, HCl, triethylamine, NaCl, toluene, THF and EtOH were used for the same purpose as described in **sub-chapter 2A, section 2A.2.1**. All these chemicals are the same as described in **sub-chapter 2A, section 2A.2.1**.

2B.2.2. Characterization

The method for evaluation of physical properties such as acid value, hydroxyl value, saponification value, viscosity, etc., as well as characterization and instrumentation procedure are same as described in **sub-chapter 2A, section 2A.2.2**.

2B.2.3. Method

2B.2.3.1. Synthesis of citric acid-based WHPE

It was synthesized by the same procedure as described for water dispersible hyperbranched polyester in **sub-chapter 2A, section 2A.2.3.2**. Here, in the second step glycerol was used in place of HBGP. Three different composition of this polyester was synthesized with respect to different weight percentages (31.6, 40.6 and 50.26%) of citric acid and coded as WHBPE30, WHBPE40 and WHBPE50 respectively. The actual compositions of the reactants for all these three resins are given in **Table 2B.1**.

2B.2.3.2. Preparation of the thermosets

The thermosets were prepared by the same procedure as described in **sub-chapter 2A, sub-section 2A.2.3.4**.

Table 2B.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 functionality	7.5	5.5	7.5
Total equivalent COOH functionality	7	4	5
Equivalent functionality ratio of OH/COOH	1.07	1.37	1.5
Gel point (%)	62	63.1	64

2B.2.3.3. Biodegradation study

Biodegradation study of the WHPE was performed using the same gram-negative and gram-positive bacterial strains by following the same procedure as described in the previous sub-chapter under the same experimental condition.

2B.2.3.4. Hemolytic Assay

Hemolytic assay was performed to investigate lysis of the red blood cell (RBC) membrane by the tested macromolecule and know about the hemocompatibility of WHPE. Goat's blood collected in heparinized tube containing 4% sodium citrate was centrifuged for 20 min at 3000 rpm ($503 \times g$). The erythrocytes were washed thrice with phosphate buffer saline. To obtain 5% hematocrit the packed erythrocytes were re-suspended 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 taken 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 ice bath for 1 min followed by centrifugation at 3000 rpm ($503 \times g$) for 5 min. Then haemoglobin 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.

2B.3. Results and discussion

2B.3.1. Synthesis of polyester

In the first step, a pre-polyester was formed by the polycondensation reaction of citric acid and PEG-200. The above pre-polyester was also further esterified in the second step with bis-MPA and glycerol which results the desired hyperbranched polyester. A probable scheme for synthesis of this polyester is shown in **Scheme 2B.1**. In this esterification reaction, glycerol, citric acid and bis-MPA act as the 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. In this case, polyester was completely soluble in water, whereas in previous case the polyol-based polyester was dispersible in water. 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

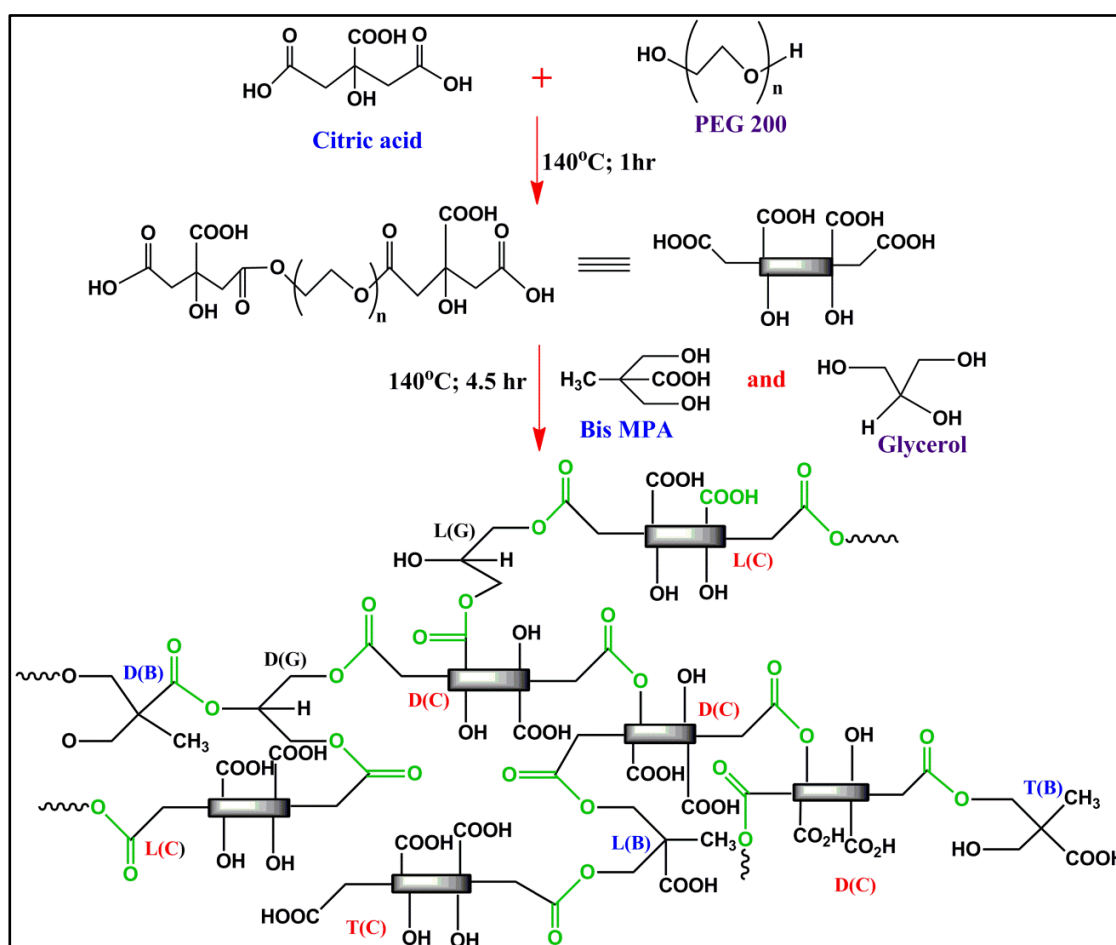
equation [36].

It is observed from **Figure 2B.1** that with the increase of reaction time the acid value decreases for all the three polyesters.

$$p = C_o - C_t / C_t \dots\dots\dots(\text{Eq. 2B.1})$$

where C_0 is the acid value at zero reaction time and C_t is the acid value after time t . The DP is given by

$$\text{DP} = 1/(1-p) \dots\dots\dots(\text{Eq. 2B.2})$$



Scheme 2B.1: Synthesis of WHPE

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, while 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**

2B.1, it is clear that the initial variation of $(1-p)^{-2}$ vs 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 non-linear portion may also represent onset period of branching that is formation of three dimensional architecture of the polyester [37]. Since 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 2B.1**, it is clear that the DP decreases with the increase of citric acid content.

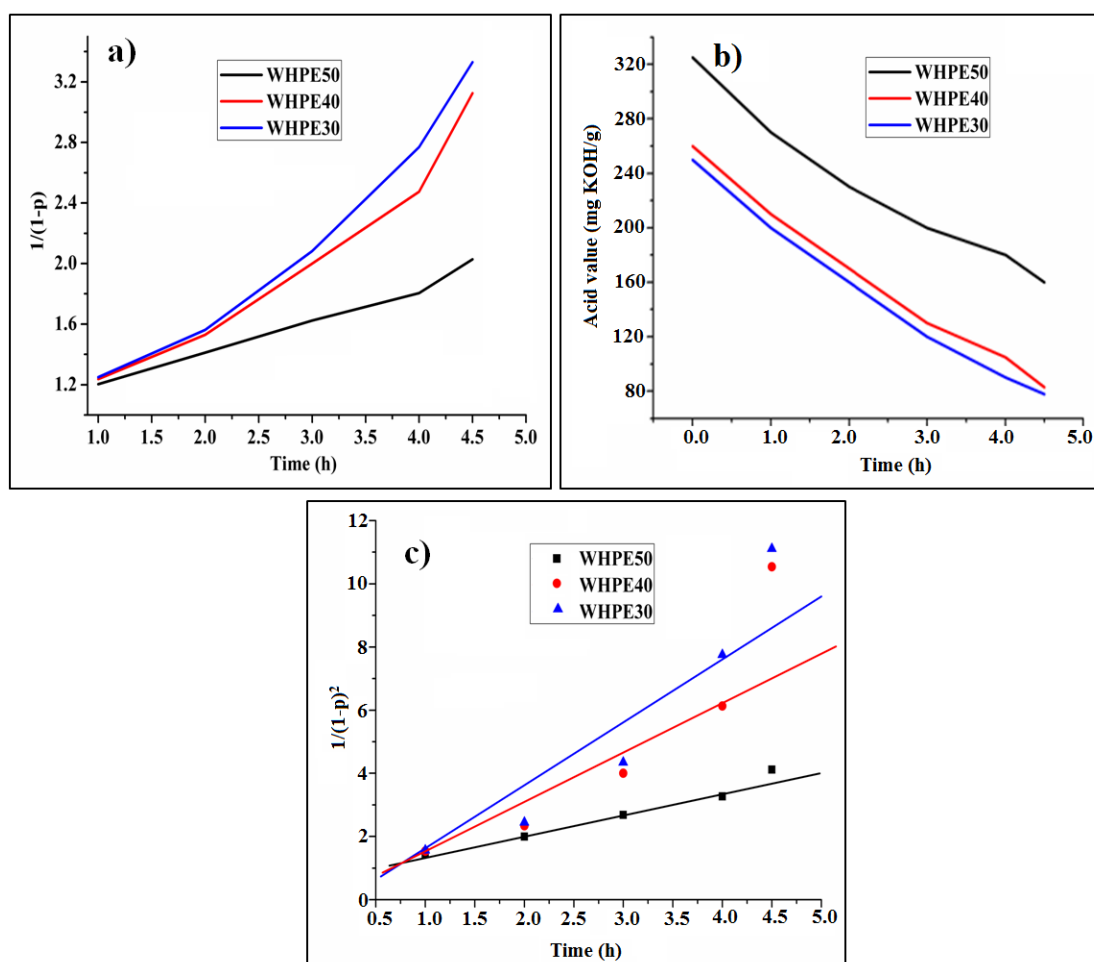


Figure 2B.1: (a) Variations of acid value with time and (b) plot of $(1-p)^{-1}$ vs time and (c) plot of $1/(1-p)^2$ vs time for polyesters

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 WHPE 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.

2B.3.2. Physical properties of the polyesters

The physical properties of the polyesters are shown in **Table 2B.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 WHPE increases with the decrease of citric acid content may be due to increase of DP which result more intra- and inter-molecular 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 Pas at 25 °C. The viscosity drops to 79 Pas by increasing the temperature to 60 °C.

Table 2B.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/cc)	1.18	1.0	0.97
Gloss at 60 ° (Thermosets)	87 ± 4	92 ± 4	96 ± 3

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 20.61, 0.59 and 0.13 Pas 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.

2B.3.3. Characterization of polyesters

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 2B.2**. The characteristics 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 $3000\text{-}2600\text{ cm}^{-1}$ are due to aliphatic symmetric and asymmetric -C-H stretching vibrations.

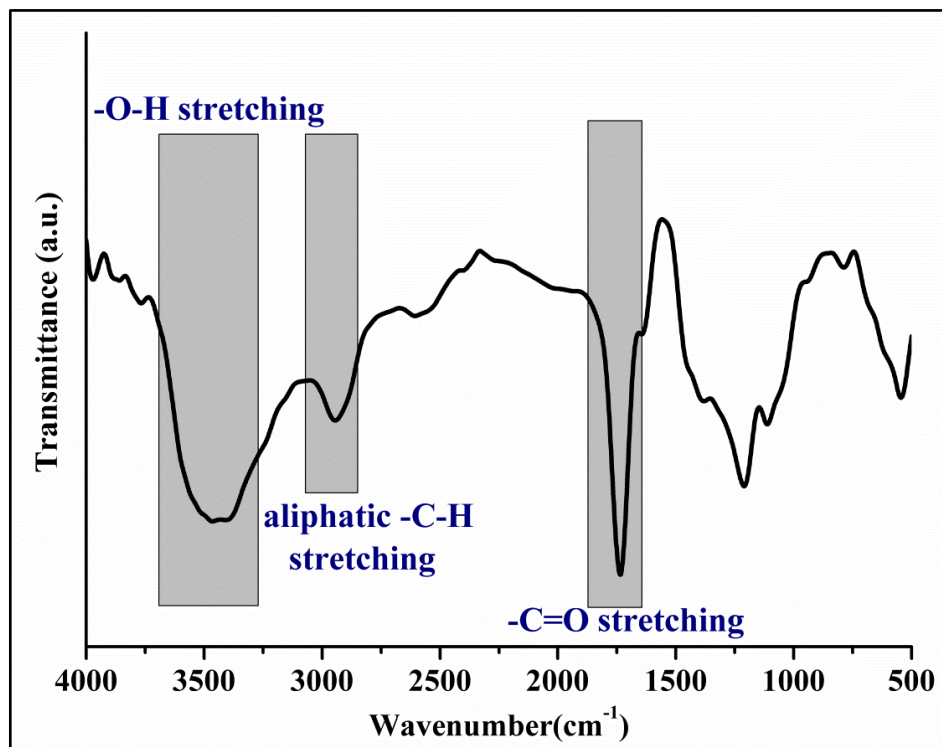


Figure 2B.2: FTIR spectrum of WHPE50

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 $3000\text{-}2600 \text{ cm}^{-1}$ (-C-H symmetric and asymmetric stretching) for WHPE40 and 3464 cm^{-1} (-O-H stretching), 1734 cm^{-1} (esters, aliphatic -C=O stretching) and $3000\text{-}2600 \text{ cm}^{-1}$ (-C-H symmetric and asymmetric stretching) for WHPE30 [37].

Protons present at different chemical environments in the structure of hyperbranched polyesters were confirmed from ^1H NMR spectral study. A representative ^1H NMR spectrum of WHPE50 is shown in **Figure 2B.3** which shows the correlation between various structural units and observed NMR peaks. The chemical shift values at $\delta = 0.98\text{-}1.14 \text{ ppm}$ are due to the methyl protons of bis-MPA moieties present in different neighbouring 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 $\delta = 3.30\text{-}4.0 \text{ ppm}$ due to different chemical environments of the neighbouring structures. The methylene protons of citric acid showed a chemical shift value at $\delta = 2.7\text{-}2.95 \text{ ppm}$. The variation is again due to the difference in neighbouring chemical structures.

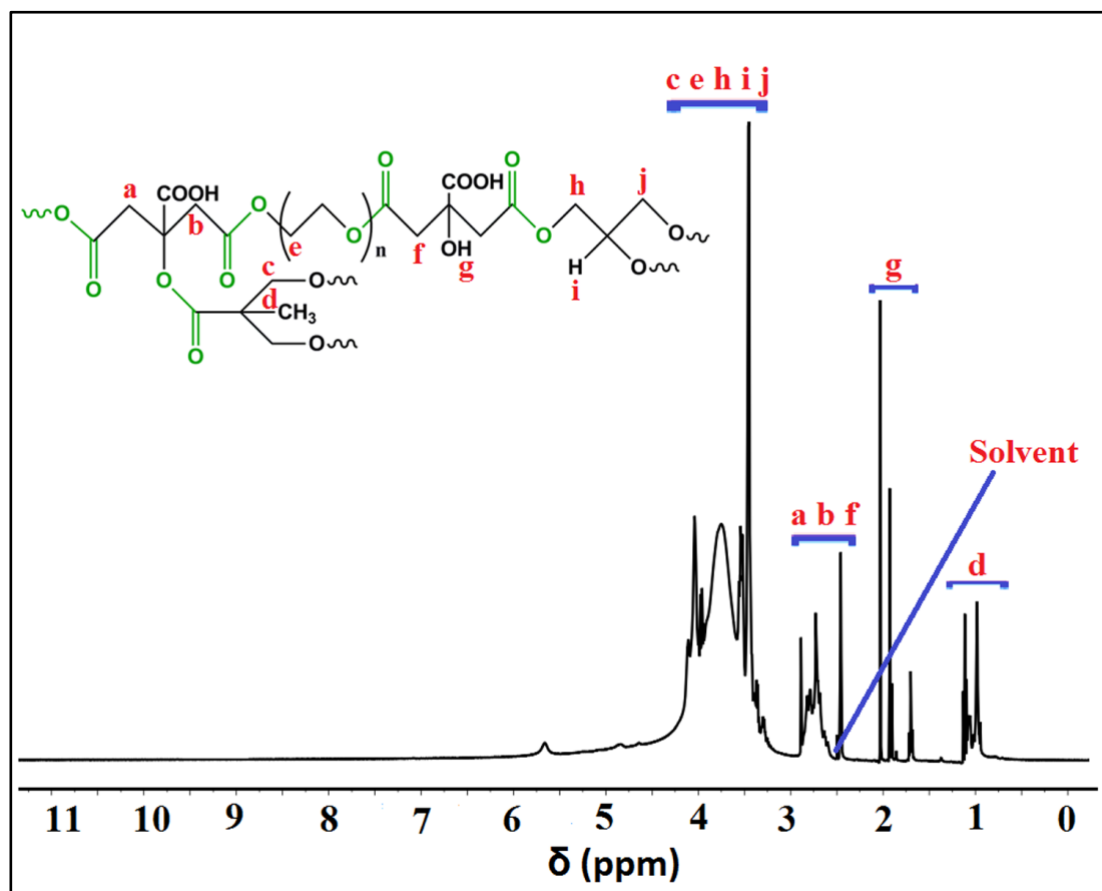


Figure 2B.3: ^1H NMR spectrum of WHPE50

The signals at $\delta = 2.04$ ppm, $\delta = 3.65$ ppm and $\delta = 4.2$ 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: δ H, ppm: 0.95-1.13 (3H, CH₃ of bis-MPA), 2.05 (1H, OH attached to CH of glycerol), 3.68 (2H, CH₂ of PEG), 4.3 (1H, OH attached to central carbon of citric acid), 2.6-2.98 (2H, CH₂ of citric acid), and 3.30-3.90 (2H, CH₂ of glycerol and bis-MPA) for WHPE40 and 0.97-1.13 (3H, CH₃ of bis-MPA), 3.65 (2H, CH₂ of PEG), 4.20-4.23 (1H, OH attached to central carbon of citric acid), 2.65-3.0 (2H, CH₂ of citric acid), 3.65 (2H, CH₂ of PEG) and 3.28-3.97 (2H, CH₂ of glycerol and bis-MPA) for WHPE30 [10, 21, 36-38].

Similarly, different chemical environments for carbon atoms present in the structure of hyperbranched polyesters were confirmed by the ¹³C NMR spectral study. Signals at $\delta = 15$ -20 ppm are due to carbon atom of -CH₃ of bis-MPA unit. The different values are due to different chemical environments of it, as substitutions are different. Carbon of -CH₂ of citric acid showed chemical shift value at $\delta = 42$ -43 ppm. The signals for carbonyl carbon of acid groups and ester groups were observed at $\delta = 170$ -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 $\delta = 47.8$, 47.9 and 48.5 ppm respectively. Similarly, the monosubstituted, disubstituted and trisubstituted glycerol units as T, L and D units were observed at $\delta = 67.5$, 68.5 and 69.6 ppm respectively. The citric acid-based T, L and D units appeared at $\delta = 72.7$, 72.9 and 73.4 ppm, respectively. These peak values of WHPE30 are shown in **Figure 2B.4**. Thus, the resulting hyperbranched polyesters in all three cases possess three D, three L and three T units. The degree of branching (DB) is the ratio of the sum of integration of D and T units to the sum of integration of D, L, and T units, i.e., $DB = (D + T)/(D + L + T)$. Here DB is calculated from three D, three L and three T 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 D, L and T units, DB 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 DP. The other two polyesters showed chemical shift value at δ C, ppm: 16-18 (CH₃, bis-MPA unit), 46-50 (monosubstituted, disubstituted and trisubstituted central carbon of bis-MPA unit), 72-74 (T, L and D unit of citric acid), 68-70 (mono, di and trisubstituted glycerol moiety) and 42-45 (CH₂, citric acid unit), and 170-180 (carbonyl carbon) for WHPE40, and 15-

18 (CH₃, bis-MPA unit), 43-45 (CH₂, citric acid unit), 46-50 (T, L and D units of bis-MPA), 68-70 (T, L and D units of glycerol moiety), 72-74 (T, L and D units of citric acid) and 170-180 (carbonyl carbon) for WHPE50 [10, 21, 22, 36-38]. The T, L and D units for WHPE40 and WHPE50 are shown separately in **Figure 2B.5**.

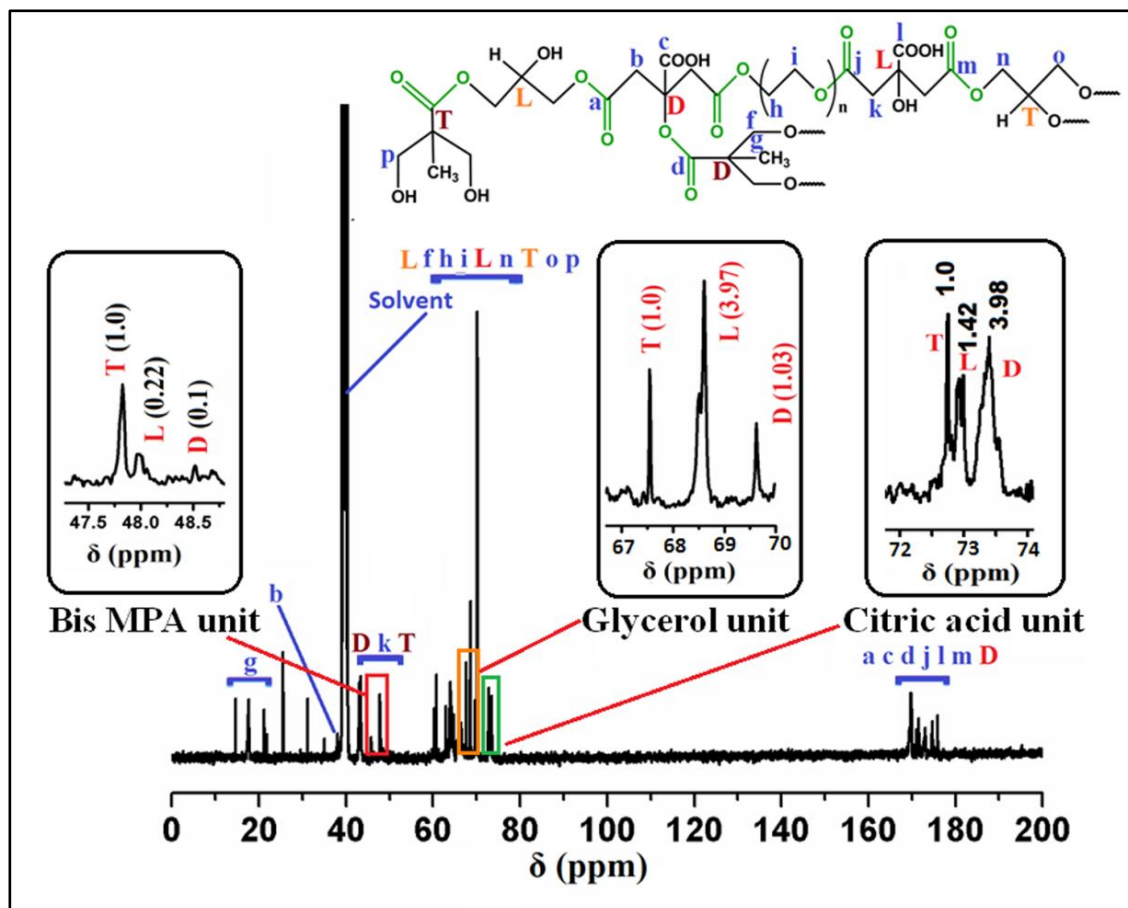


Figure 2B.4: ¹³C NMR spectrum of WHPE30

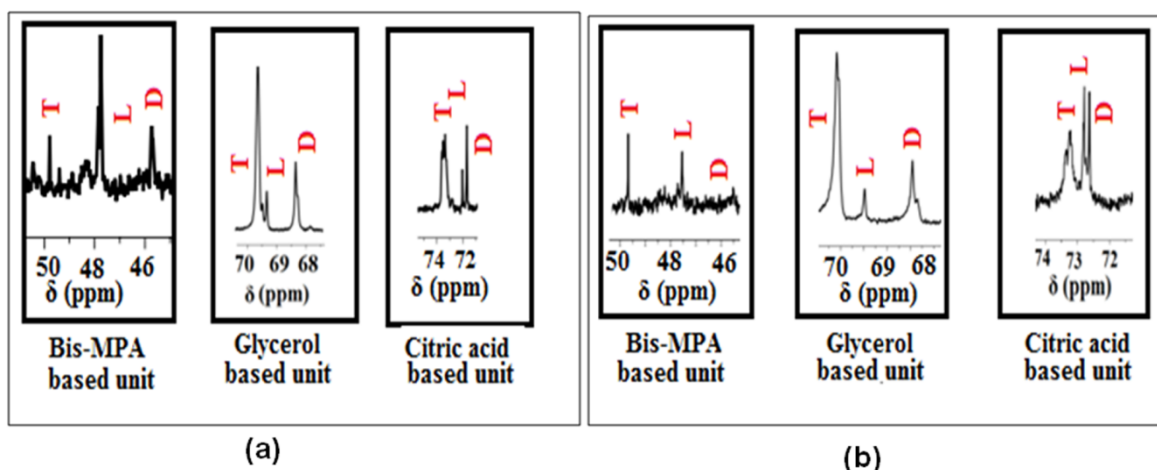
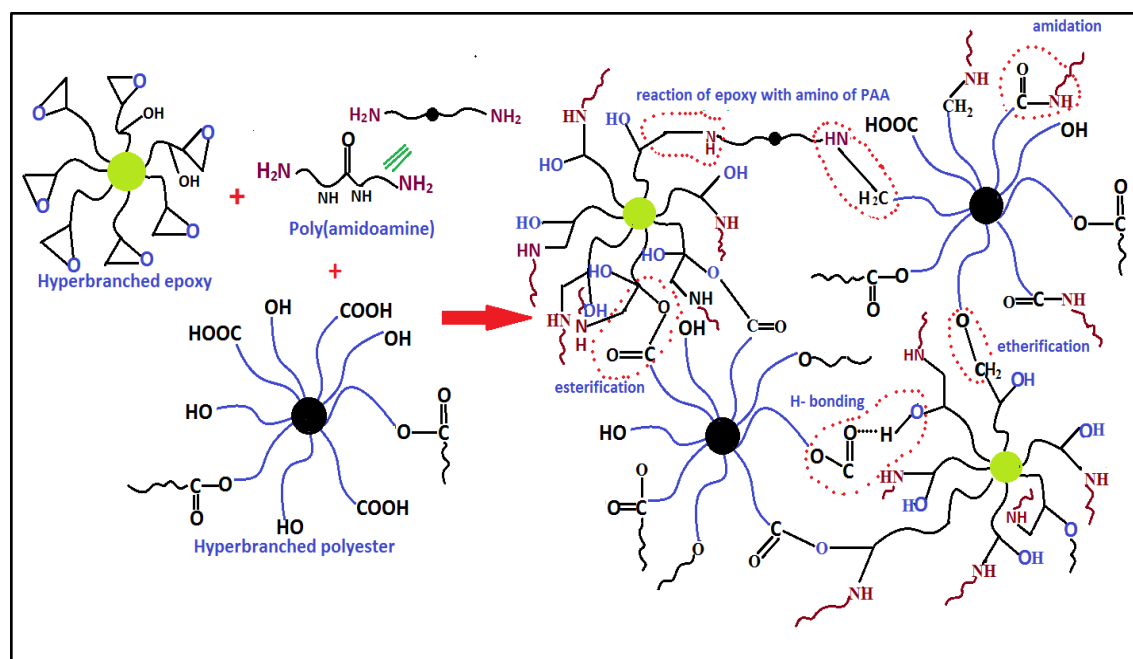


Figure 2B.5: T, L and D units of (a) WHPE50 and (b) WHPE40

2B.3.4. Curing of the polyesters

During cross-linking reactions of polyester with HBGE in presence of PAA 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 HBGE 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 presence of basic catalyst) reaction may also occur. Further, hydrogen bonding between $-C=O$ of polyester with $-OH$ of the epoxy resin was formed [32]. All the possible physico-chemical interactions taken place during curing process are shown in **Scheme 2B.2**.



Scheme 2B.2: Possible cross-linking reaction of hyperbranched polyester with HBGE and PAA hardener

In this curing reaction, PAA hardener acts as cross-linking agent and increases the basicity of the medium, thereby improving the curing efficiency of polyester [16, 19]. The curing time is the time required to attain the swelling value of 20-30% for the thermosets (**Table 2B.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.

2B.3.5. Mechanical properties

Different mechanical properties such as tensile strength, elongation at break, toughness, impact resistance and scratch hardness of the synthesized WHPE thermosets are given in **Table 2B.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 interactions also increase, as well as the presence of epoxy and PAA hardener resulted in a cross-linked network structure. This cross-linked network structure formed highly strained structure which 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 2B.3**). It is pertinent to mention that these thermosets showed better tensile strength compared to waterborne polyesters reported by Jung *et al.* [28] ($20\text{-}60 \text{ kgf/cm}^2 = 1.96\text{-}5.8 \text{ MPa}$ as $1 \text{ kgf/cm}^2 = 0.098 \text{ MPa}$) and Malar *et al.* (1.56-1.77 MPa) [39]. Further the toughness of the WHPE thermosets as calculated from stress-strain curves (**Figure 2B.6**) of them was found to be followed the same order.

Table 2B.3: Performance characteristics of WHPE30, WHPE40 and WHPE50

Properties	WHPE30	WHPE40	WHPE50
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 (MJm ⁻³)	6.55 ± 0.6	8.95 ± 0.7	17.82 ± 1
Scratch hardness (kg)	2.5 ± 0.3	3 ± 0.5	4 ± 0.7
Impact resistance (kJm ⁻¹)*	>8.3	>8.3	>8.3

*Maximum limit of the instrument

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 which is 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 bio-based resource in spite of the presence of aromatic rigid trimellitic anhydride moiety [37, 40]. The studied polyester thermosets also showed the highest limit of impact resistance (8.3 kJm^{-1} is the limit of the instrument) which clearly demonstrated their high toughness character.

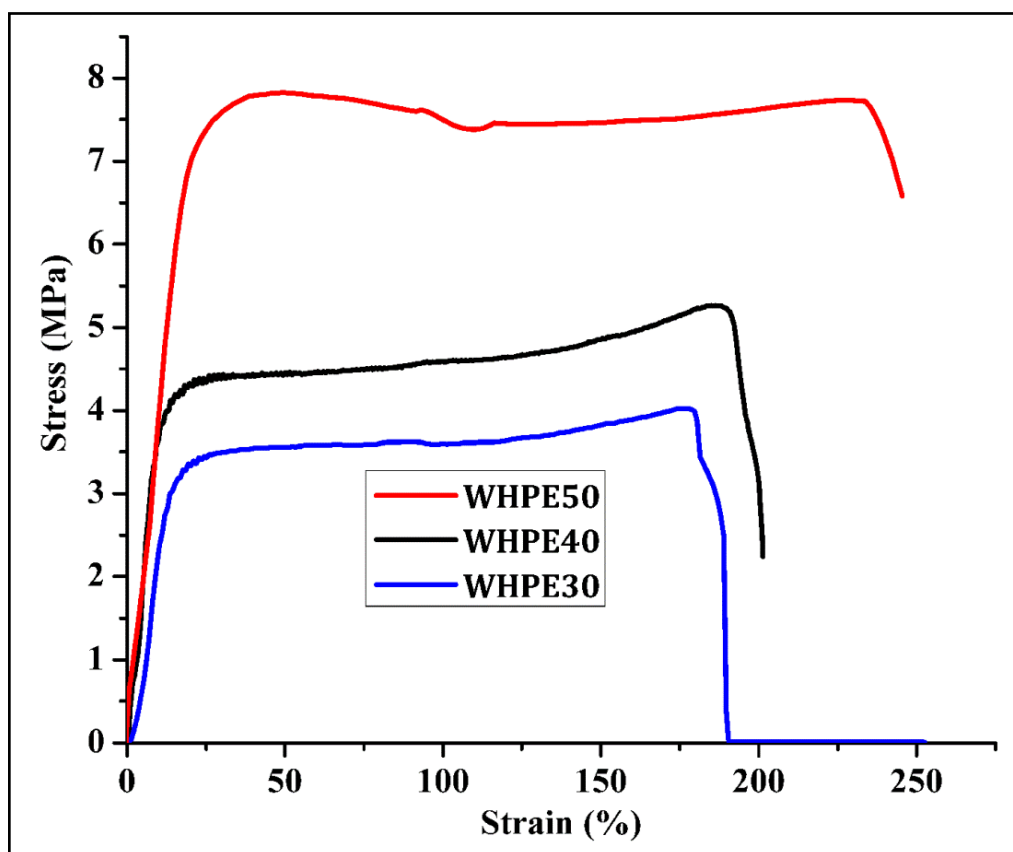


Figure 2B.6: Stress-strain profiles of the thermosets

2B.3.6. Thermal properties

The thermal degradation behaviors of WHPE thermosets are shown in **Figure 2B.7a**. All the three thermosets exhibited similar thermostability as they possess equivalent thermostable aromatic and aliphatic moieties as well as 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, HBGE and PAA hardener or may be due to the

process of aromatization or cyclization of citric acid moiety [41]. 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.

Further, DSC curves for WHPE thermosets are given in **Figure 2B.7b**. 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. 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 intra- molecular 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 °C and 46 °C respectively.

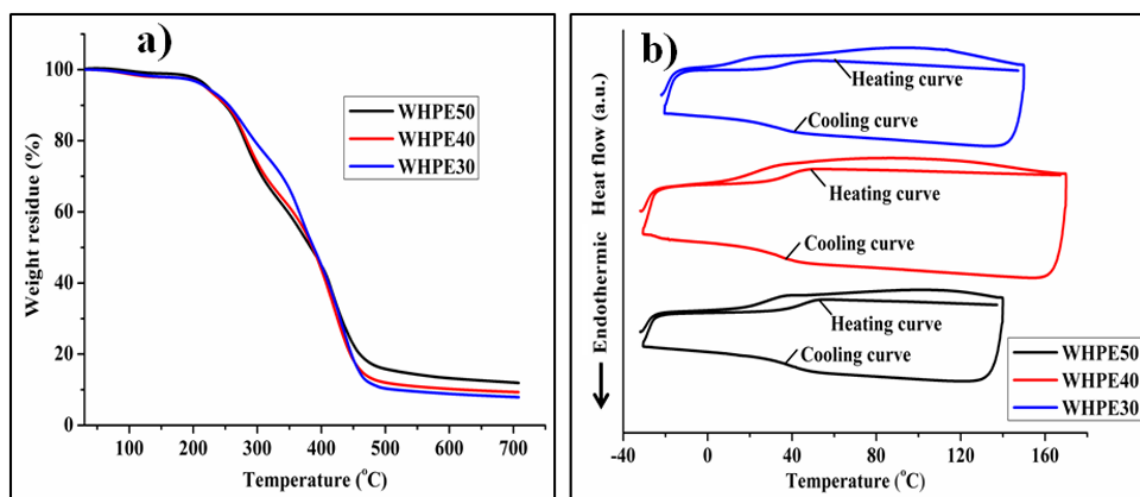


Figure 2B.7: (a) TG thermograms and (b) DSC curves of the thermosets

2B.3.7. Biodegradation study

Biodegradation of WHPE was studied by gram-negative (*Pseudomonas aeruginosa*) and gram-positive (*Bacillus subtilis*) bacterial strains and 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 case of gram-negative bacteria compared to the gram-positive bacteria is due to the difference in their cell structures. Due to the presence of hydrolysable 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 which involves four steps: 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, 40]. Therefore, the factors which increase the tendency of hydrolysis in polyester also control the biodegradation. The bacterial growth curves as measured by OD of degraded films with time are shown in **Figure 2B.8**.

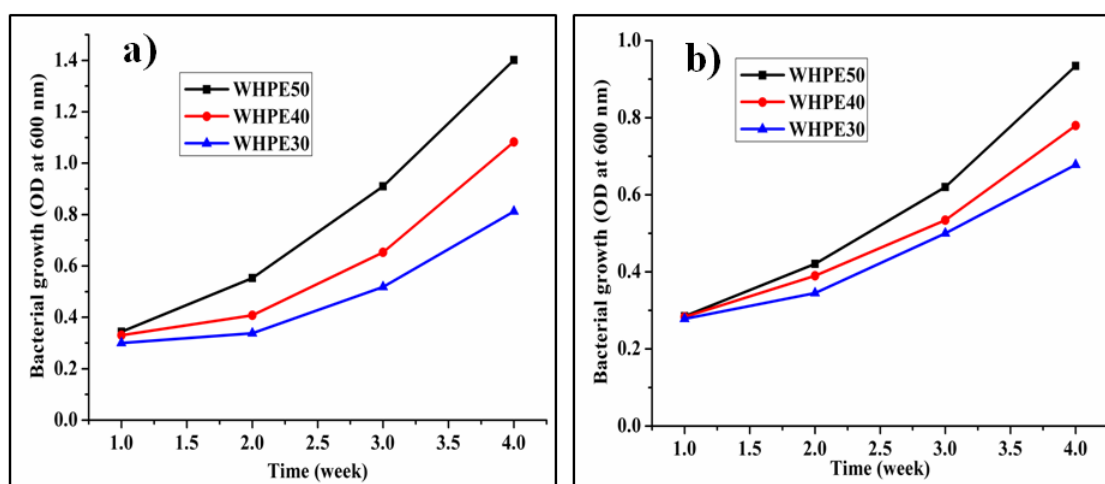


Figure 2B.8: Growth curves of (a) *Pseudomonas aeruginosa* and (b) *Bacillus subtilis* for WHPE30, WHPE40 and WHPE50

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 2B.2**). These polyesters are aliphatic in nature and hence the thermosets of them exhibited high biodegradability. Among them, 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. Representative SEM images of degraded WHPE50 by *Pseudomonas aeruginosa*

and *Bacillus subtilis* bacteria and control (WHPE50 film without bacterial medium) are shown in **Figure 2B.9**. 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 WHPE with green credits in the area of surface coating applications.

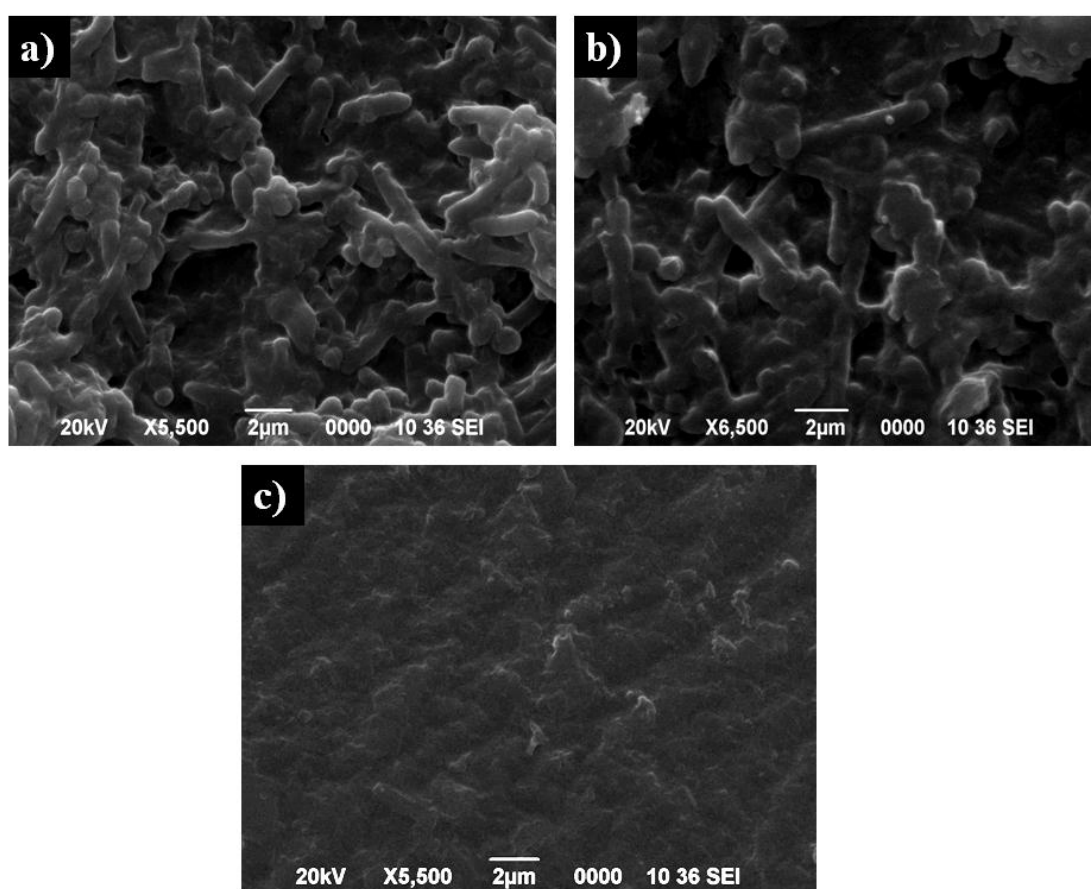


Figure 2B.9: SEM images of WHPE50 after biodegradation by (a) *Pseudomonas aeruginosa*, (b) *Bacillus subtilis* and (c) control

2B.3.8. Hemolytic assay

The hemocompatibility of the polyester thermosets were investigated by RBC hemolytic protection assay (**Figure 2B.10**) which is a type of acute toxicity assay. By detecting hemolyzation of erythrocytes it evaluates the hemocompatibility of the material

structure. 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 multi-fold destruction of RBC membrane. Thus, hemolysis assay confirmed the biocompatibility of polyester thermosets with mammalian RBC.

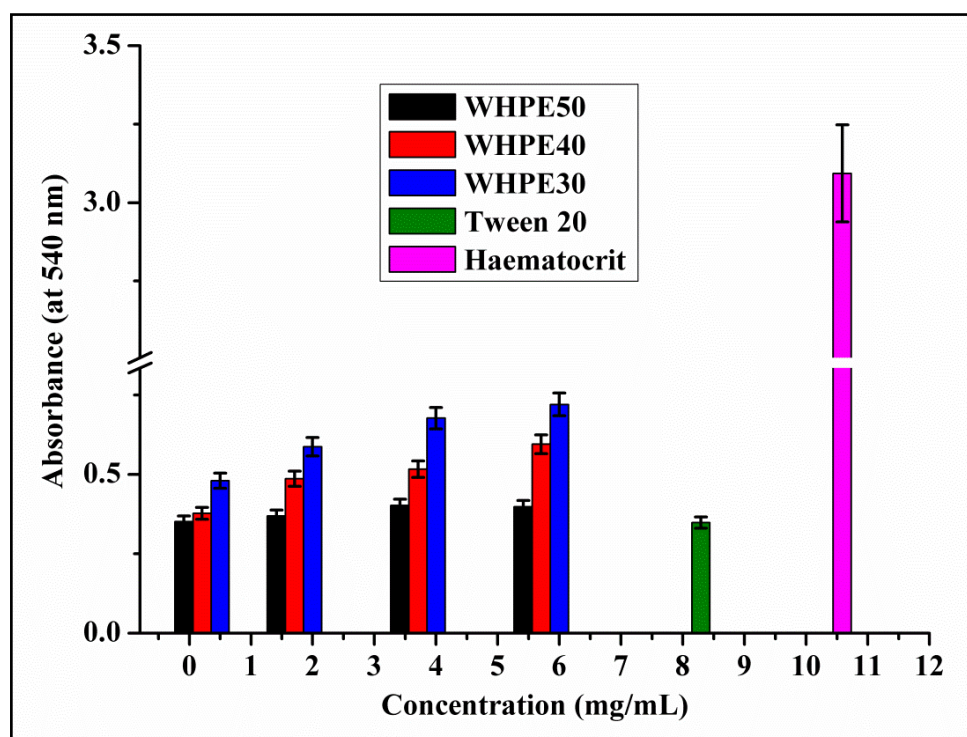


Figure 2B.10: Bar diagrams of absorbance against concentration of thermosets for anti-hemolytic activity assessment

2B.3.9. Chemical resistance

The chemical resistance of polyester thermosets was tested by exposing them in different chemical environments for 20 days at room temperature and the results as the weight losses are given in **Table 2B.4**. All the thermosets showed good resistance towards HCl,

NaCl and water. But the alkali resistance of these thermosets was poor due to the presence of hydrolysable ester bonds [10]. Among these three polyester thermosets, WHPE50 showed the best resistance towards HCl, NaCl and water due to the highest cross-linked density but the alkali resistance is the poorest owing 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 PAA. 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 2B.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

2B.4. Conclusion

In this study citric acid-based biodegradable, biocompatible WHPE 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.

Thus, from this chapter it can be inferred that among the studied polyester thermosets, citric acid-based polyester thermoset with 50 wt% citric acid may be used as the matrix for fabrication of various nanocomposites in the present work due to the

overall best performance by considering availability, cost, one step synthetic protocol and good performance. Further, this polyester was completely soluble in water which will help in fabrication of nanocomposites.

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