

Eco-friendly Hyperbranched Polyurethane

Highlight

This chapter describes synthesis, characterization and property evaluation of hyperbranched polyurethane with environment friendly attributes by using different raw materials. The chapter is divided into two sub-chapters. Sub-Chapter 2A includes synthesis of biodegradable hyperbranched poly(urea urethane) by using a dihydroxyamine compound as the branch generating moiety. The synthetic protocol followed an A₂+CB₂ approach. Synthesized polymer exhibited high mechanical and thermal properties and good chemical resistance. Biodegradability test against *Pseudomonas aeruginosa* revealed profound biodegradability. In order to improve material properties, hyperbranched poly(urea urethane) system was further modified into a solvent free two-pack system, which was used to prepare a thermosetting material by curing with a hyperbranched epoxy and fatty acid based poly(amido amine). On the other hand, Sub-Chapter 2B describes tannic acid based, low VOC containing, biodegradable waterborne hyperbranched polyurethane with moderate mechanical and thermal properties. This system was found to exhibit excellent biological properties, viz. hemocompatibility and profound biodegradability. The chapter also made a brief comparison between all these synthesized and modified systems to choose the right one to develop environmentally benign polyurethane nanocomposites for further study.

Parts of this chapter are published in

1. **Gogoi, S.,** Barua, S., & Karak, N. Biodegradable and thermostable synthetic hyperbranched poly(urethane-urea)s as advanced surface coating materials, *Prog. Org. Coat.* **77**, 1418--1427, 2014.
2. **Gogoi, S.,** Barua, S., & Karak, N. Cross-linking kinetics of hyperbranched epoxy cured hyperbranched polyurethane and optimization of reaction conversion by central composite design, *Chem. Eng. Sci.* **127**, 230--238, 2015.
3. **Gogoi, S.,** & Karak, N. Biobased Biodegradable Waterborne hyperbranched polyurethane as an ecofriendly sustainable material, *ACS Sustainable Chem. Eng.* **2**, 2730--2738, 2014.

Chapter 2A: Dihydroxyamine Based Biodegradable Hyperbranched Poly(urea urethane)

2A.1. Introduction

Chapter 1 clearly pointed out the needs and opportunities to develop novel biodegradable polyurethane (PU) based materials for various applications. It is also learnt that judicious inclusion of monomeric units often offers scope to design PU with desired properties.^{1,2} In this context, use of C_xB_y type of reactants forms an interesting tactic to obtain hyperbranched polyurethane (HBPU) with different chemical functionalities in addition to urethane.^{3,4} In many occasions, incorporation of additional chemical linkages is desirable in order to enhance various material properties. In this milieu, inclusion of urea linkages into a PU matrix seems to be advantageous. Chemically, polyurea is closely related to PU and is formed by the reaction between di/poly-isocyanate with polyamine compounds. Polyurea confers many unique properties to PU such as high mechanical strength, good chemical resistance, short curing time etc.^{5,6} Literature has shown that materials containing both urea and urethane linkages within the polymer backbone are well known and possess high industrial importance. Thus, incorporation of urea-urethane linkages within the same macromolecule may create the avenue to reap the benefits of both in a single system. This also helps to overcome the individual limitations like poor surface adhesion of PU on certain substrates and short pot-life of polyurea.^{7,8} Furthermore, inclusion of such linkages may enhance the intensity of inherent biodegradability of PU. Literature supports such view point as polyurea based materials exhibit high susceptibility for microbial degradation.^{9,10}

Practically, poly(urea urethane) (PUU) can be obtained by the reaction of di/poly-isocyanate with a mixture of polyol and polyamine or a dihydroxyamine compound. Therefore, current study describes the synthesis of aliphatic hyperbranched poly(urea urethane)s (HPUUs) following an A_2+CB_2 approach using commercially available monomers with varying weight percentages of the branching moiety. Among different routes available for the synthesis of HBPU, A_2+CB_2 is attractive because of availability of a large number of CB_2 monomers, which leads to many interesting properties.¹¹ A ϵ -caprolactam based dihydroxyamine compound

was used as the trifunctional branch generating moiety. The structural characterization and performance studies were conducted in comparison to linear analogs. Furthermore, in order to improve performance, HPUU was modified into a thermosetting form (TPUU) by curing with a glycerol based hyperbranched epoxy and fatty acid based poly(amido amine). To prevent any carbon release to the atmosphere, use of organic solvent was avoided in the modification process. Various properties, viz. mechanical, thermal, chemical etc. were evaluated and bacterial biodegradation study was conducted for these developed systems.

2A.2. Experimental

2A.2.1. Materials

Isophorone diisocyanate (IPDI) with 98% purity was used in the synthesis of HPUU. It is one of the most commonly used aliphatic diisocyanates, which provides scope to synthesize PU with high UV resistance. IPDI was procured from Sigma-Aldrich, Germany as a mixture of *trans* and *cis* isomers in the proportion of 3:1, respectively and used as received. Physically, IPDI is a colorless and odorless liquid with m.w. of 222.28 g mol⁻¹, s.g. of 1.049 (at 30 °C) and b.p. of 158 °C.

Poly(ethylene oxide) glycol with m.w. of 600 g mol⁻¹ (PEG 600) was used as the macroglycol. It is a polyether based dihydroxy compound with hydroxyl number of 178-197, m.p. of 29 °C and s.g. of 1.13 (at 20 °C). PEG 600 was procured from Merck, India and used after vacuum drying at 50 °C for 24 h.

1,4-Butanediol (BD) was used as the chain extender. It is a glycolic compound having m.w. of 90.12 g mol⁻¹, s.g. of 1.02 (at 20 °C), m.p. of 20 °C and b.p. of 230 °C. It is a colorless and odorless liquid at room temperature. BD was purchased from Merck, India and used after vacuum drying at 50 °C for 24 h.

3-Aminopropanol (AP) was used as the chain extender to prepare linear analog of HPUU. AP with m.w. of 75.11 g mol⁻¹, s.g. of 0.99 (at 20 °C), m.p. of 11 °C and b.p. of 190 °C was purchased from Merck, India. It was used after vacuum drying at 50 °C for 24 h.

A dihydroxyamine compound was used as the branch generating moiety, which was synthesized from diethanolamine (DEA) and ϵ -caprolactam using calcium

oxide (CaO) as the catalyst. DEA with m.w. of 105.14 g mol⁻¹, s.g. of 1.09 (at 30 °C), m.p. of 28 °C and b.p. of 270 °C was procured from Merck, India. ε-Caprolactam (99% assay) has m.w. of 113.16 g mol⁻¹, s.g. of 1.01 (at 80 °C), m.p. of 71 °C and b.p. of 270.8 °C. It was procured from Hi-Media, India. These chemicals were used after vacuum drying at 50 °C for 24 h. CaO with minimum assay of 99% was purchased from Merck, India and used as received.

Dibutyltin dilaurate (95% assay) (DBTDL) was used as PU catalyst. It is an organo-tin compound which is frequently used in PU reaction. DBTDL possesses m.w. of 631.56 g mol⁻¹, s.g. of 1.06 (at 30°C) and m.p. of 22 °C. DBTDL was procured from Sigma-Aldrich, Germany and used as received.

Xylene and dimethylacetamide (DMAc) were used as solvents. Xylene is a colorless solvent with m.w. of 106.16 g mol⁻¹, s.g. of 0.86 (at 20 °C), m.p. of -48 °C and b.p. of 139 °C. It was purchased from Merck, India and used after distillation. DMAc is also a colorless solvent, which has m.w. of 87.12 g mol⁻¹, b.p. of 165 °C, s.g. of 0.94 (at 20 °C) and m.p. of -4 °C. DMAc was procured from Merck, India and purified by vacuum distillation prior to use. All the solvents were stored in airtight amber glass bottles using A4 type molecular sieves obtained from Hi-Media, India.

Poly(ethylene oxide) glycol with m.w. of 200 g mol⁻¹ (PEG 200) was used in the preparation of TPUU. It is a polyether based dihydroxy compound with hydroxyl number of 535-590, s.g. of 1.12 (at 20 °C), m.p. of -38 °C and b.p. of 150 °C. PEG 200 was procured from Merck, India and used after vacuum drying at 50 °C for 24 h.

Glycerol based hyperbranched epoxy (HE) used in the modification process was prepared according to the method described elsewhere using similar grade chemicals details of which are provided in Chapter 3 of the thesis.¹² A brief preparative method of HE is included in the experimental section.

Poly(amido amine) (PAA) is a resinous, bio-based and non-volatile hardener. It was obtained from Huntsman Corporation, USA with amine value of 5-7 eq. kg⁻¹ and viscosity of 10-14 Pas. Chemically, PAA is a poly-condensation product of vegetable oil based dimer acid with diethylene triamine.

10% (w/v) Sodium chloride (NaCl) solution was used to test chemical resistance under saline condition. NaCl crystals of 99.5% purity were procured from Merck, India. It has m.w. of 58.44 g mol⁻¹ and m.p. of 108 °C.

10% (w/v) Sodium hydroxide (NaOH) solution was used to test chemical resistance in alkaline medium. NaOH pellets with purity of 97% were procured from Merck, India. It has m.w. of 39.99 g mol⁻¹ and m.p. of 319 °C.

5% (v/v) Hydrochloric acid (HCl) was used as acidic medium to check the chemical resistance under acidic condition. It has m.w. of 36.5 g mol⁻¹, s.g. of 1.19 (at 20 °C), m.p. of -28 °C and b.p. of 45 °C. HCl of 37% strength (~11.6 M) was procured from Merck, India and 5% (v/v) solution was prepared by dilution method.

The biodegradation study used bacterial strain of *Pseudomonas aeruginosa* (*P. aeruginosa*) (Code MTCC 7814). It was procured from Microbial Type Culture Collection and Gene Bank, Chandigarh, India. The bacterial culture was provided by the Department of Molecular Biology and Biotechnology, Tezpur University, Assam, India.

2A.2.2. Characterization

Fourier Transform Infrared (FTIR) spectra of the polymers were recorded in transmission mode with KBr pellets by using a Nicolet, USA, Impact 410 FTIR spectrometer. ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra of HPUU and its linear analog were recorded on a 400 MHz FT NMR spectrometer of JEOL, Japan, using dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) as the solvent and tetramethylsilane (Me₄Si, TMS) as the internal standard. Molecular weight and polydispersity index of the polymers were obtained by Gel Permeation Chromatography (GPC) in a Waters, USA instrument. Glass transition temperature (*T*_g) was measured by Differential Scanning Calorimetry (DSC) with the help of a PerkinElmer DSC 6000, USA instrument in the temperature range of -70 to 120 °C (starting temperature was 0 °C) following a cycle of heating-cooling-heating under the inert atmosphere of nitrogen and at a scanning rate of 10 °C min⁻¹. Thermal decomposition profiles of the prepared polymers were studied by Thermogravimetric Analyzer (TGA) by using a PerkinElmer TGA 4000, USA thermal instrument. The characteristic thermal decomposition temperatures were obtained by subjecting the polymer samples into a dynamic heating process at a

scanning rate of $10\text{ }^{\circ}\text{C min}^{-1}$, under an inert atmosphere of nitrogen and at a gas flow rate of 30 mL min^{-1} . A universal testing machine (UTM), Zwick Z010, Germany equipped with a 10 kN load cell and operating at a cross-head speed of 10 mm min^{-1} was employed to measure the tensile strength and elongation at break values of the polymer samples having dimension of $10\text{ cm}\times 1\text{ cm}\times 0.02\text{ cm}$. The scratch hardness of the polymeric films was measured by using a scratch hardness tester provided by Sheen Instruments, UK, Model No.705, equipped with stylus accessory and operating at a speed of $30\text{-}40\text{ mm s}^{-1}$. Impact resistance was determined by a falling weight tester manufactured by SC Dey & Co., India in accordance with ASTM D1709-16a standard protocol. Gloss was determined by using a gloss-meter, Minigloss, Sheen Instruments, UK at an incident angle of 60° . Chemical resistance test was performed in accordance with ASTM D7027-13 method under saline, basic, acidic and aqueous condition by using 10% (w/v) NaCl, 10% (w/v) NaOH, 5% (v/v) HCl and demineralized H_2O , respectively. Surface morphology of the polymers and biodegraded polymers was studied by a Scanning Electron Microscope (SEM) of JEOL, Japan, model JSM 6390LV, after platinum coating on the surfaces. The solution viscosity (0.5% (w/v) in DMAc) of the polymers was measured by using an Ubbelohde viscometer at a constant temperature of $25\pm 0.2\text{ }^{\circ}\text{C}$.

2A.2.3. Methods

2A.2.3.1. Synthesis of DHA

Vacuum dried DEA and ϵ -caprolactam in 1:1 molar ratio along with CaO (1 wt% of the total reactant weight) were taken in a three neck round bottom glass reactor immersed in a silicon oil bath, equipped with a mechanical stirrer, a nitrogen gas inlet and a thermometer. The reaction was carried out at $150\text{ }^{\circ}\text{C}$ for 4.5-5.0 h with constant mechanical agitation and under continuous nitrogen flow. Then the reaction was stopped by allowing the temperature to fall gradually. The product obtained was stored in a reagent bottle and kept inside a vacuum desiccator. It was analyzed for structural characterization by using FTIR and NMR spectroscopy.

2A.2.3.2. Synthesis of HPUU

HPUU was synthesized by a controlled pre-polymerization technique. In the first step, required amounts of PEG 600, BD and xylene were taken in a three neck glass reactor

equipped with a thermometer, a nitrogen gas inlet and a mechanical stirrer. A defined amount of IPDI was slowly injected into the reaction mixture. For different compositions, the -NCO/-OH ratio varied from 1.3 to 1.8. DBTDL (0.1 wt%) was used as the catalyst. The first step of the reaction was carried out at 70 ± 2 °C for 3 h with constant stirring under continuous flow of nitrogen. Then the reaction mixture was allowed to cool to room temperature and required amount of DHA in DMAc was added by maintaining -NCO/-OH functional ratio at 1.0. Temperature was slowly raised to 60 ± 2 °C and the reaction was continued for 3.5-4.0 h. The reaction was stopped after the formation of a sufficiently viscous polymeric solution. The overall solid content of the reaction was maintained at 30 wt%. Three different compositions of HPUU were prepared following the same method by taking different weight percentages of DHA (**Table 2A.1**). The linear counterparts of HPUU, i.e. linear poly(urea urethane) (LPUU) and linear polyurethane (LPU) were also synthesized by the same procedure except BD and AP were added in place of trifunctional moiety in the second step, respectively. The synthesized polymeric solutions were cast on glass and galvanized tin sheets to obtain thin polymeric films. These films were dried in a forced convection oven at 65 °C for 24 h and utilized for various testing.

Table 2A.1. Compositions of the reactants for the synthesized polymers*

Composition	HPUU15	HPUU10	HPUU05	LPUU	LPU
PEG 600 (mol)	1.0	1.0	1.0	1.0	1.0
BD (mol)	2.5	2.5	2.5	2.5	3.5
IPDI (mol)	6.2	5.0	4.2	6.2	4.5
DHA (mol)	1.8	1.0	0.5	-	-
AP (mol)	-	-	-	1.7	-
-NCO/-OH functional ratio	1.0	1.0	1.0	1.0	1.0

*Digit of the code indicates the weight percentage of DHA (branching moiety) in the polymer

2A.2.3.3. Thermosetting HPUU (TPUU)

A thermosetting version of HPUU was also prepared. Initially, HPUU was modified into a two-pack system, which was cured by using HE and PAA. Briefly, a -NCO terminated PU pre-polymer (PUP) with -NCO/-OH=2 was prepared by reacting IPDI (2 mol) and PEG 200 (1 mol) at 60 °C for 1.5 h without using any solvent. In the

synthesis of PUP, exactly same conditions were maintained as mentioned in the sub-section 2A.2.3.2. Such pre-polymer possessed high pot-life under dry and cool conditions (at temperature below 4°C). On the other hand, HE was prepared by reacting glycerol (0.972 g), bisphenol A (19.01 g) and epichlorohydrin (36.815 g) (at 1:2 M ratio of total -OH of glycerol and bisphenol A to epichlorohydrin) at 110 °C for 3 h with a slow addition of 5 N NaOH.¹² PUP along with DHA was used as a two-pack system for TPUU. It was cured by using HE and mixture of HE with PAA at 60 °C for 30 min (compositions are shown in **Table 2A.2**). To evaluate the effectiveness of HE and PAA as cross-linker, different kinetic parameters were further evaluated by DSC measurements. A PerkinElmer DSC 6000, USA, thermal instrument in conjugation with Advanced Pyris® 10.1 analytical software was used for the calorimetric measurements. Considering the quasi-adiabatic behavior of PU cross-linking reaction, all the measurements were done in an isothermal mode. The samples were prepared with maximum possible care following the same preparation procedure under identical condition. Exactly same amount of the reaction precursor (10.00±0.50 mg) was weighted into an aluminum pan with lid, which was hermetically sealed with the help of a crimper. The sample in the pan was placed in DSC thermal chamber preheated to a specific isothermal temperature and heating was continued for 60 min. All the measurements were done in the inert atmosphere of nitrogen and at a gas flow rate of 30 mL min⁻¹. The isothermal temperatures used for the study were 60, 80, 100 and 120 °C. Based on these measurements, kinetic parameters were calculated with the help of Pyris® 10.1 analytical software. As an attempt to bring green attribute, no solvent was used in the preparation of TPUU.

Table 2A.2. Compositions of TPUUs

Formulation	HPUU precursor		HE (g)	PAA (g)
	PUP (g)	DHA (g)		
TPUU1	1.000	0.157	0.231	-
TPUU2	1.000	0.157	0.231	0.115
HPUU	1.000	0.157	-	-

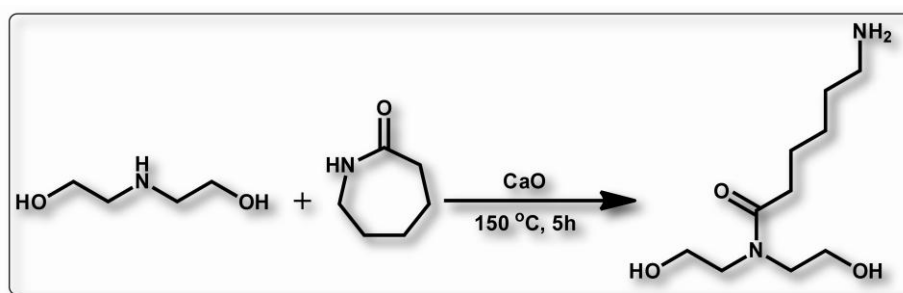
2A.2.3.4. Biodegradation

A mineral salt medium was prepared with a composition of 2.0 g $(\text{NH}_4)_2\text{SO}_4$, 2.0 g Na_2HPO_4 , 4.75 g KH_2PO_4 , 1.2 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 mg $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 100 mg $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, 70 mg $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 10 mg $\text{H}_3\text{BO}_3 \cdot 5\text{H}_2\text{O}$, 100 mg $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$, 1 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 10 mg MoO_3 , all in 1.0 L of demineralized water. This medium was then autoclaved for 15 min at 121 °C under a pressure of 15 lb and then allowed to cool to room temperature. *P. aeruginosa* strain was cultured in this prepared medium and incubated inside a shaker incubator at 37 °C for 48 h. From this bacterial culture, 100 μL (10^8 microbes mL^{-1} , as calculated by McFarland turbidity method) was inoculated into a conical flask containing 10 mL of the prepared mineral solution. Polymeric films were sterilized by exposing them to UV light at 254 nm for 15 min. After sterilization, these films were incubated in the medium under sterile conditions at 37 °C for a period of six weeks. Medium without polymeric films was kept as the negative control. Growth of the microorganism was monitored by measuring the absorbance (optical density, OD) at 600 nm with respect to the control.¹³ The readings were taken at an interval of seven days. Further, change in weight of the polymer samples was also recorded after every one week. The whole experiment was carried out for a time period of six weeks. SEM images of biodegraded films were also analyzed.

2A.3. Results and discussion

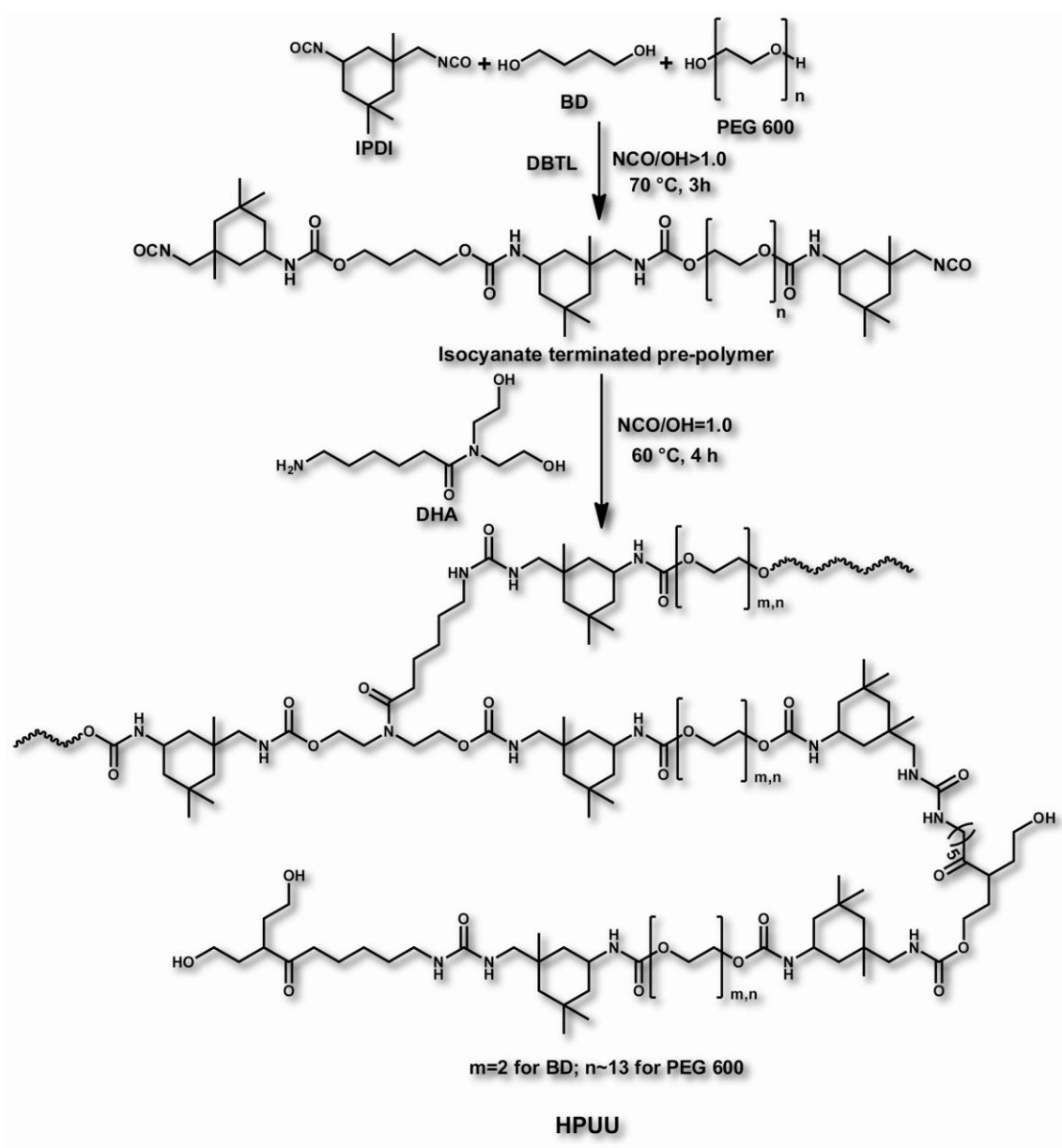
2A.3.1. Synthesis of DHA and HPUU

DHA compound was synthesized by a rearrangement reaction as shown in **Scheme 2A.1**. This DHA compound was used as a tri-functional moiety in the synthesis of HPUU. A two-step, single pot pre-polymerization technique was found fruitful for the



Scheme 2A.1. Reaction scheme for the synthesis of DHA.

successful synthesis of HPUU. The whole reaction followed an A_2+CB_2 approach. In the first step, only di-functional reactants were allowed to react. This eliminated the chance of uncontrolled reaction and hence helped to avoid gel formation. The initial reaction resulted in the formation of a -NCO terminated pre-polymer. Since in presence of DBTDL, the secondary -NCO group (-NCO_{sec}) of IPDI is known to have preferred selectively towards urethane reaction, hence, these were mainly the -NCO_{sec} groups which reacted with the hydroxyl functionalities in the pre-polymerization reaction (**Scheme 2A.2**).¹⁴ The pre-polymer formed in this step



Scheme 2A.2. Reaction scheme for the synthesis of HPUU.

acted as an A₂ type reactant. In the second step, DHA was added as the CB₂ type reactant. In order to avoid competition between different polyols and to ensure complete reaction no other hydroxyl containing compound was added. Furthermore, the concentration of the CB₂ reactant was kept low (<15 wt%), because higher concentration (>15%) increased the risk of gelation. The reaction was stopped when a sufficiently viscous polymeric solution had formed. The completion of the reaction was confirmed by taking FTIR spectra, which displayed no -NCO peak at wavenumber 2270 cm⁻¹. Weight average molecular weight (M_w), number average molecular weight (M_n), polydispersity index (PDI) and solution viscosity (0.5% in DMAc) of the synthesized polymers were evaluated as shown in **Table 2A.3**.

Table 2A.3. Weight average molecular weight (M_w), number average molecular weight (M_n), polydispersity index (PDI) and solution viscosity of HPUUs, LPUU and LPU

Parameters	HPUU15	HPUU10	HPUU05	LPUU	LPU
M _w (g mol ⁻¹)	28,500	27,900	27,300	24,700	24,100
M _n (g mol ⁻¹)	19,900	17,800	20,800	17,000	15,000
PDI (M _w /M _n)	1.43	1.57	1.31	1.45	1.61
Solution viscosity (dL g ⁻¹)	0.229	0.256	0.265	0.358	0.345

2A.3.2. Characterization

Structural characterization of the synthesized polymers was done by FTIR and NMR spectral analyses. FTIR study provided the information about the nature of the functional groups formed and presence of H-bonding within the macromolecular structures.¹⁵ The FTIR peaks were observed near 3400, 2900, 1730 and 1680 cm⁻¹, which are assigned as -N-H stretching, -C-H stretching, -C=O stretching and -N-H in plane bending frequency, respectively (**Figure 2A.1a**). Appearance of these bands gives the preliminary idea about the formation of urethane linkage. On the other hand, for the study of H-bonding in HPUUs, two major spectral regions were selected, viz. the amide-I region (-C=O stretching vibration) near 1630-1750 cm⁻¹ and the -N-H stretching vibration near 3400-3500 cm⁻¹.¹⁵ The bands in both the regions were broad, which might reflect the summation of differently H-bonded functionalities. Presence of H-bonding can be identified by following the shift in the bands towards

lower wavenumber region.¹⁶ Since bands present in the respective regions were appeared as broad multiple peaks, a Gaussian band fitting procedure was employed in order to clarify the nature of H-bonding present. After deconvolution of the IR band in the $-C=O$ region, three peaks were assigned near 1717-1726, 1641-1647 and 1572-1580 cm^{-1} , which can be attributed towards H-bonded urethane-carbonyl ($-C=O\cdots H-N-$), urea-carbonyl ($-C=O\cdots H-N-$) and $-N-H$ bending (amide-II) frequency, respectively (**Figure 2A.1b**). Deconvolution of the IR band in the 3300-3500 cm^{-1} region yielded three peaks at 3452-3485, 3410-3421 and 3368-3378 cm^{-1} , which are assigned as free $-N-H$ and $-O-H$ stretching, H-bonded $-N-H$ ($-N-H\cdots N-H-$) and H-bonded $-N-H$ ($-C-O\cdots H-N-$), respectively (**Figure 2A.1c**). The study of the peak positions in the deconvoluted spectra suggests that incorporation of urea and amide linkages caused a shift of the IR absorption peaks towards lower wavenumber region. The reason behind this is the additional polarity imparted by hydroxylamine chain extenders (both linear and branching) compared to glycolic extender by forming urea linkages, which caused extensive inter-chain association through H-bonding. In HPUUs, the shift was consistent with the increase in weight percentage of DHA branching moiety. Thus, FTIR confirmed the formation of urethane linkages as well as provided an idea about the type of H-bonding exist. Further, FTIR was used as the tool to detect the changes that had occurred during the formation of TPUU as shown in **Figure 2A.2**. Characteristic bands for urethane, i.e. $-N-H$ stretching and $-C=O$ stretching frequencies were assigned near 3400 cm^{-1} and 1740 cm^{-1} , respectively. The band at 1584 cm^{-1} is attributed to amide-II, which is mainly due to $-N-H$ in plane

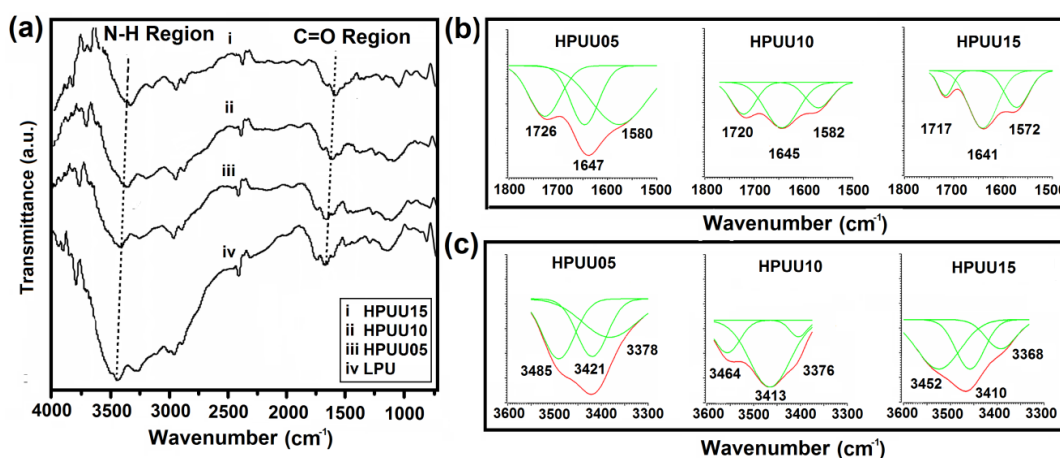


Figure 2A.1. (a) FTIR spectra of HPUUs, (b) Deconvoluted FTIR spectra for amide-I region and (c) Deconvoluted FTIR spectra for $-N-H$ region.

bending. Stretching frequency for aromatic double bond was observed at 1608 cm^{-1} . The FTIR spectrum also displayed characteristic frequency of the epoxy group near 920 cm^{-1} for the modified HPUUs before curing. However, the same was found missing after curing. This confirmed the participation of epoxy groups in the cross-linking reaction. Thus, FTIR study provides preliminary information about the structural attributes of the synthesized and modified systems.

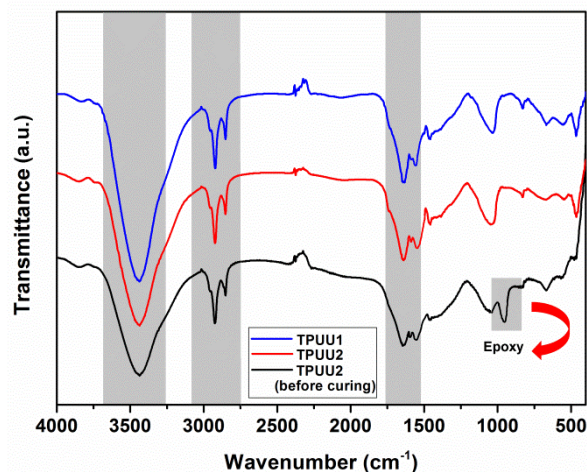


Figure 2A.2. FTIR spectra of TPUUs.

NMR spectroscopic analysis was used for structural confirmation of DHA, HPUU and its linear analogs. ^1H and ^{13}C NMR data and spectra (**Figure 2A.3**) for DHA are provided below which confirmed its structure.

(a) ^1H NMR spectroscopy data (ppm):

δ 1.46-[-CH₂-], δ 1.58-[-CH₂-CH₂-NH₂, CH₂-CH₂-C-O-], δ 2.24-[-C₂-C=O], δ 2.98-[-CH₂-NH₂], δ 2.52-[-N(CH₂)₂], δ 3.48-[-CH₂-OH] and δ 5.10-5.12 [amine and hydroxyl protons].

(b) ^{13}C NMR spectroscopy data (ppm):

δ 20.2-[-CH₂-], δ 30.2-[-CH₂-CH₂-NH₂], δ 30.5-[-CH₂-CH₂-C=O], δ 36.8-[-CH₂-C=O], δ 41.9-[-CH₂-NH₂], δ 52.1-[-N(CH₂)₂], δ 60.9-[-CH₂-OH] and δ 172-[carbonyl carbon - C=O].

However, analysis of the NMR spectrum of IPDI derived HBPU is relatively complex, since IPDI is composed of two different isomers, i.e. *cis* (*Z*) and *trans* (*E*), which exhibit variable selectivity towards the urethane reaction. Nevertheless, NMR data

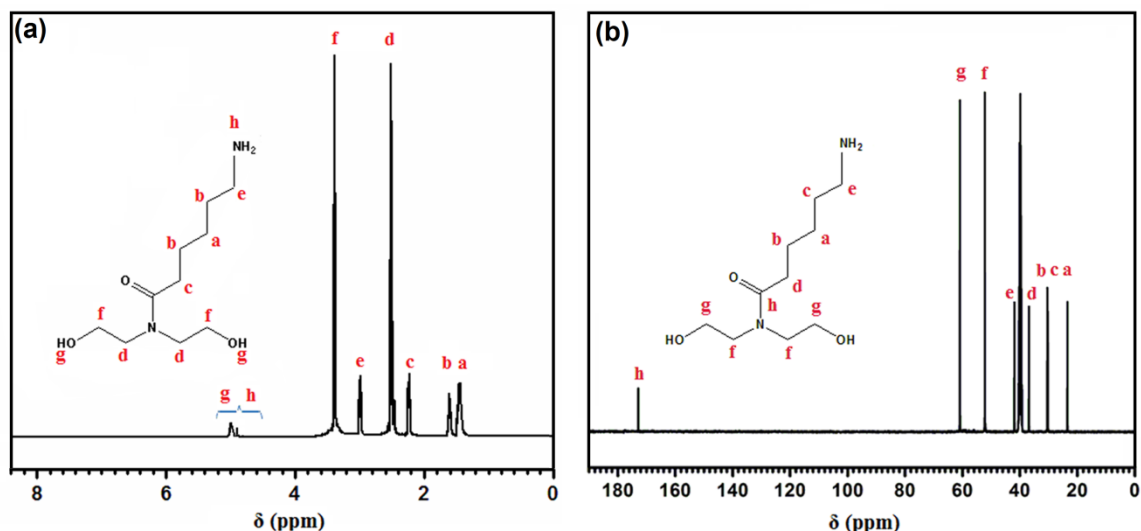


Figure 2A.3. (a) ^1H NMR and (b) ^{13}C NMR spectra of DHA.

provided valuable information about the structure of the synthesized polymer. The formation of two different types of diurethanes (*Z* or *E*) was confirmed by the appearance of peaks at δ 6.8 and 7.1 ppm, respectively (Figure 2A.4). On the other

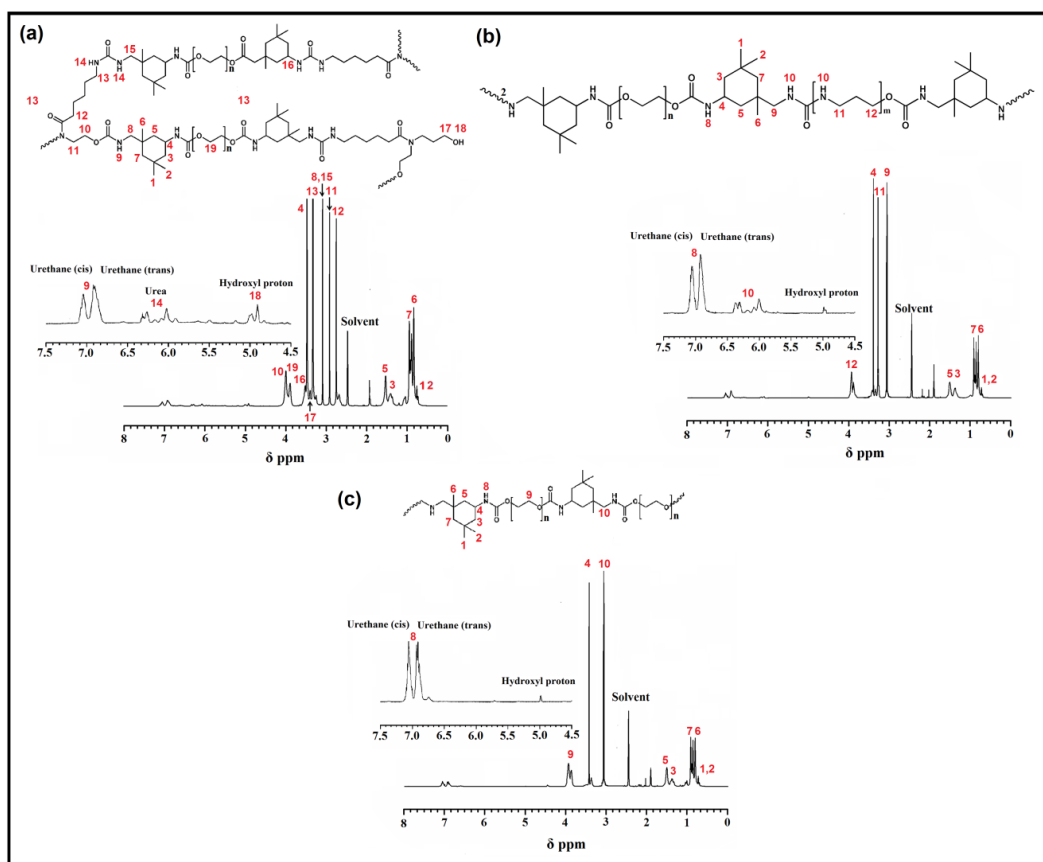


Figure 2A.4. ^1H NMR spectra of (a) HPUU15, (b) LPUU and (c) LPU.

hand, peak near δ 6.0-6.4 ppm furnished evidence for the formation of urea linkage. Comparison of the spectra of the hyperbranched (**Figure 2A.4a**) and linear (**Figure 2A.4b** and **c**) polymers reveals that several peaks were missing in LPUU and LPU, which were present in HPUU15. These missing peaks, *viz.* δ 6.0-6.4 ppm (urea proton), δ 2.92 ppm (-NCH₂), δ 2.76 ppm (N-C(O)-CH₂-CH₂-) and δ 3.31 ppm (-CH₂-NH-CO-NH-) along with the increased peak intensity of -CH₂-O-C=O compared to -CH₂-OH signal supports the hyperbranched structure for HPUU. However, a quantitative estimation of the degree of branching for IPDI derived HPUU is difficult from NMR analysis as the peaks of interest overlap and calculation of the integral area is difficult.¹¹

2A.3.3. Surface morphology

The morphological study of the synthesized HPUUs was carried out by analyzing the SEM images (**Figure 2A.5**). From the images, it is clear that the polymer surfaces were not uniform, rather there was a degree of inhomogeneity in the distribution. It is the intrinsic incompatibility or thermodynamic immiscibility of the hard and soft segments, which is responsible for phase separation. Due to their polar nature, the hard segments can form H-bonds between -C=O and -N-H linkages. Such interactions resulted in the clustering or aggregation of the hard segments into ordered hard domains.¹⁷ On the other hand, soft segments did not give rise to polar interactions and therefore they form amorphous domains. This ultimately caused phase separation. However, the light reflecting and transmitting properties of the polymers seemed to be unaffected by the degree of inhomogeneity as indicated by the good gloss values and clarity of the films.

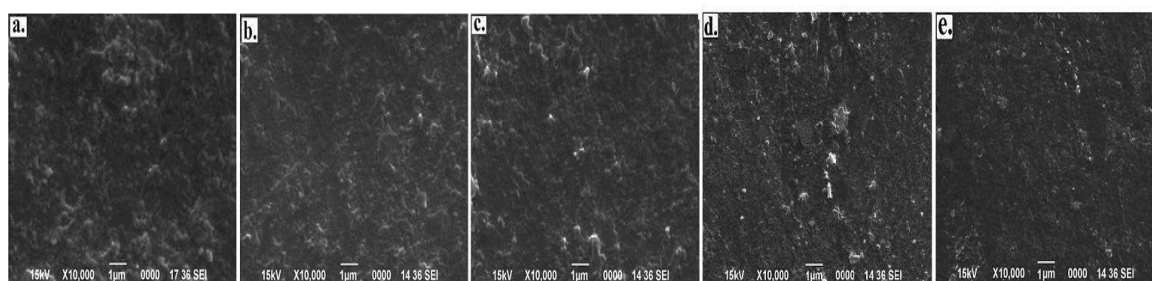


Figure 2A.5. SEM micrographs of **(a)** HPUU15, **(b)** HPUU10, **(c)** HPUU05 **(d)** LPUU and **(e)** LPU.

2A.3.4. DSC kinetics evaluation of TPUU

2A.3.4.1. Kinetic model

Cross-linking kinetics of PU/HE is complex due to involvement of many competing reactions corresponding to different kinetic equations. Hence, a phenomenological kinetic model was followed without prior knowledge on the reaction mechanism.¹⁸ Accordingly for HPUU/HE/PAA system, it was assumed that the rate of reaction is a product of two functions, *viz.* $k(T)$ and $f(x)$. Therefore, the rate equation is given by

$$\frac{d\alpha}{dt} = k(T)f(x) \dots \dots \dots \text{(Eq. 2A. 1)}$$

Where α is degree of conversion. In equation 2A.1, $k(T)$ represents the function which reveals the dependency of the reaction rate on the temperature and is given by

$$k(T) = Z \exp\left(-\frac{E_a}{RT}\right) \dots \dots \dots \text{(Eq. 2A. 2)}$$

Here, Z is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature in absolute scale. The logarithmic form of the above equation, *i.e.* $\ln k(T)$ versus $1/T$ should be a straight line with slope equal to E_a/R and intercept equal to $\ln Z$. On the other hand, the second function $f(x)$ shows the dependency of the reaction rate on the extent of reaction and is given by

$$f(x) = x^m(1 - x)^n \dots \dots \dots \text{(Eq. 2A. 3)}$$

where, m and n are the order of the reaction and x is the fraction of reactant that entered into the reaction. The sum of m and n reflects the overall order of the reaction. Equation 2A.3 represents an autocatalytic reaction, where the product initially formed can catalyze rest of the reaction and thereby increases the overall reaction rate. When $m=0$, then the reaction follows a common n^{th} order reaction mechanism.

$$f(x) = (1 - x)^n \dots \dots \dots \text{(Eq.2A.4)}$$

From literature, it is known that the reactions of $-NCO/-OH$ as well as $-NCO/-OH/-NH_2$ system follow autocatalytic kinetic model.¹⁹ Any nucleophilic reagents can catalyze various urethane reactions. Even in a catalyst free reaction, urethane groups initially formed can accelerate the rate of the reaction to a considerable extent, hence

driving the reaction to follow an autocatalytic pathway. Therefore, an autocatalytic kinetic model was followed for the PUP/DHA/HE/PAA curing reaction.

2A.3.4.2. Kinetics study

DCS kinetics study reveals the effectiveness of HE/PAA as a combined cross-linker for two-pack PU system. Time *versus* conversion curve shows more conversion in case of HE/PAA combined system than only HE (**Figure 2A.6**). The effectiveness of the used cross-linker can be best understood from the mechanism of cross-linking between HPUU and HE/PAA system. PU curing with epoxy includes different competing reactions, *viz.* addition of primary and secondary amine to epoxy as well as etherification of epoxy by hydroxyl groups as shown in **Scheme 2A.3**.^{20,21} These reactions facilitated opening of constrained epoxy rings. As a result, extensive cross-linking took place among epoxy/hydroxyl groups of epoxy, isocyanate/urethane groups of PU and amine groups of hardener forming a three dimensional network structure. As a cross-linker, the architectural features of HE also conferred significant role as its favorable attributes like low viscosity, high surface functionalities and compact structure facilitated the molecular motion for facile driving of the reactions with ease.²² The greater conversion in presence of HE and PAA as a combined system compared to only HE might be due to the greater reactivity of amine towards –NCO compared to –OH and greater efficacy of PAA to open the oxirane rings. Kinetic study also reveals that the order of PU cross-linking increases with the introduction of a cross-linker in the formulation as shown in **Table 2A.4**. The parallel reactions that proceeded in presence of HE and PAA might have an influence on the rate equation. This caused a variation in the order of rate. Further, m and n values were found

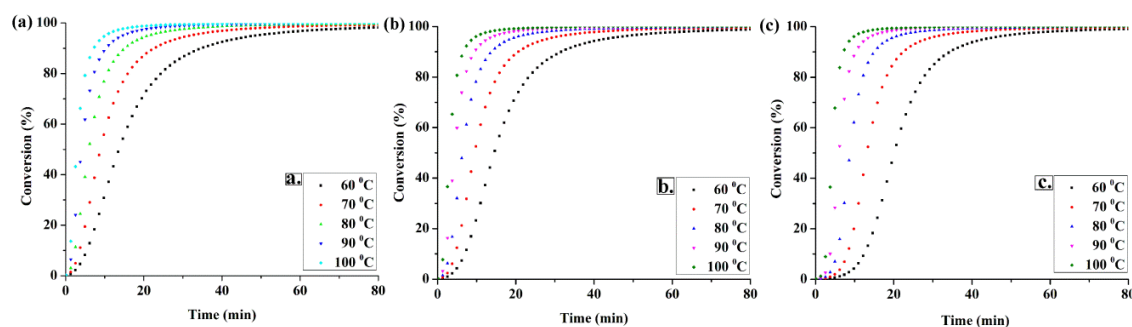
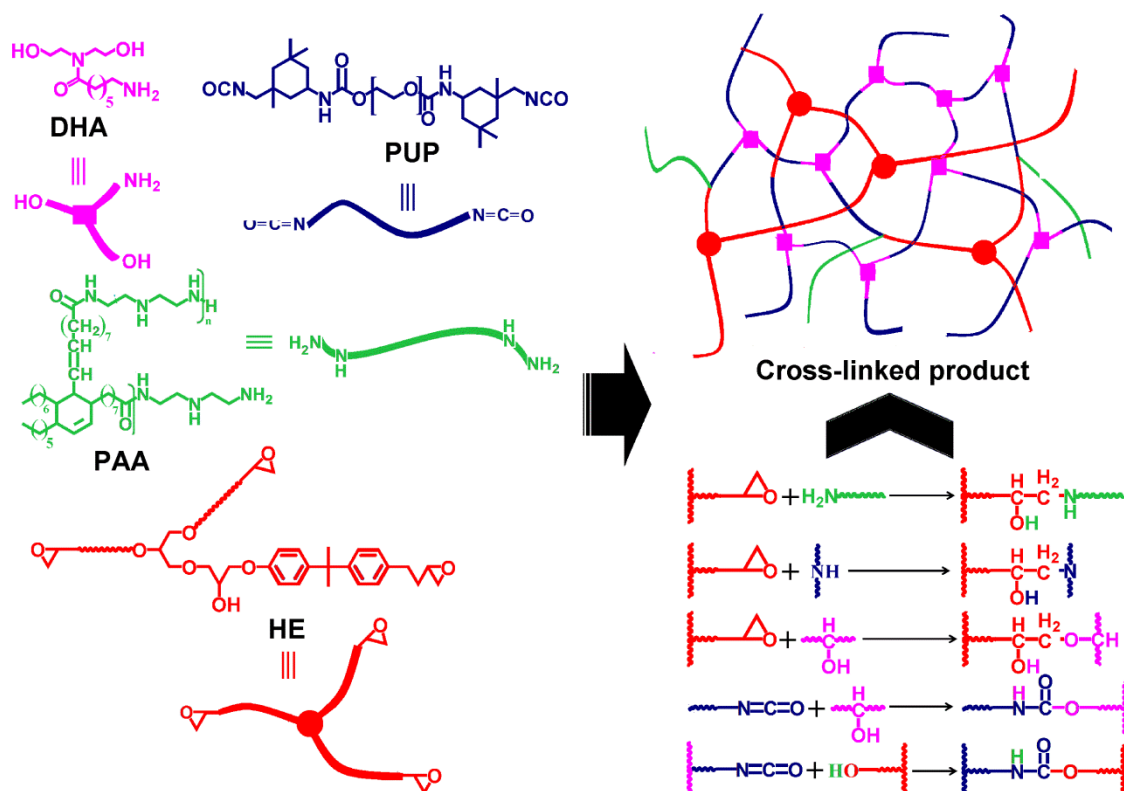


Figure 2A.6. Extent of cross-linking *versus* time curves for (a) TPUU2, (b) TPUU1 and (c) HPUU.



Scheme 2A.3. Plausible mechanism of cross-linking reactions among PUP, DHA, HE and PAA.

almost temperature independent. The m value was lower than n value, which indicates autocatalytic control over the cross-linking reaction. The rate constant k was found temperature dependent, which followed an Arrhenius pattern (**Figure 2A.7a**). $\ln k$ versus $1/T$ plot shows an acceptable linearity as shown in **Figure 2A.7b**. The energy of activation decreased with the incorporation of cross-linking agent. It is obvious because of the autocatalytic behavior of the system. Further, the large surface functionalities and low viscosity of HE allowed the molecular motion, which was effective in lowering the activation energy of the curing reaction compared to the system (HPUU) without the cross-linker.²² Thus, DSC study of cross-linking reaction reveals that a solvent free, thermosetting version of HPUU can be obtained by utilizing HE/PAA as cross-linker in a heat induced autocatalytic curing reaction, which proceeds with low energy of activation.

Table 2A.4. Kinetic parameters of cross-linking kinetics

Formulation	T (°C)	n	m	E _a (kJ mol ⁻¹)	H _{Total} (J g ⁻¹)	k
TPUU2	60	1.49±0.05	0.86±0.03	30.05	115.65	0.0159
	80	1.49±0.03	0.87±0.02	±	±	0.0291
	100	1.50±0.07	0.89±0.04	0.90	1.01	0.0495
	120	1.52±0.03	0.90±0.05			0.0835
TPUU1	60	1.45±0.04	0.75±0.03	34.98	105.45	0.0125
	80	1.46±0.05	0.78±0.03	±	±	0.0249
	100	1.47±0.05	0.79±0.05	0.75	0.95	0.0447
	120	1.47±0.03	0.80±0.05			0.0763
HPUU	60	1.35±0.02	0.52±0.03	44.78	89.97	0.0067
	80	1.37±0.08	0.53±0.02	±	±	0.0161
	100	1.38±0.05	0.55±0.04	0.88	0.55	0.0395
	120	1.39±0.04	0.56±0.03			0.0701

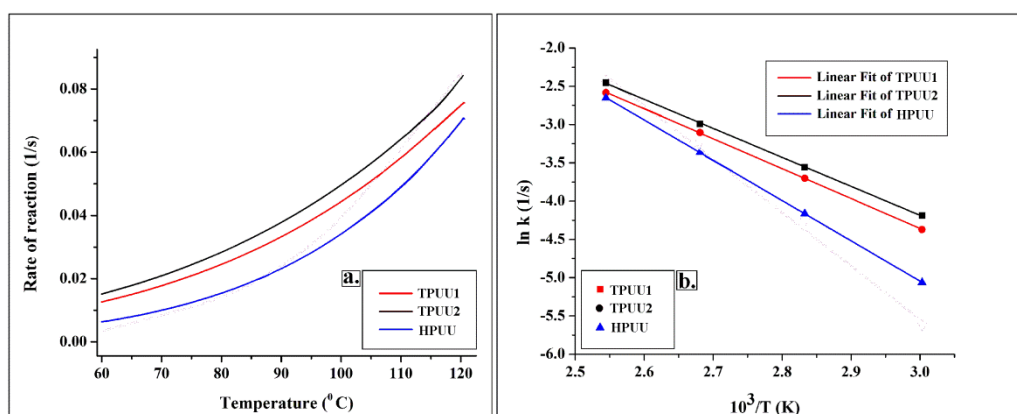


Figure 2A.7. (a) Variation of rate of cross-linking with temperature and **(b)** Arrhenius plots of the cross-linking rate constant *versus* reciprocal of absolute temperature.

2A.3.5. Mechanical properties

Mechanical properties of HBPU depend on many factors, *viz.* presence of inter and intra molecular interactions, presence of polar groups within the polymeric chains, entanglement of chains, extent of cross-linking, molecular chain length of the polymer etc.²³ Synthesized HPUUs possessed high mechanical performance such as tensile strength, scratch hardness, impact resistance, bending and gloss (**Table 2A.5**). Moreover, a dose dependent increment in mechanical properties was perceived. With

increasing amount of branching moiety, most of these properties got enhanced. Also, LPUU exhibited slightly better performance characteristics than LPU. High mechanical strength of HPUUs compared to their linear analog can be ascribed to the confined structural geometry of the former by virtue of hyperbranched architecture.²⁴ Moreover, DHA compound imparted high polarity to the polymer matrix by the formation of urea linkages. This facilitated extensive inter-chain association. This contributed significantly towards the increment of mechanical strength. With increase amount of DHA, extent of H-bonding also strengthened, which led to a dose dependent enhancement of mechanical performance. Better performance of LPUU compared to LPU also supports the influence of secondary interactions on the performance of the polymers. However, elongation at break values were found decreasing with increasing DHA compound. This might arise due to increase in rigidity of the system through different interactions. On the other hand, modification of HPUU resulted improvement of most of the mechanical properties such as tensile strength, scratch hardness and impact resistance. It is because of high level of cross-linking density introduced to the PU matrix during the curing reaction. However, elongation at break and bending values decreased drastically. This arises due to decrease in chain mobility and increase in rigidity of the polymer structure.

Table 2A.5. Mechanical properties of HPUUs, LPUU, LPU and TPUUs

Composition	Mechanical property*					
	TS (MPa)	E@B (%)	SH [†] (kg)	IR [‡] (kJ m ⁻¹)	Gloss (60°)	Bending [¶] (m)
LPU	09.5±0.2	520±2	4±0.1	7.05±0.8	97.4±0.9	<0.001
LPUU	11.6±0.2	505±5	5±0.1	7.55±0.6	97.8±0.6	<0.001
HPUU05	12.4±0.3	459±7	5±0.1	7.47±0.7	98.0±0.7	<0.001
HPUU10	13.9±0.6	444±8	6±0.2	7.88±0.3	98.0±0.3	<0.001
HPUU15	15.9±0.4	398±3	8±0.1	8.13±0.3	103±0.5	<0.001
TPUU1	20.8±0.4	42±2	>10	>8.30	88±0.8	0.005
TPUU2	22.2±0.7	54±3	>10	>8.30	85±0.3	0.005

*Mechanical properties: TS=Tensile strength, E@B=Elongation at break, SH=Scratch hardness, IR=Impact resistance; [†]Limit of scratch hardness tester was 10 kg (maximum); [‡]Limit of impact tester is 8.30 kJ m⁻¹ (maximum); [¶]Limit of the mandrel diameter was 1 mm (minimum)

TPUU2 possessed better elongation at break value compared to TPUU1, which can be attributed to the use of long chain PAA in the former.

2A.3.6. Thermal properties

The thermal stability of the synthesized HPUUs was studied by TG analysis. The thermal stability of a polymer depends on many factors such as chemical structure, type of chemical linkages, reactant composition, molecular weight, intra/inter-molecular forces etc.¹⁸ All the studied polymers showed a single step thermal degradation profile (**Figure 2A.8a**). The TG thermograms showed characteristic thermal decomposition temperatures, viz. onset decomposition and end set decomposition temperatures of the polymers. TG study clearly reveals a significant increment in the degradation temperature in presence of urea linkages in the polymers. The increment is consistent with the increase in weight percentage of the branching moiety. This can be attributed to the structural uniqueness as well as dose dependent enhancement of various secondary interactions as stated in the subsection 2A.3.5. T_g values were also increased with increase in weight percentage of the branching moiety (**Figure 2A.8b**). On the other hand, TPUUs showed much improved thermal stability compared to HPUUs. It is because of high cross-linking density, increase in rigidity of the system and introduction of aromatic moieties to the matrix (HE contains bisphenol A moieties). T_g was also increasing after modification, which reflects imposed restriction on the polymer chain mobility by the cross-linking process.

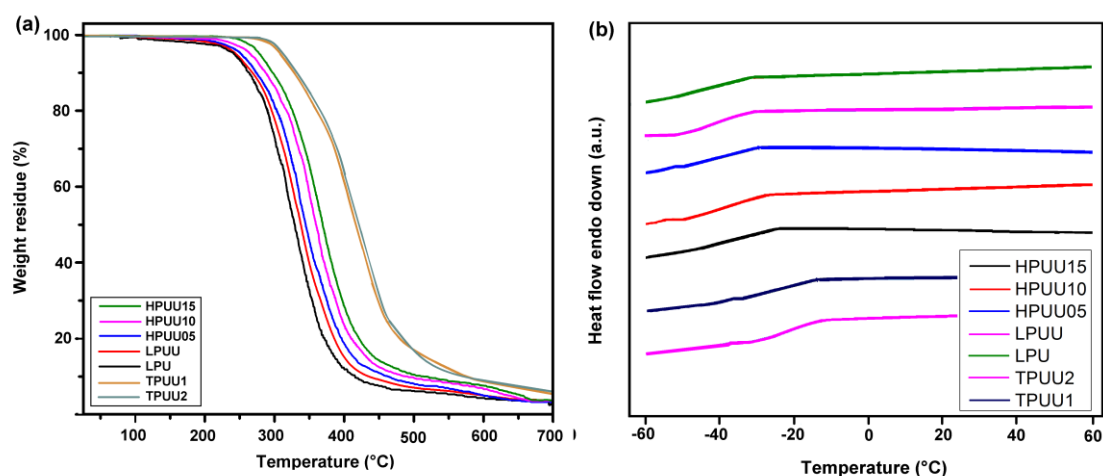


Figure 2A.8. (a) TG thermograms and **(b)** T_g of HPUUs, TPUUs, LPUU and LPU.

2A.3.7. Chemical resistance

All the polymeric compositions showed very good chemical resistance under the experimental chemical environments of 10% (w/v) NaOH, 10% (w/v) NaCl, 5% (v/v) HCl and water. The weight loss (%) after an experimental period of 10 days is shown in **Table 2A.6**. No practical weight loss was recorded in distilled water. From the data it is clear that no significant difference in terms of weight loss was observed for any of the polymeric compositions. However, thermosetting version, i.e. TPUUs showed slightly better chemical resistance compared to HPUUs due to high cross-linking density. Further, HPUUs and LPUU were found to possess slightly superior chemical properties than LPU. This may be due to the presence of urea linkages in the former, which are known to possess good chemical resistance under severe conditions.⁶

Table 2A.6. Chemical resistance (in terms of % weight loss) of HPUUs, LPUU, LPU and TPUUs

Polymer code	%Weight loss		
	10% (w/v) NaCl	10% (w/v) aq. NaOH	5% (v/v) HCl
LPU	1.55	1.85	1.98
LPUU	1.25	1.29	1.49
HPUU05	1.18	1.23	1.48
HPUU10	1.11	1.09	1.30
HPUU15	0.95	0.98	1.21
TPUU1	0.65	0.81	0.89
TPUU2	0.55	0.78	0.87

2A.3.8. Biodegradation

Biodegradation study of the synthesized polymers was carried out by determining the loss in weight due to bacterial exposure. The curve of retention of weight percentage *versus* incubation period is shown in **Figure 2A.9a**. It is quite clear that LPU showed less weight loss compared to HPUUs and LPUU. This is due to the presence of biodegradable amide and urea linkages along with urethane in HPUU and LPUU structures. On the other hand, bacterial growth profiles show a linear increment of bacterial population with time of incubation as evident from the OD data (**Figure 2A.9b**). OD values were higher for HPUUs than LPUU and LPU. This is

due to the better adherence of the microbes on the polymeric surface due to the unique architecture of HPUU compared to the linear analogs. SEM micrographs (**Figure 2A.9c**) further justified this observation. On the other hand, rate of bacterial degradation of TPUUs was found considerably slower than that of HPUUs, LPUU and LPU. The increased cross-linking density caused the process of hydrolytic biodegradation process slow. Moreover, epoxy based materials are known to possess reluctance towards microbial degradation.²⁵

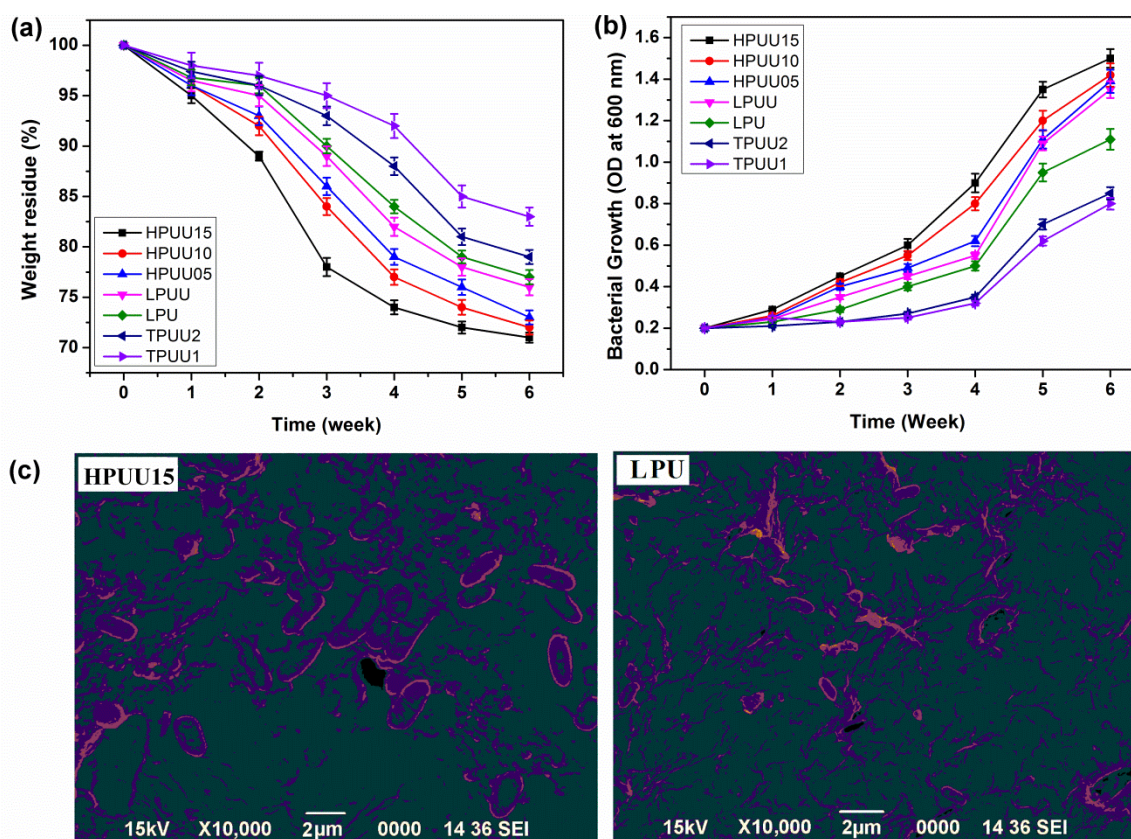


Figure 2A.9. (a) Weight loss profiles and (b) Bacterial growth curves of HPUUs, TPUUs, LPUU and LPU; (c) SEM images of biodegraded HPUU15 and LPU after experimental periods of six weeks.

2A.4. Conclusion

Hyperbranched poly(urea urethane) and its linear analogs were prepared successfully by using commercially available monomers. Comparison of hyperbranched poly(urea urethane), linear poly(urea urethane) and linear polyurethane showed that presence of both urethane and urea linkages in the first

two systems resulted more secondary interactions like hydrogen bonding. Such interactions conferred superior mechanical and thermal properties to these systems compared to linear polyurethane. The study also reveals the architectural effect of the studied polymers on various properties. Further, a high strength and thermo-stable, rigid thermosetting version of hyperbranched poly(urea urethane) was prepared by using hyperbranched epoxy and poly(amido amine) as cross-linker. All the developed polymeric materials were found biodegradable by bacterial strain of *P. aeruginosa*, however with variable rates. Rate of biodegradability was found to be promoted by the incorporation of urea linkages. In contrary, an adverse effect on bacterial biodegradation was observed upon modification. Over all, it can be concluded that biodegradable thermoplastic and thermosetting hyperbranched poly(urea urethane)s were developed with high mechanical and thermal properties. Considering good biodegradability, these materials can be said eco-friendly. However, they are incapable to address other basic environmental glitches, such as purely petroleum based synthetic route and high VOC content. Hence, these issues need to be addressed properly by developing bio-based and low VOC containing polyurethane system.

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Chapter 2B: Tannic Acid Based Waterborne Hyperbranched Polyurethane

2B.1. Introduction

The previous sub-chapter described a commercial raw material based biodegradable, solvent borne hyperbranched poly(urea urethane). Such system by virtue of biodegradability is capable of addressing environmental concern relating to its ultimate disposability after use. However, it has serious limitations to address other environmental issues, such as use of purely petroleum based raw materials and high VOC content due to the use of organic solvent in the synthetic process. Hence, it is desirable to eliminate these shortcomings, which can be achieved by developing bio-based, biodegradable and low VOC containing waterborne polyurethane (WPU) system. WPU is a binary colloidal system, where PU particles containing stabilizing groups disperse in an aqueous medium. WPU supersedes its solvent borne counterparts in terms of favorable health and environmental safety attributes.¹⁻⁴ The most auspicious aspect of this kind of PU is low VOC content, which make it possible to avoid release of volatile carbon to the atmosphere during synthesis, processing and application. In addition to the environmental benefits, WPU enjoys other advantages as well. These include non-toxicity, low viscosity, non-flammability, ease of processability etc. Nowadays, WPU finds a wide range of applications such as coating, adhesive, primer, paint additive, defoamer, associate thickener, pigment paste, biomedical etc.⁵⁻⁷

As mentioned in the introductory section of Chapter 1, use of renewable resource based raw material is desirable in the synthesis of industrially important polymers. In this context, literature shows potentiality of various bio-based compounds as raw materials for PU synthesis.⁸⁻¹² In recent years, effort is being made to utilize vegetable oils to develop WPU. Madbouly *et al.* used castor oil for the synthesis of aqueous PU dispersion.¹³ Lu and Lorock synthesized WPU from soybean oil.¹⁴ However, other bio-resources, such as naturally abundant polyphenolic compounds have not been properly utilized. Compared to vegetable oils, polyphenolic compounds possess certain advantages, e.g. most of the vegetable oils need to be converted to the desired polyol before using in PU reaction. This increases

the cost of the product. But, polyphenolic compounds do not require such pre-treatment. Therefore, the present study intends to explore the potentiality of tannic acid, a readily abundant, low cost polyphenolic compound as a bio-derived raw material in the synthesis of WPU. Industrial viability of tannic acid has already been established in pharmaceutical and food industries. It is also used as rust converter and mordant for dyeing.¹⁵⁻¹⁷ Further, the architectural construction of tannic acid is very attractive to obtain waterborne hyperbranched PU (WHPU). Generally, hyperbranched polyesters have been reportedly used in the synthesis of WHPU.¹⁸⁻²⁰ With twenty five peripheral hydroxyl groups generating from five polyester arms, TA very much resembles a hyperbranched polyester.

Thus, the present study emphasizes development of WHPU using varying weight percentages of tannic acid as the branching template. WHPU with different compositions were prepared, characterized and different properties were evaluated. Moreover, the criteria of sustainability include environmental and health safety issues.^{21,22} Hence, the study also includes hemocompatibility and bacterial biodegradability study in order to highlight its potentiality as a safe and sustainable material.

2B.2. Experimental

2B.2.1. Materials

IPDI, PEG 600 and BD were used as diisocyanate, macroglycol and chain extender, respectively in the synthesis of WHPU. All these chemicals have same grade and specifications as mentioned in Sub-Chapter 2A (Section 2A.2.1.).

Tannic acid (TA) was used as a bio-based polyol in the synthesis of WHPU. TA with m.w. of 1701 g mol⁻¹ and m.p. of 218 °C was procured from Sigma-Aldrich, Belgium. TA is extracted from pods of tetrapod. It possesses profound bioactivity with excellent biocompatibility.²³

2,2-Bis(hydroxymethyl)propionic acid (BMPA) was used as an internal emulsifier. It is a dihydroxy acid. BMPA (98% assay) with m.w. of 134.13 g mol⁻¹ and m.p. of 189 °C was purchased from Aldrich, Germany. It was recrystallized from ethanol and dried in a vacuum oven at 50 °C for 24 h prior to use.

Triethylamine (TEA) was used to neutralize the acidic groups of BMPA and to create ionic centers along the PU backbone. TEA with m.w. of 101.19 g mol⁻¹, s.g. of 0.73 (at 20 °C), m.p. of -115 °C and b.p. of 90 °C was purchased from Merck, India and used as received.

Tetrahydrofuran (THF) was used as a low boiling point solvent. It was used to reduce the viscosity of the polymer during polymerization reaction and recovered safely after the completion of the reaction. THF with m.w. of 72.11 g mol⁻¹, s.g. of 0.89 (at 20 °C), m.p. of -108.5 °C and b.p. of 66 °C was purchased from Merck, India. It was used after distillation.

Goat's blood was used in hemolytic assay. It was collected locally from slaughterhouse, Tezpur University market complex, Tezpur, India in heparinized tube containing 4% sodium citrate. Sodium citrate with m.w. of 258.06 g mol⁻¹, s.g. of 1.7 (at 20 °C) and m.p. of 300 °C was procured from Hi-Media, India.

Tween®20 (Polysorbate) was used as the negative control in hemolytic assay. It possesses m.w. of 1228 g mol⁻¹, s.g. of 1.1 (20 °C) and b.p. of >100 °C. Tween®20 was purchased from Merck, India.

Bacterial culture of *P. aeruginosa* of similar type as mentioned in Sub-Chapter 2A (Section 2A.2.1.) was used in the biodegradation study.

2B.2.2. Characterization

Same FTIR and NMR spectrometers were used in the structural study of WHPU as described in Sub-Chapter 2A (Section 2A.2.2.). D₂O was used as the solvent to record the NMR spectrum of WHPU. Besides these, a photo-spectrometer of Hitachi, model: U2001, Tokyo, Japan was used for the study of UV-visible spectra of WHPU. Molecular weights and molecular weight distribution of the synthesized polymers were determined by using same GPC as mentioned in the previous sub-chapter. On the other hand, in order to evaluate thermal and mechanical properties of WHPU, same instruments and instrumentation techniques such as TGA, DSC, UTM, scratch hardness tester, gloss meter, impact tester etc. were employed as described in Chapter 2A (Section 2A.2.2.). Surface morphology of biodegraded polymeric films was studied by using same the SEM mentioned in Sub-Chapter 2A (Section 2A.2.2.).

2B.2.3. Methods

2B.2.3.1. Synthesis of WHPU

WHPU was synthesized by a pre-polymerization technique. Required amounts of IPDI, PEG 600 and BMPA (maintaining $-NCO/-OH=1.5$) were taken in a four neck glass reactor equipped with a condenser, a nitrogen gas inlet, a thermometer and a mechanical stirrer. The pre-polymerization reaction was carried out at 85 ± 2 °C for 1.5 h without using any solvent, under nitrogen atmosphere and with constant mechanical agitation. In the second step, BD and TA in THF were introduced to the reaction mixture at 25 °C. Overall functional ratio of $-NCO$ to $-OH$ was maintained at 1 (amounts were taken in such a way that at least three $-OH$ groups of TA can participate in the reaction). Then the temperature was raised and the reaction was carried out at 70 ± 2 °C for 5 h. After completion of the reaction, TEA was added slowly at room temperature in order to neutralize the $-COOH$ groups under continuous stirring for 30 min. This was followed by a very slow addition of water to the polymeric solution with vigorous stirring for another 30 min. Then, THF was removed under reduced pressure in order to get the polymer in water. WHPU with different compositions were prepared by taking 5, 10 and 15 weight percentages of TA, which were coded as WHPU05, WHPU10 and WHPU15, respectively (**Table 2B.1**). Furthermore, a control PU (WPU0) without TA was also synthesized following the same method, except only BD was used in the second step in place of mixture of

Table 2B.1. Compositions of the reactants for the synthesized polymers*

Composition	WPU0	WHPU05	WHPU10	WHPU15
IPDI (mol)	2.00	2.00	2.00	2.00
PEG 600 (mol)	0.80	0.80	0.80	0.80
BMPA (mol)	0.53	0.53	0.53	0.53
BD (mol)	0.67	0.61	0.56	0.50
TA (mol)	-	0.04	0.07	0.11
TEA (mol)	0.53	0.53	0.53	0.53
$-NCO/-OH$ (functional ratio)	1.00	1.00	1.00	1.00

*Digit of the code indicates amount of TA in WHPU compositions

TA and BD. Synthesized polymers were cast on glass and galvanized tin sheets to obtain thin films, which were used in different tests.

2B.2.3.2. Hemolytic Assay

To get preliminary knowledge about the cytocompatibility of WHPUs, hemolytic assay was performed. The idea was to investigate the lysis of mammalian red blood cell (RBC) membrane by the tested macromolecule. Goat's blood collected in heparinized tube containing 4% sodium citrate was centrifuged for 20 min at 3000 rpm ($503\times g$) to get the erythrocytes. The erythrocytes were washed thrice with phosphate buffer saline (PBS). Then 5% hematocrit was obtained by re-suspending the packed erythrocytes in PBS (10 mM at pH of 7.4). Polymeric samples with varying concentrations, *viz.* 0.25, 0.50, 0.75, 1.00, and 5.00 mg mL⁻¹ were prepared. 100 mL of each sample was taken in microfuge tubes 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. Finally, hemoglobin concentration was determined by measuring absorbance at 540 nm, which gives the degree of hemolysis of RBC by the polymeric samples.²⁴ The experiment was performed in triplicate for each sample and analyzed by one way ANOVA. Tween® 20 was used as the negative control and hematocrit as the positive control.

2B.2.3.3. Biodegradation

Biodegradation study of WHPU was conducted by using *P. aeruginosa* as bacterial strain according to the method described in Sub-Chapter 2A (Section 2A.2.3.4.).

2B.3. Results and discussion

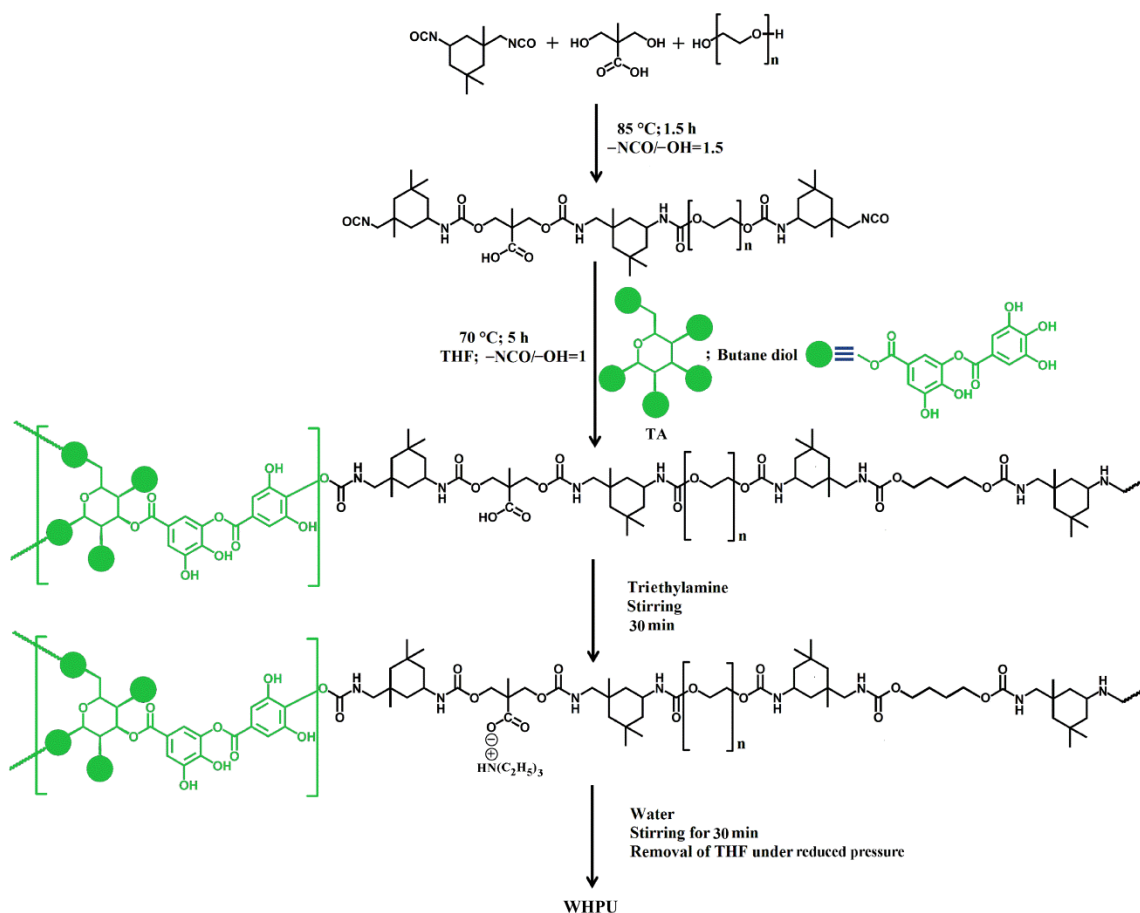
2B.3.1. Synthesis of WHPU

Generally, synthesis of WPU involves use of less reactive aliphatic diisocyanate, macroglycol, diol or diamine chain extender and an internal emulsifier which can generate ionic centers. In the present work, IPDI was used as the diisocyanate, PEG 600 as the macroglycol, BD as the chain extender and BMPA as the ion-generating moiety. On the other hand, hyperbranched polyester polyols are generally used as branching template in the synthesis of WHPU.^{19,20} The current work employed TA, a bio-based polyphenolic polyol compound for the same purpose. Structurally, TA is

very much similar to a hyperbranched polyester. It has a perfectly branched structure with five arms generating from a pyranose heterocycle, twenty five hydroxyl groups and ten ester linkages. Hence, the present synthesis tried to utilize TA instead of a synthetic polyester polyol to construct hyperbranched structure. In practice, all twenty five hydroxyl groups of TA are not equally reactive because of steric reasons. This steric factor becomes more prominent when TA reacts with long and bulky pre-polymer chains. Moreover, substitution of one hydroxyl group by a pre-polymer chain frequently reduces the reactivity of others present in the system. Hence, TA was used in a calculated amount that ensured participation of at least three hydroxyl groups in the urethane reaction. In relation to the solubility parameter, these unreacted and free -OH groups are crucial as they can enter into various secondary interactions like H-bonding with polar solvents resulting enhanced solubility of the polymer. Pre-polymerization step was carried out without using any solvent. In this step only, di-functional compounds were allowed to react, which reduced the chance for uncontrolled reaction. Further, in the first step of the synthesis, mainly -NCO_{sec} is expected to participate in the polymerization reaction; because in absence of any catalyst, -NCO_{sec} shows preferred selectivity towards urethane reaction (**Scheme 2B.1**).²⁵ A maximum of 15 wt% of TA was used in the second step as exceeding this amount can lead to an uncontrolled reaction resulting gelation. Weight average (M_w) and number average (M_n) molecular weight, polydispersity index (PDI) and solution viscosity of synthesized polymers were evaluated which are shown in **Table 2B.2**. Weight average molecular weight was obtained in the range of 22,600-5,700 g mol^{-1} with molecular weight distribution in between 1.23 and 1.39. The molecular weight was found to follow an increasing trend with the TA content of the polymer.

Table 2B.2. Weight average molecular weight (M_w), number average molecular weight (M_n), polydispersity index (PDI) and solution viscosity of WHPUs

Parameters	WHPU05	WHPU10	WHPU15
M_w (g mol^{-1})	22,600	23,300	25,700
M_n (g mol^{-1})	16,200	18,900	21,700
PDI (M_w/M_n)	1.39	1.23	1.34
Solution viscosity (dL g^{-1})	0.365	0.298	0.274



Scheme 2B.1. Reaction scheme for the synthesis of WHPU.

2B.3.2. Characterization

FTIR spectroscopy confirmed various functional groups present in the polymer matrix (**Figure 2B.1a**). Further, evidence for H-bonding was also gathered by following the change in frequency and intensity of the peaks in the mid IR spectral region. For the studied systems, absorption frequency near $1720\text{-}1730\text{ cm}^{-1}$ is attributed to -C=O stretching vibration (contribution from both amide-I and ester linkages). On the other hand, -N-H stretching and -N-H bending (amide-II) frequencies were observed at 3410 and 1580 cm^{-1} , respectively. The absorption peak for -C=C- bond was found near 1600 cm^{-1} . Similarly, amide-III, which is mainly in-phase combination of -N-H in plane bending and -C-N- stretching vibration occurred near $1230\text{-}1236\text{ cm}^{-1}$. Amide-IV and amide-V bands were observed at frequencies $773\text{-}776$ and $631\text{-}635\text{ cm}^{-1}$, respectively. On the other hand, a consistent shift of IR bands towards lower wavenumber was observed in the amide-I and -N-H stretching region with increasing TA content of the polymer. This indicates involvement of H-bonding between phenolic -O-H from TA and $\text{-N-H}/\text{-C=O}$ functionalities of urethane

linkages. With increasing TA content, there would be more -O-H groups in the polymer, which strengthened the extent of H-bonding. This causes a TA dose dependent shift of IR bands. On the other hand, UV-visible spectra of WHPUs show absorption peak near 280 nm. This confirmed the presence of catechol moieties in the synthesized polymers. The intensities of the peaks were enhanced with the increase in TA content as depicted in **Figure 2B.1b**. This indicates the presence of more catechol units in the polymer with increase amount of TA. **Figure 2B.2** shows ^1H NMR spectrum of WHPU15. However, a precise interpretation of ^1H NMR spectrum of the synthesized polymer is difficult as IPDI is composed of two isomeric forms (*Z* and *E*) and two isocyanate groups ($-\text{NCO}_{\text{prim}}$ and $-\text{NCO}_{\text{sec}}$) exhibit variable selectivity towards urethane reaction under different conditions as described in Chapter 2A (Section 2A.3.2.). Though, ^1H NMR data depicted in **Figure 2B.2** furnish valuable evidence in favor of the synthesized polymer. Urethane $[-\text{N}-\text{H}-\text{C}(=\text{O})-\text{O}]$ peaks were observed at δ 7.8-8.0 ppm, which confirmed the formation of two different urethanes, *viz.* *cis* and *trans*. The appearance of surface functional phenolic protons (Ph-OH) was marked at δ 9.7-9.9 ppm. Aromatic protons belonging to TA were observed at δ 7.0-7.2 ppm. However, from the NMR spectrum, a quantitative calculation of degree of branching is difficult for IPDI/TA derived PU, as the peaks of interest were very complex aggregates.²⁶ However, use of a perfectly branching template make the whole process highly viable towards the formation of a hyperbranched architecture.

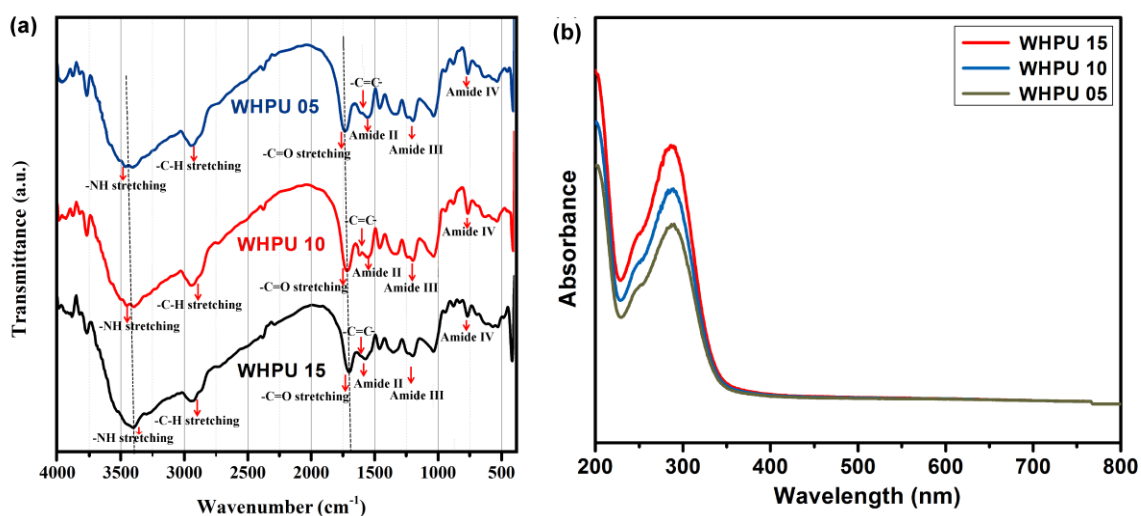


Figure 2B.1. (a) FTIR spectra and (b) UV-visible spectra of WHPUs.

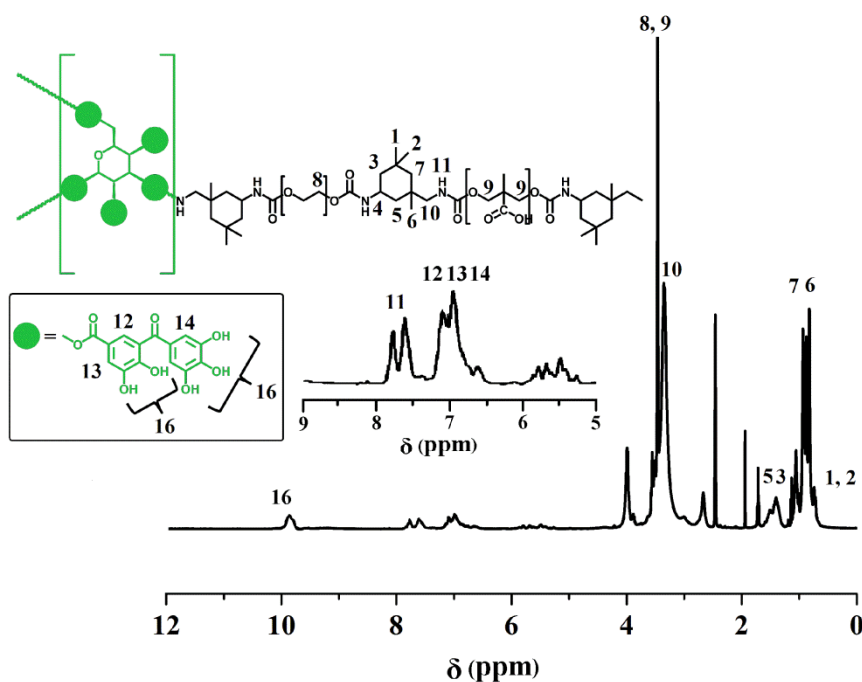


Figure 2B.2. ^1H NMR spectrum of WHPU15.

2B.3.3. Mechanical properties

Mechanical properties were evaluated for the synthesized WHPUs. Different mechanical properties are documented in **Table 2B.3**. Most of the mechanical properties like tensile strength, scratch hardness and impact resistance followed a rising trend with increasing TA content in the polymers. Generally, mechanical

Table 2B.3. Mechanical properties of WHPUs

Property*	WPU0	WHPU05	WHPU10	WHPU15
TS (MPa)	4.0±0.2	4.9±0.15	6.0±0.2	6.9±0.17
E@B (%)	520±4	508±5	457±3	315±4
SH [†] (kg)	4.0±0.1	4.0±0.2	5.0±0.2	5.5±0.2
IR (kJ m ⁻¹)	6.06±0.15	6.22±0.20	6.64±0.13	6.97±0.22
Bending [‡] (m)	<0.001	<0.001	<0.001	<0.001
Gloss (60°)	95.8±0.5	95.7±0.7	94.5±0.8	88.2±0.4

*Mechanical properties: TS=Tensile strength, E@B=Elongation at break, SH=Scratch hardness, IR=Impact resistance; [†]Limit of scratch hardness tester was 10 kg (maximum); [‡]Limit of the mandrel diameter was 1 mm (minimum).

properties of a polymer depend on certain factors, *viz.* presence of polar groups, inter and intra-molecular interactions between the polymeric chains, polymeric chain entanglement, compositions and nature of the reactants, molecular weight, rigidity of the polymer etc.²⁷ Addition of TA can favor the above factors by virtue of its high molecular structure and rigidity. Moreover, different secondary interactions such as polar-polar interaction, H-bonding, π - π stacking etc. got strengthened with the introduction of TA. This resulted high strength of the polymer. However, elongation at break values were found to follow a decreasing trend with the increasing amount of TA. High amount of TA can affect the polymer chain flexibility due to its rigid molecular structure, which caused reduction of the elongation at the break values. However, all the polymers possessed good bending values. Further, all the polymeric compositions exhibited good gloss.

2B.3.4. Thermal Properties

TG analysis showed that all the compositions of WHPU possess good thermal stability. WHPUs exhibited a two-step thermal degradation pattern as shown in **Figure 2B.3a**. The first step (in the temperature range of 250-260 °C) can be attributed to the degradation of thermo-labile aliphatic moieties, urethane bonds and ester groups. On the other hand, the second step (in the temperature range of 300-320 °C) is due to the degradation of aromatic rings belonging to TA moiety. It is clearly understood from the depicted thermograms that TA content in the polymer can enhance the thermal stability of WHPU, which is consistent with the weight percentages of TA in the polymer. Further, weight residue left after degradation at 700 °C also increases with TA content. High thermo-stability of TA imparted by the aromatic moieties, ester linkages, heterocyclic ring system as well as strong secondary interactions like H-bonding, π - π stacking etc. contributed towards the high thermal properties of WHPU. Better thermal behavior of WHPU compared to WPU0 further confirmed these facts. The DSC curves shown in **Figure 2B.3.b** indicate that T_g increases with increasing amount of TA in the polymer. This could be due to increasing inter- and intra-molecular association in the structure, which restricted polymer chain mobility.

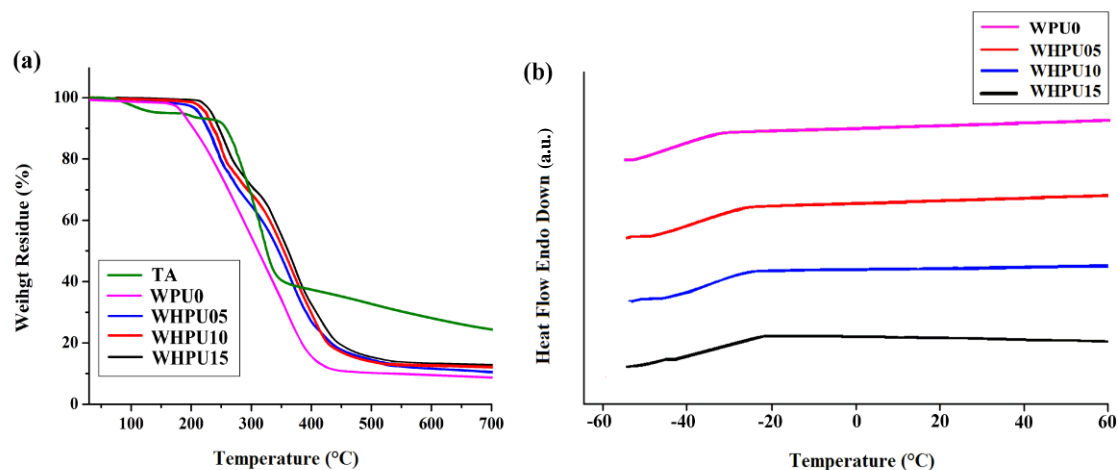


Figure 2B.3 (a) TG thermograms of WHPUs and (b) DSC curves (cooling) showing T_g of WHPUs.

2B.3.5. Biological properties

2B.3.5.1. Hemolytic assay

Human health safety is one of the major criteria for material sustainability. A material should not create any potential hazard to the living beings during its life cycle. Hence, in order to scrutinize safety of the synthesized system, hemolytic assay was performed as a representative biocompatibility test. It is a type of acute toxicity assay used to evaluate the hemocompatibility of a material by detecting hemolysis of erythrocytes.²⁸ Such study involves direct interaction of a material with the erythrocyte membrane, in which the extent of disruption of the erythrocyte membrane is considered as the direct measure of toxicity. The RBC hemolytic protection assay reveals that WHPU05, WHPU10 and WHPU15 were well compatible with the mammalian erythrocytes compared to WPU0 (**Figure 2B.4**). WHPU15 exhibited the best compatibility among the tested WHPUs, though the differences among the group were very minute. Twin[®]20, the negative control showed the highest absorbance of hemoglobin, which indicates drastic rupture of the RBC membranes. Contrarily, hematocrit, the positive control exhibited a negligible absorbance value. Thus, *in vitro* hemolytic assay confirmed the preliminary compatibility of WHPU with mammalian RBC.

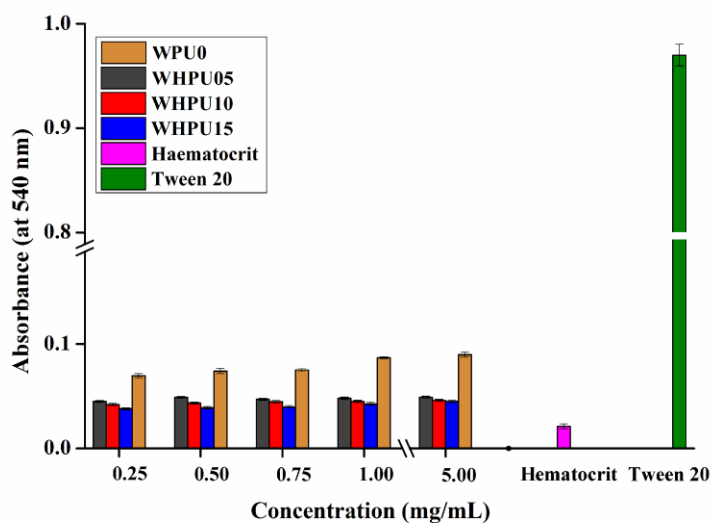


Figure 2B.4. Bar diagram of lysis of mammalian RBC membrane by WHPUs, hematocrit (positive control) and Twin[®]20 (negative control).

2B.3.5.2. Biodegradation

Biodegradation of WHPUs by *P. aeruginosa* bacteria was studied by determining the weight loss with time due to exposure of bacterial strain. The curve of retention of weight percentage *versus* incubation period as depicted in **Figure 2B.5a** clearly showed degradation of the polymeric films after six weeks of exposure. WHPU15 was found more biodegradable compared to WHPU10 and WHPU05. It is because of the fact that polyester PUs are more susceptible towards microbial degradation compared to PU alone.²⁹ As WHPU15 contains more hydrolysable ester linkages, it offered a better liable surface for bacterial growth. This was further supported by the bacterial growth curves as shown in **Figure 2B.5b**. There was a linear increment in the bacterial population with time of incubation, which was found to follow an increasing trend with TA content in the polymer. WHPU05 contains the least amount of ester linkages, hence weight loss as well as bacterial growth was minimum. Here, it is pertinent to mention that WPU0 was also found biodegradable. However, rate of biodegradability was slower than WHPUs. The bacterial biodegradation was further confirmed by SEM images taken after six weeks of degradation (**Figure 2B.6**). For all the polymer compositions, significant bacterial adherence and surface erosion were witnessed compared to the control.

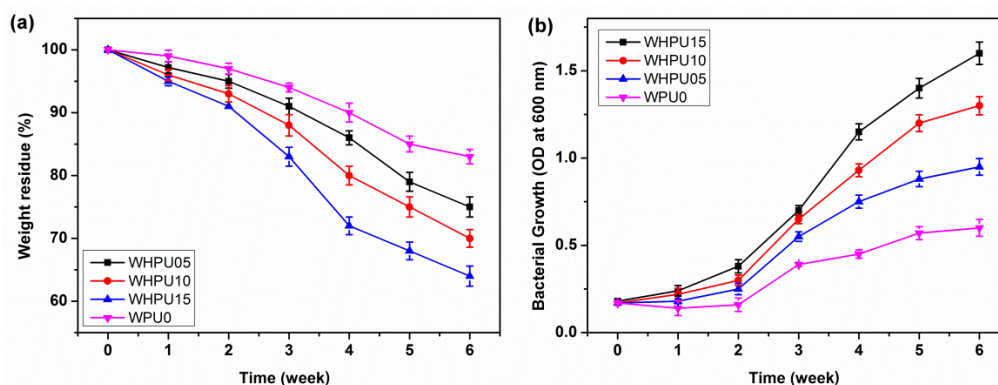


Figure 2B.5. (a) Weight loss profiles of WPU0, WHPU05, WHPU10 and WHPU15 due to bacterial degradation; (b) Growth curves of *P. aeruginosa* on WPU0, WHPU05, WHPU10 and WHPU15.

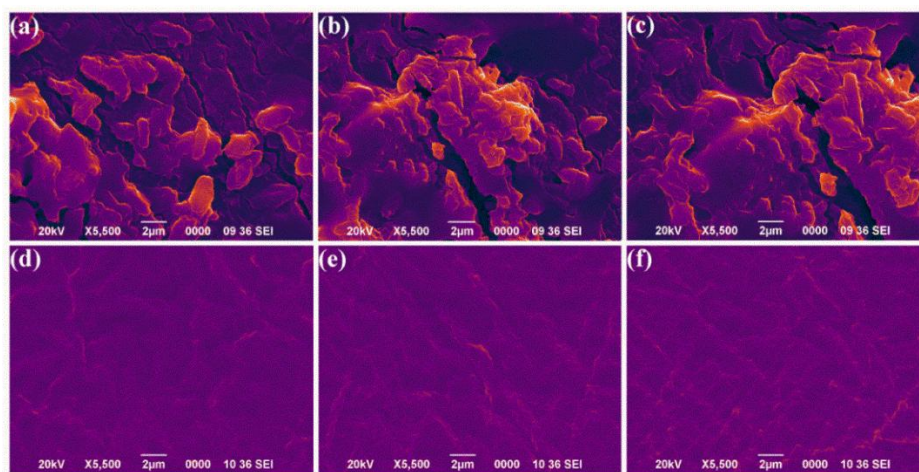


Figure 2B.6. SEM images of biodegraded (a) WHPU05, (b) WHPU10 and (c) WHPU15; SEM images of (d) WHPU05, (e) WHPU10 and (f) WHPU15 before biodegradation.

2B.4. Conclusion

The present study reports an environmentally benign approach to synthesize hyperbranched polyurethane using tannic acid as a bio-based material. The polymer exhibited acceptable thermal and mechanical properties. Hence, it can be concluded that tannic acid and other bio-based polyphenolic compounds are good alternative of vegetable oils for the development of sustainable polymeric materials. Furthermore, hemolytic assay confirmed erythrocyte compatibility of the polymer with mammalian blood cells. These results indicate the studied polymer as a safe material. Biodegradability of the polymer by bacterial strain can address genuine problems

related to land pollution and solid waste management issues. From the study it can be urged that the developed system possesses high prospective to address a cocktail of challenges ranging from sustainability to environmental footprints. Compared to previously described hyperbranched poly(urea urethane) (Sub-Chapter 2A), waterborne hyperbranched polyurethane was found superior in terms of bio-based origin and low level of VOC content. Moreover, rate of biodegradability of waterborne hyperbranched polyurethane was found faster than hyperbranched poly(urea urethane). The only inferiority witnessed was its low performance in comparison to hyperbranched poly(urea urethane) system. However, this can be corrected by its modification. Nanotechnology based routes may also be adopted to enhance the mechanical performance and to impart other special properties. Therefore, considering the environmentally benign attributes, tannic acid based waterborne hyperbranched polyurethane was selected as the material for further study.

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