

Modified Waterborne Hyperbranched Polyurethane

Highlight

Current chapter describes modification of tannic acid based waterborne hyperbranched polyurethane in order to improve its performance. A combined system of glycerol based hyperbranched epoxy and vegetable oil based poly(amido amine) was used as modifier. The modified system was obtained by chemically cross-linking at 100 °C for 45 min. FTIR spectroscopic analysis and swelling study confirmed the cross-linking reaction. A dose dependent improvement of various properties was witnessed. Modified system with 30 wt% hyperbranched epoxy and 15 wt% poly(amido amine) showed excellent improvement in mechanical properties, like tensile strength (~3.4 fold), scratch hardness (~2 fold), impact resistance (~1.3 fold) and toughness (~1.7 fold). TG study revealed enhancement of thermal properties (maximum 70 °C increment of degradation temperature and 8 °C increment of T_g). Further, it possessed better chemical and water resistance compared to the pristine polymer. An adequate biodegradation was witnessed for the modified system against *Pseudomonas aeruginosa* as the test organism. The work showed the way to develop environmentally benign waterborne hyperbranched polyurethane as a high performance material by incorporating a reactive modifier into the polymer network. Use of benign solvent and bio-based materials as well as good biodegradability justified eco-friendliness of the modified system.

Parts of this chapter are published in

Gogoi, S., & Karak, N. Bio-based high-performance waterborne hyperbranched polyurethane thermoset, *Polym. Adv. Technol.* **26**, 589--596, 2015.

3.1. Introduction

The previous chapter (Sub-Chapter 2B) described the development of a tannic acid based waterborne hyperbranched polyurethane (WHPU) system. Such polymeric system possesses various eco-friendly attributes like bio-based origin, profound biodegradability and low VOC content. However, despite of all these environmental benefits, it has serious limitation of low performance, which creates obstacle towards its utilization in many modern applications. Waterborne polyurethanes (WPU) are primarily thermoplastics with little or no gel fraction and contain a large number of hydrophilic ionic groups along the polymer backbone.¹ Hence, they are very sensitive towards moisture and other chemical environments. This leads to inferior mechanical property, thermal stability and poor chemical resistance of WPUs compared to their solvent borne counterparts.^{2,3} Such limitations restrict practical applicability of WPU in many advanced applications.⁴ Therefore, tannic acid based WHPU requires special attention to overcome the aforementioned shortcomings in order to develop it as a high performance eco-friendly material.

Literature has shown different routes for polyurethane (PU) modification, which may be used to bring preeminence in the performance of WHPU. This can be achieved by physical or chemical means.^{5,6} Generally, window of widespread properties of PU can be broadened by modifications like blending, creating a cross-linking reaction or forming of an interpenetrating network system.⁷⁻¹² Modification of WPU should result in the formation of a chemically cross-linked structure, which can resist influence of moisture and other chemical environments as well as provide high mechanical and thermal properties. However, methods such as blending and interpenetrating network formation do not provide the scope for cross-linked system as these methods do not involve formation of covalent bond between the host and modifier.⁵ In this context, formation of extensive cross-linking within WPU matrix by incorporating a reactive and compatible polymeric system may form an interesting tactic. WPU has been reported to be cross-linked by using different modifiers such as carbodimide, aziridine, hexa(methoxymethyl)melamine, amino-formaldehyde, melamine-formaldehyde resins etc.¹³⁻¹⁵ In this milieu, epoxy may be a promising candidate.¹⁶⁻²⁰ Epoxy is an industrially important resinous polymeric material. Most importantly epoxy is compatible with PU system by virtue of various polar groups,

which can interact with each other either physically or chemically. As a modifier, epoxy resin possesses many advantageous properties like good mechanical and thermal performance, high adhesive strength, low shrinkage during curing, low creep, excellent corrosion and weather resistance, good chemical resistance, dimensional stability, ease of processability etc.²¹⁻²³ Thus, inclusion of such high performance epoxy into WHPU may bring superior material properties. Further, use of epoxy with hyperbranched architecture may confer other favorable attributes as well. These include low solution and melt viscosity, high peripheral functionality and compact geometry, which may be helpful to achieve an exceedingly compatible WHPU/epoxy system with high degree of cross-linking.²⁴ Hence, hyperbranched epoxy can be used as a novel, low viscous modifier for a low performing WHPU system.

Considering these facts, a modifying system comprising of glycerol based hyperbranched epoxy (HE) and fatty acid based poly(amido amine) (PAA) was employed to improve various properties of WHPU. Inclusion of PAA in the modifying system is desirable as it is known as an epoxy hardener and initiates the cross-linking process. Different weight percentages of HE/PAA were used to obtain various compositions of modified WHPU. Use of bio-based materials (host polymer and modifier) justified the eco-friendliness and sustainability of the resultant material. Different properties such as mechanical, thermal, chemical etc. were evaluated and compared with the pristine WHPU. Further, bacterial degradation study with *P. aeruginosa* bacterial strain was conducted to find out the effect of induced cross-linking on the rate of bio-disposability of the neat system. Such approach may create avenue towards the development of high performance environmentally benign PU for various applications.

3.2. Experimental

3.2.1. Materials

IPDI, PEG 600 and BD of similar grade and specifications were used as described in Sub-Chapter 2A (Section 2A.2.1.). Other chemicals used in the preparation of WHPU were TA, TEA, BMPA and THF. All these chemicals possessed similar grade and specifications as described in Sub-Chapter 2B (Section 2B.2.1.). Similar graded NaCl,

NaOH and HCl along with ethanol (C₂H₅OH, Merck, India) were used in the chemical resistance test as mentioned in Sub-Chapter 2A (Section 2A.2.1.). Same type of bacterial culture of *P. aeruginosa* was used in the biodegradation study as mentioned in Sub-Chapter 2A (Section 2A.2.1.).

On the other hand, glycerol based HE was prepared by using glycerol, bisphenol A and epichlorohydrin. Glycerol with m.w. of 92.10 g mol⁻¹, s.g. of 1.26 (at 20 °C), m.p. of 18 °C and b.p. of 290 °C was purchased from Merck, India. Bisphenol A (≥99% assay) with m.w. of 228.29 g mol⁻¹, m.p. of 218 °C and b.p. of 220 °C was purchased from Sigma-Aldrich, Germany. It was used after recrystallizing from ethanol. Epichlorohydrin with m.w. of 92.52 g mol⁻¹, s.g. of 1.18 (at 20 °C), m.p. of -57 °C and b.p. 116.5 °C was procured from Merck, Germany. It was used as received. On the other hand, fatty acid based PAA was used a hardener in the modification process. It had similar grade and specification as described in Sub-Chapter 2A (Section 2A.2.1.).

3.2.2. Characterization

Same FTIR spectrometer as mentioned in Sub-Chapter 2A (Section 2A.2.2.) was employed to study the changes that had occurred during the cross-linking reactions between WHPU and HE/PAA system as well as to detect the functional groups that are present in the modified systems. TGA and DSC were used to study the thermal stability and to evaluate T_g of modified WHPU system, respectively. Same thermal instruments and experimental conditions were used in the evaluation of thermal properties as mentioned in Sub-Chapter 2A (Section 2A.2.2.). Various mechanical properties of the modified systems, viz. tensile strength, elongation at break, scratch hardness and impact resistance were evaluated using the same UTM, scratch hardness tester and impact tester as described in Sub-Chapter 2A (Section 2A.2.2.). Chemical resistance test was carried out under similar chemical environments as mentioned in Sub-Chapter 2A (Section 2A.2.2.) following standard protocol of ASTM D543-14. Same SEM was employed for the visual study of the biodegraded polymeric films as described in Sub-Chapter 2A (Section 2A.2.2.). In addition to these, an ultrasonicator (Hielscher, Model: UP200S, Germany with acoustic power density of 460 W cm⁻²) at 60% amplitude and 0.5 cycle was used to prepare the uniform mixtures of WHPU, HE and PAA systems.

3.2.3. Methods

3.2.3.1. Preparation of WHPU

WHPU was prepared by following a pre-polymerization technique as described in Sub-Chapter 2B (Section 2B.2.3.1.). Considering good strength and elongation at break value, WHPU10 was selected as the composition to be modified with HE/PAA system. However, a more general code, *viz.* WHPU has been used in this chapter to define the mentioned composition instead of WHPU10.

3.2.3.2. Preparation of HE

HE was prepared by following the method described elsewhere.²⁵ Briefly, the required amount of glycerol (0.972 g) and bisphenol A (19.01 g) were reacted with epichlorohydrin (36.815 g) in a three neck round bottom glass reactor fitted with a pressure-equalizing funnel and a condenser as mentioned in Sub-Chapter 2A (Section 2A.2.3.3.). Reaction was carried out for 3 h at 110 °C with constant magnetic stirring. 5 N NaOH solution was added drop wise through the pressure-equalizing funnel. The viscous mass obtained at the end of the reaction was separated, washed and dried by following the standard procedures. FTIR and NMR (¹H and ¹³C NMR) spectroscopic data confirmed the structure of prepared HE.

- (a) FTIR (cm⁻¹): 911 (epoxy ring), 1035 (alkyl-aryl ether group), 1241 (aryl ether linkage), 3441 (-O-H) and 1608 (-C=C-).
- (b) ¹H NMR (ppm): δ 2.71, δ 2.72, δ 3.13 (oxirane protons).
- (c) ¹³C NMR (ppm): δ 44.68, δ 50.43 (oxirane ring C atoms), δ 68.68 (dendritic tri-substituted glycerol), δ 68.49 (linear di-substituted glycerol) and δ 67.9 (terminal mono-substituted glycerol); Degree of branching was 0.88.

These spectroscopic data were confirmed by comparing with those reported previously.²⁵

3.2.3.3. Modification of WHPU

WHPU with 50 wt% of solid content was mixed with the desired amount of HE and PAA according to the compositions shown in **Table 3.1**. A thorough mixing of the polymeric components was done by sonicating the mixture for 15 min at room

temperature. This gives a homogeneous dispersion of HE and amine hardener in the WHPU system. The dispersed mixture was cast on glass plates. Coated films were then kept under open atmospheric condition for removal of the solvent. To ensure the removal of the last trace of entrapped solvent, the coated strips were degassed under vacuum. Then, the films were chemically cross-linked by heating at 100 °C for 45 min. The cured films were cooled in a desiccator and kept overnight. The films were then peeled off from the glass plates by immersing in hot water and dried again in a vacuum oven. They were utilized for various tests and the modified system was coded as modified waterborne polyurethane (MWPU).

Table 3.1. Compositions of MWPU

Composition*	WHPU (g)	HE (g)	PAA (g)
WHPU	100	0	0
MWPU10	90	10	5
MWPU20	80	20	10
MWPU30	70	30	15

*Digit of the code indicates amount of HE used as cross-linker

3.2.3.4. Swelling study

Cross-linking density of MWPU was estimated by measuring swelling value of the modified polymer. ASTM D2765-11 method was followed to determine swelling value. The swelling test was carried out by immersing weighed amount (W_D) of cured film in THF. The samples were removed from the solvent after attaining equilibrium and the weight of the swollen film (W_S) was measured. The swelling value was calculated by using the following formula:

$$\text{Swelling value (\%)} = \frac{(W_S - W_D)}{W_D} \times 100 \dots \dots \dots \text{(Eq. 3.1)}$$

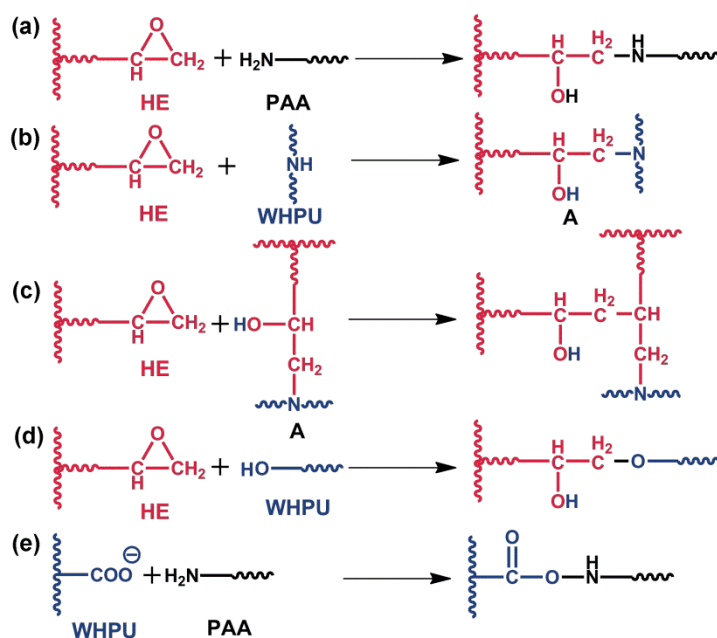
3.2.3.5. Biodegradation

Microbial biodegradation test of MWPU films was carried out by using *P. aeruginosa* as the bacterial strain for a period of seven weeks according to the method described in Sub-Chapter 2A (Section 2A.2.3.4.). Biodegradation study was performed in order to study the effect of modification on the rate of bacterial degradation of WHPU.

3.3. Results and discussion

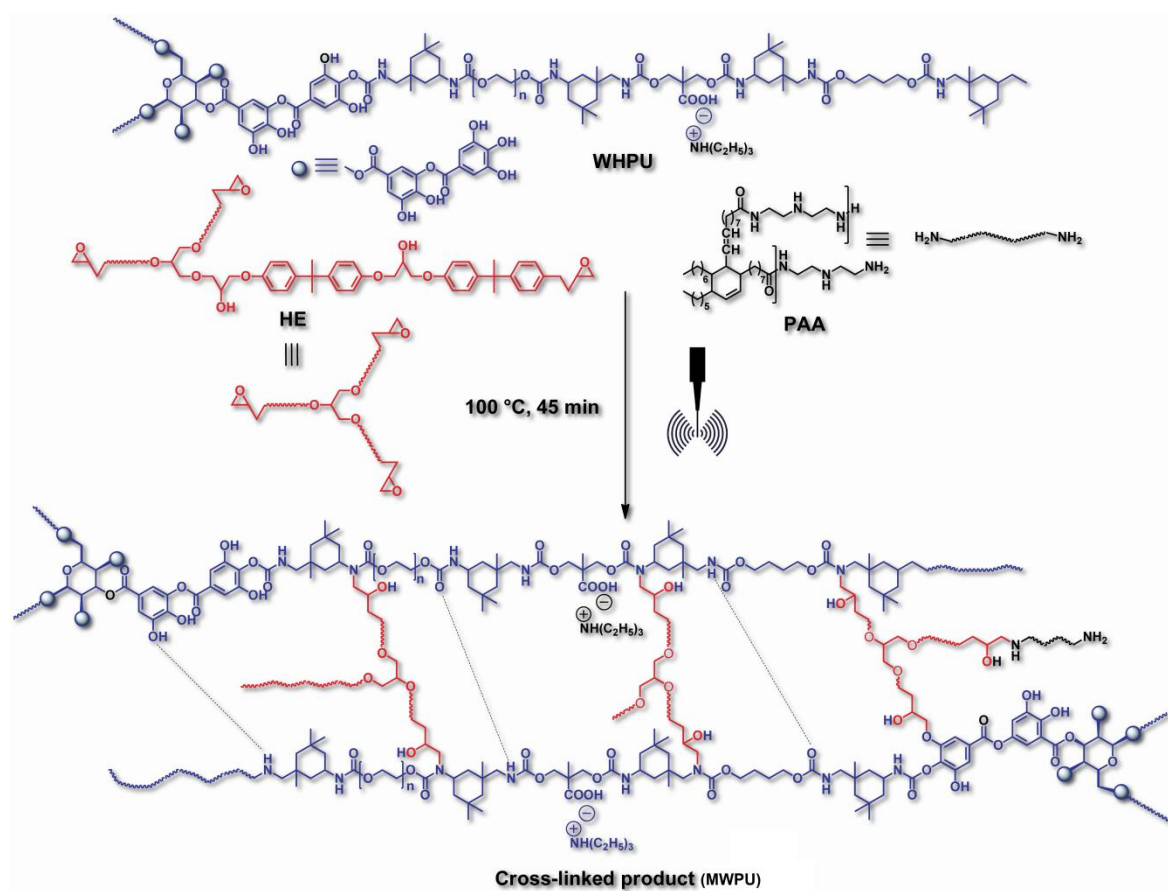
3.3.1. Modification of WHPU

The modified WHPU system, i.e. MWPU is expected to have significantly improved properties compared to the unmodified system. The extent of improvement depends on the nature and extent of cross-linking in the resultant system. Hence, for such modified system, introduction of high level of cross-linking is desirable in order to manipulate different material properties. To achieve such highly cross-linked, compatible and single phase modified system, physical and chemical properties of the modifier and host polymer should be alike.⁵ Further, both the systems must contain suitable chemical functionalities, which can serve as the active sites for cross-linking reactions to occur. In this context, use of HE/PAA system as a modifier for WHPU based material is found attractive. Epoxy based resin contains a large number of strained oxirane rings. These rings are extremely reactive towards nucleophilic attack and readily undergo ring opening reaction with amine and hydroxyl groups as shown in **Scheme 3.1**.^{26,27} WHPU system contains various nucleophilic groups within its structure, such as -N-H functionality of carbamate linkage, free -O-H groups of TA etc. Therefore, in a combined system of WHPU, HE and PAA, extensive cross-



Scheme 3.1. Plausible reactions of cross-linking among WHPU, HE and PAA.

linking reactions occur between the epoxy/hydroxyl groups of epoxy and hydroxyl/urethane groups of WHPU resulting in the formation of a highly cross-linked three-dimensional network structure as shown in **Scheme 3.2**. Further, in such modification process, architectural features of polymers played a significant role. Generally, hyperbranched structure possesses low viscosity and facilitates molecular motion, which can act as a driving force for cross-linking reaction to occur with ease. Oh *et al.* verified superiority of HE as a modifier over its linear analog in their study.²⁴ Different secondary forces, such as polar-polar interaction, H-bonding, π - π stacking etc. also contributed significantly towards the formation of a highly compatible and closely packed structure. On the other hand, from chemical kinetics point of view, such modification can be considered as an auto-catalytic process as mentioned in Sub-Chapter 2A (Section 2A.3.4.2.).^{28,29} The -O-H groups formed initially can further participate in the cross-linking reaction and thereby enhanced the reaction rate (reaction (b) in **Scheme 3.1**). With increase amount of HE/PAA,



Scheme 3.2. Schematic presentation of modified WHPU.

extent of cross-linking also increased. This is reflected by a decrease in the touch free time (it is the minimum time required by a coating surface to resist thumb impression on touching) and drying time (it is measured by indenting the cured film by an indenter) with an increase in the amount of HE and PAA (**Table 3.2**). Swelling study of the modified system also confirmed this fact, as these values also followed a decreasing trend with the increase amount of modifier in the system. It can be attributed to the increase in number of epoxy functionalities in the system with increase amount of modifier, which initiates more cross-linking reactions to occur according to the mechanism shown in **Scheme 3.1**.

Table 3.2. Curing parameters of MWPU

Composition	Touch free time (min)	Drying time (min)	Swelling (%)
MWPU10	30	37	23
MWPU20	25	35	22
MWPU30	20	30	19

3.3.2. FTIR spectroscopic study

FTIR spectroscopy was used as the tool to identify the nature of the functional groups present in MWPU as well as to detect the functional changes that had occurred during the modification process (**Figure 3.1**). Characteristic bands for urethane, i.e. -N-H stretching (amide-A) and -C=O stretching (amide-I) frequencies were assigned at 3300-3400 cm^{-1} and 1725-1750 cm^{-1} , respectively. Stretching frequency for aromatic double bond was observed at 1604 cm^{-1} . On the other hand, the characteristic frequency of the epoxy group appeared at 916 cm^{-1} for the HE/PAA modified WHPU before curing, whereas the same was missing after cross-linking. This confirmed the participation of epoxy groups in the cross-linking process. Further, a shift of the FTIR bands towards lower wavenumber was observed in the amide-A and amide-I regions with the increasing amount of HE/PAA in the polymer. This indicates the involvement of H-bonding between free -O-H groups originated by the opening of oxirane and -N-H and -C=O functionalities of carbamate. There would be more -O-H groups in the polymer matrix with increasing HE/PAA content, which

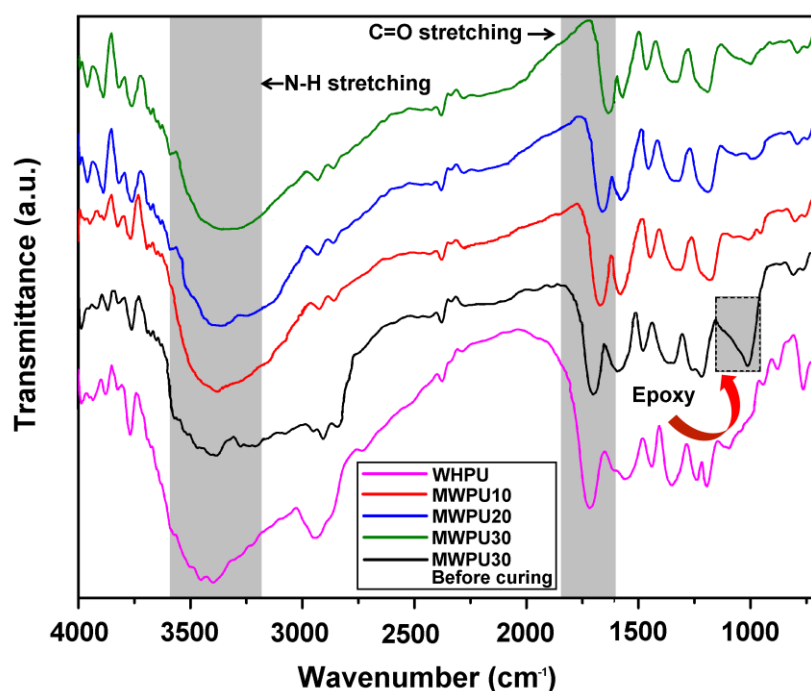


Figure 3.1. FTIR spectra of WHPU and MWPU.

further enhanced the extent of H-bonding. Thus, a dose dependent shift in the FTIR spectra was observed in the mentioned regions. FTIR spectroscopy thus confirmed the modification of WHPU system by HE/PAA system.

3.3.3. Mechanical properties

For polymeric materials, mechanical properties are very important for their various applications. Generally, WPU suffers from inferior mechanical properties. It is because of the presence of hydrophilic groups in the polymer chains, which causes the hygroscopic nature of the dried films, resulting in poor mechanical performance. However, we have found improved mechanical properties of WHPU system after modification with HE/PAA system. The stress-strain profiles of MWPU are shown in **Figure 3.2**. The data presented in **Table 3.3** show that most of the mechanical parameters such as tensile strength, toughness, scratch resistance and impact resistance were enhanced after modification. Further, a dose dependent enhancement in performance was achieved, as these properties increased with increase amount of HE/PAA in the system. Similar trend of improvement of mechanical performance was previously observed by Kalita and Karak during the

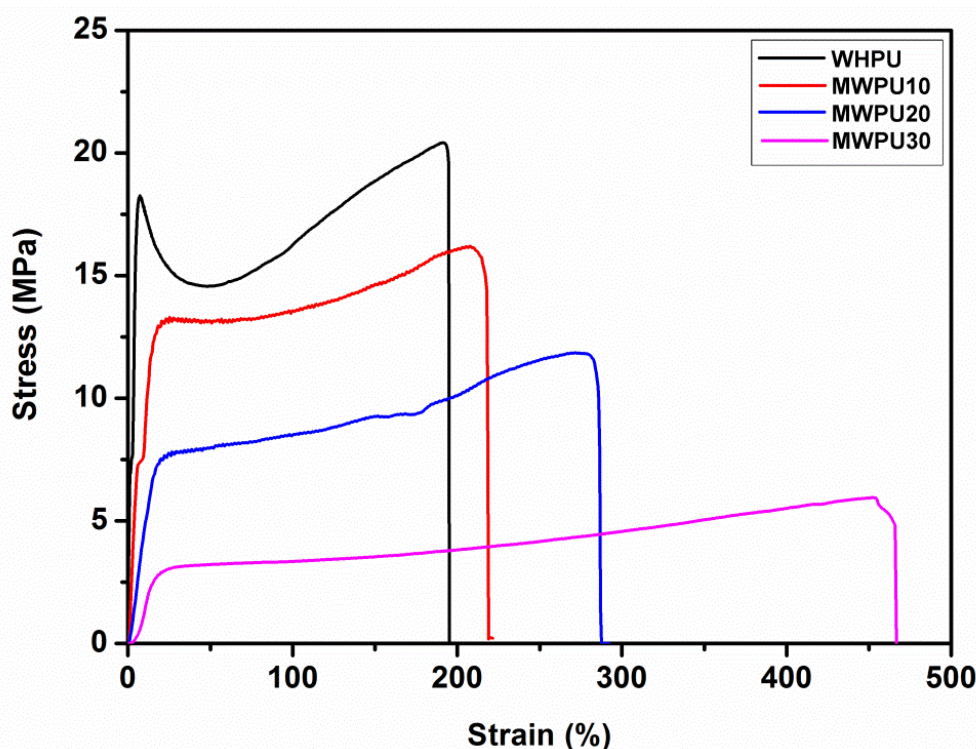


Figure 3.2. Stress-strain profiles of MWPU.

modification of *Mesua ferrea* L. seed oil based PU by using bisphenol A based linear diglycidyl ether epoxy resin and cycloaliphatic amine.⁸ Generally, mechanical properties of such modified material depend on several factors such as cross-linking density, nature of the reactants and modifier used, composition, intensity of secondary interactions that exist within the polymer network etc.³⁰ In the present modification, cross-linking density played a vital role towards the enhancement of mechanical properties. As discussed in the previous section (Section 3.2.1.), HE/PAA system is highly capable of inducing a chemically cross-linked structure. Formation of such new covalent linkages which connected various branches of WHPU imparted high degree of concreteness to the polymer matrix. This ultimately results in high performance by the modified system. Blank and Tramntano established such favorable effect of cross-linking on mechanical properties of a water dispersible PU.³ In addition to the cross-linking density, presence of aromatic moieties also contributed towards high performance of MWPU. HE contains aromatic rings (due to the presence of Bisphenol A) which provided a structural stiffness and thus helped to bring strength to the polymer. However, values of elongation at break were found to

Table 3.3. Mechanical properties of MWPU

Property*	WHPU#	MWPU10	MWPU20	MWPU30
TS (MPa)	6.0±0.2	11.8±0.6	17.0±0.5	20.4±0.3
E@B (%)	457±3	292±1	220±2	195 ± 1
Toughness [§] (MPa)	19.36	25.2	28.74	32.43
SH [†] (kg)	5.0±0.2	7.5±0.2	9.0±0.2	10 ± 0.3
IR [‡] (kJ m ⁻¹)	6.64±0.13	7.47±0.15	8.25±0.12	>8.30
Bending [¶] (m)	<0.001	0.002	0.002	0.003
Gloss (@ 60°)	94.5±0.8	95.0±0.5	95.2±0.3	98.1 ± 0.3

*Mechanical Properties: TS=Tensile strength, E@B=Elongation at break, SH=Scratch hardness, IR=Impact resistance; [§]Calculated by integrating the area under stress-strain curve; [†]Limit of scratch hardness tester was 10 kg (maximum); [‡]Limit of impact tester was 8.30 kJ m⁻¹ (maximum) for film of thickness 1mm; [¶]Limit of the mandrel diameter was 1 mm (minimum), #Data reproduced from Sub-Chapter 2B for comparison.

follow a decreasing trend after the modification. This is due to the increase in rigidity and decrease in chain mobility of the structure. Despite of the fact, elongation and bending values recorded were good enough for various utilization of MWPU as shown in **Table 3.3**. Further, the bending test confirmed the retention of sufficient flexibility even after the formation of the modified system. Retention of good flexibility and elongation is partly due to the presence of PAA and PEG 600 as the long segments, which helped in the entanglement of polymeric chains. On the other hand, increase in toughness of MWPU indicates overall gain in mechanical performance. Toughness is a measure of stress and flexibility of the system together. Thus, increase in toughness indicates that extent of gain in tensile strength is greater than that of loss in elongation due to the modification. The secondary interactions, like π - π stacking, polar-polar interactions and H-bonding also played a significant role towards an improved performance of the modified systems. Thus, the overall effect of high cross-linking density, presence of aromatic moieties and long chain segments, presence of strong secondary interactions as well as homogeneous distribution of the cross-linker contributed towards the improved mechanical properties of the modified system. Gloss values were found better for MWPU than WHPU. This is due to the formation of dimensionally stable surface with better water repellency.

3.3.4. Thermal

The thermal decomposition profiles show improved thermal stability of the polymer after modification (**Figure 3.3a**). The unmodified polymer exhibited a two-step thermal degradation pattern. The first step of the degradation (in the temperature range of 190-220 °C) primarily represents degradation of urethane bonds, ester groups along with other thermo-labile aliphatic moieties present in the matrix, whereas the second step (in the temperature range 240-300 °C) is attributed to the degradation of aromatic moieties belonging to TA as discussed in Sub-Chapter 2B (Section 2B.3.4.). However, MWPU seemed to follow an almost one-step degradation pattern with enhanced thermo-stability. This is due to the structural integrity of MWPU achieved by the modification process. The increment in thermo-stability was consistent with the amount of HE/PAA used in the modification reaction. The enhanced thermal properties of MWPU can be explained considering three factors, *viz.* cross-linking density, presence of thermo-stable moiety and availability of free volume in the system.^{30,31} Cross-linking density has a marked influence on the thermal degradation process. In a highly cross-linked network structure, molecular chain excitation and motion generated during exposure to thermal energy are prohibited significantly. This makes the thermal degradation process energy consuming. High cross-linking density also effectively reduces the free space available within a macromolecular structure. Similarly, introduction of thermo-stable moiety to a polymer can enhance its thermal stability. In this milieu, aromatic ring

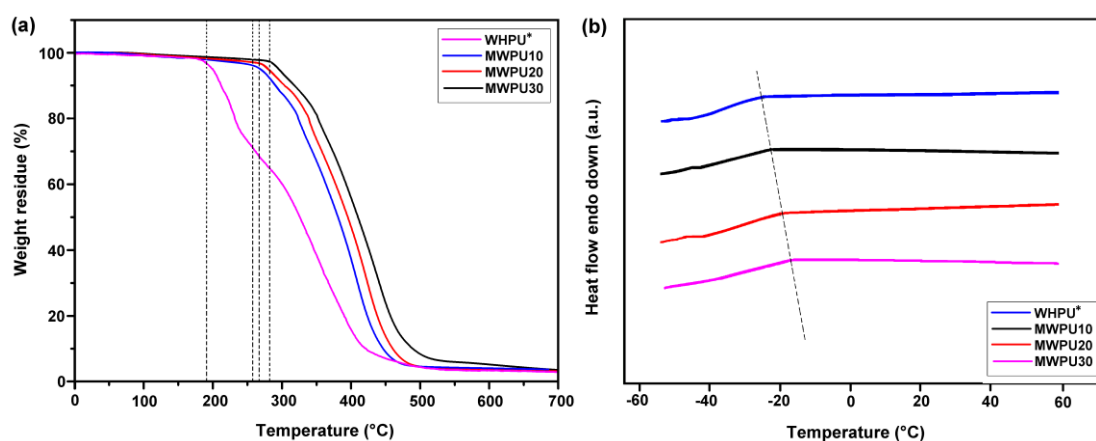


Figure 3.3. (a) TG thermograms of MWPU and (b) DSC curves (cooling) showing T_g of MWPU. *Data reproduced from Sub-Chapter 2B for comparison.

is known as highly thermo-resistance entity with a high stabilizing effect against thermal degradation. We have seen that introduction of HE/PAA system can favor all these factors positively, which results in superior thermal properties of MWPU compared to the neat polymer system. Secondary interactions like H-bonding, polar-polar interactions and π - π stacking also played a vital role towards the enhanced thermal properties of MWPU. On the other hand, DSC study shows the increase in T_g with increase amount of modifier in MWPU (**Figure 3.3b**). It is again due to the enhanced rigidity and molecular chain restriction of the modified polymer arising from different interactions as described above. All the modified systems possessed single T_g , which suggests a highly compatible and single phase cross-linked system. Similar kind of thermal behavior was also achieved by Deka and Karak during the modification of a bio-based hyperbranched PU system with bisphenol A based epoxy and PAA.⁹

3.3.5. Chemical resistance

Chemical resistance of WHPU was poor. Because, this is a thermoplastic with large number of hydrophilic ionic groups, which can be easily hydrolyzed. Moreover, it contains hydrolysable ester linkages due to the use of TA as polyol in the synthetic process. This further reduced the resistance of WHPU towards different chemical environments including water. Hence, it is very much desirable to improve this inferiority of WHPU. This can be achieved by chemical cross-linking of WHPU. Blank and Tramontano showed that cross-linking modification of water dispersible PU leads to superior chemical resistance.³ They used an amino formaldehyde resin as modifier. Chemical resistance of modified and unmodified WHPU towards different chemical environments was tested, which include 10% (v/v) C_2H_5OH , 5% (w/v) NaOH, 10% (w/v) NaCl, 5% (v/v) HCl and distilled water. Results for chemical resistance are included in **Table 3.4**. It was found that all the modified polymers have better resistance towards the experimental chemical environments compared to the unmodified version. However, resistance was comparatively poor in alkali medium. It might be due to the presence of TA with hydrolysable ester linkages in the polymer matrix. On the other hand, in aqueous medium, resistance was significantly improved. Good chemical resistance of the modified polymers can be attributed to the high cross-linking density, presence of aromatic moiety, compact structure and

presence of strong secondary interactions like H-bonding and polar-polar interactions as discussed in the above subsections (Section 3.2.1 and 3.2.3).

Table 3.4. Chemical resistance (in terms of % weight loss) of MWPU

Chemical environment	Weight loss (%)			
	WHPU	MWPU10	MWPU20	MWPU30
5% (w/v) NaOH	7.59	2.01	1.67	1.55
10% (v/v) C ₂ H ₅ OH	5.98	0.85	0.65	0.35
5% (v/v) HCl	6.78	1.01	0.78	0.69
10% (w/v) NaCl	6.98	0.61	0.51	0.29
H ₂ O	5.67	0.57	0.35	0.22

3.3.6. Biodegradation

Biodegradation study of MWPU was carried out by exposing the polymer films with the bacterial strain of *P. aeruginosa* over a period of seven weeks. The objective of the study was to ensure biodegradability of the modified system. The weight loss profiles of the polymer films clearly reveal an adequate degradation by the test organism over the experimental period (**Figure 3.4a**). However, compared to the pristine system, weight loss percentage of the modified system was less. The chemical structure of WHPU is the key for the observed biodegradation as it contains large numbers of hydrolysable ester linkages.^{32,33} But, in a modified system, the degree of ester linkages is less compared to the neat system. Further, the high degree of cross-linking induced during the modification can also affect the hydrolysis process, making biodegradation slightly slower. Among different modified systems, MWPU10 recorded the maximum weight loss, while MWPU30 exhibited the minimum. It is because, MWPU10 contains the highest number of ester linkages among the tested compositions, while MWPU30 the least. The bacterial growth curves as depicted in **Figure 3.4b** also support the aforementioned observation. A linear increment of the bacterial population with time of incubation was found, which indicates susceptible polymer surface for bacterial growth. SEM images confirmed significant bacterial adherence as well as surface erosion after the experimental period (**Figure 3.5**).

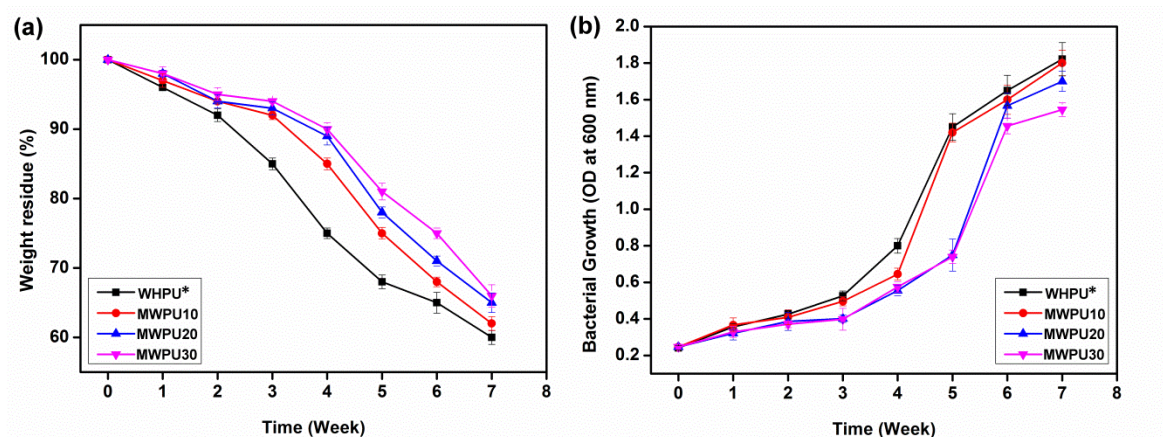


Figure 3.4. (a) Weight loss profiles of MWPU10, MWPU20, and MWPU30 due to bacterial degradation and (b) Bacteria growth curves of *P. aeruginosa* on MWPU10, MWPU20, and MWPU30. *Data reproduced from Sub-Chapter 2B for comparison.

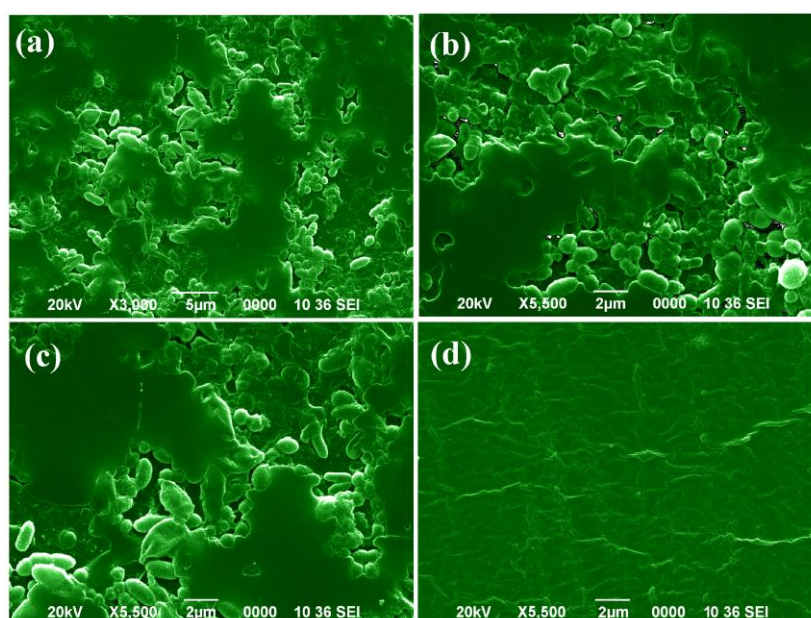


Figure 3.5. SEM images of biodegraded (a) MWPU10, (b) MWPU20 and (c) MWPU30; (d) Representative SEM image of MWPU30 before biodegradation.

Hence, no significant adverse effect of modification was witnessed on the inherent biodegradability of the original polymer system.

3.4. Conclusion

The study showed that bio-based hyperbranched epoxy along with vegetable oil based poly(amido amine) can be effectively used for the modification of bio-based waterborne hyperbranched polyurethane system by using ultra-sonication and heat

energy. Different material properties like mechanical, thermal and chemical including hydrophobicity were significantly enhanced by the modification. Such modification can lift the developed waterborne hyperbranched polyurethane as a high performance, eco-friendly polymeric material for many advanced applications. Further, use of bio-based modifier such as glycerol based hyperbranched epoxy and vegetable oil based poly(amido amine) adds eco-friendly behavior to the overall process with high degree of sustainability. Retention of biodegradability at an adequate rate further ensures its acceptability as a bio-disposable material. Thus, this modified system can be considered as a suitable candidate for the development of high performing polyurethane nanocomposites for modern day applications.

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