

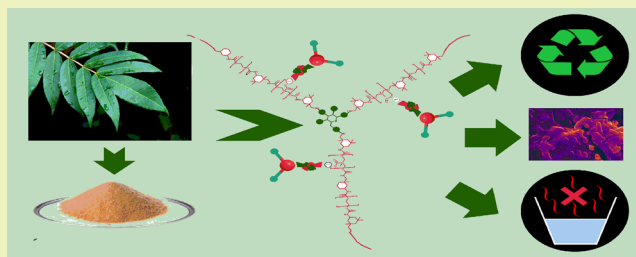
Biobased Biodegradable Waterborne Hyperbranched Polyurethane as an Ecofriendly Sustainable Material

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ABSTRACT: Research thrust to address the problems confronting the use of conventional polymers like high volatile organic compound (VOC) content still remains a challenge. In this context, the authors report the synthesis of a sustainable and biodegradable waterborne hyperbranched polyurethane (WHPU) using polyphenolic tannic acid in lieu of vegetable oil as the biobased component. The chemical structure of WHPU was characterized by nuclear magnetic resonance and Fourier transform infrared spectroscopy. An UV–visible peak at the wavelength of 282 nm confirmed the presence of catechol moiety in WHPU. WHPU exhibited pronounced thermostability and desirable performance (tensile strength, 6.87 MPa; elongation at break, 315%; scratch hardness, 5.5 kg for 15 wt % tannic acid based WHPU). The radical scavenging and hemolytic assays of WHPU showed their potent antioxidant activity and cytocompatibility with the erythrocytes, respectively. Furthermore, WHPU exhibited bacterial degradation by *Pseudomonas aeruginosa*. Thus, the above results forward the synthesized WHPU as a potent ecofriendly and sustainable polymeric material by a simple approach that possesses a higher degree of sustainability over a purely petrochemical route.

KEYWORDS: Tannic acid, sustainable polymer, low VOC polyurethane, bacterial degradation, antioxidant



INTRODUCTION

Since its inception, polyurethane has emerged as the material of interest in colossal domains owing to its versatile properties.^{1,2} However, the growing consciousness regarding environmental issues has created serious concerns with respect to the use of conventional solvent borne polyurethanes, particularly due to high volatile organic compound (VOC) content.^{3–5} The processing and application of solvent borne polyurethanes involve evaporation of organic solvents, which adds to VOC content in the atmosphere. Thus, different environment protection agencies have taken serious steps to reduce VOC emission from the industrial sector and issued guidelines to combat the same.⁶ Under such circumstances, a paradigm shift in research has been observed in the develop ecofriendly polymeric materials. As a result of such efforts, waterborne polyurethane (WPU) has emerged out as one of the greener alternatives.⁷ WPU supersedes their solvent borne counterparts in terms of nontoxicity, nonflammability, and low or no content of organic solvent.^{8–11} Today, WPU has applications across the globe as a coating, adhesive, primer, paint additive, defoamer, associate thickener, pigment paste, biomaterial, etc.^{12–14}

On the other hand, the global concern with respect to the dwindling petro-based resources and research according to tenets of green chemistry has instigated the utility of sustainable feedstock in the synthesis of industrially important polymers. Literature reports the use of various biobased raw materials including vegetable oils for the synthesis of WPU.^{15–19} Madbouly et al. used castor oil for the synthesis of aqueous

polyurethane dispersion.⁴ Lu and Lorock synthesized WPU from soybean oil.⁵ However, in such cases, oil needs to be transferred to the desired polyols, which increases the cost of the product. In this context, inexpensive, readily available biobased polyols may prove to be potent candidates for polyurethane synthesis. Thus, the present study intends to explore the potentiality of tannic acid, a readily abundant, low cost polyphenolic compound, as a bioderived raw material. The industrial viability of tannic acid has already been established in pharmaceutical and food industries and as a rust converter and mordant for dyeing.^{20–22}

Further, literature cites use of hyperbranched polyester polyols for the synthesis of waterborne hyperbranched polyurethane (WHPU), a novel class of macromolecules with unique physical and chemical properties.^{23–25} In this regard, the structure of tannic acid is interesting because of its architectural similarity with hyperbranched polyester polyols. Moreover, criteria of sustainability include environmental and health safety issues.^{26,27} In this context, designing of tannic acid based hyperbranched polyurethane seems to be an interesting proposition because of significant bioactivity and biocompatibility.²⁸ Tannic acid can also act as a redox active material. Therefore, the potential interactions of tannic acid based WPU

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with biological systems need to be carefully examined to develop it as a safe and sustainable material.

The present study henceforth emphasizes the development of WHPU using tannic acid as a branch generating moiety, which is the first attempt in the field as per the author's knowledge. The study also made an effort to evaluate the hemocompatibility, radical scavenging activity, and biodegradability in order to highlight its potential as a safe and sustainable material.

EXPERIMENTAL SECTION

Materials. Isophorone diisocyanate (IPDI, Aldrich, Germany) and triethylamine (TEA, Merck, India) were used as received. Poly(ethylene glycol) with $M_n = 600$ (PEG-600, Merck, India); butane diol (BD, Merck, India), and tannic acid (TA, Sigma-Aldrich, Belgium) were dried in a vacuum oven at 55 °C prior to use. 2,2-Bis(hydroxymethyl)propionic acid (BMPA, Aldrich, Germany) was recrystallized from ethanol and dried before used. Tetrahydrofuran (THF, Merck, India) was distilled and stored in 4A molecular sieves for further use. Other chemicals like 1,1-diphenyl-2-picrylhydrazyl (DPPH), trichloroacetic acid and ferric chloride were purchased from Himedia, India and used as received. The bacterial strain of *Pseudomonas aeruginosa* (*P. aeruginosa*, MTCC 7814) was collected from the Department of Molecular Biology and Biotechnology, Tezpur University.

Synthesis of WHPU. WHPU was synthesized by a prepolymerization technique. Required amounts of IPDI, PEG-600, and BMPA (NCO/OH = 1.5) were taken in a four-necked round-bottomed flask equipped with a condenser, a nitrogen inlet, a thermometer, and a mechanical stirrer. The reaction was carried out at 80–90 °C for 2 h in nitrogen atmosphere with constant mechanical agitation. In the second step, BD and TA in THF were introduced to the reaction mixture at 25 °C, so that overall functional ratio of –NCO to –OH becomes 1 (considering three –OH groups of tannic acid participate in the reaction). Then the temperature was maintained at 65–70 °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 45 min. This was followed by slow addition of water to the reaction mixture with vigorous stirring for another 30 min. Then, THF was removed under reduced pressure in order to get the polymer in water. Three different compositions viz. WHPU05, WHPU10 and WHPU15 were prepared taking different weight percentages of TA (Table 1). Furthermore, control polyurethane

Table 1. Composition of the Reactants for the Synthesized Polyurethanes

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	0.60	0.54	0.50
TA (mol)	0	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

(WPU0) without TA was also synthesized following the same method, except only BD was added in the second step in place of mixture of TA and BD. The synthesized polymers were cast on glass and a galvanized tin sheet to obtain a film thickness of 1–2 mm.

Characterization. Fourier transform infrared (FTIR) spectra were recorded on Nicolet (Madison, USA) FTIR Impact 410 spectrometer in absorbance mode using KBr pellets. The ^1H NMR spectrum was recorded on a 400 MHz FT NMR (Jeol, Japan) at 25 °C using trimethyl silane as the internal standard and D_2O as the solvent. UV spectra were recorded at room temperature (25 °C) using a Hitachi spectrophotometer (U2001, Tokyo, Japan). Thermal properties were

evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) study. Thermogravimetric study was carried out by using a PerkinElmer 4000 thermal instrument in the temperature range 25–700 °C, at a scanning rate of 10 °C/min, maintaining an inert atmosphere of nitrogen at a gas flow rate of 30 mL/min. The differential scanning calorimetry study was done by a PerkinElmer DSC 6000, USA instrument in the temperature range –70 to +120 °C (starting temperature = 0 °C) following a cycle of heating–cooling–heating under an atmosphere of nitrogen and at a scanning rate of 5 °C/min. Mechanical properties, such as tensile strength and elongation at break were measured by a Universal Testing Machine (UTM, Zwick Z010, Germany) equipped with a 5 kN load cell operated at a crosshead speed of 50 mm/min. Samples with dimensions 10 × 1 × 0.02 cm were used for the same. The scratch hardness of the polymeric films was measured by using a scratch hardness tester, Model No.705 (Sheen instrument limited, UK) with a stylus accessory at a travel speed of 30–40 mm/s. An Ubbelohde viscometer was used to determine the intrinsic viscosity of the synthesized polymers. Molecular weight of the polymer was determined by gel permeation chromatography (GPC, Waters, UK). On the other hand, images of the biodegraded polymer films were obtained by scanning electron microscopy (SEM, model JSM-6390LV (JEOL)), after platinum coating on the surface.

Radical Scavenging Assay. For DPPH radical scavenging assay, 1 mL of 0.1 M DPPH (in 50% ethanol solution) was mixed with 1 mL of polymer solution (0.2–2.0 mg/mL in double distilled water). The reaction mixture was vortexed and incubated at room temperature for 20 min under dark conditions. Then the absorbance was measured at 517 nm.²⁹ The scavenging activity was measured by using the following formula

$$\text{scavenging effect (\%)} = \left[1 - \frac{A_{S-517}}{A_{C-517}} \right] \times 100$$

where A_{S-517} is the absorbance of the samples and A_{C-517} is the absorbance of the control.

For hydroxyl radical scavenging assay, 1 mL of polymeric solution (0.2–2.0 mg/mL in double distilled water) was mixed with 2.4 mL of 0.1 M phosphate buffer (pH 7.4) and 0.6 mL of 0.4 M H_2O_2 solution. The mixture was vortexed and incubated for 10 min at room temperature. The absorbance was measured at 230 nm.²⁹ The scavenging ability for hydroxyl radicals was calculated by using the following formula

$$\text{scavenging effect (\%)} = \left[1 - \frac{A_{S-230}}{A_{C-230}} \right] \times 100$$

where A_{S-230} is the absorbance of samples and A_{C-230} is the absorbance of the control.

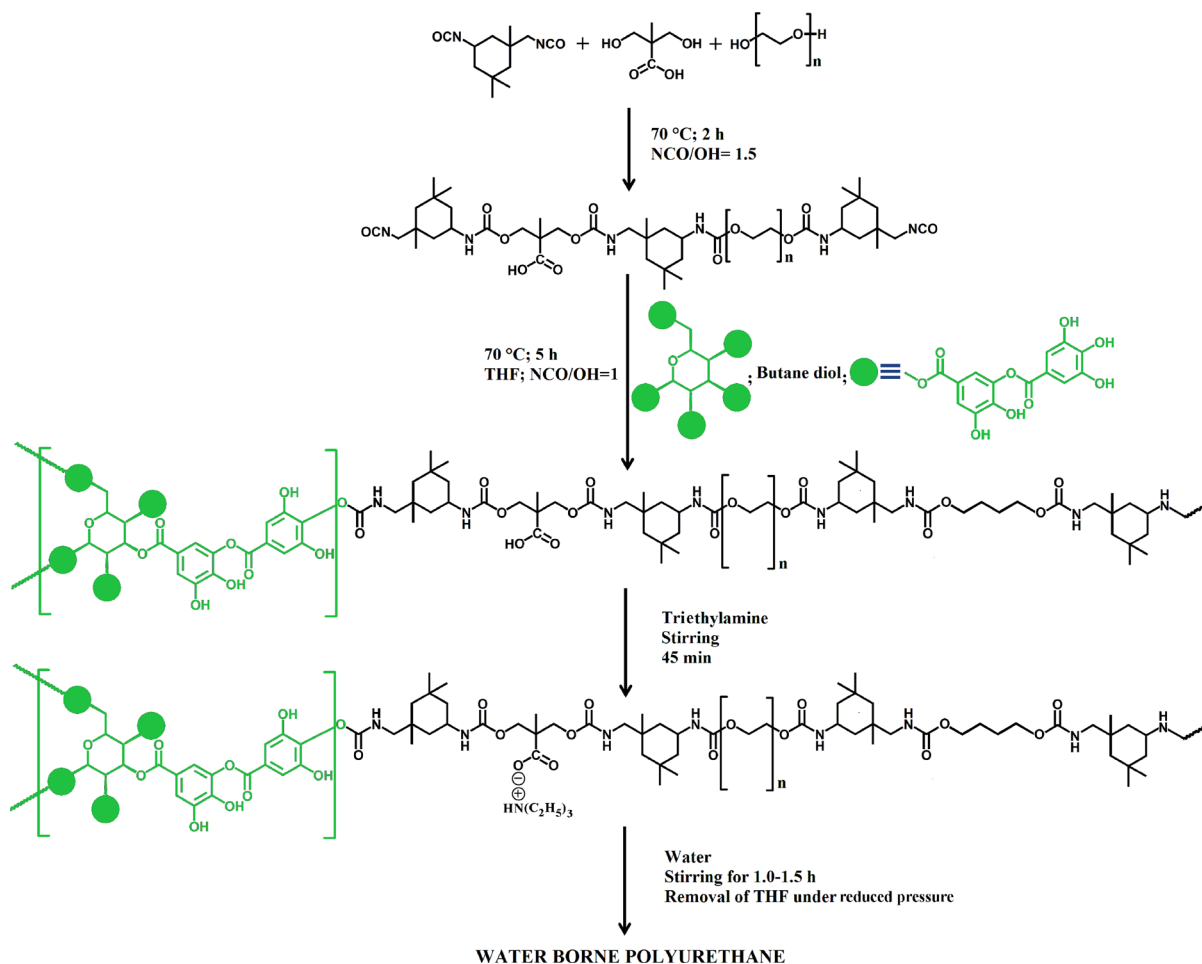
The reduction potential of WHPU was determined by mixing 1 mL of polymer solution (0.2–2.0 mg/mL in double distilled water) with 1 mL of 0.2 M phosphate buffer (pH 6.6), 0.5 mL of 1% (w/v) potassium ferricyanide. The mixture was incubated at 50 °C in a water bath for 20 min. Then it was cooled, followed by addition of 1 mL of 10% (w/v) trichloroacetic acid and 0.2 mL of 0.1% (w/v) freshly prepared ferric chloride solution. The resulting solution was shaken well and the absorbance was measured at 700 nm.²⁹ The reducing power was calculated by using the following formula

$$\text{reducing power} = A_{S-700} - A_{C-700}$$

where A_{S-700} is the absorbance of the sample and A_{C-700} is the absorbance of the control with replacement of FeCl_3 by water. For all the experiments, ascorbic acid (As) was taken as the standard to compare the radical scavenging activity of WHPU compositions.

Hemolytic Assay. To get preliminary knowledge about the cytocompatibility of WHPU, hemolytic assay was performed. The idea was to investigate lysis of the 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 g). The erythrocytes were washed thrice with phosphate buffer

Scheme 1. Synthesis of WHPU



saline. Then 5% hematocrit was obtained by resuspending the packed erythrocytes in PBS (10 mM at pH of 7.4). Samples with varying concentrations viz. 0.25, 0.50, 0.75, 1.00, and 5.00 mg mL⁻¹ were prepared. Then 100 mL of each sample was taken in a microfuge tube along with 1900 mL of the hematocrit and the solutions were incubated at 37 °C for 30 min. After completion of the incubation period, cells were placed in ice bath for 1 min followed by centrifugation at 3000 rpm (503 g) for 5 min. Then hemoglobin concentration was determined by the help of UV absorbance at 540 nm as a measure of hemolysis.³⁰ The experiment was performed in triplicate and analyzed by one way ANOVA.

Biodegradation Study. Biodegradation study was done by McFarland turbidity method using *P. aeruginosa* as the bacterial strain.^{31,32} A medium of mineral salts containing 2.0 g of (NH₄)₂SO₄, 2.0 g of Na₂HPO₄, 4.75 g of KH₂PO₄, 1.2 g of MgSO₄·7H₂O, 0.5 mg of CaCl₂·2H₂O, 100 mg of MnSO₄·5H₂O, 70 mg of ZnSO₄·7H₂O, 10 mg of H₃BO₃·5H₂O, 100 mg of CuSO₄·7H₂O, 1 mg of FeSO₄·7H₂O, and 10 mg of MoO₃, all in 1.0 L of demineralised water, was prepared. It was sterilized for 15 min at 120 °C under a pressure of 15 lb and then allowed to cool to room temperature. Bacterial strain of *P. aeruginosa* was cultured in the medium inside an incubator shaker at 37 °C for 48 h. 100 μL (10⁸ microbes/mL, as calculated by McFarland turbidity method) of the cultured medium was taken in a conical flask containing 10 mL of the prepared salt medium. The polymeric films were sterilized by exposing them to UV light of wavelength 254 nm. The sterilized films were incubated inside the medium under sterile condition at 37 °C. Medium without polymeric films was used as the negative control. The increase in turbidity of the medium with time indicates bacterial growth. The optical density (OD) of the microorganism was monitored by measuring the absorbance of the medium at 600 nm with respect to the control. The experiment was

conducted in triplicate for an experimental period of 6 weeks. FTIR analysis of the degraded films was also conducted to study the functional changes occurred due to bacterial degradation.

RESULTS AND DISCUSSION

Synthesis. Synthesis of WHPU involves use of low reactive aliphatic diisocyanate, a diol or diamine chain extender and a component with ionogenic center. In the present work, IPDI was used as the diisocyanate, PEG-600 and BD were used as the diol, and BMPA was used as the ion generating moiety. The literature demonstrates the use of hyperbranched polyester polyols for the synthesis of WHPU. The current work used TA as a bio-based raw material for the same. TA is structurally very much similar to a hyperbranched polyester, with five branches generating from a pyranose heterocycle, 25 hydroxyl groups, and 10 ester linkages. Hence, the present synthesis tried to utilize TA instead of a synthetic polyester polyol to construct hyperbranched structure. In practice, all 25 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 prepolymer chains. Moreover, substitution of one hydroxyl group by a prepolymer chain frequently reduces the reactivity of others, present in the system. Hence, TA was used in a calculated amount that ensures participation of at least three hydroxyl groups in the urethane reaction. In relation to the solubility parameter, the unreacted and free -OH groups are crucial as they can enter into secondary interactions like hydrogen bonding with polar solvents causing enhanced

solubility of the polymer. Further, in the first step of the synthesis, mainly $-\text{NCO}_{\text{secondary}}$ is expected to react, since in absence of catalyst $-\text{NCO}_{\text{secondary}}$ is known to have preferred selectivity toward urethane reaction (Scheme 1).³³ A maximum of 15 wt % of TA was used, as exceeding this amount can lead to an uncontrolled reaction and may cause gelation. Weight-average (M_w) and number-average (M_n) molecular weight; polydispersity index (PDI) and solution viscosity of synthesized polymers are given in Table 2. Weight-average molecular

Table 2. Weight Average (M_w), Number Average (M_n) Molecular Weight; Polydispersity Index (PDI) and Solution Viscosity of WHPUs

parameter	WHPU05	WHPU10	WHPU15
M_w (g/mol)	22600	23300	25700
M_n (g/mol)	16200	18900	21700
PDI	1.39	1.23	1.34
solution viscosity (dL/g)	0.365	0.298	0.274

weight was obtained in the range of 22 600 to 25 700 with molecular distribution between 1.23 and 1.39 using THF as the solvent. The molecular weight was found to follow an increase in trend with the tannic acid content of the polymer.

FTIR Study. FTIR spectroscopy was used to confirm the variety of chemical functionalities present in the polymer matrix (Figure 1). Further, evidence of hydrogen bonding was also

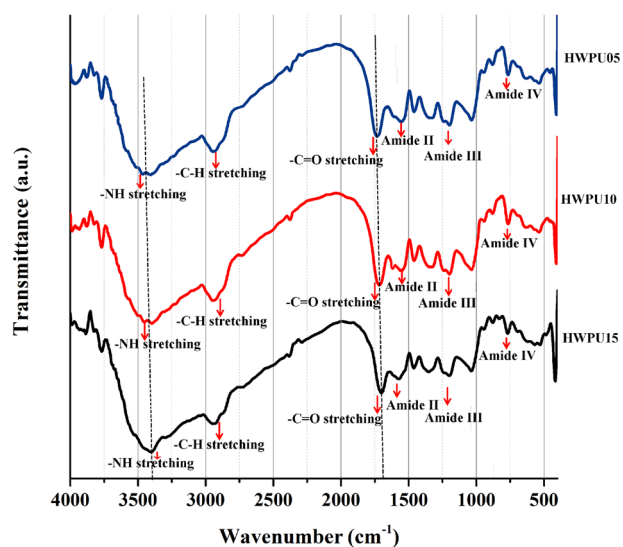


Figure 1. FTIR spectra of WHPU05, WHPU10, and WHPU15.

gathered by following the change in frequency and intensity of the peaks in the mid-IR spectral region.³¹ For the studied systems, the absorption band near $1720\text{--}1730\text{ cm}^{-1}$ can be attributed to $-\text{C}=\text{O}$ stretching frequency (contribution from both amide I and ester linkages). Further, the $-\text{N}-\text{H}$ stretching and $-\text{N}-\text{H}$ bending (amide II) frequencies were observed at 3410 and 1580 cm^{-1} , respectively. The absorption peak for $\text{C}=\text{C}$ bond was near 1600 cm^{-1} . Similarly, amide III, which is mainly due to in-phase combination of $\text{N}-\text{H}$ in plane bending and $\text{C}-\text{N}$ stretching vibration occurred near $1230\text{--}1236\text{ cm}^{-1}$. Amide IV and amide V bands were observed at frequencies of $773\text{--}776$ and $631\text{--}635\text{ cm}^{-1}$, respectively. On the other hand, a shift of IR band toward lower wavenumber was witnessed in the amide I and $\text{N}-\text{H}$ stretching region with

increase of TA content in the polymer. This indicates involvement of hydrogen bonding between phenolic $-\text{OH}$ from TA and urethane $-\text{NH}$ and $-\text{C}=\text{O}$ groups. With increasing TA content, there will be more $-\text{OH}$ groups in the polymer matrix by which the extent of hydrogen bonding gets strengthened.

^1H NMR Study. The interpretation of ^1H NMR spectrum of the synthesized WHPU is difficult, as IPDI is composed of two isomeric forms (Z and E) and two isocyanate groups ($-\text{NCO}_{\text{primary}}$ and $-\text{NCO}_{\text{secondary}}$) that exhibit variable selectivity toward urethane reaction under different conditions.³³ Though, ^1H NMR data depicted in Figure 2 furnish valuable evidence in favor of the synthesized polymer. It is well understood from the mechanism of urethane reaction that in absence of any catalyst, $-\text{NCO}_{\text{secondary}}$ of IPDI has preferred selectivity toward urethane reaction. Hence, in the first step of synthesis, mostly $-\text{NCO}_{\text{secondary}}$ is expected to react with $-\text{OH}$ functionality. The $-\text{NH}$ urethane peaks were observed at δ $7.8\text{--}8.0$ ppm, which confirmed the formation of two different urethanes viz. cis and trans. The appearance of surface functional phenolic protons ($\text{Ph}-\text{OH}$) was marked at δ $9.7\text{--}9.9$ ppm. Aromatic protons belonging to TA were observed at δ $7.0\text{--}7.2$ ppm. However, from the ^1H NMR spectrum, a quantitative calculation of degree of branching is difficult for IPDI/TA derived polyurethane, as the peaks of interest were very complex aggregates.

UV-Visible Spectroscopy. The catechol units of TA produce an absorbance peak near 280 nm , which can be used to detect and evaluate quantitative amount of TA present in the polymer. For the synthesized polymer, absorbance was observed near 282 nm in the UV-visible spectrum. The intensity of the peak for the catechol moiety increases with the increase of TA content, as depicted in Figure 3. This indicates the presence of more catechol units in the polymer with increase in wt % of TA.

Thermal Properties. Thermogravimetric analysis showed that WHPU exhibited a two-step thermal degradation pattern, as shown in Figure 4a. The first step (in the temperature range $250\text{--}260\text{ }^\circ\text{C}$) can be attributed to the degradation of thermolabile aliphatic moieties, urethane bonds, and ester groups, whereas the second step (in the temperature range $300\text{--}320\text{ }^\circ\text{C}$) 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 wt % of TA in the polymers. Further, weight residue left after degradation up to $700\text{ }^\circ\text{C}$ also increases with TA content. High thermostability of TA imparted by aromatic moieties, ester linkages, heterocyclic ring system, as well as enhanced secondary interactions like hydrogen bonding, contribute toward the thermal properties of WHPU. Better thermal behavior of WHPU compared to WPU0 further confirmed the fact. The glass transition temperature (T_g) measurement was made by using DSC at the heating rate of $5\text{ }^\circ\text{C}/\text{min}$ in a nitrogen atmosphere for the temperature range of -70 to $+200\text{ }^\circ\text{C}$. The DSC curves shown in Figure 4b indicate that T_g increases with increase in wt % of TA. This could be due to increase in inter- and intramolecular interactions in the structure.

Mechanical Properties. Mechanical properties were evaluated for the synthesized WHPUs. The different mechanical properties are documented in Table 3. The tensile strength and scratch hardness increase, and elongation at break

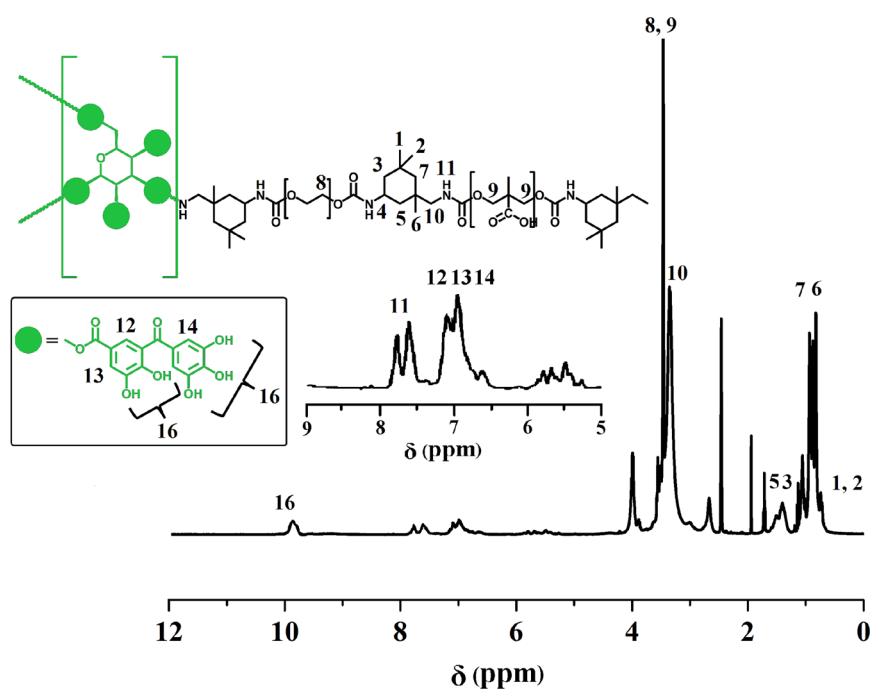


Figure 2. ^1H NMR spectrum of WHPU15.

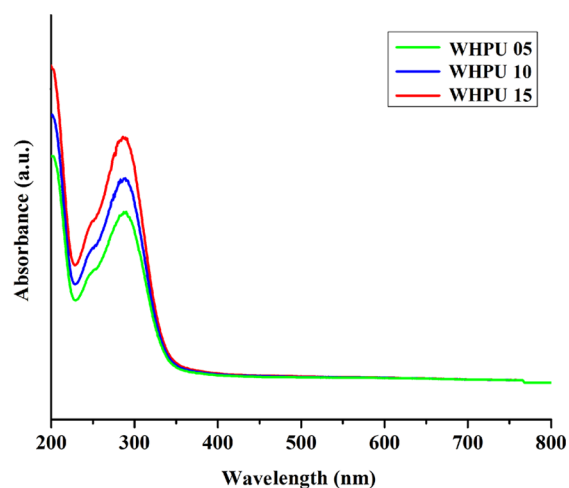


Figure 3. UV-visible spectra of WHPU05, WHPU10, and WHPU15.

decreases with increase in wt % of TA in WHPUs. Generally, mechanical properties depend on many factors viz. presence of polar groups within the polymeric chains, existence of inter and intramolecular interactions, entanglement of chains, compositions and nature of reactants, molecular weight, rigidity of the polymer, etc. Addition of TA can favor the above factors by virtue of its high molecular structure and rigidity. Moreover, different intermolecular interactions, e.g., polar–polar, hydrogen bonding between macromolecular chains get strengthened with the TA content. This results high strength of the polymer. However, TA content can affect the polymer chain flexibility due to molecular rigidity, which results in reduction of the elongation at the break values. However, all the polymers possess good bending and gloss values.

Radical Scavenging Assay. The antioxidant potency of a compound relies on its ability to donate labile electron to a radical. Radical scavenging assay of WHPU against DPPH and hydroxyl radical shows profound antioxidant activities (Figure

5a,b). It is obvious, because the polymer contains a large number of free catechol moieties. These catechol fractions can act as an electron donor that reacts with free radicals to convert them into more stable products with the termination of radical chain reactions. WHPU15 exhibits the best radical scavenging activity whereas WHPU05 shows the least. This is due to the greater tannic acid content of the former than the latter. The reducing power assay also reflects the overall antioxidant activity of a compound. It is based on reduction of Fe^{3+} to Fe^{2+} with change in color of the mixture from yellow to various shades of blue or green according to the reducing power of the sample. The results obtained are in accordance with the radical scavenging assay data (Figure 5c). Among tested polymers, WHPU15 exhibited a greater reducing power than WHPU10 and WHPU05 and, at higher concentrations, it is comparable with the reducing ability of ascorbic acid (As). WPU0 did not exhibit any radical scavenging activity, which confirms that TA is the vital component of the polymer responsible for antioxidant activity of WHPUs. This radical scavenging ability of the macromolecule is significant in multiple respects. The literature shows use of natural, antioxidant polyphenolic polymers in the control of glucose intolerance and diabetes.³⁴ Polymers with antioxidant activity have also been reported as a medium to suppress oxidative stress injury to the cells.³⁵ In this context, TA based synthetic WPU shows the promise as a potent sustainable material with profound bioactivity. Moreover, polyphenolic antioxidants have reportedly used to enhance thermo-oxidative stability of different polymeric materials.³⁶ Hence, the presence of the polyphenolic fraction within the same macromolecular structure adds the advantage of high thermo-oxidative stability to the developed polymer.

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 material safety of the synthesized system, hemolytic assay was performed as a representative biocompatibility test. It is a type of acute toxicity assay used to

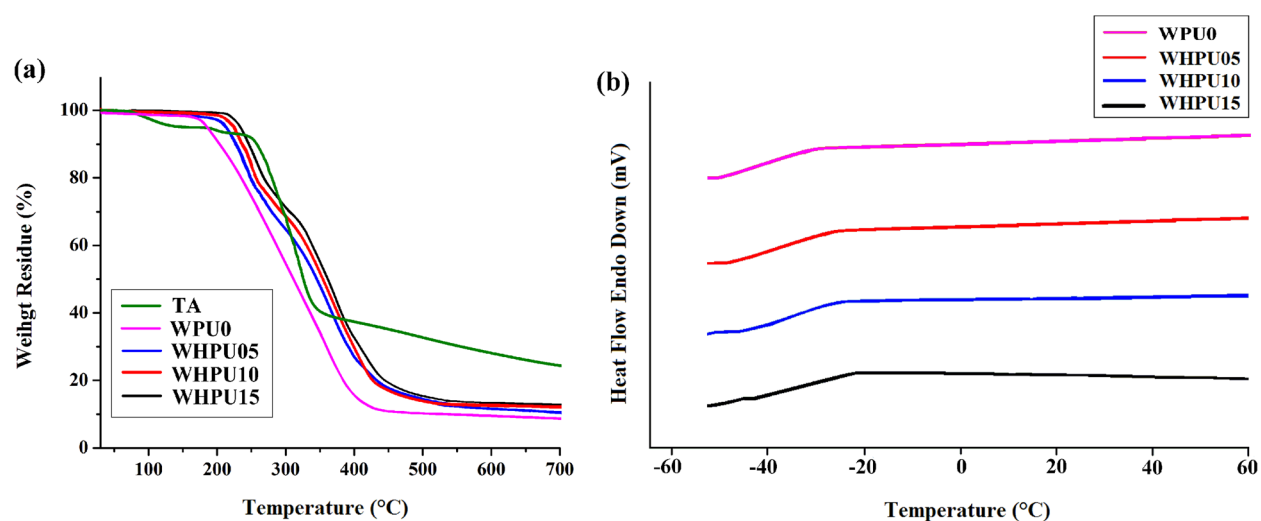


Figure 4. (a) TGA thermograms of WPU0, WHPU05, WHPU10, WHPU15, and TA. (b) Glass transition temperatures of WPU0, WHPU05, WHPU10, and WHPU15.

Table 3. Mechanical Properties of WHPUs

property	WHPU05	WHPU10	WHPU15
tensile strength (MPa)	4.93 ± 0.15	6.02 ± 0.20	6.87 ± 0.17
elongation at break (%)	508 ± 5	457 ± 7	315 ± 4
scratch hardness (kg)	4.0 ± 0.2	5.0 ± 0.1	5.5 ± 0.2
gloss (60 °C)	98.7 ± 0.7	94.5 ± 0.8	88.2 ± 0.4

evaluate the hemocompatibility of material by detecting hemolysis of erythrocytes. Such study involves direct interaction of a material with the erythrocyte membrane in which the extent of disruption of the erythrocyte membrane is a direct measure of toxicity. The RBC hemolytic protection assay reveals that WHPU15, WHPU10, and WHPU05 were well compatible with the mammalian erythrocytes compared to WPU0 (Figure 6). WHPU15 exhibited the best compatibility among the tested WHPUs, though the differences are very minute. Tween 20, the negative control, showed high absorbance of hemoglobin, which indicated drastic rupture of the RBC membrane. Contrarily, the positive control (hematocrit) exhibited a negligible absorbance value. Thus, *in vitro* hemolytic assay confirmed the compatibility of the polymer with mammalian RBC.

Biodegradation Study. Biodegradation of WHPU by *P. aeruginosa* bacteria was studied by determining the weight loss

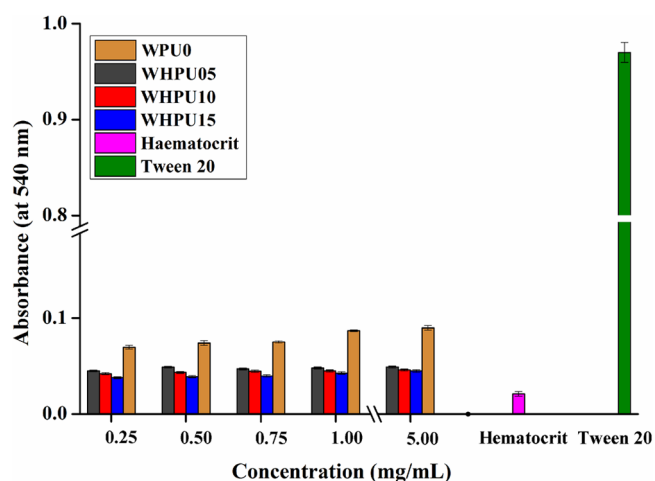


Figure 6. Antihemolytic activity assessment.

with time due to exposure of bacterial strain. The curve of retention of weight percentage versus incubation period depicted in Figure 7a clearly showed degradation of the polymeric films after 6 weeks of exposure. WHPU15 is found more biodegradable compared to WHPU10 and WHPU05. It is because of the fact that polyester polyurethanes are more

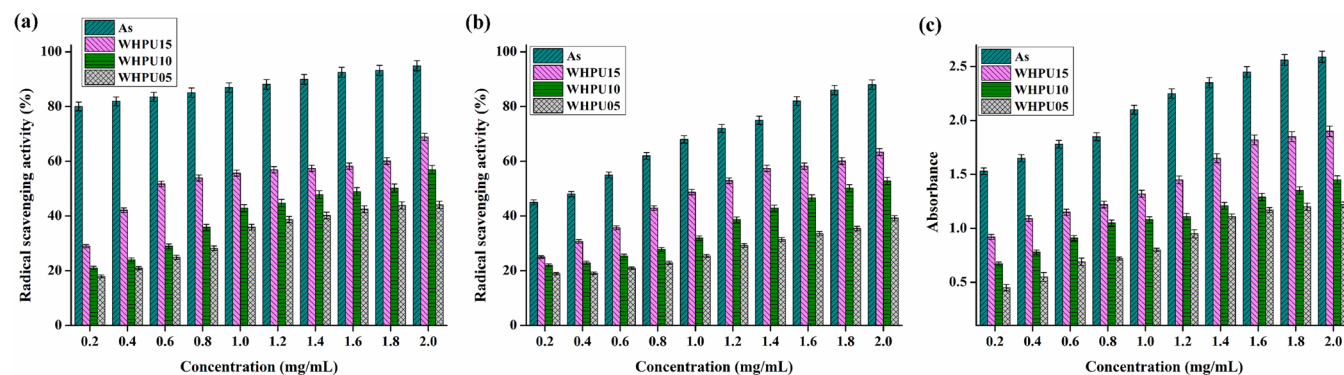


Figure 5. (a) DPPH radical scavenging activity, (b) hydroxyl radical scavenging activity, and (c) reducing power assay of WHPU05, WHPU10, and WHPU15.

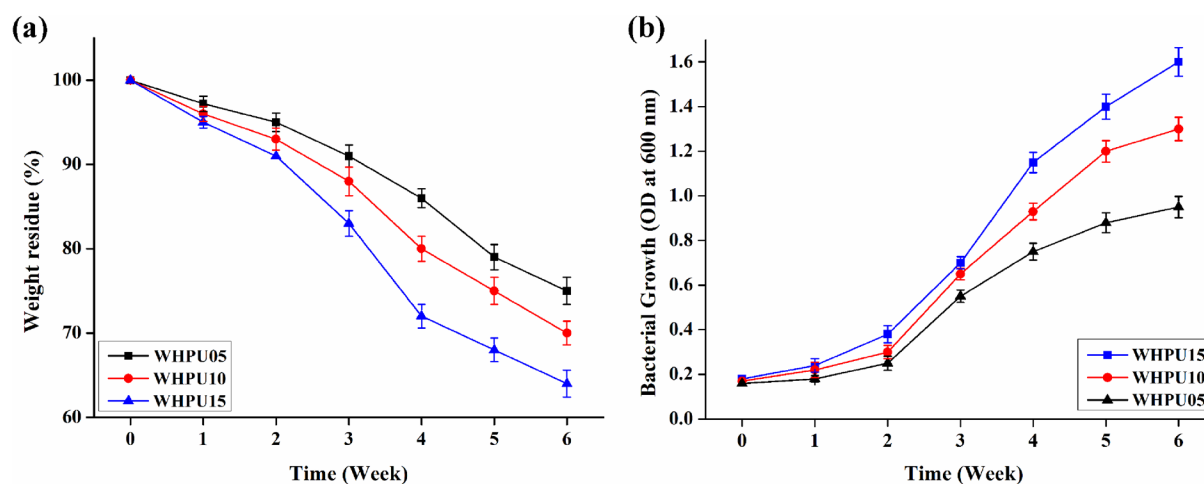


Figure 7. (a) Weight loss profile of WHPU05, WHPU10, and WHPU15 due to bacterial degradation. (b) Growth curve of *P. Aeruginosa* on WHPU05, WHPU10, and WHPU15.

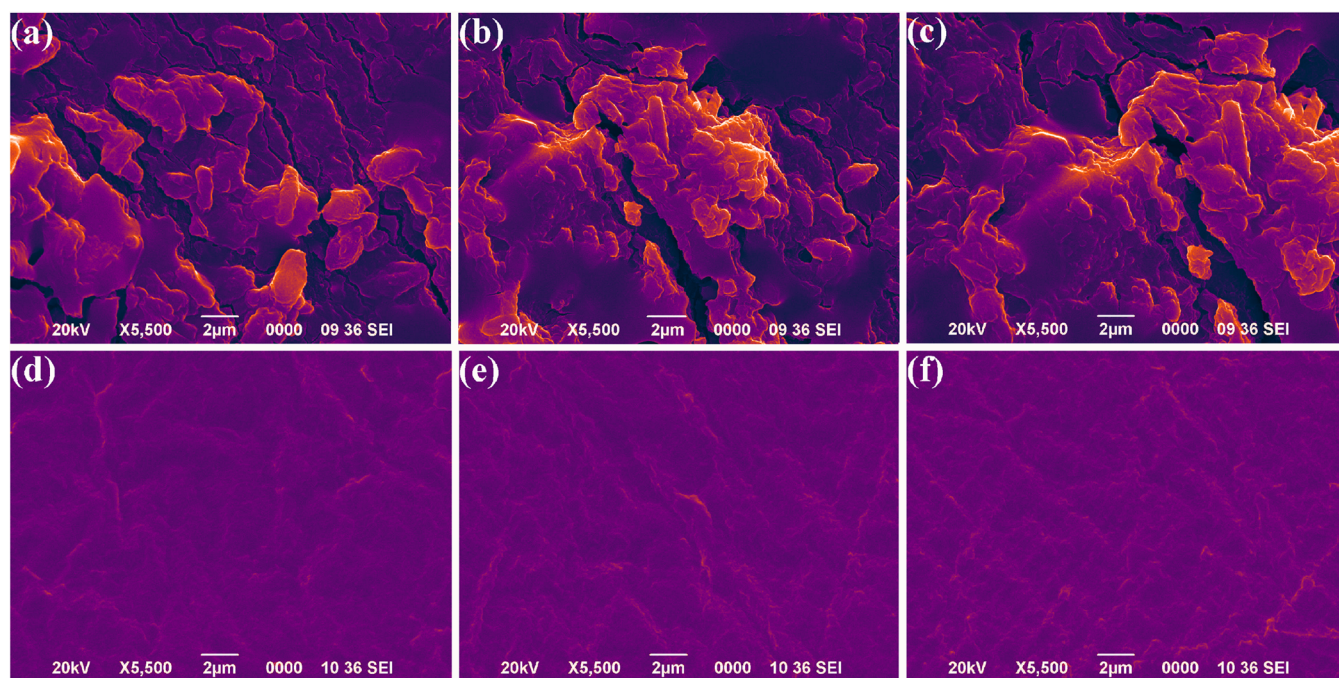


Figure 8. SEM images of biodegraded (a) WHPU05, (b) WHPU10, and (c) WHPU15, and respective controls of (d) WHPU05, (e) WHPU10, and (f) WHPU15.

susceptible toward microbial degradation compared to polyurethane alone.³⁷ As WHPU15 contains more hydrolyzable ester linkages, it offers a better liable surface for bacterial growth. This is further supported by the OD curves shown in Figure 7b. There is 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 less ester linkages, hence weight loss as well as bacterial growth is the least. The bacterial biodegradation was further confirmed by SEM images taken after 6 weeks of degradation (Figure 8). For all the polymer compositions, significant bacterial adherence and surface erosion was witnessed compared to the controls. Here it is pertinent to mention that WPU0 is also biodegradable, though within 10 days, no significant degradation was observed. FTIR study of the degraded film further confirmed the bacterial degradation as a number of significant

changes have been observed in the spectra (Figure 9). The most distinct change was observed for the carbonyl stretching frequency ($1720\text{--}1730\text{ cm}^{-1}$) with significant diminution in peak intensity over the experimental period. On the other hand, the absorbance peaks resulting from urethane (--NH) and aryl groups remain unchanged. This primarily indicates that degradation is mainly occurred by the rupturing of the ester linkages.

CONCLUSIONS

The present study reported a more environmentally benign approach over the conventional petrochemical routes to synthesize a hyperbranched waterborne polyurethane using tannic acid as a biobased material. The polymer exhibited acceptable thermal and mechanical properties. Hence, it can be concluded that tannic acid and other biobased polyphenolic

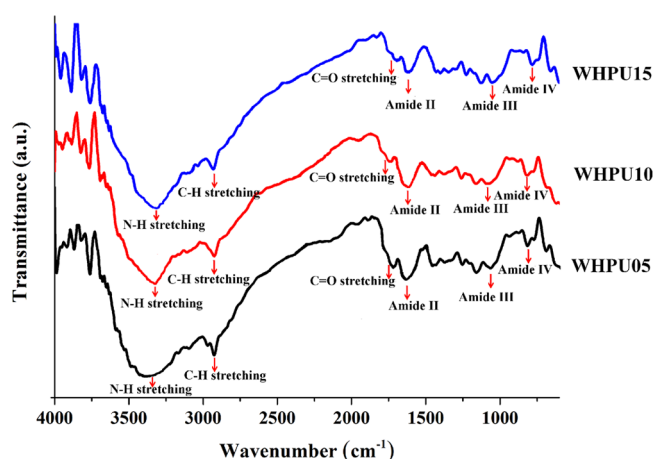


Figure 9. FTIR spectra of biodegraded WHPUs after 6 weeks of bacterial exposure.

compounds could be good alternative of vegetable oils for the development of sustainable polymeric materials. Furthermore, hemolytic assay confirmed the erythrocyte compatibility and radical scavenging assay revealed potent antioxidant activity of the polymer. These results indicate the polymer as a safe material. Biodegradability of the polymer by bacterial strain can address genuine problems of land pollution and solid waste management issues. The overall results mandate the synthesized waterborne hyperbranched polymer as a step toward sustainability.

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Notes

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