

Synthesis, characterization, and properties evaluation of tannic acid-based epoxy and its thermoset

Highlights

This chapter concerns the preparation of a bio-based epoxy by employing a nature-derived polyhydric phenol, i.e., tannic acid (TA), as the prime reagent. TA, being highly rich in hydroxyl and aromatic moieties, was epoxidized through the conventional taffy process, and the obtained epoxy resin was characterized using various instrumentation techniques. Meanwhile, three contrast samples were prepared using different stoichiometric amounts of TA and bisphenol A, and their properties were analogized with those of the fully TA-containing epoxy. The latter interestingly possesses better thermal, mechanical, and chemical resistivity in comparison to the partially bio-based ones. Moreover, good biodegradability and adhesive properties ensured its application in the field of eco-friendly coatings.

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2.1. Introduction

As evinced from the comprehensive discussion of **Chapter One**, epoxy resins portray an active role in some crucial disciplines of science. Concurrently, being dependent on petroleum resources, the commercial epoxy, made up of bisphenol A (BPA), has been suffering from resource scarcity and biodegradability issues that need to be resolved immediately in order to contribute toward maintaining a green planet [1]. Moreover, BPA-containing epoxy resins are employed in manufacturing reusable plastic bottles, as coatings in food and beverage cans, as filling material or sealants, etc., which, on hydrolysis or exposure to high temperatures, acidic environments, or basic conditions may release BPA and subsequently contaminate the food products during storage or serving [2]. Eventually, it enters the living body and initiates some serious complications in the human body because of its estrogenic properties. These difficulties restrict the extensive use of BPA-based epoxy resins and encourage scholars to hunt for benevolent alternatives [3]. Various renewable starting materials, as shown in **Table 1.2** of **Chapter One**, are utilized in the synthesis of bio-based epoxy resins, inclusive of different plant oils [4-6], lignin [7], rosins [8], vanillin [9], polyphenols [3], etc. Tannic acid (TA) is one such prolific biomolecule, a polyphenol obtained from beverages (including red wine, beer, coffee, and tea) and other plant-resources like grapes, nuts, galls, seeds, tree barks, etc., that has received tremendous attention as a precursor for epoxy preparation or as a crosslinking or curing agent. Being extracted from tannins having a high natural abundance and being merely specific to the plant kingdom, TA has ample potential as a renewable substrate [10]. Additionally, the presence of high functionality and aromatic rings gives TA a hyperbranched structure with considerable rigidity. TA has 25 hydroxyl groups of different reactivities that make it prone to structural tweaking. Moreover, ester linkages present in the structure are easily hydrolyzed and offer flexibility to the molecule. Epoxidation of TA by epichlorohydrin was done earlier by Esmaeili et al. using tetrabutylammonium bromide as a phase transfer catalyst (PTC) [11]. Recently, Saleh and his coworkers have epoxidized TA by a similar procedure without using a PTC [12]. However, the process required a high amount of tetrahydrofuran (THF) as a solvent for dissolving epichlorohydrin and toluene for extraction of the resin, which was inconsistent with the solvent-free concept currently emerging in the field of synthetic polymers. Furthermore, these studies remained silent on the structure-property relationship of these TA-based epoxies.

In the study reported herein, an attempt was made to synthesize a BPA-free bio-based epoxy from TA using it as the core hyperbranched unit and further crosslinking with a bio-based hardener to obtain an epoxy thermoset with high bio-content. An extensive study was subsequently performed on the epoxy thermosets using characterization and analytical techniques to gain a clear insight into their structural, mechanical, thermal, and biodegradable behaviors. To have a transparent understanding, a comparative study was done alongside preparing three different compositions of epoxy containing BPA (in 50, 25, and 10% loadings) along with TA. The high mechanical performance, good thermostability, and excellent adhesive nature of the resin may urge consideration for designing bio-based biodegradable coatings and adhesives for diverse applications.

2.2. Experimental

2.2.1. Materials

TA is a form of hydrolysable tannin, or gallotannin, obtained from various plant tissues, specifically the bark, leaves, and fruits of certain plants. TA possesses a complex structure with a core glucose unit to which esterified gallic acid units are connected. It has a molecular weight (m.w.) of 1701.2 g/mol with a density of 1.42 g/cm³ at room temperature (RT) and melts at 218 °C. It has the typical look of a light-yellow amorphous powder. In this study, TA was received from Sigma Aldrich and was used as the prime reactant for the epoxidation process to get a bio-based epoxy resin.

BPA is a synthetic dihydric phenol, a white solid at RT that melts at 159 °C. It has a m.w. of 228.29 g/mol and a density of 1.20 g/cm³. BPA, in the form of white granules, was purchased from Sisco Research Laboratory (SRL) Private Ltd., India and recrystallized from toluene before use. It is generally employed for the production of diglycidyl ether of BPA (DGEBA), as discussed in **Section 1.3.1.1. (a)**. In the present study, it is used as a co-reactant with TA in different stoichiometric contents to prepare the partially bio-based epoxy resins.

Epichlorohydrin or 1-chloro-2,3-epoxypropane, as described in **Section 1.3.1.1. (b)** of **Chapter One**, is an organochlorine compound with a m.w. of 92.52 g/mol and a density of 1.18 g/cm³. It boils at a temperature of 115 °C and has a low viscosity and transparent appearance. Epichlorohydrin was purchased from SRL Private Ltd., India, and was used as a reactant for the epoxidation of TA and BPA.

Sodium hydroxide (NaOH) is a colorless crystalline solid with a m.w. of 39.99 g/mol, a density of 2.13 g/cm³, and a melting point (m.p.) of 318 °C. It has high water solubility, is hygroscopic, corrosive, and strongly basic in nature. It is used as a catalyst in the epoxidation process for extracting protons from the polyhydric compounds. Moreover, it is used in determining the epoxy equivalent weight (EEW) of the prepared epoxy resins and for finding the chemical resistivity of the thermosets. Here, NaOH was procured from Merck, India, with a 97% purity index.

Sodium chloride (NaCl), commonly known as table salt, is a highly water-soluble inorganic compound with a crystalline white appearance. It has a m.w. of 58.44 g/mol and melts at a temperature of 801 °C. In the present investigation, NaCl, purchased from Merck, India, with a purity grade of 98%, was used in the form of a 16% aqueous solution to wash the resin during its workup process and to test the chemical resistance of the thermosets.

Sodium sulfate (Na₂SO₄), commonly referred to as Glauber's salt, is a highly water-soluble white crystalline salt. Anhydrous Na₂SO₄ was used in the workup phase to remove the excess water present in the resin during the washing process. It was obtained from Merck in India with 99% purity.

Poly(amido amine), also known as HY 840, is a polycondensation product of diethylene triamine and dimer acid. It is a resinous, light-yellow liquid that is widely used for curing commercial epoxy. The hardener is famous for its good pot life and the highly thermostable finish it offers to epoxy resins upon curing. It has an amine value of 6.6-7.5 eq/kg and a density of 0.98 g/cm³. Poly(amido amine) was received as a gift sample from Asian Paints, India, and was specifically applied for the curing of epoxy resins.

Potassium hydroxide (KOH) is a base with a m.w. of 56.11 g/mol. It is a white solid that has a density of 2.12 g/cm³ at RT and a m.p. of 360 °C. It was obtained from Merck, India, to use as a secondary standard for the hydroxyl value determination of the resin.

Oxalic acid, the simplest dicarboxylic acid with the chemical formula C₂H₂O₄ can be obtained from different plants. It has a m.w. of 126.06 g/mol and appears as a white crystalline solid at RT but melts at 189 °C. It was purchased from Rankem, India and used as a primary standard in the titrimetric processes for determining the strengths of NaOH and KOH.

Maleic anhydride is an organic compound that is highly soluble in water and produces maleic acid in water. It is a white, crystalline solid with a pungent odor that melts at 52.6 °C. It was obtained from Loba Chemie, India, to employ in the determination of hydroxyl value.

Triethylamine, abbreviated as Et₃N, is a colorless, volatile liquid with a strong fishy odor similar to ammonia. It has a basic nature with a pKa value of 10.7. The m.w. and density of triethylamine are 101.19 g/mol and 0.725 g/cm³, respectively. It was purchased from Merck in India and used in the evaluation of the hydroxyl value of the epoxy resins.

Hydrochloric acid (HCl) was used as received from Merck, India, with a purity grade of >35%. It has a formula weight of 36.46 g/mol and a density of 1.16-1.18 g/cm³ at RT. HCl was used in the process of EEW determination and in the chemical resistance test.

THF is a heterocyclic organic compound with the chemical formula C₄H₈O. It is a volatile solvent with a boiling point (b.p.) of 66 °C and a density of 0.886 g/cm³. THF is highly miscible in water making it usable for a wide range of applications. It was used, post drying, for extracting the epoxy resin from the aqueous emulsion. It was also used in very minute amounts during the curing process to attain a homogeneous amalgamation of the resin and the hardener.

2,2-Diphenyl-1-picrylhydrazyl (DPPH) is a stable free radical with a deep violet appearance. It is highly used as a trap or scavenger for other radicals and thus has potential utility in determining the antioxidizing activity of biomolecules. In this study, it was also applied for the same purpose: to find the antioxidant activity of the thermosets, as obtained from HiMedia Laboratories Private Ltd., India.

Ethanol, or ethyl alcohol (EtOH), is an organic solvent belonging to the alcohol homologous series. It is naturally produced during the fermentation of sugars by yeasts. Chemically, it can be obtained from the hydration of ethylene. It is a colorless, volatile liquid with a wine-like, pungent smell that boils at 78 °C and has a density of 0.789 g/cm³. In the present study, ethanol was obtained from Merck, India, for the evaluation of antioxidant activity, chemical resistance, and solubility tests.

Other important solvents like toluene (m.w.: 92.14 g/mol, density: 0.866 g/cm³, b.p.: 110.6 °C), hexane (m.w.: 86.18 g/mol, density: 0.659 g/cm³, b.p.: 68.7 °C), acetone

(m.w.: 58.08 g/mol, density: 0.79 g/cm³, b.p.: 56.5 °C), dimethyl sulfoxide (DMSO) (m.w.: 78.13 g/mol, density: 1.10 g/cm³, b.p.: 189 °C), N,N-dimethylacetamide (DMAc) (m.w.: 87.12 g/mol, density: 0.937 g/cm³, b.p.: 164 °C), etc. are procured from Merck, India and used for experimenting the solubilities of the resins. Furthermore, hexane and acetone were also used for the specific gravity and EEW-determination tests, respectively.

2.2.2. Instrumentation

Structural analysis of the epoxy resins and thermosets was performed utilizing Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) spectroscopy, and gel permeation chromatography (GPC) techniques. FTIR and attenuated total reflectance (ATR)-FTIR spectra of the prepared resins and thermosets, respectively, were recorded in the range 4000-500 cm⁻¹ on a Nicolet FTIR spectrophotometer (Impact-410, USA). ¹H and ¹³C NMR spectra of the resins were obtained from a 500 MHz AV500 AVANCE III FT-NMR spectrometer using d₆DMSO as the solvent and tetramethylsilane as the standard. GPC (Waters Corporation, USA) analysis of the resins was done in THF using linear polystyrene as the standard. The mechanical properties like scratch hardness and impact strength of the prepared thermosets were measured by using a scratch hardness tester (Sheen Instrument Ltd., UK) and an impact tester (S C Dey & Co.) by the standard falling ball method using a weight of 850 g with a maximum height of 100 cm. Using a mini gloss meter from Sheen Instrument Ltd., the gloss of the cured films was measured with an incident angle of 60°. Tensile strength and elongation at break (%) of the thermosets were measured by a Universal testing machine (UTM) (WDW10, Jinan, China) with a load cell of 0.5 kN and a crosshead speed of 5 mm/min. Two interfaces, metal-metal (aluminum) and wood-wood were used to measure the adhesive strength of the resin with an overlapping area of 25 × 25 mm² and a thickness of 0.10-0.20 mm. The surfaces were polished with sandpaper, followed by cleaning and washing with acetone. When the solvent was evaporated, a homogeneous mixture of epoxy and hardener was applied to the surfaces and allowed to cure at RT, using certain weights to hold the lap shear joints in place. The adhesive strengths were then measured by the UTM machine with a load cell of 10 kN and a crosshead speed of 5 mm/min. The thermal stability of the thermosets was determined by the thermogravimetric analyzer (TGA) (Netzsch, Germany) and differential scanning calorimeter (DSC) (Perkin Elmer, DSC 6000). The transparency of the prepared thermosets was evaluated by measuring the transmittance percentage of 25 mm × 10 mm × 0.3 mm thermosets by an Evolution-300 UV-visible spectrophotometer (Thermo

Fischer, USA) in the wavelength range of 200-800 nm. To check the resistivity of the thermosets in different chemical environments, a chemical resistance test was carried out. For the same reason, the thermosets were placed in different chemical media, such as aqueous solutions of HCl (5%), NaOH (5%), NaCl (10%), EtOH (10%) and freshwater, at RT for 30 days, and their weight loss percentages were measured after the completion of the test period.

2.2.3. Methods

2.2.3.1. Preparation of the epoxy

The epoxy resin was prepared by adhering to the typical epoxide formation process, as per the narrative in **Section 1.3.2.1 (c)**, involving the polycondensation reaction between a polyhydric compound (in this case TA) and epichlorohydrin. An amount of 10 g TA (0.00587 mol) in a minimum volume of 0.5 N NaOH solution (7 mL) was taken in a 250 mL three-neck round bottom flask equipped with a mechanical stirrer. A 23.0 mL of epichlorohydrin (0.29390 mol, two times the total hydroxyl groups of TA) was then allowed to be added dropwise to the mixture using a pressure-equalizing funnel at 40 °C to obtain a clear solution. When the temperature was raised to 65 °C, 28.4 mL of 5 N aqueous solution of NaOH was introduced into the flask through a pressure-equalizing funnel, maintaining a slow dropping rate to sustain the pH of the reaction mixture at 7.4. The addition was continued to 2.5–3 hours (h) by maintaining the temperature at 80 °C until a resinous product started to form. Continuous heating was applied for another 1 h after the accomplishment of complete NaOH addition, followed by cooling down to RT under a continuous stirring. The resin was transferred to a separating funnel, the aqueous layer was decanted off, and the resin was washed with a brine solution followed by distilled water for 2–3 times to remove the water-soluble impurities along with any residual reactants present. Finally, the resin was dissolved in THF, added anhydrous Na₂SO₄ for trapping the residual water, and dried using a rotary evaporator to remove the excess epichlorohydrin and entrapped water. The final product was codified as TAE100 and preceded for further studies.

Following the same procedure, three other compositions were prepared using 50, 25, and 10 weight percent (wt%) of BPA along with TA and codified as TAE50, TAE75, and TAE90, respectively, as given in **Table 2.1**.

2.2.3.2. Curing of the epoxy

The epoxy thermosets used for the physical testing were prepared by mixing the epoxy with the bio-based curing agent or hardener poly(amido amine), which is available commercially. The required amount of epoxy resin for curing was adjusted from the EEW value. The resin and the hardener were taken in a small beaker and mixed via hand stirring using a minimum amount of distilled THF. For a 5 g mixture of resin and crosslinker, only 1 mL THF was used. After uniform mixing, the solvent and air were then removed by degassing the mixture in a vacuum desiccator for about 5-10 minutes (min), and the bubble-free homogeneous mixtures obtained were coated uniformly on glass and metal plates of dimensions 75 mm × 25 mm × 1.3 mm. The remaining solvent was allowed to evaporate, keeping the cast films at RT. After 48 h, when the films became touch-free, they were subject to high-temperature curing at 100 °C for a definite time period, followed by post-curing at 120 °C. These films coated on glass were further utilized for measuring gloss, and scratch hardness, and films coated on metal plates for calculating impact strength, while for other analyses, films were peeled off from the glass plates and placed in a desiccator before use.

Table 2.1: Composition of the prepared epoxy resins

Sample Code	TA (mol)	BPA (mol)	Epichlorohydrin (mol)	wt% of TA
TAE50	0.00235	0.01752	0.18758	50.00
TAE75	0.00293	0.00729	0.17566	75.04
TAE90	0.00293	0.00243	0.15622	90.00
TAE100	0.00587	-	0.29390	100

2.2.3.3. Determination of physical properties

As outlined in **Section 1.4.4.1**, the EEWs of the resins were determined by following ASTM D1652, where 0.2-0.8 g of the resin was taken in a flask and 20 mL of acetone was added to dissolve the resin. 10 mL of 2 N HCl was added to the flask, and the contents were refluxed for 1 h at 80 °C. After attaining RT, 5 mL aliquots of the mixture were titrated against a 0.5 N NaOH solution using a phenolphthalein indicator to measure the amount of HCl from which EEWs were calculated. The hydroxyl values of the resins were

also measured following the standard methods, using maleic anhydride, triethylamine, and KOH [13].

The swelling values of the cured thermosets were reckoned by submerging previously weighted thermosets in THF for a period of 48 h and thereafter recording their weight gain percentages using **Equation 2.1**. These swelling values were used to optimize the cure timing.

$$\text{Swelling (\%)} = [W_f - W_i] / W_i \times 100 \quad \text{Equation 2.1}$$

where W_i and W_f are the initial and final weight of the thermosets, respectively.

2.2.3.4. Determination of antioxidation activity

The antioxidant activity of the prepared thermosets was studied via the radical scavenging method using DPPH as the active radical [14]. A 100 μM solution of DPPH in a 50% ethanolic solution was prepared and stirred for 30 min. Then 2 mg of the thermoset with a 1 mm \times 1 mm dimension was added to 5 mL of DPPH solution and vortexed for 30 min. A blank solution, an ascorbic acid solution, and a TA solution were also prepared to be used as a blank, standard and for comparison purposes, respectively. The solutions were then incubated in a dark place. The scavenging process was completed when the color of the solution turned from violet to yellow and the absorbance was recorded at 517 nm by a UV-visible spectrophotometer. The scavenging activity was obtained by the expression provided in **Equation 2.2**.

$$\text{Radical scavenging (\%)} = (1 - A_s / A_b) \times 100 \quad \text{Equation 2.2}$$

where A_s and A_b are the absorbances of the sample and blank solution, respectively.

2.2.3.5. Biodegradation study

Biodegradability of the prepared thermosets was studied by the McFarland turbidity method using *Pseudomonas aeruginosa* (*P. aeruginosa*, gram-negative) and *Bacillus subtilis* (*B. subtilis*, gram-positive) bacterial strains [13, 14]. The strains were received from the Department of Microbiology and Biotechnology (MBBT), Tezpur University. To prepare the culture medium, a combination of different salts such as 2 g of $(\text{NH}_4)_2\text{SO}_4$, 2 g of Na_2HPO_4 , 4.75 g of KH_2PO_4 , 1.2 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 g of $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, 0.1 g of $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$, 10 mg of $\text{H}_3\text{BO}_3 \cdot 5\text{H}_2\text{O}$, 70 mg of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 10 mg MoO_3 , 1 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.5 mg $\text{CaCl}_2 \cdot 7\text{H}_2\text{O}$ was added to 1 L of demineralized water, and then the solution was sterilized for 30 min in an autoclave under a pressure of 15 lb at 120 $^\circ\text{C}$.

This sterilized mixture was then used for culturing the strains in the incubator for 48 h at 37 °C. A 100 µL aliquot (10^8 microbes per mL) of the cultured bacterial medium was added to a conical flask containing 10 mL of the sterilized medium. The next step is to sterilize the thermosets to be tested under UV radiation of 254 nm wavelength and to add them to the conical flask, followed by incubation at 37 °C. The same amount of the above bacterial medium was used as the control. The rate of growth of the bacterial strain was determined by repeatedly measuring the absorbance of the thermoset-containing medium at 600 nm in the form of optical density (OD) of the microbes for 4 weeks. After completion of the test, the surface morphology of the degraded thermosets was studied by a JOEL JSM-6390LV scanning electron microscope (SEM). Meanwhile, the final weight loss percentages of the thermosets were recorded using **Equation 2.3**.

$$\text{Weight loss (\%)} = [W_i - W_f]/W_i \times 100 \quad \text{Equation 2.3}$$

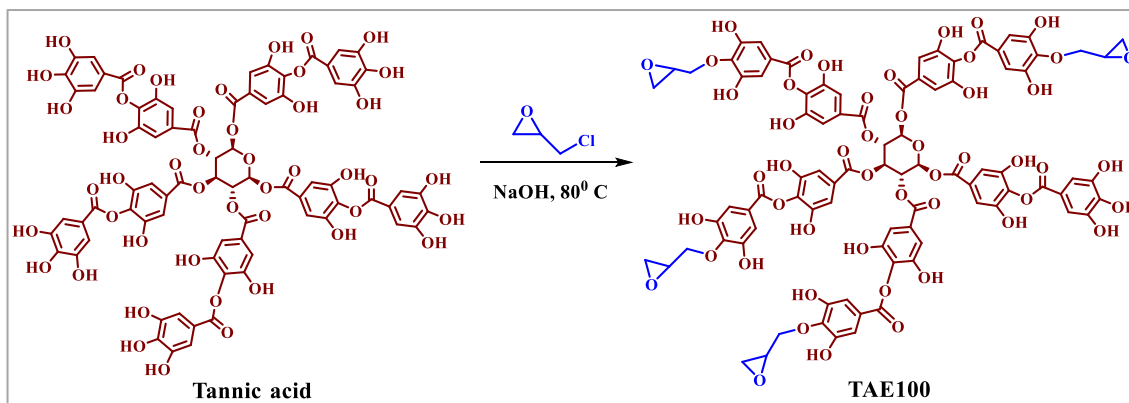
where W_i and W_f are the initial and final weight of the thermosets, respectively.

2.3. Results and discussion

2.3.1. Synthesis and inspection of the resin

In this work, the epoxide formation reaction of TA was conducted in an alkaline medium without using any organic solvent, by controlling the pH of the medium at 7.4, which ensured minimum hydrolysis. The use of PTC was avoided without compromising the reaction yield (92.6% yield for TAE100). Epoxidation resulted in surface modification of TA by substituting glycidyl groups in some of the hydroxyl groups of TA, preferentially in the outer layer, as represented by the probable structure of the TAE100 in **Scheme 2.1**. The protocol followed was thus straightforward and facile, with a comparatively lower reaction temperature (80 °C) which satisfied the concept of energy conservation to a certain degree.

However, in the presence of BPA, the epoxidation was expected to take place first in the -OH groups of BPA followed by the -OH groups of TA in the case of TAE50, TAE75, and TAE90 resins. This is due to the high reactivity and availability of hydroxyl groups in BPA compared to sterically crowded TA hydroxyl groups. Hence, TA is supposed to act as the branch-generating unit, the hydroxyl groups of which could open the epoxy rings of DGEBA supplementary to end group modification [15]. However, with an increasing percentage of TA, surface epoxidation became more prominent, which can be understood from the ^1H NMR spectra of the resins as described in the latter sections.



Scheme 2.1: Synthesis route of TA-based epoxy (TAE100)

Figure 2.1(a) shows the FTIR spectra of the four epoxy resins, displaying the presence of different functionalities in their structure. The characteristic absorption bands appeared at 3450 cm^{-1} (-OH stretching), 1719 cm^{-1} (-C=O stretching), $1635/1594\text{ cm}^{-1}$ (-C=C- aromatic ring) and two peaks in the range $830\text{-}911\text{ cm}^{-1}$ for the asymmetric stretching of the oxirane ring, which were indicative of a successful epoxide ring formation with the TA moiety [16]. Two aliphatic absorption peaks appeared at 2930 cm^{-1} and 2871 cm^{-1} for -CH₂ asymmetric and symmetric vibrations, respectively. These -CH₂ vibrations originated from the oxirane ring, which was initially absent in TA, supported the success of the epoxidation process that introduced aliphatic methylene groups into the resin. Moreover, the weakened intensity of the -OH stretching band detected in the resins compared to TA further suggested an effectual epoxidation. A clear insight into the FTIR spectrum of TAE100, as displayed in **Figure 2.1(d)**, revealed the presence of an overlapping band with a shoulder near 860 cm^{-1} which can be attributed to the presence of two closely situated peaks at 866.4 cm^{-1} and 852.2 cm^{-1} . The first one originated from the out-of-plane deformation of -C-H of benzene rings of TA (**Figure 2.1(c)**) and the later from -C-O-C- stretching of oxirane rings. Whereas the second characteristic -C-O stretching peak appeared at 909.4 cm^{-1} [17]. In contrast, these two peaks were absent in the spectrum of TAE100 thermoset, as depicted in **Figure 2.1(e)**. Crosslinking of the resin with the hardener resulted in opening up of the epoxy rings because of which the characteristic epoxy peaks disappeared and only the peak originating from the -C-H bond deformation of the benzene rings of TA was observed [13]. Similar outcomes have also been reported in other studies, demonstrating the synthesis of bio-based epoxy resins and their curing with potential hardeners [16, 17].

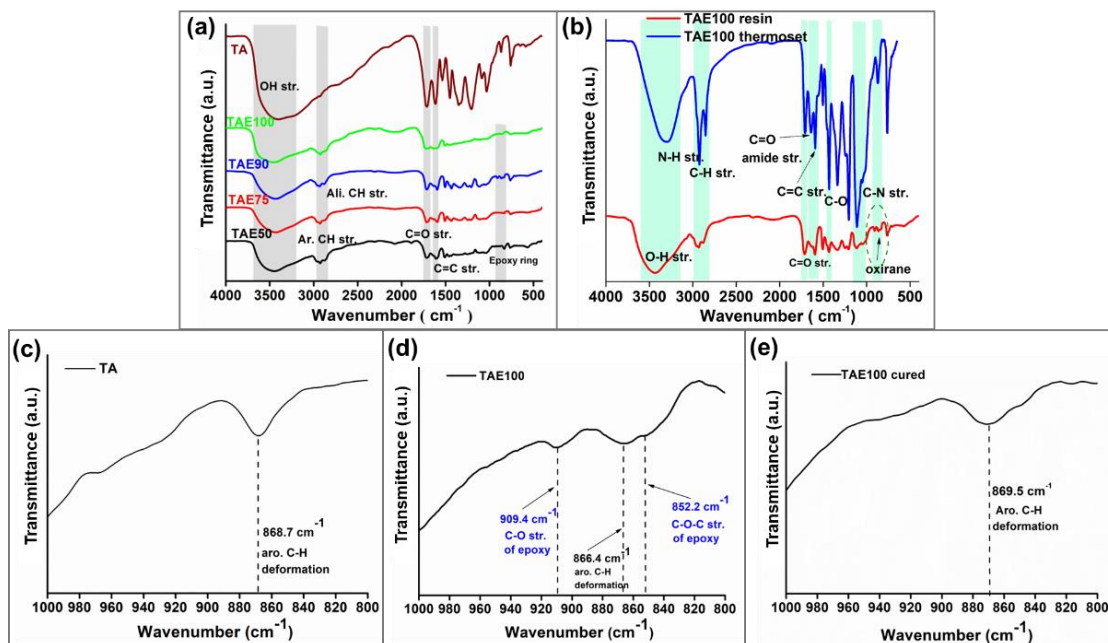


Figure 2.1: FTIR spectra of (a) all four epoxy resins with TA, (b) TAE100 resin and thermoset after curing, enlarged FTIR spectra of (c) TA, (d) TAE100 resin, and (e) TAE100 thermoset (after curing) in the range $1000\text{--}800\text{ cm}^{-1}$

The ^1H NMR (500 MHz, d_6 -DMSO as solvent) spectrum of TAE100 is shown in **Figure 2.2(a)**. The peaks appearing at δ values (in ppm) are depicted as: 2.69 and 2.82 (2H, CH_2 of oxirane ring), 3.65 and 3.75 (2H, CH_2 next to oxirane ring), 3.71 and 4.03 (CH_2 of opened oxirane ring), 3.95 (hydroxyl group's H of opened oxirane), and 5.55 (hydroxyl group's H of TA). The peaks in the region at 7.14 and 7.34 ppm corresponded to aromatic protons of TA. The solvent d_6 -DMSO appeared at $\delta = 2.50$ ppm and the peak for absorbed moisture appeared at 3.31 ppm, while for the entrapped THF used during NMR sample preparation, two distinct peaks showed up at 1.71 and 3.56 ppm. The ^{13}C NMR (d_6 -DMSO) spectrum of TAE100 is shown in **Figure 2.2(b)**, from which different peaks corresponding to different chemically surrounded carbons (Cs) can be depicted. The peaks (δ in ppm) at 43.88 and 49.98 are for oxirane ring Cs, 68.86 for C next to oxirane, and 70.38 for opened oxirane ring Cs. Complex multiplets at 106.09, 108.61, and 112.09 ppm are attributed to the unsubstituted Cs of benzene rings. Similarly, signals at 121.44 and 124.68 ppm are assigned to the benzene ring Cs next to $\text{C}=\text{O}$, while 137.93, 141.84, and 143.60 ppm are due to the benzene ring Cs next to $-\text{C}-\text{O}-$; peaks at 147.94 and 152.04 ppm are for benzene ring Cs attached to $-\text{OH}$ groups. The signals appearing at δ values of 164.80 and 165.45 ppm indicated the carbonyl Cs of the TA moiety.

The gradual replacement of BPA with TA can be understood from the proton NMR peaks, as displayed in **Figure 2.3**. The aromatic hydrogen peaks appearing near δ values 6.64-7.10 ppm corresponded to the BPA aromatic protons, while the TA aromatic protons appeared near $\delta = 7.19$ -7.29 ppm. With the gradual increase in TA concentration in the epoxy resins, the intensity of this second set of peaks started mounting. Contrarywise, the peaks due to the aromatic BPA protons are seen to be diminishing progressively from TAE50 to TAE90, finally vanishing in TAE100.

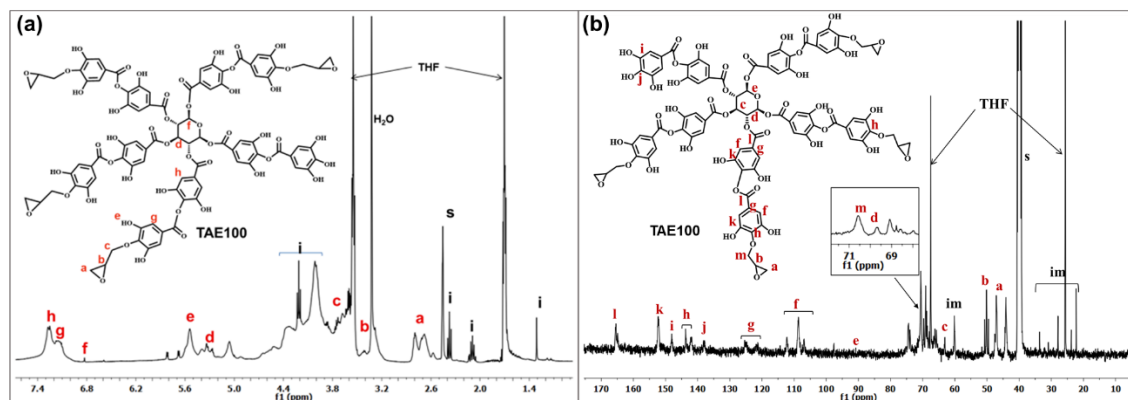


Figure 2.2: (a) ^1H NMR and (b) ^{13}C NMR spectra of TAE100

2.3.2. Physical properties of the resins and the thermosets

The TA-derived bio-based epoxy resin was obtained as a brown-colored viscous product that is stable at RT for a long period of time. The physical properties like EEW, hydroxyl value, m.w., specific gravity, gloss, etc. of the resins were determined by standard techniques, and the results obtained are tabulated in **Table 2.2**. The experimentally obtained EEW of the TAE100 resin was 623.6 g/eq, which suggested the

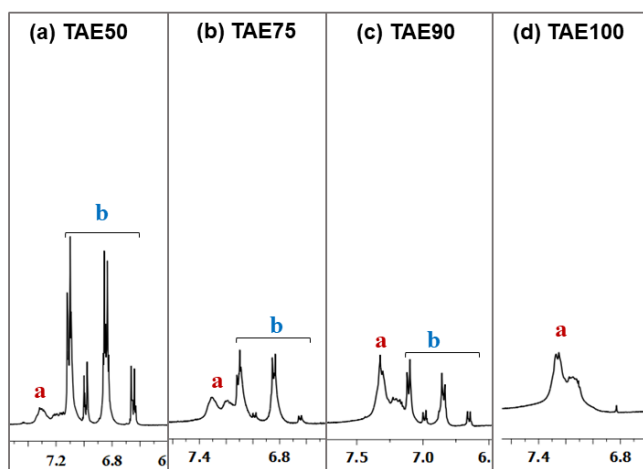


Figure 2.3: Intensity changes of aromatic protons (a: TA protons; b: BPA protons) with change of TA loading in all four resins

presence of nearly four epoxy groups in the structure. This value was much higher than the theoretical EEW (477.7 g/eq). This may be due to the fact that the unsubstituted hydroxyl groups of one TAE100 monomer interacted with the epoxy groups of another monomer via hydrogen bonding and made the oxirane ring unavailable for hydrolysis by HCl. Also, the analytical methods followed for EEW measurement might result in only partial hydrolysis, leading

Table 2.2: Physical properties of the synthesized resins and their thermosets

Parameter	TAE50	TAE75	TAE90	TAE100
Yield (%)	87.8	89.3	88.9	92.6
Theoretical m.w. (g/mol)	1187	1430	1709	1911
Number average m.w. from GPC (M_n in g/mol)	1460	1651	1468	1804
Polydispersity index	1.37	1.63	1.46	1.55
Theoretical EEW (g/eq.)	395.6	476.6	427.2	477.7
Experimental EEW (g/eq.)	255.0	416.6	423.2	623.6
Hydroxyl value (mg of KOH/g)	169.2	154.7	158.7	189.6
Gloss (60°)	95.7	91.1	42.3	49.7
Specific gravity of resin	1.36	1.32	1.30	1.36
Specific gravity of thermoset	1.71	1.73	1.78	1.85

to erroneous results. However, for BPA containing three compositions, EEWs were decreasing with rising amounts of BPA, which indicated the presence of DGEBA, leading to a lower EEW value [18]. The hydroxyl value of TAE100 was found to be 189 mg KOH/g, indicating the presence of 10 hydroxyl groups, whereas the theoretically obtained hydroxyl value from the proposed structure is 175 mg KOH/g corresponding to 11 -OH groups in the structure. The M_n of TAE100 obtained from GPC measurement using THF as the solvent was found to be 1804 g/mol and the polydispersity index was 1.55, as shown

in **Table 2.2**. However, M_n obtained from GPC measurement is supposed to deviate from the actual molecular weight of the resin as only linear polystyrene is used as the standard for the measurement compared to the branched structure of the resin [19].

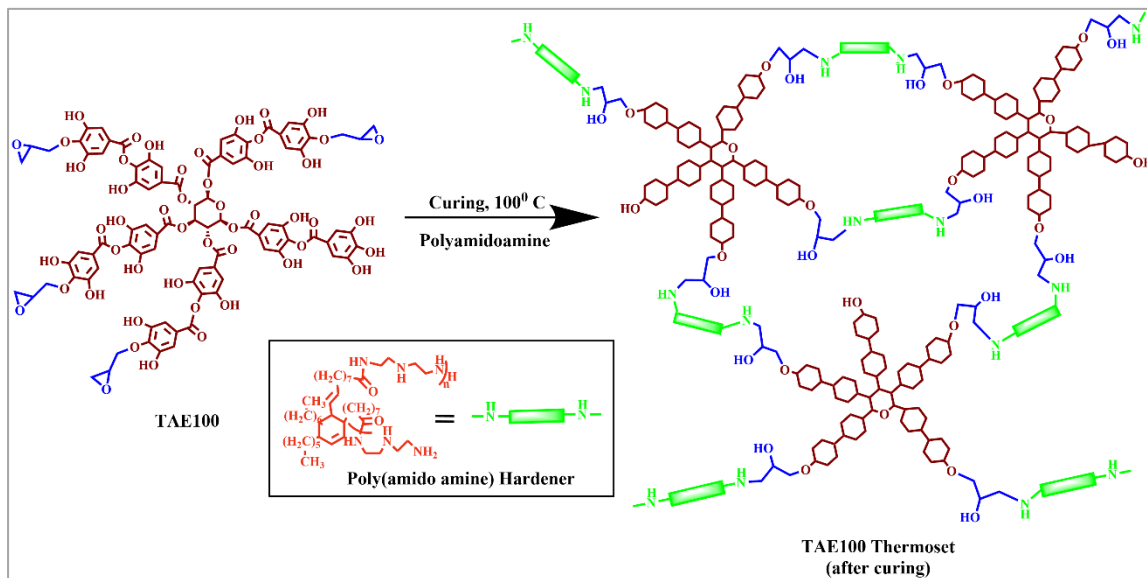
The good solubility of the resin in most of the polar solvents such as THF, acetone, DMSO, DMAc, ethanol, etc., while its dispersibility in water, ethyl acetate, methanol, etc., indicates its high polarity on account of the highly polar functionality (-OH) present, as well as the hyperbranched structure originated from the TA component [20]. This was further established by the zero solubility of the resin obtained for non-polar solvents like hexane, toluene, xylene, etc.

2.3.3. Curing study

To obtain a three-dimensional network structure, the resin prepared was cross-linked with a bio-based hardener, poly(amido amine) with an epoxy to amine ratio of 2:1. Due to the high viscosity, integrating the resin with the hardener via hand stirring was difficult, and to obtain a homogeneous mixture, good flowability was necessary. The addition of THF during the mixing of the resin and hardener lowered the viscosity of the mixture, making the stirring smooth and resulting in homogenous mixing that further facilitated uniform crosslinking throughout the thermoset. However, before casting the film on the glass or metal plates, the solvent was removed using a vacuum desiccator. This was necessary to avoid entrapping the solvent molecules inside the polymer network during the crosslinking process at high temperatures. Evaporation of the solvent molecules would have resulted in the formation of blisters on the surface of the coated films. These blisters make the films rough and aberrant, and have adverse effects on the mechanical, thermal, and chemical properties of the thermosets, which were avoided by removing the solvent. After the films became touch-free, on applying a temperature of 100 °C for a substantial amount of time, which varied for the different compositions according to their structural complexity; rigid epoxy thermosets in the form of homogeneous brown transparent films were obtained. The applied elevated temperature causes the highly strained oxirane rings to be opened up by the nucleophilic amine groups present in the hardener, resulting in a cross-linkage as shown in **Scheme 2.2**, demonstrating a mere probable structural representation of the TA-based epoxy thermosets.

Figure 2.1(b) shows the ATR-FTIR spectrum of TAE100 after curing, compared with that of the resin. Two peaks appearing at 852.2 and 909.4 cm^{-1} for epoxy ring vibrations vanished with curing, as seen from the enlarged spectrum of TAE100 thermoset

in **Figure 2.1(e)**, and the intensity of the hydroxyl peak at 3300 cm^{-1} seemed to become narrower compared to the resin.



Scheme 2.2: Possible crosslinking of TAE100 with poly(amido amine) hardener at elevated temperature

To optimize the curing time and obtain the desired crosslinking density, the swelling value of the thermosets was measured. Accordingly, they were subject to post-curing at $120\text{ }^{\circ}\text{C}$ until desired swelling values, ranging between 20 and 30% were reached. **Table 2.3** displays the various curing parameters for all four compositions of epoxies along

Table 2.3: Curing parameters for TAE resins

Parameters	TAE50	TAE75	TAE90	TAE100
Touch free time at RT (h)	48	36	24	21
Curing time at $100\text{ }^{\circ}\text{C}$ (min)	100	80	65	60
Post cure time at $120\text{ }^{\circ}\text{C}$ (min)	10	7	5	3
Swelling value (%)	29	27	28	22

with swelling values measured after post-curing. The times consumed for curing and post-curing were the shortest for TAE100. With decreasing TA content, the duration of curing increased for TAE90, TAE75, and TAE50. The last one displayed the longest curing profile. The low curing time required for TAE100 signified a high epoxy content as well

as presence of highly polar functionality in it that resulted in a highly crosslinked structure. However, the results exhibited a complementary relationship to EEW obtained by analytical techniques. Generally, crosslinking density increases with decreasing epoxy content. Partially bio-based resins required a relatively longer curing time, although they had lower EEW, which was due to the presence of the DGEBA moiety, that required a longer curing time.

2.3.4. Mechanical properties and adhesive strength

A thorough inspection of the mechanical properties, such as tensile strength, elongation at break, scratch hardness, impact strength, and adhesive strength of the prepared thermosets was performed and the obtained results are presented in **Table 2.4**. **Figure 2.4(a)** represents the stress-strain profiles of all four epoxy thermosets, showing tensile strength and elongation at break values. TAE100 thermoset, the one with the highest bio-content, displayed the maximum tensile strength of 18.4 MPa; nevertheless, elongation was recorded to be lowest for the same. This reciprocal relationship between tensile strength and elongation is typical of most epoxy thermosets, as evident from the literature [21]. High tensile strength suggested an optimum crosslinking level, which was also perceptible from the curing profile and swelling value, as mentioned earlier. The elevated tensile strength came from the high aromatic content originating from ten galloyl units and the dynamic ester linkages present in the TA moieties [22]. The high-mass epoxy monomers were strongly held together by amine linkages in the hardener and thus required considerable force to break these linkages. Moreover, the presence of polar functionalities coming from the TA moiety as well as an amine-based aliphatic hardener enhances the crosslinking density through intra- and inter-molecular secondary interactions that play a crucial role in determining the tensile properties. Henceforth, as the TA content dropped from TAE100 to TAE50, a gradual decrease in tensile strength was observed due to the lowering of aromatic and polar group content. Nevertheless, the low elongation of TAE100 was anticipated owing to the lack of flexible fragments in the TAE100 epoxy monomer, while the BPA moiety played the same role in the other three compositions to impart flexibility to some extent, as reflected in the gradually improving elongation values. Thus, a continuous decrease in elongation was observed as the BPA percentage dropped from TAE50 to TAE100, with the maximum elongation being shown by TAE50. Although the obtained tensile strength was low compared to DGEBA thermosets as reported by Duarah et al. [13], it was still better compared to some other bio-based BPA-free epoxies [23].

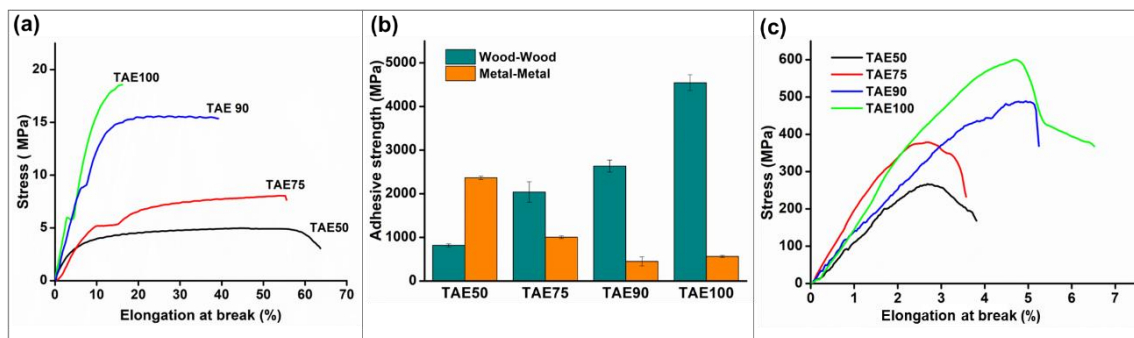


Figure 2.4: (a) Stress versus elongation at break plots, (b) adhesive strengths in wood-wood and metal-metal surfaces for epoxy thermosets and (c) stress-elongation at break curves for adhesive strength in wood substrates

The scratch hardness and impact resistance of epoxy thermosets maintain a linear relationship with tensile strength [24]. The impact resistance measures the capability of the thermoset to withstand a sudden applied force and its dissipation throughout the system. Both tensile strength and elongation contribute to the impact resistance of the thermoset [25]. Thus, TAE100, having the highest tensile strength, displayed the maximum scratch hardness and impact resistance among all the compositions. It could withstand, without cracking, a shock or impact up to 100 cm (19.3 kJ/m impact energy), which was the maximum limit of the instrument. This could be attributed to the presence of rigid aromatic systems of TA and flexible aliphatic chains of the hardener that offered both rigidity and flexibility at the molecular level [26]. Highly dense cross-linking and interactions between the terminal hydroxyl groups also contributed to good impact and scratch hardness.

The adhesive behavior of epoxy resin is of vital importance in regard to coating and adhesive-based applications. So, the synthesized epoxies were subject to an adhesive test for joining different substrates, viz., wood and aluminum sheets, as demonstrated in **Table 2.4**. Such adhesive studies of TA-based epoxies were previously done by Saleh et al. on aluminum and carbon fiber-reinforced polymer adherends [12]. Although they used a mixture of 15% of TA-based epoxy components and the rest DGEBA in the adhesive formulation, this put limits on their applicability from a sustainability viewpoint. In this work, the use of DGEBA was avoided, and pure TAE100 bio-epoxy was applied on the 25 mm × 25 mm area of the adherends, mixing in a 2:1 ratio with the hardener. The curing was allowed to occur at RT, and then the lap shear adhesive test was performed. Similarly, three other contrast epoxies were also subject to the test. As evident from **Figure 2.4(b)** and **Table 2.4**, the adhesive strength for wood substrates showed a steady increase with

Table 2.4: Mechanical properties and adhesive strength of TAE thermosets

Sample	TAE50	TAE75	TAE90	TAE100	
Tensile strength (MPa)	4.8 ± 1.1	8.0 ± 1.6	15.3 ± 1.5	18.4 ± 1.1	
Elongation at break (%)	63.5 ± 1.4	55.0 ± 2,9	39.1 ± 0.4	16.0 ± 0.6	
Toughness (J/m³)	277.1	353.4	509.3	190.1	
Impact energy (kJ/m)	4.5 ± 0.3	6.9 ± 0.2	16.5 ± 1.5	19.3 ± 1.9	
Scratch hardness (kg)	4 ± 0.5	6 ± 0.5	8 ± 0.5	8 ± 0.5	
Adhesive strength (MPa)	Wood-wood	881 ± 15	2040 ± 23	2715 ± 29	4545 ± 37
	Metal-metal	2366 ± 18	1007 ± 27	450 ± 17	565 ± 24

increasing TA percentage, while a reverse trend was recorded for aluminum substrates. The highest adhesive strength of 4545 MPa was recorded for TAE100, which might be attributed to the presence of highly polar hydroxyl groups that could interact with the cellulose hydroxyls via hydrogen bonding, leading to a better adhesion. This is nearly five times higher than DGEBA cured with the same hardener (863 MPa) and also higher than the starch-based epoxy as reported by Duarah et al. [13]. The absence of polar functionalities in comparison to TAE100, which can enhance adherence to the cellulosic surface, is the reason for such differences in adhesive strength. With the decrease in TA content, a lowering in adhesive strength was observed owing to the diminution of polar-polar interactions via hydroxyl groups. This can be observed from the stress-strain curves recorded for the wood substrates shown in **Figure 2.4(c)**. The adhesive strengths obtained on metal substrates were also good, but TAE100 displayed a lower adhesive strength followed by cohesive failure than TAE50 and TAE75. The reason for this behavior was probably due to the high viscosity and sterically complex shape of the epoxy monomer, which hampered mechanical interlocking with the metal surfaces [21]. On the contrary, the DGEBA moiety, being less bulky than the TAE monomer, can adhere to the rough metal surface, leading to better adhesion. This clearly justifies the observed trend of adhesive strength on the metal surfaces.

2.3.5. Thermal properties

Understanding the thermostability of the epoxy thermoset extends its end-use to a wide range of temperatures. TGA was performed in a temperature range of 30-600 °C. **Figure 2.5(a)** displays the outcomes as a weight loss percentage versus temperature plot, and the corresponding data are presented in **Table 2.5**. All four thermosets revealed two-stage degradation profiles, with an initial 2-3% degradation attributed to the loss of small molecules like water, THF, and volatiles entrapped inside the polymer network [13]. Though actual degradation started after temperatures of 230 °C and TAE100 showed the lowest onset degradation temperature (T_{ON}) of 232 °C. The peak temperature for the first-stage degradation profile varied from 299 °C to 330 °C which corresponds to the depolymerization of the TA moiety via cleavage of ester bonds. As it is clear from the

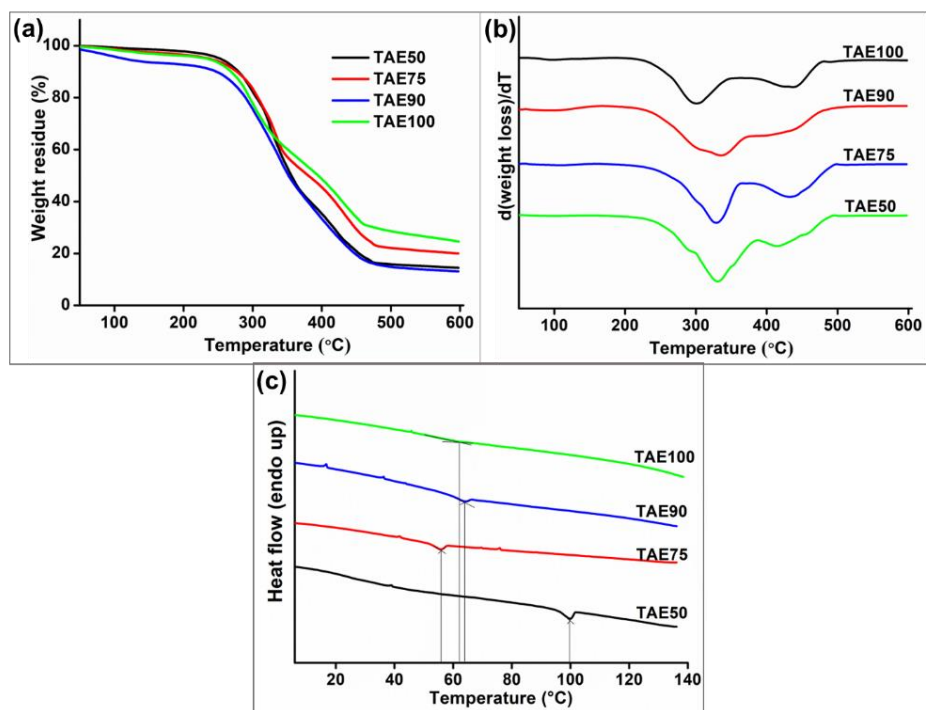


Figure 2.5: (a) TGA thermograms, (b) DTG curves showing two stage degradation profiles, and (c) DSC curves showing glass transition temperatures (T_g) for the thermosets data, with the upsurge in TA concentration, the first peak degradation temperature shifted to a lower temperature region, and TAE100 showed the lowest value [27]. The next step of degradation started from 320 °C to 384 °C and is due to the decomposition of rigid aromatic rings of TA for TAE100 and both TA and BPA moieties for the other three compositions, as well as amide linkages of poly(amido amine) hardener, with a peak temperature of 340 °C [28, 29]. The TGA thermogram of TAE100 revealed its weight loss at a comparatively higher temperature than others. Moreover, the highest weight residue

value of 24.57% was recorded for TAE100, concluding its better thermostability, for which greater crosslinking density and aromatic content might be the reasons.

The DSC thermograms shown in **Figure 2.5(c)** disclosed the T_g values of the thermosets. The values are given in **Table 2.5**. Based on earlier reports, the T_g values of the epoxy thermosets were expected to be high with the incorporation of TA into DGEBA when it was used as a crosslinker [11]. In this study, where only TA was present, TAE100 was found to have a T_g of 61.9 °C due to its high aromatic content and presence of polar functionality, which led to a denser network and reduced flowability [30]. However, the other, three compositions appeared to have random T_g s, not following any definite order which might be due to the presence of different amounts of DGEBA in the system along with TA.

Table 2.5: Thermal parameters for TAE thermosets obtained from TGA and DSC analyses

Parameters	TAE50	TAE75	TAE90	TAE100
T_{ON} (°C)	244	241	230	232
1 st stage degradation peak temperature (°C)	330	328	334	299
2 nd stage degradation peak temperature (°C)	414	434	401	440
Weight residue at 600 °C (%)	14.47	19.97	13.06	24.57
T_g (°C)	99.4	55.7	63.5	61.9

2.3.6. Chemical resistance

The epoxy thermosets were exposed to different chemical media to understand their durability in harsh environments for widespread applicability, and the results obtained are listed in **Table 2.6**. The existence of hydrolysable ester linkages in the epoxy monomers affected their behavior in alkaline and acidic conditions, which could be understood from the weight loss percentages. Although the relatively higher crosslinking density and structural compactness of TAE100 offered comparatively better resistance in the used conditions [31].

2.3.7. Transparency

The transmittance of a material depends on its ability to transmit light through it without absorbing or diffracting it. The prepared bio-based epoxy thermosets exhibited excellent

Table 2.6: Chemical resistance results of TAE thermosets in terms of weight loss (%)

Sample	5% NaOH	5% HCl	10% NaCl	10 % EtOH	Water
TAE50	5.05 ± 0.36	2.94 ± 0.16	0.03 ± 0.00	0 ± 0	0 ± 0
TAE75	5.01 ± 0.03	3.23 ± 0.20	0.26 ± 0.02	0.55 ± 0.03	0 ± 0
TAE90	4.97 ± 0.04	2.18 ± 0.07	0.95 ± 0.05	0.12 ± 0.02	0 ± 0
TAE100	3.73 ± 0.06	2.14 ± 0.03	0.80 ± 0.02	0.47 ± 0.02	0 ± 0

transparency, enabling their application to optical devices as well as packaging materials. **Figure 2.6(a)-(d)** depicts the digital photographs of the thermosets taken by placing each thermoset on a piece of paper with their written code tags. **Figure 2.6(e)** displays the corresponding transmittance curves of the thermosets recorded in the 200-800 nm wavelength region. The transmittance percentage of the bio-based epoxy thermoset TAE100 was recorded to be 81.12%, which was slightly lower than the partly bio-based ones. The presence of abundant aromatic ring systems and polar groups acting as auxochromes resulted in absorbing the visible radiation with increasing TA loading, which in turn led to a lowering of transparency.

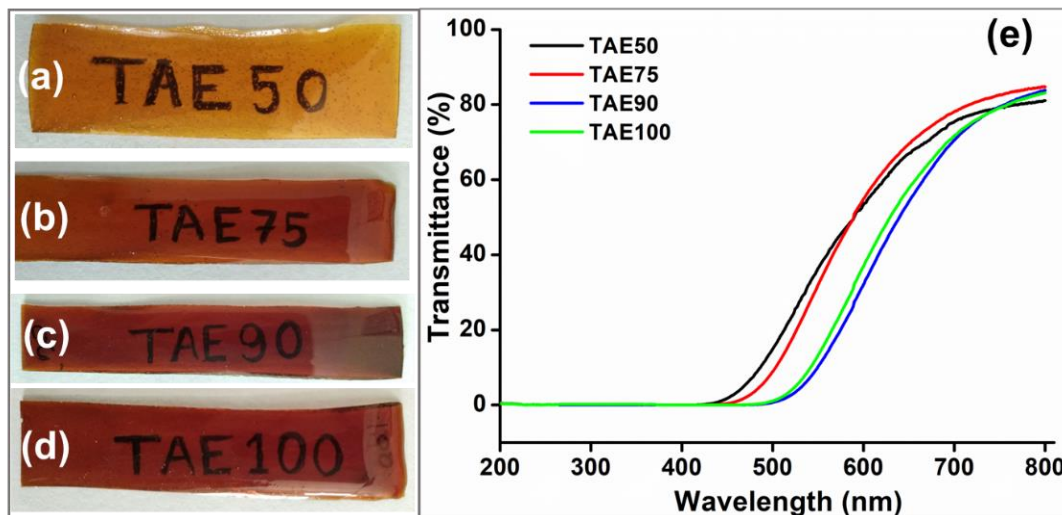


Figure 2.6: Digital photos of transparent epoxy thermosets; (a) TAE50, (b) TAE75, (c) TAE90, (d) TAE100 and (e) variation of their transmittance percentages with wavelength

2.3.8. Antioxidant activity

The antioxidant activity of the prepared epoxy thermosets was examined by monitoring the quenching ability of the stable DPPH radical by the thermosets. DPPH appears violet in color with a characteristic absorption at a wavelength of 517 nm. Quenching of DPPH by an antioxidant result in the formation of yellow-colored DPPH-H by absorbing a H radical from the antioxidant [10]. In this instance, TA, being a polyphenol, has the potential to serve as a H provider for DPPH and thus act as an antioxidant. This is evident from its expeditious radical scavenging activity (94.32%) obtained for TA just after the addition of DPPH solution [11]. The prepared epoxies, however, evinced relatively lower scavenging activity compared to TA, as revealed by **Figure 2.7**. Surface epoxidation of TA as well as high crosslinking density gradually lowered the number of unsubstituted hydroxyl groups in the TA moiety of the thermosets that can serve as the H donor to DPPH.

Thus, the thermosets required a 48 h incubation period in dark conditions to show a moderate quenching of DPPH. A reciprocal relationship was observed between scavenging activity and TA concentration. Henceforth, TAE100 displayed the lowest radical scavenging ability (31.87%) due to high TA loading and a higher number of epoxy groups present in its structure. Further increasing the incubation time increases the scavenging ability, with > 80% ability recorded for all four thermosets after 72 h.

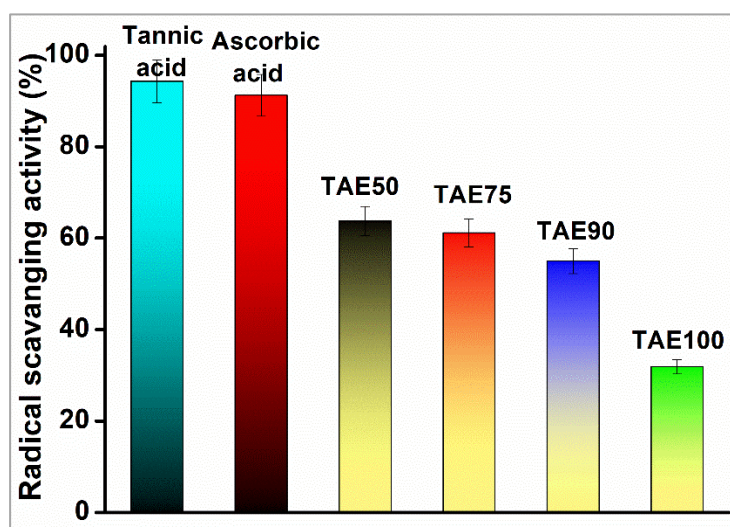


Figure 2.7: Radical scavenging activity of epoxy thermosets (after 48 h), TA and ascorbic acid

2.3.9. Biodegradation study

To judge the compatibility of the epoxy thermosets with the environment, a biodegradation study was carried out with two different bacterial strains, viz. gram-

positive *B. subtilis* and gram-negative *P. aeruginosa*, using the McFarland turbidity method. As per the reports obtained from the literature, TA is found to have significant antibacterial activity against certain gram-negative bacteria (including *P. aeruginosa*) [31, 32] and to a certain extent against the gram-positive bacteria like *B. subtilis* [33]. Therefore, the presence of the TA moiety in the prepared epoxy thermosets offered the latter a certain degree of antibacterial activity, which is supposed to affect the biodegradability of the thermosets. As elucidated by the results, *B. subtilis* displayed a good biodegradation profile with increasing exposure time. The results obtained for *P. aeruginosa* were comparatively lower because of the high antibacterial nature of TA against it and thus are not presented. *B. subtilis* is a petroleum-originated thermophilic bacteria with weak cell hydrophobicity capable of bioremediation of hydrocarbons [34]. The OD curves achieved for *B. subtilis* as an indicator for bacterial growth are displayed in **Figure 2.8(a)**. Initially, a gradual increase in bacterial growth was recorded until a maximum level was reached, decreasing thereafter with the increase in exposure time. The observed trend is possibly due to the presence of the nutrient medium as the source of energy for the microbes, that enhanced their growth. But as the nutrients ran out, the thermosets were left as the only source of carbon and energy for the bacteria [35]. The initial stages of degradation of the four thermosets were affected by the simultaneous and opposing effects of several factors. *B. subtilis* being weakly hydrophobic in nature, the bacterial cells might have faced difficulties in absorbing the hydrophilic thermosets to initiate the breakage [34]. Again, with an increasing TA percentage in the thermosets, the antibacterial activity had a tendency to resist bacterial growth. The highly crosslinked structure and smooth, glossy surface of the epoxy thermosets also offered resistance to the easy accessibility for bacterial attack by resisting the initial adherence of the bacteria to the bulk through the smooth surface. The presence of the nonbiodegradable BPA moiety in TAE50, TAE75, and TAE90 lowered the rate of degradation for these thermosets, although TAE100, being the bio-based one, did not suffer the same. On the contrary, the presence of easily hydrolysable ester linkages originating from the TA moiety and effortlessly cleavable amide linkages of the hardener system tends to accelerate the degradation of the thermosets [13]. The alkane chains present in the bio-based hardener serve as the carbon source for the bacteria and facilitate the breakage of the crosslinking [34]. The result of these counter-effects considerably affected the degradation profile of the thermosets, as reflected in the weight loss values, shown in **Figure 2.8(b)**. The SEM

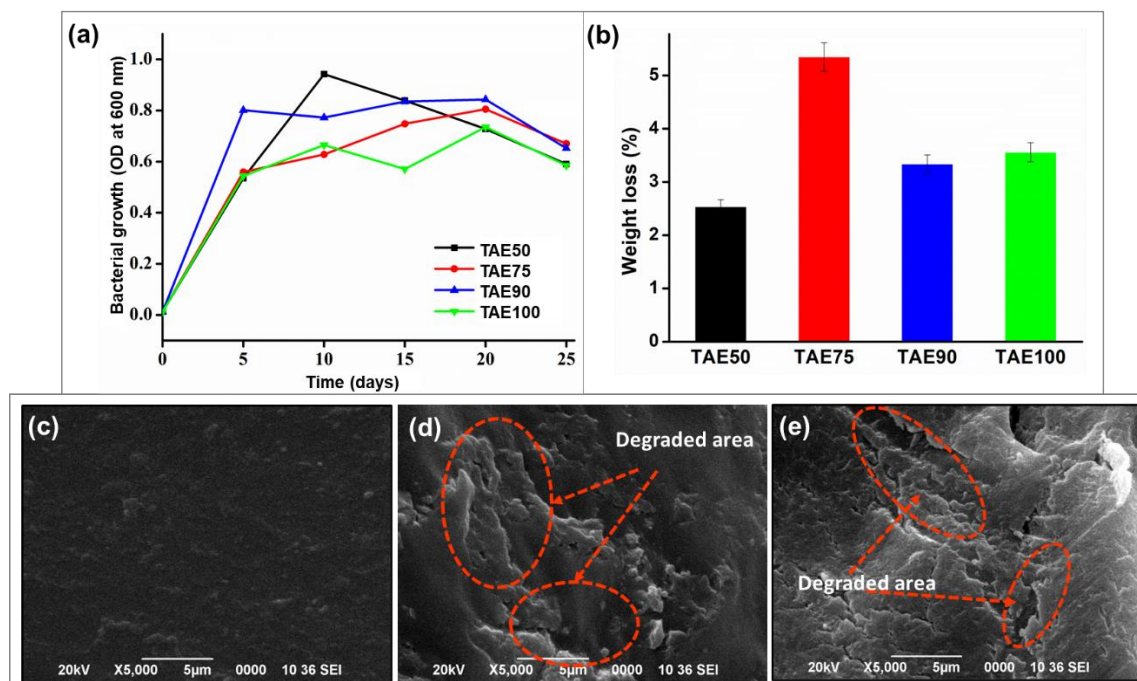


Figure 2.8: Bacterial degradation profiles of the thermosets by *B. subtilis*; (a) bacterial growth against exposure time for the thermosets after 30 days, (b) weight loss after biodegradation, and (c) and (d)-(e) SEM images of TAE100 thermoset before and after bacterial degradation, respectively

images of the degraded TAE100 thermoset were recorded after 4 weeks of incubation in the *B. subtilis* bacterial solution. The image screened in **Figure 2.8(d)-(e)** revealed the presence of a substantial amount of surface erosion in the TAE100 thermoset compared to the control, where a smooth and uniform surface was observed (**Figure 2.8(c)**). The SEM images confirmed that a partial biodegradation was effectively taking place over the surface of the thermosets; however, complete degradation demanded a prolonged incubation period.

2.4. Conclusion

In this study, a TA-derived bio-based epoxy resin was prepared, which was subsequently crosslinked with a bio-based hardener to achieve a bio-based epoxy thermoset. TA and fatty acid-based hardeners provided sustainability to the epoxy thermoset, as the resultant thermoset is also biodegradable. Further, its high mechanical strength and good thermal behavior revealed its great potential for different structural applications. The excellent transparency as well as the good adhesive character further broadened its applicability to eco-friendly optical devices and coating materials. Thus, the prepared epoxy may be employed as a high-performance material in various engineering domains. In addition, the study inclined toward exploring possible opportunities for further modification that may

lead to enormous potential applications.

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