

Synthesis and Physicochemical Study of Polyester Polyols of Epoxy Resin of 2,4,6-Tris(4-hydroxyphenyl)-1,3,5-Triazine and Their Polyurethanes

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ABSTRACT: Polyester polyols of ricinoleic acid (ETPRA), oleic acid, linoleic acid (ETPLA), and rosin (ETPR) and epoxy resin of 2,4,6-tris(4-hydroxyphenyl)-1,3,5-triazine (ETP) and their polyurethanes (PUs) were synthesized and characterized by Fourier transform infrared spectroscopy, NMR, differential scanning calorimetry, and thermogravimetric analysis techniques. The PU films showed the following density order: ETPRPU600 > ETPRAPU600 > ETPLAPU600. ETPLAPU600 showed good tensile strength and volume resistivity values compared to ETPRAPU600 and ETPRPU600. All three PUs showed good electric strength. ETPLAPU600 showed almost double the electric strength of ETPRAPU600 and ETPRPU600. The incorporation of soft-segment poly(ethylene glycol) 600 into PU chains resulted in the flexibility of the films. The PU films showed a high water absorption tendency in water, acidic, and saline environments, and they degraded in an alkaline environment. The weight gain tendency of the films was due to surface solvolysis and was also probably due to microcrack formation. The polyester polyols and PUs were thermally stable up to about 167–221 and 184–214°C, respectively, and followed multistep degradation reactions with either fractional or integral order (0.43–2.71) degradation kinetics. Thus, the structure of the PUs affected the studied physicochemical properties of the films. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40203.

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INTRODUCTION

Polyurethanes (PUs) are a versatile class of polymers, which find a broad range of applications, for example, as elastomers, sealants, fibers, foams, coatings, adhesives, and biomedical materials. The synthesis of PUs is carried out by a variety of methods, although the most widely used method starts from difunctional or polyfunctional hydroxyl compounds (polyols) with difunctional or polyfunctional isocyanates, which are usually industrially produced from petroleum. The progressive dwindling of fossil resources, coupled with the drastic increase in oil prices in the long term, has driven researcher to develop alternatives based on renewable resources for the production of polymer materials. A major drawback of these materials is their ease of flammability and the toxic nature of the gases, which are evolved. PU foams, in particular, are widely used in upholstery and home furnishings and, as a result, are often major contributors to fires.¹

In recent years, the utilization of renewable materials, such as plant oils and natural fatty acids, for replacing petroleum-derived raw materials for the production of polymeric materials

has attracted great attention because of social, environmental, and economic considerations. Considerable work has been reported on biobased PUs;^{2–9} this work has focused on the preparation of such types of polyols derived from vegetable oils in combination with petrochemical-based diisocyanates. It has been shown that biobased PUs have comparable properties in many aspects with PUs derived from petrochemical-based polyols.^{10,11}

Fatty acids (soft segments) derived from vegetable oils are useful for the development of PUs with dangling chains as their constitutive characteristics.^{12–16} Such PUs are ecologically sustainable and potentially biodegradable polymers. Materials derived from renewable resources play an important role in saving the environment and preventing natural calamities. Vegetable oils are one of the cheapest and most abundant biological sources available in large quantities, and their use as starting materials has numerous advantages for example, low toxicity, inherent biodegradability, and high purity.¹⁷ They are considered to be one of the most important classes of renewable resources for the production of biobased thermosetting PUs. For natural oils

to be used as raw materials for polyol production, multiple hydroxyl functionality is required.¹⁸

During the thermal degradation of PUs, many pyrolyzates can be generated because of secondary reactions, such as chain breaking, isomerization, and dehydrogenation.^{19,20} It is generally accepted in the literature that the thermal degradation of the urethane linkages within PU (the primary degradation step) occurs over the temperature range from 200 to 250°C. Depolymerization results in major volatile diisocyanate species, and PU can also undergo secondary decomposition reactions. Depolymerization of the urethane linkages leave a residue containing almost exclusively regenerated polyol. The diisocyanate cannot volatilize; it will be trapped within the pyrolysis zone and the reverse reaction can occur. That is, the polyol and isocyanate can recombine to reform the urethane bond, and equilibrium will, therefore, become established.¹

A literature survey revealed that no work has been reported on the synthesis and properties of PUs of polyester polyols based on multifunctional epoxy resins containing *s*-triazine moieties, which encouraged us to undergo this investigation. In this study, we used fatty acids derived from renewable resources for the syntheses of PUs of epoxy polyester polyols. We expected that multifunctional epoxy resins would possess a high crosslink density and, hence, a rigid and brittle nature. The brittle and rigid properties could be improved by the incorporation of soft segments in the polymer chain. To improve the properties of the PUs, we modified a trifunctional epoxy resin [epoxy resin of 2,4,6-tris(4-hydroxyphenyl)-1-3-5-triazine (ETP)] and converted it into polyester polyols with fatty acids and further with poly (ethylene glycol) 600 (PEG600). We successfully modified the PUs with improved properties to some extent. The main objective of this study was to use sustainable and biodegradable fatty acids and PEG600 to synthesize PUs with improved physicochemical properties.

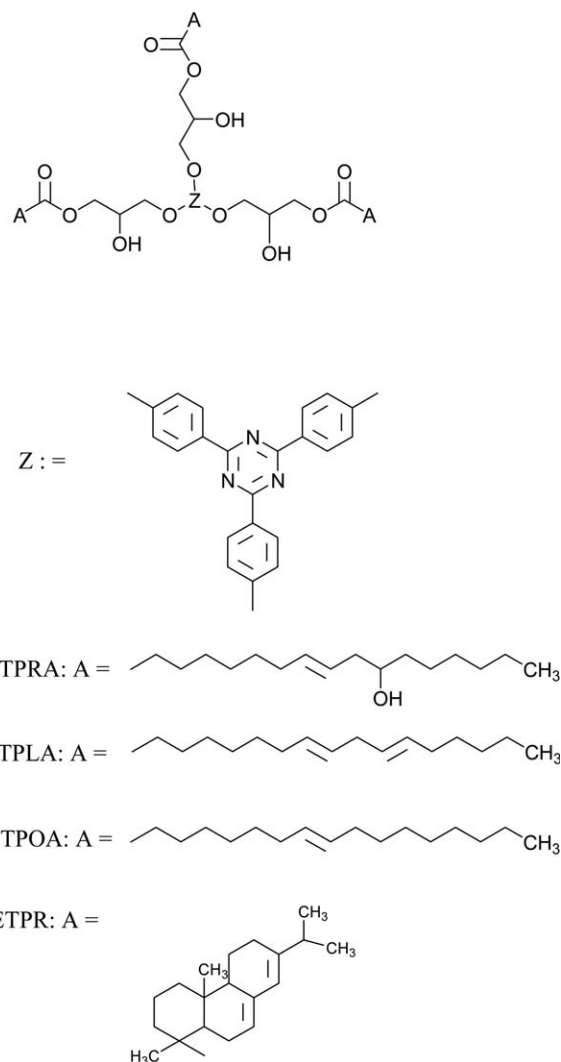
EXPERIMENTAL

Reagents and Materials

Tetrahydrofuran (THF; Spectrochem, Mumbai, India) and 1,4-dioxane (Allied Chemicals, Vadodara) were laboratory grade and were purified according to reported methods.²¹ ETP (EE 771) was synthesized according to a recent publication.²² Oleic acid (Allied Chemicals, Vadodara), ricinoleic acid, linoleic acid, and rosin (National Chemicals, Vadodara), toluene diisocyanate (TDI; 80% 2,4-toluene diisocyanate and 20% 2,6-toluene diisocyanate; Narmada Chematur Petrochemicals, Ltd., Bharuch), PEG600 (Spectrochem, Mumbai, India), and triethylamine (Spectrochem, Mumbai, India) were used as received.

Syntheses of the Epoxy Polyester Polyols

Polyester polyols (Scheme 1) having acid values of less than 30 were synthesized as follows. A 500-mL, three-necked, round-bottomed flask equipped with a condenser, a stirrer, and a thermometer was placed in an oil bath. To this flask, 0.04 equiv of ETP; 0.14 mol of ricinoleic acid, linoleic acid, oleic acid, or rosin; 40 mL of 1,4-dioxane; and 1 mL of triethylamine catalyst were charged, and the temperature of the



Scheme 1. General structure of the polyester polyols of ETP.

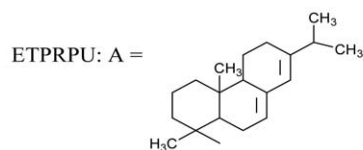
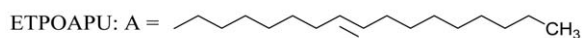
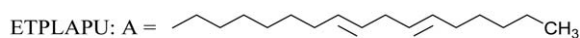
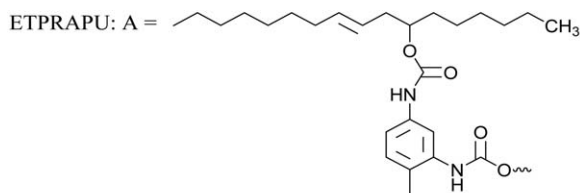
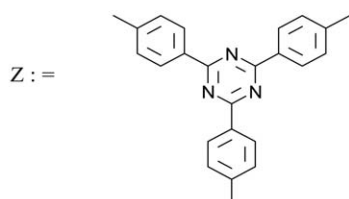
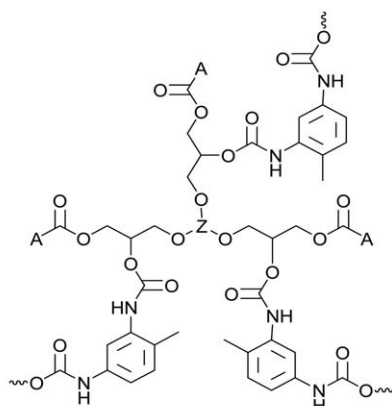
oil bath was increased to reflux with stirring. The reaction was refluxed for 2–6 h, and excess solvent was distilled off and cooled to room temperature. The solid resin was isolated from an excess of cold water, filtered, washed well with saturated bicarbonate solution, and finally washed well with distilled water and dried in an oven at 50°C. The resin was purified three times from a 1,4-dioxane–water system. Polyester polyols are hereafter designated as ETpra for that of ricinoleic acid, ETpla for that of linoleic acid, ETpoa for that of oleic acid, and ETPR for that of rosin. Polyester polyols are highly soluble in common solvents such as 1,4-dioxane, methyl ethyl ketone, *N,N*-dimethylformamide, dimethyl sulfoxide (DMSO), and THF.

The acid and hydroxyl values of the purified polyester polyols were determined according to reported methods.²³ For the determination of acid values, THF was used as the solvent, and 0.1N alcoholic potassium hydroxide was used as a titrant, whereas for the hydroxyl values, a mixture of acetic anhydride and pyridine (1:3 v/v) was used as a solvent, and 1N alcoholic potassium hydroxide was used as a titrant. Phenolphthalein was

Table I. Acid and Hydroxyl Values of the Polyester Polyols

Time (h)	Acid value (mg of KOH ⁻¹)				Hydroxyl value (mg of KOH ⁻¹)			
	ETPRA	ETPLA	ETPOA	ETPR	ETPRA	ETPLA	ETPOA	ETPR
2	24.7	60.6	30.3	46.0	235.8	73.8	126.6	49.2
3	18.4	52.7	22.4	34.9	395.4	126.5	284.8	193.3
4	15.7	41.5	17.9	30.3	536.9	291.8	386.7	393.7
5	10.1	25.8	11.2	15.7	627.6	474.6	453.5	478.1
6	7.8	16.8	9.0	9.0	707.4	576.5	597.6	566.0

used as an indicator. Titration was carried out in triplicate, and the mean values of the acid and hydroxyl values were considered. The acid and hydroxyl values of the polyester polyols are

**Scheme 2.** General structure of the PUs of the ETP polyols.

presented in Table I, in which it is shown that acid values decreased and the hydroxyl values increased with the extent of the reaction time. This indicated the practical conversion of epoxide groups into ester groups.

Syntheses of the PUs of Polyester Polyols

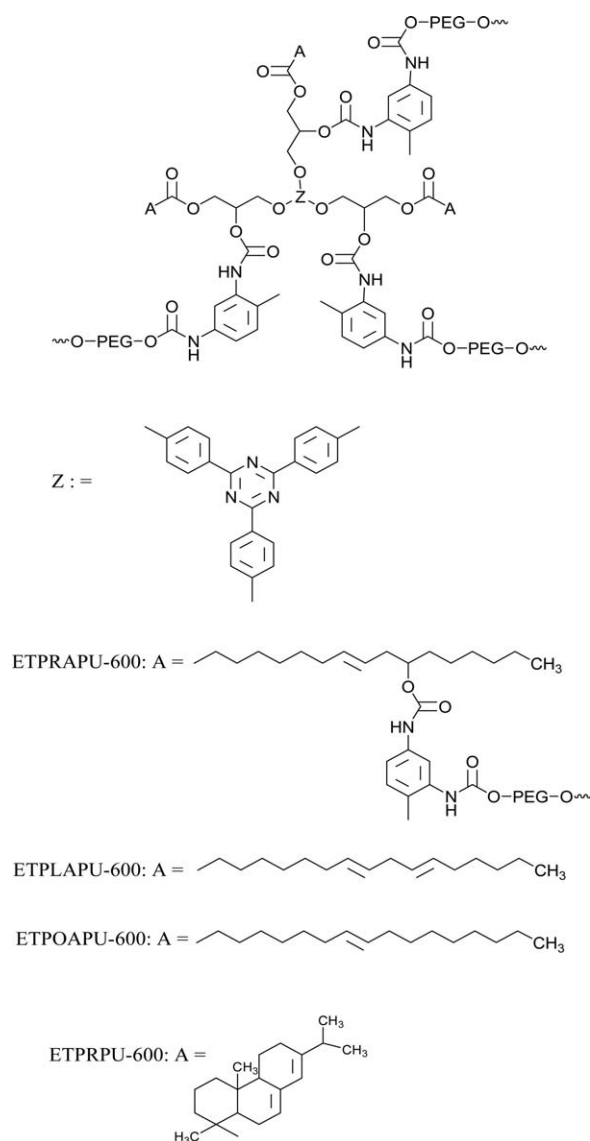
Into a 100-mL beaker, a required quantity of ETPRA (acid value 7.8), ETPLA (acid value 16.8), ETPOA (acid value 9.0), or ETPR (acid value 9.0; Table II) was dissolved in 20 mL of THF. To this solution, 0.3 mL of TDI in 5 mL of THF was added dropwise with stirring. The resulting solution was stirred manually for 15 min and poured into a leveled 15 × 15 cm² glass mold. The solvent was allowed to evaporate with a controlled rate at room temperature. After 24 h, the film was peeled from the mold. The PU films were found to be rigid and brittle. Hereafter, PUs (Scheme 2) are designated as ETPRAPU for that of ricinoleic acid, ETPLAPU for that of linoleic acid, ETPOAPU for that of oleic acid, and ETPRPU for that of rosin.

Syntheses of the Copolyurethanes of Polyester Polyols

To improve the flexibility of the PU films, efforts were made to synthesize copolyurethanes with various proportions of PEG600 as a soft segment. Thus, into a 100-mL beaker, required quantities (Table II) of ETPLA, ETPRA, or ETPR and (0.0005 mol) PEG600 was dissolved in 20 mL of THF at room temperature. To this solution, 0.001 mol of TDI in 5 mL of THF was added dropwise with stirring. The resulting solution was stirred manually for 15 min and poured into a leveled 15 × 15 cm² glass mold. The solvent was allowed to evaporate at a controlled rate. After 24 h, the film was peeled from the mold. A high concentration of PEG600 (>0.0005 mol) resulted in rubberlike PU films. Hereafter, the

Table II. Experimental Details of the Synthesized Copolyurethanes

PU	Polyol (g)	PEG-600 (g)	TDI (g)	NCO/OH
ETPRAPU	1.414	-	0.364	0.23
ETPLAPU	1.152	-	0.364	0.35
ETPOAPU	1.194	-	0.364	0.33
ETPRPU	1.132	-	0.364	0.37
ETPRAPU-600	7.07	3.05	1.712	0.73
ETPLAPU-600	5.76	3.05	1.712	0.88
ETPOAPU-600	5.97	3.05	1.712	0.85
ETPRPU-600	5.66	3.05	1.712	0.90



Scheme 3. General structure of the copolyurethanes of the polyester polyols and PEG600.

copolyurethanes (Scheme 3) are designated as ETPRAPU600, ETPLAPU600, and ETPRPU600. ETPOAPU600 was found to be very difficult to peel from the glass mold because of its strong adhesion with the glass surface, so its properties were not studied.

Measurements

The IR (KBr pellets) spectra of the polyester polyols and their PUs were scanned on a Shimadzu FTIR-8400 spectrometer over the frequency range from 4000 to 400 cm^{-1} . The $^1\text{H-NMR}$ spectra of the polyester polyols were scanned on a Bruker AVANCE II (500-MHz) spectrometer with hexadeuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) as a solvent and TMS as an internal standard. The density measurements of the PU films were carried out by a flotation method at $35 \pm 0.1^\circ\text{C}$ and were accurate to $\pm 0.0001 \text{ gcm}^{-3}$. Into six different wide-mouth stoppered test tubes, a small piece of film and about 5 mL of CCl_4 were placed, and *n*-hexane was added dropwise with shaking

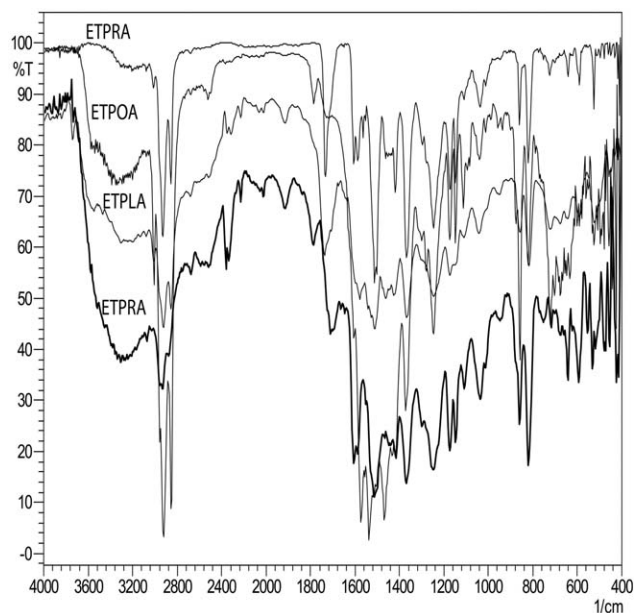


Figure 1. Fourier transform infrared spectra of the ETPLA, ETPLA, ETPOA, and ETPLA resins.

until the film remained suspended throughout and was allowed to equilibrate at room temperature for 24 h. The densities of the resulting mixtures were measured according to our previous report,²⁴ and the average values with standard deviations were considered. The chemical resistance of the films against water and 10% each of HCl , H_2SO_4 , HNO_3 , CH_3COOH , NaOH , KOH , NaCl , and NaHCO_3 was measured by a change-in-weight method at 35°C . Tensile tests were carried out on a Shimadzu Autograph universal tensile testing machine (model AG-X Series) at a speed of 0.5 mm/min according to the ASTM D 638-91 method. Four to five specimens of each of the films were tested, and the mean values with standard deviations are reported. The volume resistivity (ASTM D-257-2007) and electric strength [IEC:60243(pt-1)-1998] measurements were carried out on a Hewlett-Packard high-resistance meter in air at 25°C after charging for 60 s at a 500-V direct-current applied voltage and on a high-voltage tester (Automatic Electric, Mumbai, India) in air at 27°C with 25/75 mm brass electrodes, respectively. Differential scanning calorimetry (DSC) measurements were carried out on a Shimadzu DSC60 at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere (flow rate = 20 mL/min) with standard aluminum pans. Known amounts (2–3 mg) of the samples were sealed with the help of a crimper. The DSC thermograms were scanned over the temperature range from 50 to 350°C . Thermogravimetric analysis (TGA) experiments were conducted on a PerkinElmer TGA (model Pyris-1) at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere (flow rate 20 mLmin $^{-1}$). TGA thermograms were scanned over the temperature range from 50 to 700°C with samples of 7–10 mg.

RESULTS AND DISCUSSION

IR Spectral Analysis

IR spectra of the polyester polyols (ETPLA, ETPLA, ETPOA, and ETPLA) and PUs of polyester polyols (ETPRAPU, ETPLAPU, ETPOAPU, and ETPLA) are presented in Figures 1 and 2,

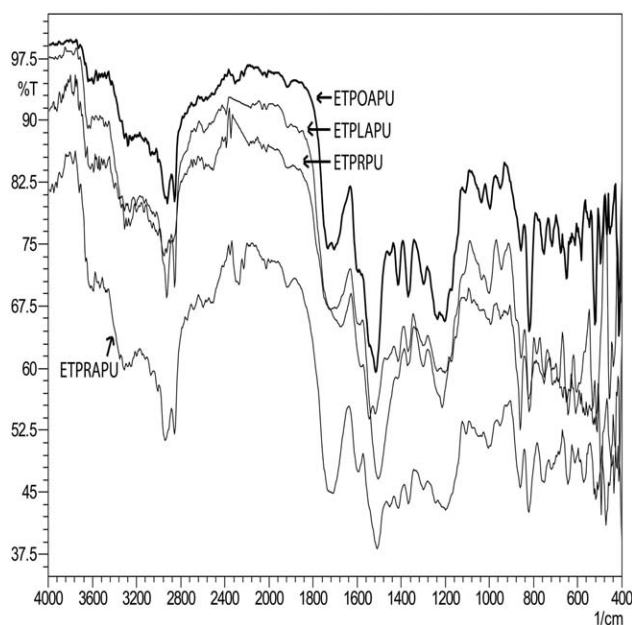


Figure 2. Fourier transform infrared spectra of ETPLAPU, ETPRAPU, and ETPOAPU.

respectively. The polyester polyols showed characteristic IR absorption frequencies at $3346\text{--}3302\text{ cm}^{-1}$ (--OH stretching), $1786\text{--}1734\text{ cm}^{-1}$ (ester --C=O stretching), $1248\text{--}1246\text{ cm}^{-1}$ (C--O--C stretching), and $1041\text{--}1036\text{ cm}^{-1}$ (C--OH deformation), and those of the PUs showed absorption peaks at $3306\text{--}3308\text{ cm}^{-1}$ (--N--H stretching), $1734\text{--}1674\text{ cm}^{-1}$ (ester and urethane stretching), and $1234\text{--}1207\text{ cm}^{-1}$ (C--O--C stretching) in addition to the normal modes of aliphatic, alicyclic, and aromatic groups. Urethane formation resulted in a decrease in the absorption frequencies of OH, ester, and ether groups.

Thus, the IR spectral data supported the formation of polyols and their PUs.

$^1\text{H-NMR}$ Spectral Analysis

A representative $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) spectrum of ETPOA is presented in Figure 3, in which it is shown that the spectrum is highly complex. The complexity was due to the three different aromatic and aliphatic moieties present in the ETPOA molecule. However, efforts were made to interpret the NMR data. The observed signals were in accordance to the expected ones. Different types of protons, their chemical shifts, and multiplicities were assigned as follows: Methyl protons (H1) of oleic ester appeared as a triplet at $0.836\text{--}0.863\text{ ppm}$. Methylene protons H2–H7 and H12–H15 ($1.153\text{--}1.263\text{ ppm}$), H16 ($1.35\text{--}1.45\text{ ppm}$), and H8 and H11 ($1.964\text{--}1.978\text{ ppm}$) gave multiplets. Methylene protons (H17) appeared as a triplet at 2.093 ppm . The alcoholic protons (H20; --CH--OH) and methylene protons (H21) bonded to an ether linkage overlapped and gave multiplets at $4.0\text{--}4.2\text{ ppm}$. The methine protons ($\text{--CH}_2\text{--CH--OH}$, H19) and methylene protons (H18) bonded to ester linkage overlapped and gave a multiplet at $4.2\text{--}4.4\text{ ppm}$. The aromatic protons (H22 and H23) gave doublet of doublet patterns at $6.958\text{--}7.201$ and $8.533\text{--}8.653\text{ ppm}$, respectively. The residual DMSO and moisture present in it gave intense signals at 2.50 and 3.40 ppm , respectively, which masked the aliphatic proton signals to a great extent. The masking effect in other polyols resulted in very low intensity signals. Thus, the $^1\text{H-NMR}$ data supported the expected structure of ETPOA.

Density of the Copolyurethane Films

The densities of the PU films along with the standard deviations are reported in Table III. The observed density trend was $\text{ETPR-PU600} > \text{ETPRAPU600} > \text{ETPLAPU600}$; this confirmed the different PU structures. The packing density depended on degree

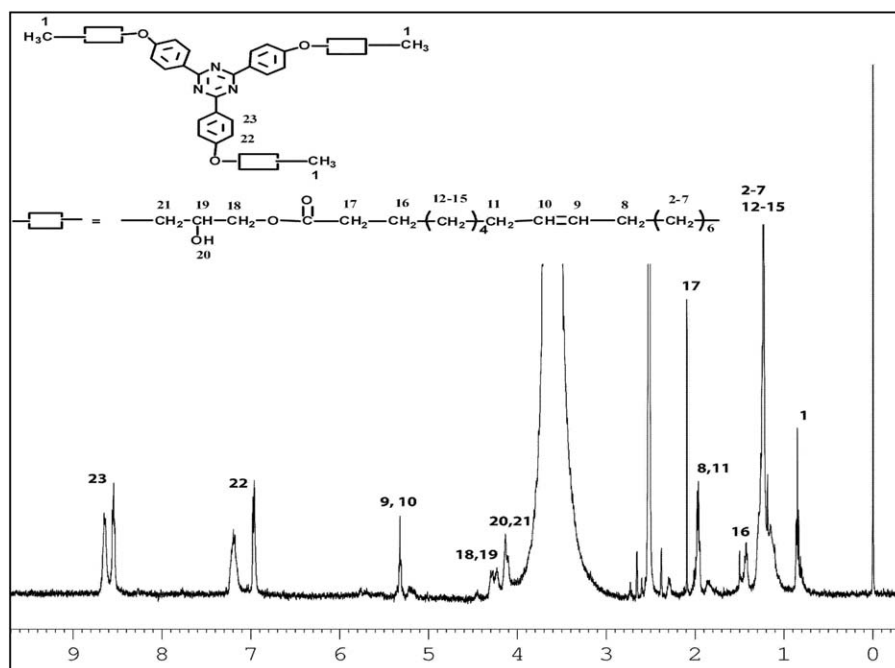


Figure 3. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) spectrum of ETPOA.

Table III. σ , Electric Strength, and Volume Resistivity Data for the Copolyurethane Films

PU film	σ (MPa)	Electric strength (kVmm ⁻¹)	Volume resistivity (Ω cm)	Density (gcm ⁻³)
ETPRAPU-600	5.02	10.1	5.0×10^{09}	1.1931 ± 0.002
ETPLAPU-600	28.73	20.7	2.7×10^{13}	1.1032 ± 0.0003
ETPRPU-600	1.21	11.5	2.5×10^{10}	1.2361 ± 0.0021

of crosslinking density and also on the degree of branching. Generally, the physical properties of PUs largely depend on the chain length of polyol, the extent of crosslinking, and the nature of diisocyanate.

Mechanical and Electrical Properties of Copolyurethanes

Tensile, flexural, and electrical properties of the materials are very useful for the engineering design and in classifying materials with respect to their bending strength and stiffness and in predicting the relative insulation quality characteristic of the selection of materials for specific applications. The tensile strength (σ) of the composites was determined according to eq. (1):

$$\sigma = W/A \quad (1)$$

where W is the load value at break and A is the original cross-sectional area of the sample.

The electric strength and volume resistivity of the composites were determined according to eqs. (2) and (3), respectively:

$$\text{Electric strength} = V/t \quad (2)$$

where V is the puncture voltage (volts) and t is the sample thickness (mm).

$$\text{Volume resistivity} = (R_v A)/t \quad (3)$$

where R_v is the volume resistance (ohms), A is the area of the electrodes, and t is the sample thickness (cm).

The σ , electric strength, and volume resistivity of the ETPRAPU600, ETPLAPU600, and ETPRPU600 films were determined according to eqs. (1)–(3), and the mean values are reported in Table III. As shown in Table III, it was clear that the ETPLAPU600 film possessed relatively good tensile and electrical properties compared to the ETPRAPU600 and ETPRPU600 films. The observed variation in said properties may have been due to the variation in the structural constitution and degree of crosslinking. The low tensile properties were mainly due to the rigid and brittle nature of the ETPRAPU600 and ETPRPU600 films. The relatively high degree of crosslinking was expected in the case of ETPRA because of the doubled hydroxyl functionality compared to the cases of ETPRA and ETPR. Recently, Maminsky et al.²⁵ reported the effect of the NCO/OH ratio (0.29–0.68) on the wood adhesion properties of the PUs on the basis of hyperbranched polyglycerols (hydroxyl functionalities = 4, 7, and 12) and diisocyanates. They also observed low σ s, ranging from 2.7 to 12 MPa, depending on the degree of crosslinking, that is, on the hydroxyl functionality of the polyols. The high degree of crosslinking resulted in the brittleness of the PUs. The ETPLAPU600 film possessed almost doubled electric strength compared to those of the

ETPRAPU600 and ETPRPU600 films. Similarly, the ETPLAPU600 film possessed 5400 and 5 times better volume resistivities compared to those of the ETPRAPU600 and ETPRPU600 films. The vast variation in the electric strength and volume resistivity of the PU films indicated a different structural constitution and hence different polarity of the PUs.

The incorporation of the soft segment (PEG600) into the PU chains resulted in the flexibility of the films.²⁶ Flexibility with improved tensile and electrical properties was achieved to a considerable extent in case of the ETPLAPU600 film but failed in case of the ETPRAPU600 and ETPRPU600 films. The increasing amount of hard segments usually increased the intermolecular attraction, rigidity, and brittleness.²⁷ When a load was applied to the PU film, soft segments threw away the load to hard segments, and as a consequence, the load was concentrated at the junction of the soft and rigid segments. This resulted in rupture, even at a low load. Because of a lack of coordination between the soft and hard segments, there was a nonuniform distribution of stress transfer.

The nature and molecular structure of the polymer chains, molecular weight, degree of crosslinking, test conditions, sample thickness, electrode area and geometry, voltage application rate, imperfection, impurities, and so on affect the mechanical and electrical properties of copolyurethanes.²⁸ In this case, the nature, molecular structure, and degree of crosslinking played important roles in determining the studied properties of the PU films. The fairly good σ , electric strength, and volume resistivity values of the ETPLAPU600 film signified its industrial importance as an insulating material.

Chemical Resistance

The chemical resistance of the PU films against various reagents, such as water and 10% aqueous HCl, HNO₃, H₂SO₄, CH₃COOH, NaHCO₃, NaOH, KOH, and NaCl was studied at 35°C. The percentage weight gain with the passage of time for ETPRAPU600, ETPLAPU600, and ETPRPU600 films are presented in Figures 4–6. The equilibrium time and equilibrium water content data are presented in Table III. The high equilibrium water content in the PU films was due to the presence of polar groups in the PU chains, which underwent solvolysis. As shown in Table IV, we observed that a high equilibrium water content was observed in water and acid environments, and the films broke down into pieces in an alkaline environment; this confirmed the hydrolysis of ester and urethane linkages. In a saline environment, the PU films became slightly green. In acidic environments, the ETPRAPU600 and ETPRPU600 films became slightly orange after 48 h and turned black after 144 h. The weight gain tendency of the films was due to the surface

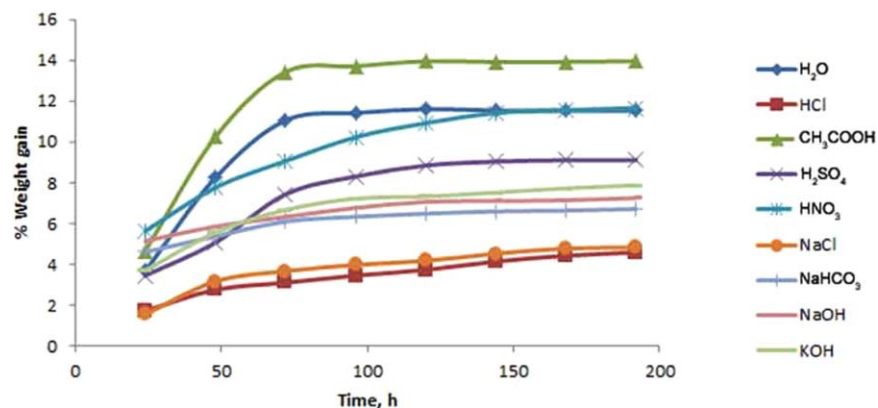


Figure 4. Plots of weight gain (%) against time in different solvents for the ETPLAPU600 films at 35°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solvolysis and probably also microcrack formation.^{29,30} The absorbed water indulged irreversible changes, such as chemical degradation, cracking, and blistering. The presence of electrolytes in water affect the water structure and, hence, the water uptake behavior in the PUs.

Thermal Analysis

DSC curves of the polyester polyols and PUs at a $10^{\circ}\text{Cmin}^{-1}$ heating rate in a nitrogen atmosphere are presented in Figures 7 and 8, respectively, and the observed transitions are reported in Table IV. The broad endothermic transitions at 72.5°C (ETPRA), 77°C (ETPLA), 85°C (ETPOA), and 67.3°C were assigned as melting transition of corresponding polyester polyols. More broad endothermic transitions at 121.3°C (ETPRA), 148°C (ETPOA), and 124.5°C (ETPR) were assigned to some physical change, and we further confirmed this by the lack of weight loss observed over those temperatures in the corresponding TGA curves (Figure 9). Other broad transitions at 249.3°C (endothermic) and 375°C (exothermic) of ETPRA, 267.3°C (endothermic) and 346.5°C of ETPLA, 257°C (exothermic) of ETPOA, and 285.6°C (endothermic) and 365.2°C of ETPR were due to the decomposition reactions and were further confirmed by the weight loss over those temperatures in the corresponding TGA curves (Figure 9).

Broad and shallow endothermic transitions at 88.3°C (ETPRAPU), 78.6°C (ETPLAPU), and 86.9°C (ETPOAPU) were

assigned as the melting transitions of untransformed residual polyester polyols. The broad and shallow endothermic transition of ETPRAPU at 107.6°C was due to some physical change that was probably due to the partial melting of PU. Other broad transitions at 294.7°C (endothermic) and 374.6°C (exothermic) of ETPRAPU; 301.8°C (exothermic) of ETPLAPU; 208.4°C (endothermic), 283.6°C (endothermic), and 378.9°C (exothermic) of ETPOAPU; and 221.9°C (endothermic), 299.9°C (endothermic), and 362.1°C (exothermic) of ETPRAPU were due to decomposition reactions and were further confirmed by weight loss over those temperatures and corresponding to the TGA curves (Figure 10). The endothermic transition of ETPOA at 85°C disappeared in ETPOAPU and confirmed the conversion of polyol into PU.

The TGA curves of the polyester polyols and their PUs at a $10^{\circ}\text{Cmin}^{-1}$ heating rate and in a nitrogen atmosphere are presented in Figures 9 and 10, respectively, where it is shown that both the polyols and their PUs showed different degradation patterns. As shown in Figure 9, we observed that ETPLA and ETPR followed three-step degradation reactions, whereas the ETPRA and ETPOA followed four-step degradation reactions. ETPRAPU, ETPLAPU, ETPOAPU, and ETPRPU followed three-step degradation reactions. The initial decomposition temperature (T_0), decomposition range, temperature of maximum weight loss (T_{max}), percentage weight loss involved in each step,

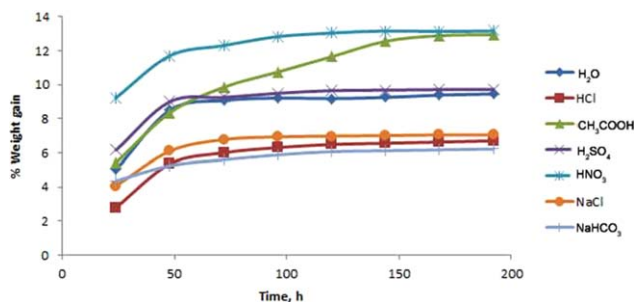


Figure 5. Plots of the weight gain (%) against time in different solvents for the ETPRAPU600 films at 35°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

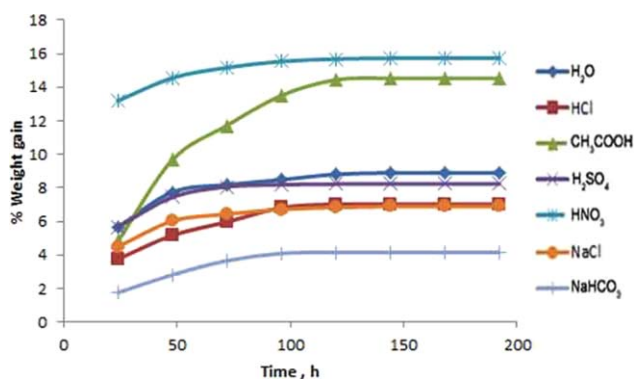


Figure 6. Plots of the weight gain (%) against time in different solvents for the ETPLAPU600 films at 35°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Equilibrium Time and Equilibrium Water Content Data for the Copolyurethane Films

Reagent	Equilibrium time (hr)			Equilibrium water content (%)		
	ETPRAPU-600	ETPLAPU-600	ETPRPU-600	ETPRAPU-600	ETPLAPU-600	ETPRPU-600
H ₂ O	120	72	96	8.8	11.0	9.2
HCl	120	144	96	7.0	4.1	6.3
CH ₃ COOH	144	72	168	14.5	13.4	12.9
H ₂ SO ₄	120	144	120	8.3	9.0	9.7
HNO ₃	96	120	120	15.5	10.9	13.0
NaCl	96	120	96	6.7	4.2	6.9
NaHCO ₃	120	96	144	4.1	6.3	6.1
NaOH	-	120	-	-	7.1	-
KOH	-	96	-	-	7.2	-

and percentage residue left at 700°C are recorded in Table V. The polyester polyols and their PUs were thermally stable up to about 167–221 and 184–214°C, respectively. ETPRAPU (196°C) and ETPRPU (214°C) were somewhat more thermally stable than those of ETPRA (171°C) and ETPR (167°C). ETPLA (203°C) and ETPLAPU (204°C) had practically the same thermal stability. ETPOAPU (184°C) showed less thermal stability than ETPOA (221°C). Ricinoleic acid, linoleic acid, and oleic acid were linear and had one, two, and one double bonds, respectively, whereas rosin was a polycyclic compound containing two double bonds. Ricinoleic acid possessed one additional hydroxyl group, which was responsible for the increase in the crosslinking density. The high thermal stability of ETPRPU was due to the rigid and cyclic structures of the rosin moiety and the strong intermolecular hydrogen bonding. Comparatively, ETPRAPU, ETPLAPU, and ETPOAPU were flexible because of the linear alkyl chains of the fatty acids. Thus, the observed variation in the thermal stability was mainly due to the different molecular structures of the polyols and their PUs. The T_{max} values for each step were determined from differential thermogravimetric (TG) curves. The T_{max} and percentage residue values were found to be different for the polyols and their PUs because of their different chemical constitutions.

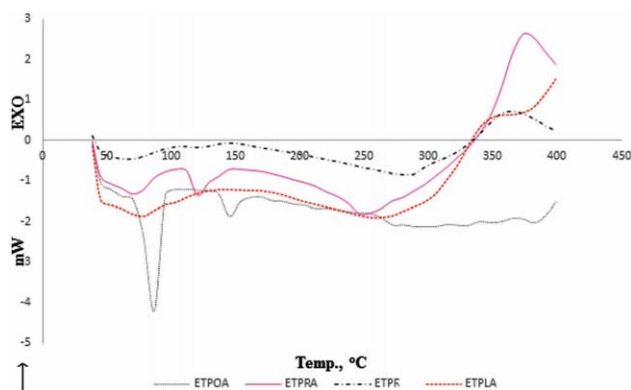


Figure 7. DSC thermograms of ETPLA, ETPOA, ETPRA, and ETPR in a nitrogen atmosphere at 10°Cmin⁻¹. (mw: milliwatt) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The associated kinetic parameters, such as the energy of activation (E_a), frequency factor (A_f), and degradation order (n), were derived according to the Freeman–Anderson method:³¹

$$\Delta \ln dw/dt = n \Delta \ln W_a - (E_a/R) \Delta(1/T) \quad (4)$$

$$A_f = (E_a \beta / RT^2) e^{E_a/RT} \quad (5)$$

$$\Delta S^* = R \ln (A_f h / kT) \quad (6)$$

where dw/dt is the weight loss with time, W_a is the active weight of the substance, β is the heating rate, R is the gas constant, h is Planck's constant, T is the temperature, ΔS^* is the entropy change, and k is Boltzmann's constant. The least squares values of E_a , A_f , and n are reported in Table VI. ΔS^* was determined at the corresponding T_{max} and is also reported in Table VI along with the regression coefficients (R^2 's). In Table VI, it is shown that the n , E_a , and A_f values were found to be different for the subsequent degradation reactions. Different magnitudes of the kinetic parameters indicated different chemical structures of the fatty acid moieties. The degradation reactions followed either fractional or integral order degradation kinetics depending on chemical constitutions of the polyols and their PUs. In accordance with theory, the high values of E_a

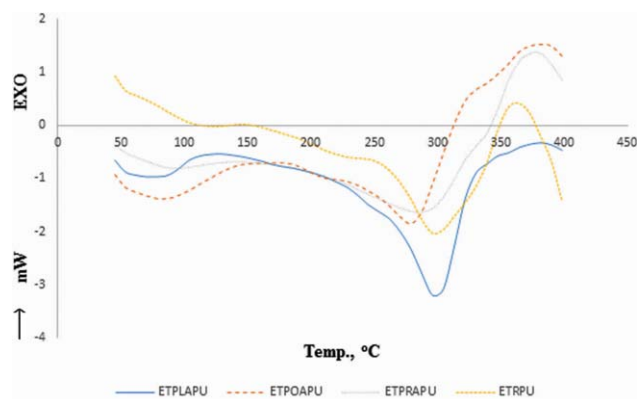


Figure 8. DSC thermograms of ETPLAPU, ETPOAPU, ETPRAPU, and ETPRPU in a nitrogen atmosphere at 10°Cmin⁻¹. (mw: milliwatt) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

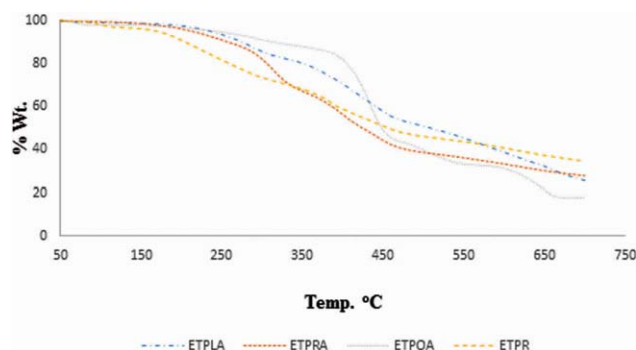


Figure 9. TG thermograms of ETPLA, ETPOA, ETPRA, and ETPR at a $10^{\circ}\text{Cmin}^{-1}$ heating rate in a nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reflected high values of A_f in all cases. From E_a values, we concluded that the larger the rigid value was, the larger the structure was, and vice versa. The magnitudes of ΔS^* indicated the orderliness of the transition state. The large and positive values

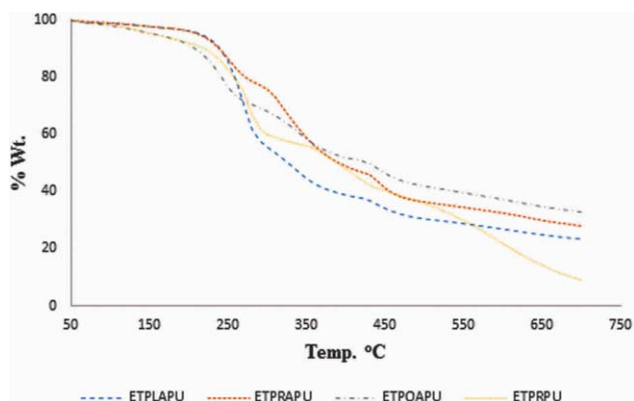


Figure 10. TG thermograms of ETPLAPU, ETPOAPU, ETPRAPU, and ETPRPU at a $10^{\circ}\text{Cmin}^{-1}$ heating rate in a nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of ΔS^* suggested that the transition states were in a more disorderly state than those of polyol or PU molecules and vice versa.³²

Table V. TGA Data for ETPLA, ETPOA, ETPRA, ETPR, ETPRAPU, ETPLAPU, ETPOAPU, and ETPRPU

Sample	DSC transitions (°C)	Endo/Exo	T_o (°C)	Decomposition range (°C)	T_{max} (°C)	Weight loss (%)	Residue at 700°C (%)
ETPRA	72.5	Endo	171	171-337	311.0	28.4	27.9
	121.3	Endo		337-415	398.0	17.4	
	249.3	Endo		415-478	441.1	11.8	
	375.0	Exo		478-700	607.9	12.3	
ETPLA	77.0	Endo	203	203-311	282.4	12.7	25.8
	267.3	Endo		330-475	421.3	29.4	
	346.5	Exo		536-700	588.9	21.8	
ETPOA	85.0	Endo	221	221-313	291.8	6.3	17.9
	148.0	Endo		380-465	431.0	41.8	
	257.0	Exo		485-551	505.0	8.7	
				600-663	644.2	13.8	
ETPR	67.3	Endo	167	167-298	224.3	21.5	34.7
	124.5	Endo		349-475	395.7	20.7	
	285.6	Endo		475-700	619.7	13.0	
	365.2	Exo					
ETPLAPU	78.5	Endo	204	204-295	265.9	38.6	23.3
	301.8	Endo		295-393	332.9	18.1	
				428-479	441.1	5.5	
ETPOAPU	86.9	Endo	184	184-270	244.9	21.2	32.8
	208.4	Endo		270-404	336.6	19.7	
	283.6	Endo		424-490	443.7	7.8	
	378.9	Exo					
ETPRAPU	88.3	Endo	196	196-281	250.4	18.1	28.0
	294.7	Endo		293-403	325.6	28.4	
	374.6	Exo		427-476	441.1	8.7	
ETPR	107.6	Endo	214	214-307	273.3	31.6	9.1
PU	221.9	Endo		364-430	398.0	11.8	
	299.9	Endo		521-700	596.4	24.8	
	362.1	Exo					

Table VI. Kinetic Parameters for ETPLA, ETPOA, ETPRA, ETPR, ETPRAPU, ETPLAPU, ETPOAPU, and ETPRPU

Sample	E_a (kJmol ⁻¹)	A (s ⁻¹)	ΔS^* (J K ⁻¹ mol ⁻¹)	n	R^2
ETPRA	133.0	5.4×10^{20}	151.6	0.99	0.962
	96.4	5.5×10^{10}	-41.6	0.57	0.970
	167.9	1.3×10^{18}	98.7	1.17	0.993
	39.9	5.8	-236.2	0.47	0.999
ETPLA	85.6	1.4×10^{14}	26.8	0.97	0.98
	45.7	2.4×10^3	-183	0.48	0.983
	58.2	4.8×10^2	-199.1	1.01	0.990
ETPOA	60.7	1.0×10^9	-72.0	0.43	0.96
	156.3	1.4×10^{17}	80.6	0.81	0.982
	134.7	8.9×10^{11}	-20.44	0.93	0.978
	249.4	2.0×10^{18}	99.0	0.59	0.986
ETPR	23.2	2.6×10^5	-177.7	0.68	0.939
	24.9	1.9×10^3	-232.0	0.45	0.969
	264.3	1.9×10^{22}	140.0	2.71	0.996
ETPLAPU	104.7	1.1×10^{20}	120.7	0.81	0.977
	86.4	5.7×10^{11}	-20.6	1.0	0.993
	23.6	2.2×10^{26}	256.1	1.4	0.978
ETPOAPU	109.7	9.1×10^{21}	177.2	0.82	0.974
	83.9	1.5×10^{11}	-31.4	1.12	0.973
	295.9	2.1×10^{33}	389.7	1.95	0.986
ETPRAPU	98.1	9.1×10^{18}	119.5	0.98	0.972
	98.9	1.3×10^{14}	25.1	1.48	0.970
	272.6	5.4×10^{30}	340.3	1.31	0.949
ETPRPU	76.5	8.5×10^{12}	3.4	0.97	0.990
	68.1	7.6×10^6	-115.5	0.51	0.970
	73.1	1.0×10^4	-173.6	0.93	0.987

Endo: Endothermic, Exo: Exothermic, T_0 : Initial decomposition temperature

Ether and ester linkages are weak points in polyols, whereas ether, ester, and urethane linkages are weak points in PUs, which degrade selectively and form radicals. These radicals further undergo a variety of reactions, such as branching, cross-linking, rearrangement, and recombination, and as a consequence, new products formed, which further degraded at elevated temperatures. The weight loss of the polyols in the temperature range 167–478°C was due to the decomposition of ester and ether linkages and the moisture content; these led to the formation of CO₂, alcohols, aldehydes, CO, and so on.^{33,34} The weight loss in the temperature range 475–700°C was due to the decomposition of the product formed previously as a result of the degradation of the original polyester polyols. Conventional PUs are known to exhibit poor resistance to heat and poor thermal stability. Thermal degradation occurs above 200°C.^{35,36} The weight loss in the temperature range 184–430°C was due to the decomposition of ether, ester, and urethane linkages and the moisture content; these led to the formation of CO₂, alcohols, amines, aldehydes, CO, and so on.^{33,34} The weight loss in the temperature range 430–700°C was due to the decomposition of the product formed previously as a result of the degradation of the original PUs of polyester polyols. The thermal degradation of polyols and PUs resulted in a number of

products because of the aforementioned reactions.^{19,20} We believed that the primary thermal degradation of the urethane linkages occurred below 250°C, and depolymerization resulted in the volatile diisocyanate species leaving polyol, which could also undergo secondary decomposition reactions at elevated temperatures. The decomposition of ester and urethane linkages resulted in the elimination of carbon dioxide, carbon monoxide, alcohols, amines, aldehydes, and so on. The other degradation species resulted in low-molecular-mass hydrocarbons. The dehydration of secondary hydroxyl groups with the formation of allylic bonds underwent a crosslinking reaction or aromatization. The dehydration and cleavage of allylic bonds involved a relatively low E_a . The repetition of the bond cleavage of the epoxy network led to the evolution of low-molecular-mass fragments. The residue (~9–35%) left at 700°C confirmed the formation of highly thermally stable crosslinked products. Thus, because of this complex nature, the polyester polyols and their PUs underwent complex degradation kinetics.

CONCLUSIONS

The polyester polyols of epoxy resin containing *s*-triazine ring and their PUs were synthesized successfully. The low acid values

and high hydroxyl values confirmed the conversion of epoxide groups into polyols. The PUs of synthesized polyols were found to be rigid and brittle, and therefore, their flexibility was improved by the incorporation of PEG600 as a soft segment. The PU films showed a moderate to good σ , electric strength, and volume resistivity. The PU films showed a high water absorption tendency in water, acidic, and saline environments, whereas they were found to degrade in an alkaline environment. Polyester polyols and their PUs were found to be thermally stable up to about 167–221 and 184–214°C and followed multistep degradation reactions with either integral or fractional order degradation kinetics

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