

Synthesis and Characterization of Ricinoleamide-Based Polyurethane

Mohammad Kashif · Eram Sharmin ·
Fahmina Zafar · Sharif Ahmad

Received: 8 December 2010 / Revised: 25 May 2011 / Accepted: 26 May 2011 / Published online: 14 June 2011
© AOCS 2011

Abstract *Ricinus communis* (RC) oil-based materials are currently receiving increasing attention because of economic and environmental concerns. In the present work, RC oil—a natural triol has been utilized for the development of an advanced polymeric material—poly(urethane-ricinoleamide) (PUR) through very simple synthesis and curing strategy, omitting derivatization steps or side reactions, chain extenders and crosslinkers. The synthesis of PUR was carried out in two steps. The first step is the introduction of an amide group in the RC oil (89.5% ricinoleic acid) via base catalyzed amidation, which results in *N, N*-bis (2-hydroxyethyl) ricinoleamide (HERA). The second step is urethanation of HERA by the reaction of toluene-2,4-diisocyanate (TDI) in minimal possible organic solvent by one-shot technique, which results in the formation of polyurethane along with amide linkages. The physico-chemical and spectral studies (FT-IR, ¹H-NMR and ¹³C-NMR techniques) confirm these two reactions and the structure of PUR. The resin was cured at ambient

temperature without any cross linker. Solubility of the resin was investigated in different polar and non-polar solvents. Thermo-gravimetric analysis (TGA)/differential thermal analysis (DTA) and Differential Scanning Calorimetry (DSC) were used to determine the thermal stability and curing behavior of PUR. An ambient cured ricinoleamide modified polyurethane resin exhibited thermal resistance up to 200–220 °C.

Keywords *Ricinus communis* oil · Ricinoleamide · Polyurethane · Spectral · TGA · Antimicrobial

Introduction

The strict environmental regulations imposed on the industries by governments and international agencies all over the world have focused the interests of scientists and researchers towards the utilization of sustainable resources for the preparation of eco-friendly polymeric materials. Among the sustainable resources, vegetable oils (triglycerides of fatty acids) are expected to be an ideal alternative to petro-chemical feed stock [1]. They represent one of the cheapest biological feed stocks available in large quantities and their use as starting materials offers numerous advantages, such as low toxicity, inherent biodegradability and high purity [2]. They have several excellent properties that can be utilized for the preparation of a number of value-added polymers and other materials that have found various applications in different fields. A variety of vegetable oils such as Linseed, Tung, Soybean, Sunflower, Karanj, Castor, etc., have been used for this purpose [3, 4].

Polyurethane is one of the important classes of polymers that possess a unique structure and have versatile applications. They generally comprise soft segments (di-/poly-ol)

Electronic supplementary material The online version of this article (doi:10.1007/s11746-011-1867-z) contains supplementary material, which is available to authorized users.

M. Kashif · E. Sharmin · S. Ahmad (✉)
Materials Research Laboratory, Department of Chemistry,
Jamia Millia Islamia, New Delhi 110025, India
e-mail: sharifahmad_jmi@yahoo.co.in

M. Kashif
e-mail: kashif_jmi25@yahoo.co.in

E. Sharmin
e-mail: eramsharmin@gmail.com

F. Zafar
Department of Chemistry, Jamia Millia Islamia,
New Delhi 110025, India
e-mail: fahmzafar@gmail.com; fahm_zafar@yahoo.com

and hard segments (di-/poly-isocyanates). The desirable properties of polyurethanes can be obtained by altering these segments [5]. Vegetable oil-based polyols [6] can be obtained by introducing several modifications such as hydroxylation, ozonolysis, amidation, etc., and are becoming important as an alternative to petro-based soft segments [7, 8]. Commercially available natural polyol such as *Ricinus communis* (RC) oil comprises about 90% ricinoleic acid (12-hydroxy-cis-9-octadecenoic acid) of the total triglyceride fatty acids of the oil. It is considered as a non-drying oil and has an effective hydroxyl functionality of 2.7. It can be used directly as a raw material for the preparation of polyurethanes without any further modification [9]. It has potential for the syntheses of variety of polyurethane products, ranging from coatings, cast elastomers, thermoplastic elastomers, rigid foams, semi-rigid foams, sealants and adhesives to flexible foams [7–9]. RC-based polyurethane obtained from the direct utilization of RC oil has advantages along with some disadvantages, such as low functionality, low reactivity due to the secondary hydroxyl groups, thus leading to semi-flexible and semi-rigid materials [7]. Therefore, several modifications have been done to overcome these drawbacks [5–9].

In the present work, we report the modification of RC oil by amidation that yields triol [*N, N*-bis (2-hydroxyethyl) ricinoleamide, HERA], which consists of two primary and one secondary hydroxyl group along with an amide linkage. HERA, considered as soft segment for polyurethane, by the urethanation reaction with toluene-2,4-diisocyanate (TDI) yields polyurethane which has recurring amide linkages. It is expected that such modification can improve the performance of RC oil based polyurethanes. Literature survey reveals that no such work is reported on RC oil [9].

Materials and Methods

Chemicals

RC oil [Number average molecular weight (Mn): 930; hydroxyl value: 160–168 mg KOH g⁻¹; acid value: 2.45 mg KOH⁻¹g], sodium metal, diethyl ether, diethanol amine (DEA), ethyl methyl ketone (EMK) (s.d. fine chemical) and TDI (Merck India) of analytical grade were used as such.

Synthesis of HERA (Amidation of *Ricinus communis* Oil)

As reported in the literature [10], a calculated amount of RC oil (0.1 mol), DEA (0.32 mol) and freshly prepared sodium methoxide (0.007 mol) solution (in methanol) were kept in a three-necked conical flask (fitted with a

thermometer and condenser) over a magnetic stirrer at 110 °C. Progress of the reaction was monitored by TLC (Thin Layer Chromatography) [10]. After the completion of the reaction (3 h), HERA was cooled down to room temperature and purified with the help of a separatory funnel through solvent and non-solvent methods [11].

In the purification step, firstly, HERA was dissolved in a suitable solvent (diethyl ether or xylene) then treated with a non-solvent (15% aqueous NaCl solution and water, in which HERA does not dissolve), transferred to a separatory funnel (to remove water) and left to stand for some time. After some time, two layers were obtained—one top solvent layer (HERA with solvent) and another of aqueous layer (non-solvent). In the next step the solvent layer is separated out with the help of the separatory funnel and then dried over anhydrous sodium sulfate. Finally, the solvent is evaporated off using a rotary vacuum evaporator to obtain the product HERA (yield 87 ± 1%).

FTIR (cm⁻¹): 3,369.3 (broad -OH), 3,010 (v, C=C-H), 2,923(v, -CH₂ asym), 2,853 (v, -CH₂ sym), 1,636.2 (v, >C=O amide), 1,078.9 cm⁻¹ and 1,052.9 cm⁻¹ (v, C-OH, primary and secondary).

¹H-NMR (CDCl₃/TMS, δ, ppm): 5.5–5.3 {m, -CH=CH-}, 5.26{s, -CH(OH)}, 4.85 (s, -CH₂-OH), 3.59 (s, -CH(OH)}, 3.77 and 3.84 (t, -CH₂-N<), 3.56 and 3.49 (t, -CH₂-OH), 2.36 (m, -CH(OH) CH₂-), 2.2 {t, -CH₂-C(=O)-N-}, 2.03(m, -CH₂-CH=CH-), 1.62 (m, -OCCH₂ CH₂) 1.45 {m, =CHCH₂CH(OH)}, 1.30 (m, -CH₂-, fatty acid chain), 0.88 (t, -CH₃).

¹³C-NMR (CDCl₃/TMS, δ, ppm): 130–127.7(-HC=CH-; olefin carbon), 71.4 {(-CH(OH))}, 59.376 (CH₂-OH), 47–40 (CH₂-N), 33.69 {CH₂-C(=O)-N-}, 29 (CH₂ fatty acid chain), 24.8 [CH₂ CH₂ C(=O)-N], 27.2 (CH₂-C=C-).

Synthesis of PUR (Urethanation of *Ricinus communis* Oil Modified Monomer, HERA) (Table 1)

Pure HERA (1 mol) was reacted with different amounts of TDI (0.8, 1 and 1.2 mol) in a minimal amount of EMK (20 ml, for dilution and homogenous mixing of reaction mixture) placed in a three-necked flat bottom flask fitted with the dropping funnel, thermometer and condenser. The reaction was carried out under a nitrogen environment along with continuous stirring at room temperature. The progress of the reaction was monitored by TLC (Thin Layer Chromatography) [11] and hydroxyl value determination at regular time intervals. The reaction was stopped on reaching the desired hydroxyl value of the product. The solvent (EMK) was removed by a rotary vacuum evaporator to obtain light yellow-colored liquid PUR (yield 96 ± 1%) designated as PUR-0.8, PUR-1 and PUR-1.2, the numerals stand for the moles of TDI.

Table 1 Chemical composition for the synthesis of PUR

Composition	HERA (mole)	TDI (mole)	[NCO]/[OH] ratio
PUR-0.8	1.0	0.8	1.6/3
PUR-1.0	1.0	1.0	2.0/3
PUR-1.2	1.0	1.2	2.4/3

The synthesized PUR were dissolved in the solvent (EMK) and filtered, repeatedly for purification. The solvent was removed from the filtrate with the help of rotary vacuum evaporator to obtain pure PUR-0.8, PUR-1 and PUR-1.2, which were taken for characterization. This operation was performed to remove any impurity (gel fraction, if any), which was not obtained here.

FTIR (cm^{-1}): 3,290.9 (weak, residual $-\text{OH}$), 3,339 (ν , N–H of urethane), 3,069 (ν , Ar C=C–H), 3,010 (ν , C=C–H), 1,716 (ν , $>\text{C}=\text{O}$ urethane), 1,636.2 (ν , $>\text{C}=\text{O}$ amide), 2,923 (ν , $-\text{CH}_2$ asym), 2,853 (ν , $-\text{CH}_2$ sym), 2,273 (ν , free NCO), 1,605, 744.5 (ν , and bending, Ar–C=C), 1,622 ($>\text{C}=\text{O}$, amide), 1,228 (ν , NCOO–), 697 (bending, N–H urethane).

$^1\text{H-NMR}$ (CDCl_3/TMS , δ , ppm): 5.53–5.35 (q, $-\text{CH}=\text{CH}-$)[h], 5.29 and 4.85 (s, low intensity, $-\text{OH}$)[k, a], 4.01–4.43 (m, $-\text{CH}_2\text{O C}(=\text{O})\text{NH}-$ and $-\text{CH}_2\text{O C}(=\text{O})\text{NH}-$, urethane)[n, p], 3.77 and 3.9 (t, $-\text{CH}_2-\text{N}<$)[c, c'], 3.5 (t, low intensity, $-\text{CH}_2-\text{OH}$)[b], 3.6 (t, $-\text{CHOH}$)[j], 2.4 (t, $-\text{CH}_2(\text{C}=\text{O})\text{N}<$)[d], 2.33 {t, $=\text{CHCH}_2\text{CH}(\text{OH})$ }[i], 2.2 (s, $-\text{CH}_3$ of TDI)[t], 2.02 (m, $-\text{CH}_2-\text{CH}=\text{CH}-$)[g], 1.61 (m, $-\text{OCCH}_2\text{CH}_2$)[e], 1.44 (m, $-\text{CH}(\text{OH})\text{CH}_2-$)[l], 1.31 (m, $-\text{CH}_2-$, fatty acid chain)[f, f'], 0.88 (t, $-\text{CH}_3$)[m].

$^{13}\text{C-NMR}$ (CDCl_3/TMS , δ , ppm): 173.2 ($>\text{C}=\text{O}$ amide)[c], 149–152 ($>\text{C}=\text{O}$ urethane and free $-\text{NCO}$)[q, n], 130, 126 ($-\text{HC}=\text{CH}-$; olefin carbon)[h, i], 127–132 (aromatic ring carbons)[r, s, t, u, v, w], 65–69 ($-\text{CH}_2-\text{O}$ and $-\text{CH}-\text{O}-$)[a', p], 71.4, 59.376 (residual, $\text{CH}-\text{OH}$ and CH_2-OH)[k, a], 50–55 (CH_2-N)[b, b'], 36–20 (chain CH_2)[j, d, l, f, m, g, e, n], 18.5 (CH_3 attached to aromatic ring)[x], 14 ($-\text{CH}_3$)[o].

Characterization

Standard laboratory methods of TLC was used to monitor the progress of the reactions [11].

Solubility of the resin was tested in various polar and non-polar solvents by taking 50 mg of resin in 10 ml of different solvents in a closed test tube and set aside for a day. Physico-chemical tests such as hydroxyl value, specific gravity and refractive index were performed by standard laboratory methods [11].

FT-IR spectra of resins were obtained with a Perkin-Elmer 1750, FTIR spectrophotometer (Perkin Elmer Instruments, Norwalk, CT) using an NaCl cell. $^1\text{H-NMR}$

and $^{13}\text{C-NMR}$ spectra were recorded on a JEOL GSX 300 MHz FX-1000 spectrometer using deuterated chloroform (CDCl_3), as a solvent, and tetramethylsilane as an internal standard.

Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using the SII EXSTAR 6000, TG/DTA6300 (Japan) from 40 to 750 °C in a nitrogen atmosphere at 10 °C min^{-1} heating rate. Differential Scanning Calorimetry (DSC) was done with SII EXSTAR 6000, DSC620 (Japan) from 30 to 400 °C in a nitrogen atmosphere at 10 °C min^{-1} heating rate.

Results and Discussion

Generally, synthesis and application of polyurethanes requires volatile organic compounds (VOC), through cumbersome multistep processes. In the present work, synthesis and curing of ricinoleamide based polyurethane was achieved at room temperature. The overall process, which almost reduces use of VOC to 50%, is simple and environmentally friendly.

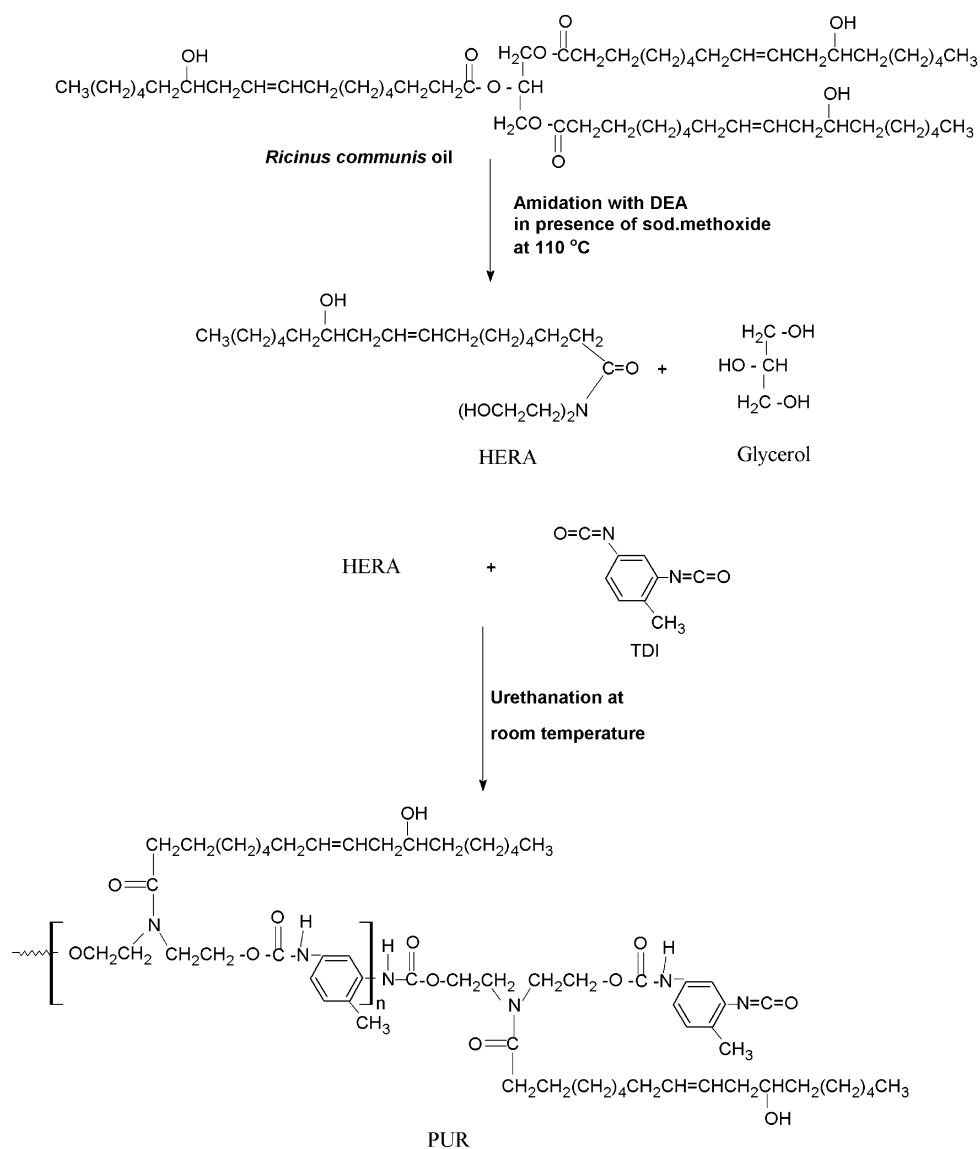
Synthesis (Fig. 1)

Figure 1 a shows the synthesis of PUR from RC oil. The amidation of the oil was carried out without VOC by the reaction of diethanolamine at 110 °C in the presence of sodium methoxide (acts as a catalyst) that results in the formation of HERA. The amidation reaction proceeds through the base-catalyzed nucleophilic acyl substitution bimolecular ($\text{S}_{\text{N}}2$) reaction mechanism while urethanation was carried out in a minimal possible amount of solvent via the addition reaction between the primary and the secondary $-\text{OH}$ group of HERA and the NCO– group of TDI (in different mole ratios) that result in the formation of PUR [12, 13]. It was found that the addition of TDI above 1.2 mol caused the formation of lumpy aggregates resulting in PUR that are too viscous [12].

In the formation of PUR, a different amount of TDI was used. However, PUR-1 was found to be the optimum composition. Thus, it was subjected to characterization as described in the proceeding section.

Generally, in polyurethane chemistry a particular ratio of functional groups is used: $[-\text{N}=\text{C}=\text{O}]/[\text{OH}]$ groups and this ratio is close to 1 or a maximum 1.1; the best properties are when one equivalent weight of isocyanate reacts with one equivalent weight of polyol. In other words, the best properties are obtained when the NCO/OH ratio is equal to one (to get the highest molecular weight). Nevertheless, for some applications, it is required to be below the stoichiometry as in the polyurethanes described here. Thus, this ratio may be altered according to the end use application

Fig. 1 Synthesis of PUR through amidation and urethanation reactions



requirement of polyurethanes, i.e., to prepare high or low molecular weight polyurethane. In this case, at each ratio, we have an excess of hydroxyl groups (Table 1), which based on general principles of polyaddition reactions lead to low molecular weight PUR, which may find applications as coating and adhesive materials [14].

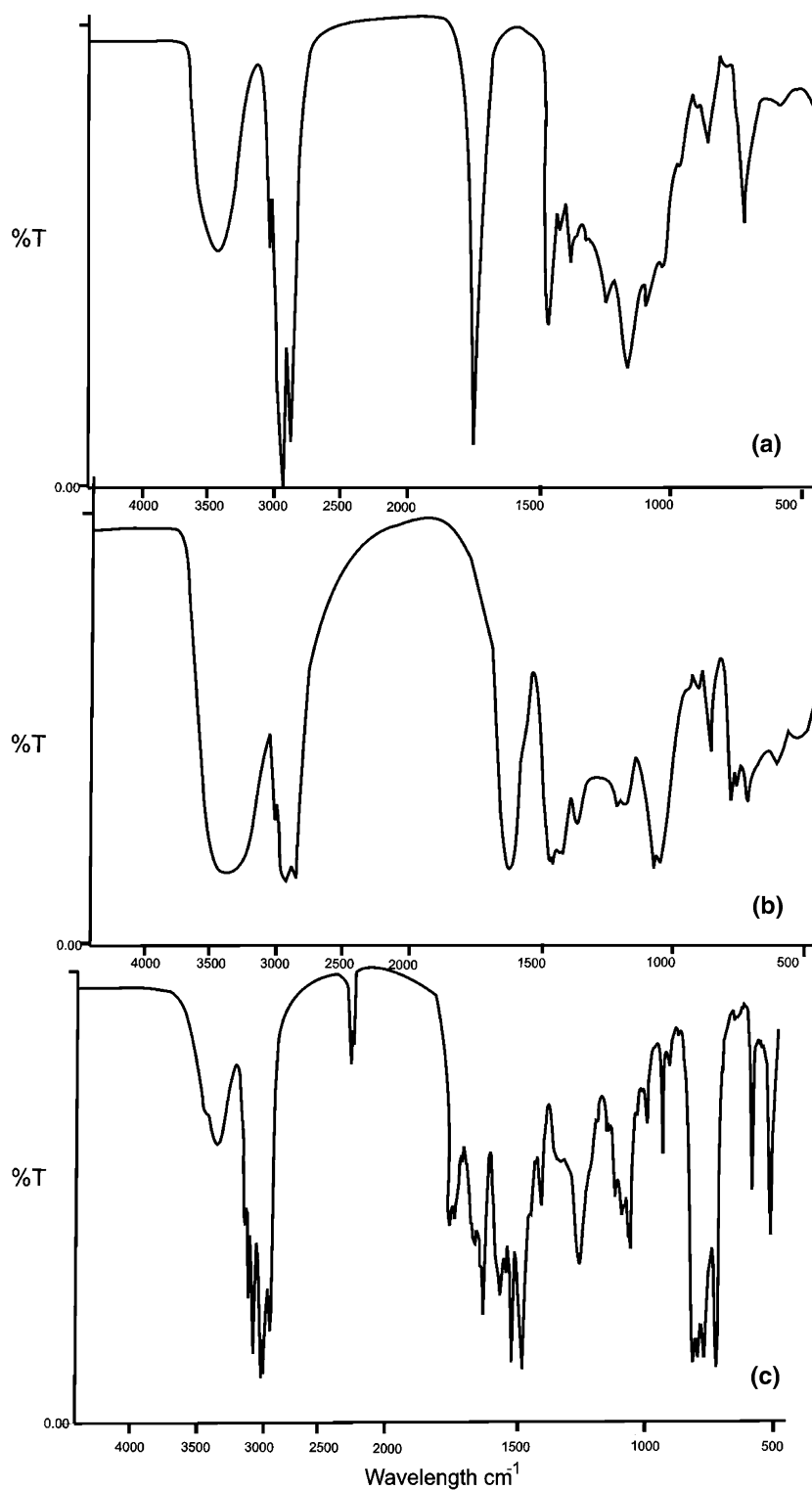
It is worth mentioning that the urethanation reaction was carried out by using a “one-shot” technique. In this method, all the ingredients (HERA and TDI) are mixed simultaneously and the resulting mixture is allowed to polymerize directly. The advantage of using this method is that no intermediate prepolymer preparation is necessary [15].

Spectral Analysis

FTIR spectra (Fig. 2): It is observed in the spectra of HERA that the characteristic bands of ester carbonyl (at 1,745,

1,241, 1,164 and 1,097 cm^{-1}) of RC oil disappeared with the appearance of new bands at 1,622, 1,078.9, 1,052.9 cm^{-1} for amide carbonyl, primary and secondary alcoholic groups (C–O stretching), respectively, as well as the presence of a broad band at 3,369 cm^{-1} instead of 3,422.1 cm^{-1} confirming the amidation of RC oil. In PUR spectra, the hydroxyl band of HERA (3,369.3 cm^{-1}) diminished and was centered at 3,290.9 cm^{-1} . The presence of new bands at 3,339 cm^{-1} (N–H stretching of urethane linkages), 1,716 cm^{-1} (urethane carbonyl stretching), 1,228 cm^{-1} (NCO– stretching), 2,273 (free NCO stretching), and 697 (N–H of urethane) [13, 16, 17] as well as bands at 3,069, 1,605.5, and 744.5 for aromatic ring of TDI confirm the urethanation of HERA. $^1\text{H-NMR}$ (Fig. 3) spectra of pure PUR-1 shows the characteristic peaks at 4.01–4.43 ppm {m, $-\text{CHOC}(=\text{O})\text{NH}-$ and $-\text{CH}_2\text{OC}(=\text{O})\text{NH}-$, urethane}[n, p], 2.2 ppm (s, $-\text{CH}_3$ of TDI)[t], and 6.9–7.38 ppm

Fig. 2 FTIR spectra of RC oil (a), HERA (b) and pure PUR-1 (c)



(aromatic peaks)[r, s, q] while ^{13}C -NMR (Fig. 4) spectra of pure PUR-1 shows the spectral peaks at 149–152 ppm ($>\text{C}=\text{O}$ urethane and free $-\text{NCO}$)[q, n], 127–132 ppm (aromatic ring carbons)[r, s, t, u, v, w], 65–69 ppm ($-\text{CH}_2-\text{O}$ and $-\text{CH}-\text{O}$)[a', p] and 18.5 ppm (CH_3 attached to aromatic ring)[x]. These spectral bands are the characteristic

bands of TDI based polyurethanes [13, 17]. Closer examination of ^1H -NMR spectra of HERA and PUR-1 reveals that pure PUR-1 shows suppressed characteristic peaks of $-\text{OH}$, $-\text{CH}-\text{OH}$ and CH_2-OH compared to HERA (sect. 2.1) at 5.26 ppm [$-\text{CH}(\text{OH})$], 4.85 ppm and ($-\text{CH}_2-\text{OH}$), 3.59 ppm [$\text{CH}(\text{OH})$], 3.56 and 3.49 ppm ($-\text{CH}_2-\text{OH}$), while

^{13}C -NMR spectral analysis of pure PUR-1 also support the suppression of the characteristic peaks of $-\text{CH}-\text{OH}$ and CH_2-OH of HERA (sect. 2.1) at 71.4 ppm ($-\text{CH}-\text{OH}$) and 59.376 ppm (CH_2-OH). The suppression of these peaks can be correlated to the consumption of $-\text{OH}$, $-\text{CH}-\text{OH}$ and CH_2-OH of HERA with $-\text{NCO}$ of TDI in the formation of polyurethane.

These spectral studies are correlated to the formation of PUR, through the addition reaction of $-\text{OH}$ groups of HERA and $-\text{NCO}$ of TDI [13, 17].

Physico-chemical Properties and Solubility

The data for physico-chemical properties of HERA and different compositions of PUR are given in Table 2. It reveals that the percent hydroxyl content of PUR decreases gradually from PUR-0.8 to PUR-1.2, that is, with increases in the amount of TDI. The trend can be attributed to the consumption of hydroxyl groups of HERA during urethration reaction with TDI. The specific gravity and refractive index of PUR increase with the increased content of

Fig. 3 ^1H NMR spectra of pure PUR-1

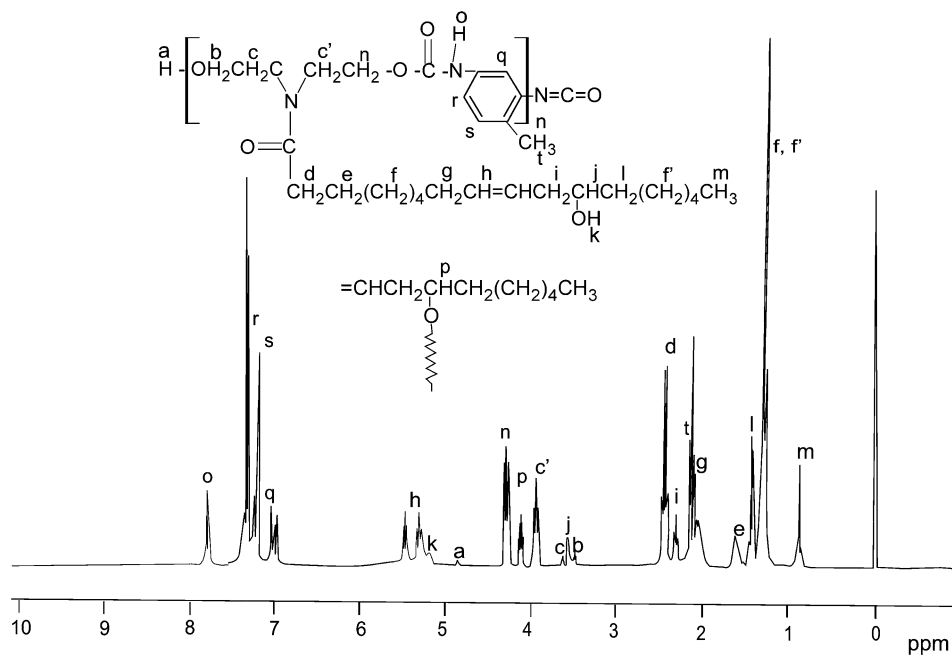


Fig. 4 ^{13}C NMR spectra of pure PUR-1

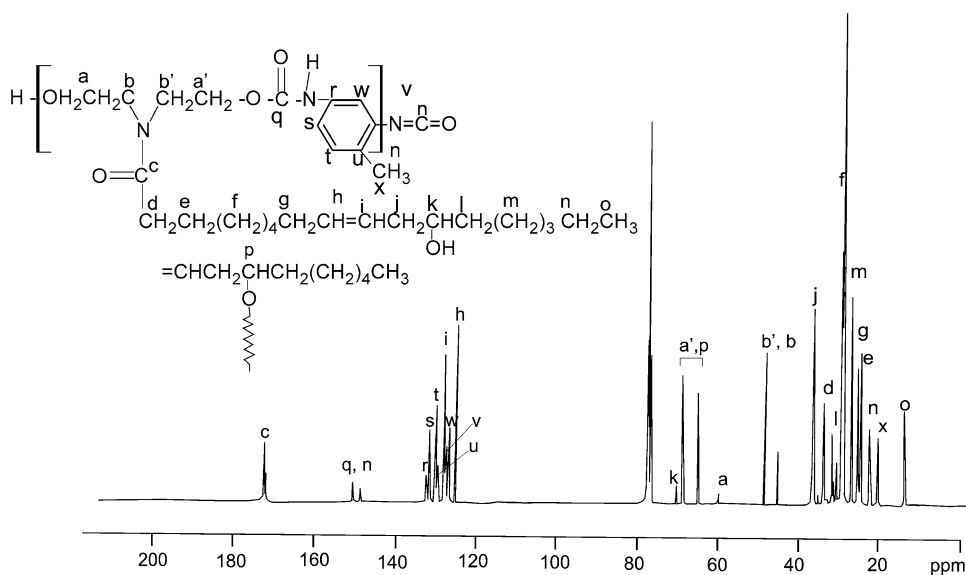


Table 2 Physico-chemical tests of HERA and different compositions of PUR

Resin code	HERA	PUR-0.8	PUR-1	PUR-1.2
Hydroxyl value (mg KOH g ⁻¹)	438.9	154.05	109.725	62.7
Specific gravity (g ml ⁻¹)	0.8654	0.8912	0.8965	0.8987
Refractive index	1.6120	1.6230	1.636	1.639

TDI attributed to the inclusion of increased urethane content in the polymer backbone.

The solubility test reveals that all PUR compositions (before curing) are completely soluble (100%) in EMK, chloroform, carbon tetrachloride, DMF (Dimethylformamide), DMSO (Dimethyl sulfoxide), THF (Tetrahydrofuran) and diethyl ether while they have 20% solubility in methyl alcohol, ethyl alcohol, and insoluble in water. The higher solubility of these resins in polar and non-polar solvents except H₂O and alcohol is due to the presence of long fatty acid hydrocarbon chains and polar groups of the resin.

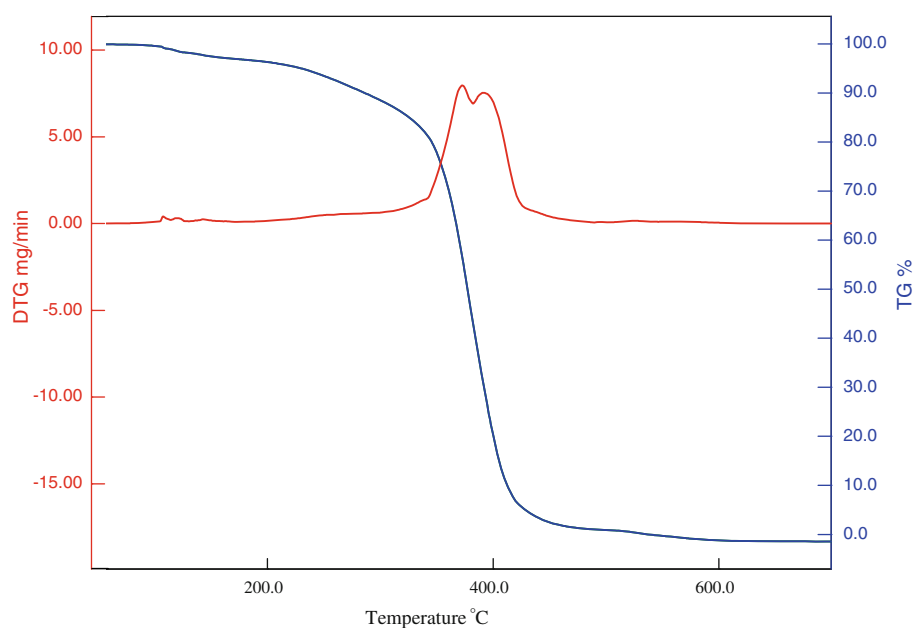
Curing of Film

The solution of PUR in EMK was applied on mild steel strips. It was cured at ambient temperature without any modifier. The curing time for PUR was found to be 10–20 min. The curing process of PUR resin occurs through the chemical reaction of free –NCO of PUR with atmospheric moisture and –OH of the other chains after the solvent evaporation. This chemical reaction is followed by other characteristic reactions that are the formation of urethane, amine, urea, allophanate and biuret [13]. All

these chemical reactions are collectively responsible for the three dimensional optimum cross linked structure of PUR.

Thermal Analysis

The thermal stability of PUR-1 is shown in Fig. 5. It reveals that the degradation of PUR-1 was observed in the range of 150–390 °C. This may be correlated to the decomposition of urethane bonds followed by the volatilization of the decomposition products. It is reported that polyurethanes generally exhibit relatively low thermal stability due to the presence of labile urethane groups. The onset of this bond dissociation occurs around <300 °C through the dissociation of isocyanate and alcohol, the formation of primary amine and olefins, or the formation of secondary amines that result in the loss of CO₂ from the urethane bond, depending upon the type of isocyanate and polyol employed [18]. The decomposition of the urethane bond in PUR-1 takes place at quite high temperatures due to any allophanate and biuret linkages formed during the curing reaction, they reopen quite readily on heating at a relatively high temperature as they are most thermolabile [18]. The degradation in the range of 390–410 °C may be correlated to the decomposition of the amide bond, aromatic ring and aliphatic alkyl chain of the fatty acid followed by the volatilization of the decomposition products, respectively. The polyol used in this study is based on HERA. So, the main chain cleavage may result in the formation of 16-undecanoic acid and heptanal as evident by the thermal degradation of ricinoleic acid [19]. Derivative TGA curves (DTG) of PUR-1 shows almost single step thermal degradation, which matches with TGA of the same. This step incurs about 85 wt% loss correlated to a cross-linked, homogenous

Fig. 5 TGA and DTA thermogram of PUR-1

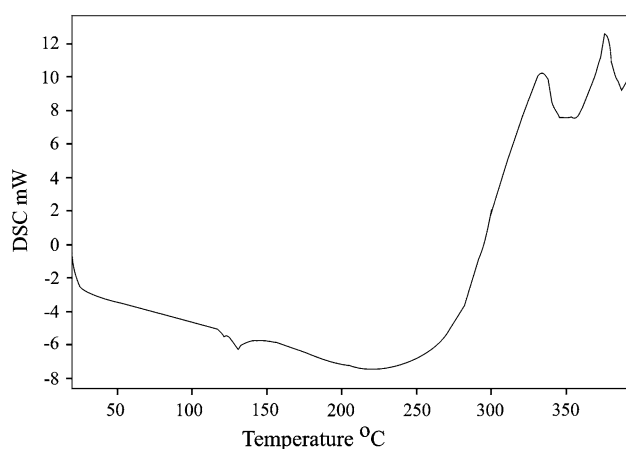


Fig. 6 DSC thermogram of PUR-1

network of cured PUR-1 (Sect. 3.2) that results in their single-step thermal degradation behavior as (not separate but one) single entity favored by chain entanglements. DSC thermograms (Fig. 6) show small endotherms at 115–140 °C (centered at 129.5 °C) followed by an exotherm attributed to the reaction of the remaining unreacted groups in the PUR-1 backbone. TGA/DTG thermograms do not show significant decomposition in the former temperature range. After 230 °C, a strong exothermal reaction is observed due to the degradation of the PUR-1 backbone. The temperature range between 300–420 °C shows a maximum weight loss in the TGA/DTG thermogram.

Conclusion

The non-edible and non-drying RC oil was utilized for the preparation of environmentally friendly, room-temperature cured, ricinoleamide-modified polyurethane using a one-shot technique in a minimal amount of organic solvent. The synthesis and curing strategy were very simple omitting derivatization steps or side reactions (at optimum loading of TDI), crosslinkers, and chain extenders. The synthesized polymer shows moderate antibacterial activity. Thermal degradation of the resin was more or less similar to virgin polyurethane, indicating that this modification of RC oil has not influenced the thermal stability. The resin can safely be used up to 200–220 °C. It can be utilized for eco-friendly adhesives, protective paints and coating material. The application studies of ricinoleamide-modified polyurethane as an advanced coating material will be published soon.

Acknowledgments Dr. Fahmina Zafar and Dr. Eram Sharmin are thankful to the Council of Scientific and Industrial Research (CSIR) India for a Senior Research Associateship (SRA) and a Research Associateship (RA) against Grants No: 13(8385-A)/Pool/2010 and 9/466(0102) 2K8-EMR-I, respectively. The authors also acknowledge

the University Grant Commission (UGC). SAP for TGA and DSC facilities.

Conflict of interest None.

References

- Lopes RVV, Loureiro NPD, Zamian JR, Fonseca PS, Macedo JL, Santos MLD, Sales MJA (2009) Synthesis and characterization of polymeric materials from vegetable oils. *Macromol Symp* 286:89–94
- Sharm V, Kundu PP (2006) Addition polymers from natural oils: a review. *Prog Polym Sci* 31:983–1008
- Huang K, Xia J, Yang X, Li M, Ding H (2010) Properties and curing kinetics of C21-based reactive polyamides as epoxy-curing agents derived from tung oil. *Polym J* 42:51–57
- Guner FS, Yagci Y, Erciyas AT (2006) Vegetable oil-based thermosetting polymers. *Prog Polym Sci* 31:633–670
- Sharm V, Kundu PP (2008) Condensation polymers from natural oils. *Prog Polym Sci* 33:1199–1215
- Lligadas G, Ronda JC, Galia M, Cadiz V (2010) Plant oils as platform chemicals for polyurethane synthesis: current state-of-the-art. *Biomacromolecules* 11:2825–2835
- Petrović ZS (2008) Polyurethanes from vegetable oils. *Polym Rev* 48:109–155
- Narine SS, Yue J, Kong X (2007) Production of polyols from canola oil and their chemical identification and physical properties. *J Am Oil Chem Soc* 84:173–179
- Mutlu H, Meier MAR (2010) Castor oil as a renewable resource for the chemical industry. *Eur J Lipid Sci Technol* 112:10–30
- Bharathi NP, Alam M, Tasleem Jan A, Hashmi AA (2009) Bioactive organotin materials: synthesis, characterization and antimicrobial investigation. *J Inorg Organomet Polym* 19:187–195
- Vogel AI, Tatchell AR, Furnis BS, Hannaford AJ, Smith PWG (1996) *Vogel's textbook of practical organic chemistry*, 5th edn. Prentice Hall, New York, ISBN 0582462363
- Sharmin E, Ashraf SM, Ahmad S (2007) Epoxidation, hydroxylation, acrylation and urethanation of *Linum usitatissimum* seed oil and its derivatives. *Eur J Lipid Sci Technol* 109:134–146
- Sharmin E, Ashram SM, Ahmad S (2007) Synthesis, characterization, antibacterial and corrosion protective properties of epoxies, epoxy-polyols and epoxy-polyurethane coatings from linseed and *Pongamia glabra* seed oils. *Int J Bio Macromol* 40:407–422
- Poul S (1996) *Surface coatings: science and technology*, 2nd edn. Wiley, Chichester
- Vermette P, Griesser HJ, Laroche G, Guidoin R (2001) Biomedical applications of polyurethanes, tissue engineering intelligence uni, unit 6, EUREKAH.COM, Landes Bioscience, Georgetown
- Lu Y, Larock RC (2009) Soybean oil based waterborne polyurethane dispersion: effect of polyol functionality and hard segment content on properties. *Biomacromolecules* 9:3332–3340
- Akram D, Sharmin E, Ahmad S (2008) Synthesis, characterization and corrosion protective properties of boron-modified polyurethane from natural polyol. *Prog Org Coat* 63:25–32
- Somani K, Kansara S, Parmar R, Patel N (2004) High solid polyurethane coatings from castor oil based polyester polyols. *Int J Polym Mater* 53:283–293
- Szycher M (1999) *Szycher's Handbook of polyurethane*, 2nd edn. CRC Press, Sterling Biomedical, Inc, Lynnfield MA, Michael Szycher, Cardio-Tech International, Woburn, Massachusetts