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ORIGINAL PAPER

Structure and Thermal Properties of Polyurethanes Synthesized from Cardanol Diol

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Abstract Amorphous polyurethanes (PUs) were prepared from isophorone diisocyanate and various diols based on ethylene glycol, containing phenol (PD), hydrogenated cardanol (HCD) and cardanol (CD) as side groups. The influence of side groups on thermal and thermo-oxidative stability was studied by thermogravimetric analysis and differential scanning calorimetry. The finding revealed that pendent C15 alkyl side groups of HCD–PU and CD–PU improved thermal stability of PUs. The possible crosslinks of olefinic side groups enhanced both thermal and thermo-oxidative stability of CD–PU. Both EG–PU and CD–PU exhibited good oxidative resistance. The glass transition temperature arranged in the order of EG–PU > PD–PU > HCD–PU > CD–PU. Cardanol molecules on PU backbones acted as an internal plasticizer and elevated the flexibility of PUs.

Keywords Cardanol · Cashew nut shell liquid · Thermally oxidative stable · Renewable resource

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Introduction

Polyurethanes (PUs) are versatile materials, having a wide range of mechanical properties from flexible to rigid materials, which depend on the chemical structure [1]. PUs are mostly utilized in the production of foams, insulators, furniture, synthetic leathers, engineering plastics, coatings, sealants and adhesives. A polymerization of thermoplastic PUs is generally undergone through a step-growth polymerization by the reaction of diisocyanate and diol [2], which are mainly obtained from petrochemical industries [3]. To solve the problem of the high consumption and price of oil and natural gas, sustainable materials are of great interest to replace petrochemical based materials. Recently, to produce PUs, monomers (i.e., diols or polyols) obtained from renewable resources, such as vegetable oil, glycerol, solid lignin, cork and other cellulose products, have attained significant interest [4].

Cardanol (CD) is one interesting natural phenol separated from the dark brown oil of cashew nut shell liquid (CNSL), which is obtained from the cashew nut waste. The chemical structure of cardanol is phenol derivatives having C15 alkyl chains at the meta-position with different degrees of unsaturations, monoene (∼36 %), diene (∼20 %) and triene (∼41 %) [5, 6]. Cardanol has been experimentally used to synthesize various polymers, such as formaldehyde resins, epoxy resins, acrylic resins, polyesters and polyurethanes [5] because it is inexpensive and easy to modify. In addition, the long carbon chain of cardanol provides not only a flexible property but also a good solubility in organic solvent and good processability [7].

The chemical modification of cardanol to di- or polyol compounds has been used to prepare PUs [8, 9]. Cardanol was firstly reacted with formaldehyde to produce cardanol-formaldehyde resin with many free hydroxyl groups. The

resin was then reacted with the diisocyanate to yield a good chemical resistance and high hardness rigid PUs [8, 9]. To prepare low density and high compressive strength PU foams, cardanol has been modified to polyol by peracid-epoxidation, followed by hydrolysis processes [10]. To increase hydroxyl functionalities, monoglycidyl ether based cardanol (epicard) has been used as a precursor for diol/triol and diethanolamine preparation [11]. An incorporation of double bonds at cardanol side chains during a polymerization is capable of promoting the crosslink density of UV-curable PUs [12]. Furthermore, the synthesis of semi-crystalline PUs has been achieved via cardanol diol, prepared by diazotization and hexamethylene diisocyanate or diphenylmethane diisocyanate [13, 14].

Although there are many studies relating to the synthesis of PUs based on cardanol [8–14], the influence of various side chains of cadanol based diols on thermal and thermo-oxidative stabilities has not been deeply investigated. Understanding the thermal and thermo-oxidative behavior of cardanol based PUs can be further applied to develop high performance polymeric materials with environmental concern. Therefore, in the present work, we focused on the effect of diol side groups on the thermal and thermo-oxidative stability of PUs synthesized from isophorone diisocyanate and phenol diol derivatives based on ethylene glycol, containing phenol, cardanol, and hydrogenated-cardanol as side groups along with dibutyl tin dilaurate catalyst. The chemical structure of PUs was examined using nuclear magnetic resonance (NMR), mass spectrometer (MS), gel permeation chromatography (GPC), Fourier transform infrared spectrometer (FTIR), and wide angle X-ray diffraction (WAXD). Thermal properties of PUs were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Experimental

Materials

Cashew nut shells were received from Jearleung cashew nut factory (Chonburi, Thailand). 3-chloropropane-1,2-diol (Aldrich, Singapore), sodium hydroxide (NaOH, QRëC, Thailand), calcium hydroxide [$Ca(OH)_2$, Lobachemie, India], palladium hydroxide adsorbed on carbon [$Pd(OH)_2$/C, Aldrich, Singapore] and phenol (Rankem, India) were used as received. Isophorone diisocyanate 98 % (IPDI, Aldrich, Singapore) and dibutyl tin dilaurate (DBTDL, Aldrich, Singapore) were stored under N_2 gas and kept in a desiccator to avoid humidity. Ethylene glycol (EG, POCH, Poland) was distilled and kept under N_2 atmosphere. Anhydrous dimethylformamide (DMF, ORëC, ThailandIndia) and chloroform-d (CDCl$_3$, Aldrich, Singapore) was used as received. Solvents (ORëC, Thailand) including ethyl acetate

(EtOAc), hexane, dichloromethane (CH_2Cl_2) and ethanol (EtOH) were distilled before used.

Synthesis of Polyurethane Based on Cardanol Diol

Recovery of Cardanol

CNSL was obtained from cashew nut shells by heating at 150 °C for 4 h with the presence of $Ca(OH)_2$ to promote decarboxylation of anacardic acid to cardanol [15]. Cardanol was separated from CNSL by column chromatography using 15 % ethyl acetate: hexane as an eluent. The chemical structure of CD was confirmed by ^{1}H-NMR, FTIR and MS and the finding is consistent with the data in previous research [11]. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.15 (t, 1H, Ar*H*), 6.76 (d, 1H, Ar*H*), 6.68 (s, 1H, Ar*H*), 6.65 (d, 1H, Ar*H*), 5.90–5.78 (m, C*H*=CH$_2$), 5.50–5.29 (m, C*H*=C*H*), 5.10–4.93 (m, CH=C*H*$_2$), 2.90–2.74 (m, CH=CHC*H*$_2$ CH=CH), 2.55 (t, 2H, ArC*H*$_2$), 2.10–1.92 (m, C*H*$_2$C*H*$_2$CH=CH), 1.68–1.51 (m, 2H, ArCH$_2$ C*H*$_2$), 1.46–1.20 (m, (C*H*$_2$)$_n$), 0.96–0.85 (m, C*H*$_3$). FTIR (neat) v_{max}/cm^{-1}: 3,351, 3,009, 2,926, 2,854, 1,589, 1,487, 1,456, 1,265, 1,154, 912, 874, 780, 694. MS: m/z (% relative intensity): 304 (M$^+$ saturated, 4), 302 (M$^+$ monoene, 17), 300 (M$^+$ diene, 8), 298 (M$^+$ triene, 8), 147 (37), 120 (36), 108 (100), 107 (84), 91 (29), 79 (45), 77 (44).

Hydrogenation of Cardanol

Cardanol (30 g) was dissolved in EtOAc (120 mL) and 5 % $Pd(OH)_2$/C was then added slowly. After hydrogenation for 14 days, the solution was filtered through a Celite bed to obtain the catalyst-free solution. This solution was evaporated under vacuum to obtain crude solids of saturated cardanol, which was reprecipitated in hexane. White powder of hydrogenated cardanol (HCD) was obtained. The chemical structure of HCD was examined by ^{1}H-NMR, FTIR and MS. The absence of the double bond signal at 5.50–4.03 ppm of hydrogenated-cardanol in ^{1}H-NMR spectra was observed because of the completion of catalytic hydrogenation of cardanol [16]. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.15 (t, 1H, Ar*H*), 6.79 (d, 1H, Ar*H*), 6.68 (s, 1H, Ar*H*), 6.67 (d, 1H, Ar*H*), 2.58 (t, 2H, ArC*H*$_2$), 1.69–1.55 (m, 2H, ArCH$_2$C*H*$_2$), 1.41–1.20 (m, 24H, (C*H*$_2$)$_{12}$), 0.90 (t, 3H, C*H*$_3$). FTIR (CHCl$_3$) v_{max}/cm^{-1}: 3,341, 2,952, 2,917, 2,849, 1,591, 1,473, 1,463, 1,375, 1,264, 1,154, 942, 866, 788, 748, 719, 697. MS: m/z (% relative intensity): 304 (M+, 13), 149 (15), 108 (100), 107 (60), 79 (13), 77 (14).

Synthesis of Phenol Diol Monomers

EG structure was modified to phenol diol derivatives by coupling phenolic OH groups with 3-chloropropane-1,2-diol in the presence of sodium hydroxide followed by reflux for 36 h [12].

Synthesis of Phenol Diol (PD)

Phenol (0.033 mol) was added to a mixture of 3-chloro-propane-1,2-diol (0.066 mol) and NaOH (0.066 mol) in ethanol–water mixture (1:1, 30 mL). The solution was refluxed for 36 h. The refluxed product was poured into water and extracted with CH_2Cl_2. The sample was dried and obtained as white solid with 62 % yield. The chemical structure of phenol diol was examined by ^{1}H-NMR, FTIR and MS. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.29 (t, 2H, ArH), 7.00 (t, 1H, ArH), 6.91 (d, 2H, ArH), 4.15–4.08 (m, 1H, CHOH), 4.05 (s, 1H, ArOCH_2), 4.04 (d, 1H, ArOCH_2), 3.90–3.80 (m, 1H, CH_2OH), 3.80–3.70 (m, 1H, CH_2OH). ^{13}C NMR (75 MHz, CDCl$_3$): δ 158.4 (C), 129.6 (CH), 121.3 (CH), 114.6 (CH), 70.6 (CH), 69.1 (CH$_2$), 63.7 (CH$_2$). FTIR (CHCl$_3$) ν_{max}/cm^{-1}: 3,367, 2,933, 2,879, 1,599, 1,588, 1,497, 1,457, 1,292, 1,245, 1,173, 1,118, 1,079, 1,045, 932, 881, 811, 754, 691. MS: m/z (% relative intensity): 169 (M$^+$+1, 20), 168 (M$^+$, 100), 133 (10), 94 (27), 91 (9), 66 (10), 65 (11).

Synthesis of Hydrogenated Cardanol Diol (HCD)

The process of HCD synthesis is similar to that of PD synthesis, except HCD was used instead of phenol. HCD was purified through column chromatography (using 30 % Hexane: 30 % CH_2Cl_2: 40 % EtOAc as a solvent system). About 75 % yield of white solid was obtained. The chemical structure of HCD diol was examined by ^{1}H-NMR, FTIR and MS. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.20 (t, 1H, ArH), 6.82 (d, 1H, ArH), 6.78 (s, 1H, ArH), 6.77 (d, 1H, ArH), 4.17–4.10 (m, 1H, CHOH), 4.08 (s, 1H, ArOCH_2), 4.06 (d, 1H, ArOCH_2), 3.91–3.83 (m, 1H, CH_2OH), 3.83–3.73 (m, 1H, CH_2OH), 2.58 (t, 2H, ArCH_2), 1.69–1.55 (m, 2H, ArCH$_2$CH_2), 1.40–1.20 (m, 24H, (CH_2)$_{12}$), 0.90 (t, 3H, CH_3). ^{13}C NMR (75 MHz, CDCl$_3$): δ 158.4 (C), 144.9 (C), 129.3 (CH), 121.6 (CH), 114.8 (CH), 111.5 (CH), 70.4 (CH), 69.2 (CH$_2$), 63.7 (CH$_2$), 36.0 (CH$_2$), 31.9 (CH$_2$), 31.4 (CH$_2$), 29.7–29.4 (10 × CH$_2$), 22.7 (CH$_2$), 14.1 (CH$_3$). FTIR (CHCl$_3$) ν_{max}/cm^{-1}: 3,329, 2,956, 2,918, 2,850, 1,614, 1,583, 1,490, 1,471, 1,451, 1,297, 1,244, 1,230, 1,158, 1,065, 1,038, 931, 864, 781, 770, 757, 717, 688, 618. MS: m/z (% relative intensity): 378 (M+, 2), 305 (25), 182 (9), 150 (7), 149 (15), 146 (9), 145 (12), 133 (15), 121 (16), 108 (100), 107 (60), 91 (20), 85 (14), 80 (11), 79 (20), 77 (20), 71 (20), 57 (25).

Synthesis of Cardanol Diol (CD)

The process of CD synthesis is similar to PD synthesis, except cardanol was used instead of phenol. The crude product was obtained as yellow oil. It was then purified through column chromatography (using 30 % Hexane:

30 % CH_2Cl_2: 40 % EtOAc as a solvent system) and provided approximately 71 % yield of yellowish viscous oil. The chemical structure of cardanol was examined by ^{1}H-NMR, FTIR and MS. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.15 (t, 1H, ArH), 6.79 (d, 1H, ArH), 6.75 (s, 1H, ArH), 6.71 (d, 1H, ArH), 5.91–5.75 (m, CH=CH$_2$), 5.52–5.29 (m, CH=CH), 5.12–4.96, (m, CH=CH_2), 4.14–4.06 (m, 1H, CHOH), 4.00 (s, 1H, ArOCH_2), 3.99 (d, 1H, ArOCH_2), 3.85–3.78 (m, 1H, CH_2OH), 3.77–3.69 (m, 1H, CH_2OH), 2.90–2.80 (m, CH=CHCH_2CH=CH), 2.55 (t, 2H, ArCH_2), 2.12–1.95 (m, CH_2CH$_2$CH=CH), 1.68–1.51 (m, 2H, ArCH$_2$CH_2), 1.46–1.20 (m, (CH_2)$_n$), 0.96–0.85 (m, CH_3). ^{13}C NMR (75 MHz, CDCl$_3$): δ 158.5 (C), 144.8 (C), 136.8 (CH), 130.4–126.8 (CH of double bond), 129.3 (CH), 121.5 (CH), 114.8 (CH$_2$ of vinyl group), 114.7 (CH), 111.5 (CH), 70.6 (CH), 70.0 (CH$_2$), 63.8 (CH$_2$), 36.0 (CH$_2$), 31.8 (CH$_2$), 31.5 (CH$_2$), 31.4 (CH$_2$), 29.8–22.7 (CH$_2$ of methylene groups), 14.1 (CH$_3$), 13.8 (CH$_3$). FTIR (neat) ν_{max}/cm^{-1}: 3,378, 3,010, 2,927, 2,855, 1,602, 1,584, 1,487, 1,449, 1,261, 1,159, 1,119, 1,050, 912, 874, 776, 695. MS: m/z (% relative intensity): 376 (M+, 6), 182 (30), 133 (29), 108 (70), 107 (100), 91 (33), 79 (32), 77 (36).

Synthesis of Polyurethanes

Polyurethanes were synthesized by a solution polymerization using IPDI and prepared diols in the presence of DBTDL catalyst as shown in Scheme 1. The stoichiometric molar ratio of IPDI: diol was kept constant at 1:1 (assuming 100 % purity of monomers). The required amount of diol was placed in a round-bottom flask and purged with N$_2$. The required amount of IPDI dissolved in DMF was added to diol solution with 1–2 drops of DBTDL and kept at a temperature around 80–85 °C for 4 h. PU films were prepared by solution casting and further dried at 60 °C for 24 h under vacuum to eliminate the solvent. All films were kept in desiccators for further characterization. PUs synthesized from EG, PD, HCD and CD are referred to as EG–PU, PD–PU, HCD–PU and CD–PU, respectively.

Characterization

^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on a Bruker 300 MHz using CDCl$_3$ as a solvent with tetramethylsilane (TMS) as an internal standard.

Fourier transform infrared (FTIR) spectra were measured on a PerkinElmer system 2,000 infrared spectrometer in a range of 400–4,000 cm^{-1} with a resolution of 4 cm^{-1}.

Mass spectra were performed on a Thermo Finnigan Polaris Q mass spectrometer (MS) using EtOAC as a solvent.
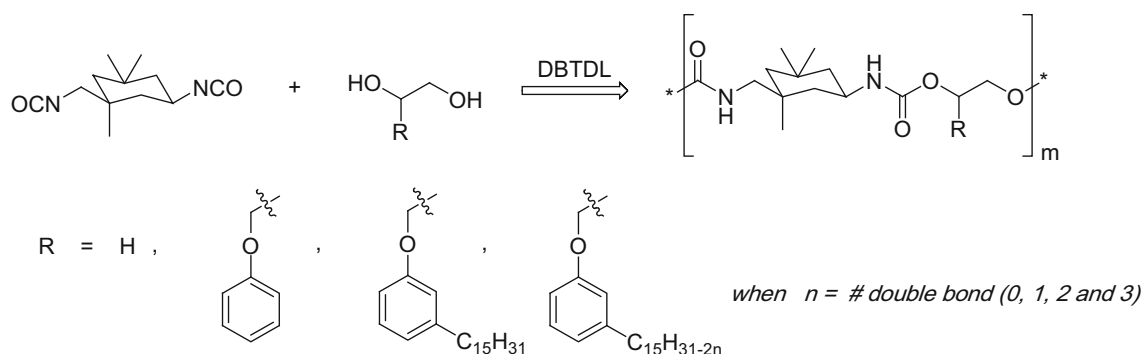
Scheme 1 Synthesis of PUs from cardanol diol

The number and weight average molecular weights (M_n and M_w, respectively) of PUs were determined by gel permeation chromatography (GPC) using Styragel column (Styragel HR5E, 7.8×300 mm) and tetrahydrofuran (THF) as an eluent with polystyrene standards.

Wide-angle X-ray diffraction (WAXD) patterns were acquired using a Scintag Pad V diffractometer with CuKα radiation ($\lambda = 0.154$ nm) at 35 kV and 30 mA. Samples were scanned continuously at a scanning rate of 2°/min in the 2θ range of 10°–30°.

The glass transition temperature (T_g) was determined using a Seiko differential scanning calorimeter (DSC) 220 under N_2 gas with a heating and a cooling rate of 10 °C/min. Results shown in this paper were taken from the second scan of DSC thermograms.

The thermal and thermo-oxidative stability was measured using a thermogravimetric analyzer TA -Q500 TGA under N_2 and O_2, respectively with a heating rate of 10 °C/min. The measurements were repeated twice for each sample.

The oxidative induction time (OIT) was measured using DSC and TGA for comparison. About 5 mg of samples were loaded and heated from 30 to 200 °C at 20 °C/min under N_2. The sample was held at 200 °C under N_2 for 3 min and the purge gas was then switched from N_2 to O_2 at 50 mL/min and held for 60 min. The time during oxygen exposure to the onset of oxidation is taken as the OIT value.

Results and Discussion

Chemical Structure of Prepared Diol Compounds

^{1}H-NMR was used to investigate the chemical structure of diol compounds as shown in Fig. 1a–c. PD exhibits ^{1}H-NMR spectra of aromatic proton signals around 7.29–6.91 ppm and methylene proton (CH and CH_2) signals around 4.15–3.70 ppm (see Fig. 1a). Figure 1b displays ^{1}H-NMR spectra of HCD. The presence of long chain alkyl groups in HCD structure is confirmed by the signal of $(CH_2)_n$ and CH_3 at chemical shift about 1.69–0.90 ppm. The triplet signal at 2.58 is attributed to protons of benzylic carbons. The low intensity of HCD spectra was observed due to the poor solubility of HCD in $CDCl_3$. As shown in Fig. 1c, a double bond of CD structure is confirmed by the signal around 5.91–4.96 ppm. A signal at 2.90–2.80 corresponds to CH_2 groups between double bonds.

PD and HCD samples were obtained as white solids, whereas a CD product was obtained as yellow oil. This is due to the bending of *cis* conformations on CD side chains of CD samples preventing an orderly arrangement of main chains, while no such double bonds exist in PD and HCD side chains. Similar results were previously observed for C_{18} fatty acid [17] that a single *cis* double bond in C_{18} fatty acid molecules is able to reduce a melting point from 70.1 °C (stearic acid) to 16.3 °C [(*z*)-octadec-9-enoic acid].

Structural Characterization of Polyurethanes

FTIR was used to confirm the formation of urethane linkages. Figure 2 shows comparative spectra between diol monomers and PUs prepared from those diol compounds. Figure 2a displays PU structure prepared from a commercial EG monomer (EG–PU), which was used as a reference here. An absence of isocyanate peaks at 2,260 cm^{-1} (N=C=O) was observed for all samples. Characteristic of urethane functionality is confirmed by peak signals at 3,325 cm^{-1} (N–H stretching), 1,702 cm^{-1} (C=O stretching), 1,541 cm^{-1} (N–H bending), and 1,237 cm^{-1} (C–N stretching & N–H bending) [18]. As shown in Fig. 2b–d, aromatic signals at 1,600, 1,580, 1,500 and 1,480 cm^{-1} (C=C bending) were observed for PD–PU, HCD–PU and CD–PU samples. Peaks at 754 and 691 cm^{-1} correspond to mono-substituted benzene rings of PD–PU, whereas peaks at ∼860, 771 and 695 cm^{-1} are associated to 1,3-di-substituted benzene rings of HCD–PU and CD–PU. Both HCD–PU and CD–PU exhibit a peak at 720 cm^{-1}, which corresponds to the CH_2 rocking mode of ethylene side chains.
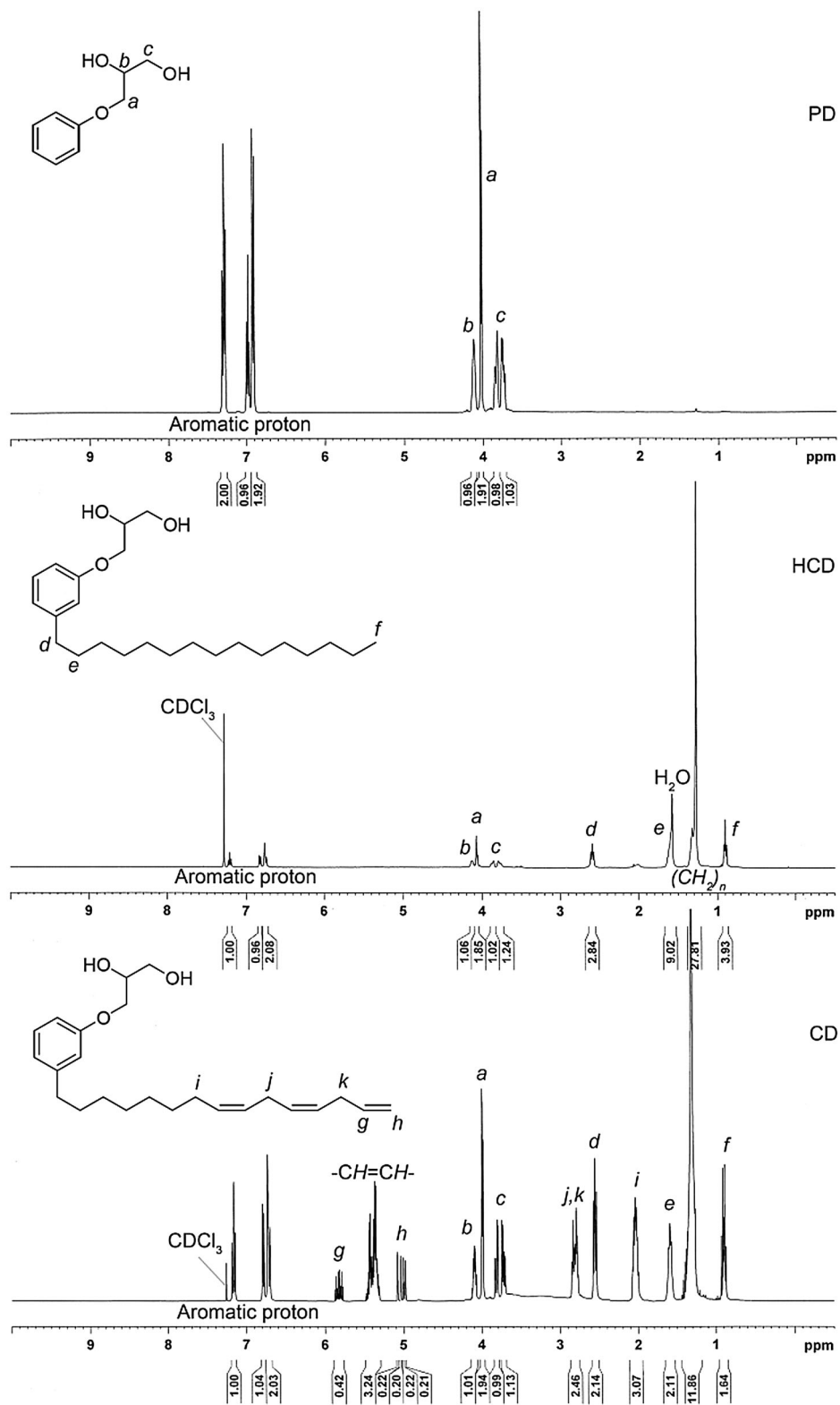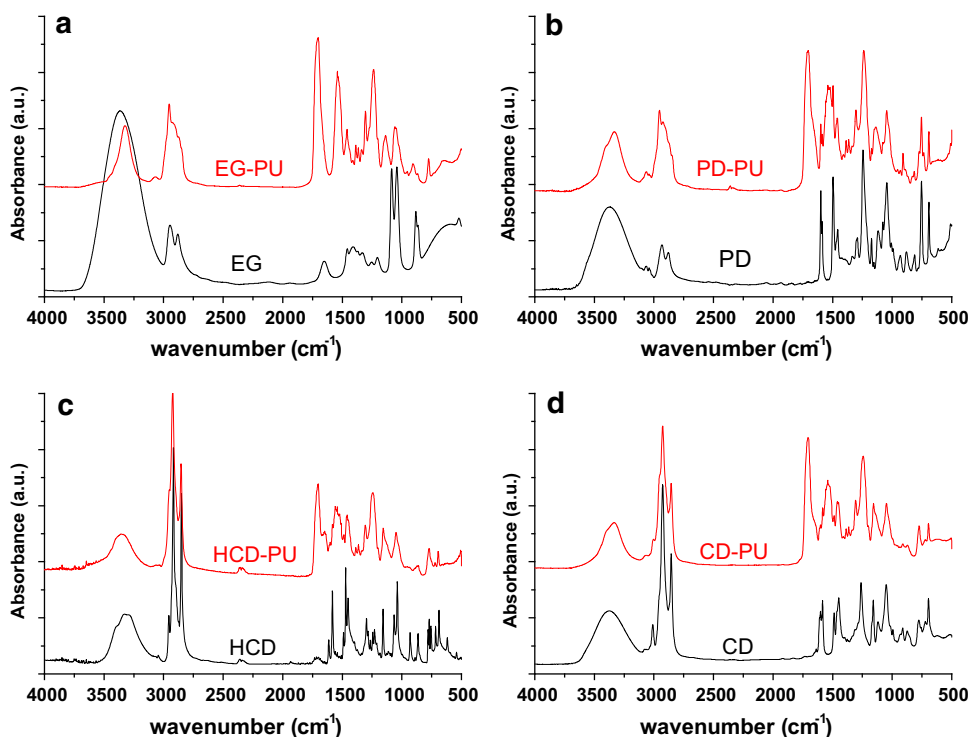
Fig. 1 ¹H-NMR spectra of PD, HCD and CD

Fig. 2 FTIR spectra of diol and PUs prepared from that diol of **a** EG–PU/EG, **b** PD–PU/PD, **c** HCD–PU/HCD and **d** CD–PU/CD

Properties of Polyurethanes

As expected, GPC results show that EG–PU has a higher number average molecular weight ($M_n \sim 15,000$ g mol^{-1}) than the other three samples because EG is a pure compound and contains two primary hydroxyl groups, whereas all other diols contain one primary and one secondary and have long side groups. Typically, the reaction rate of the primary hydroxyl group is faster than the secondary hydroxyl group because of steric effect [19]. Also, the side group of PD–PU, HCD–PU and CD–PU could possibly prevent the reaction between hydroxy and isocyanate during polymerization [20]. In addition, the low molecular weight of all samples is probably due to IPDI itself as it contains both primary and secondary isocyanate groups. The latter has lower reactivity toward the reaction than the primary isocyanate group [2], and a short reaction time. The low molecular weight indicates that all PU samples were obtained as prepolymers, which are similar to previous work reported by Athawale and Shetty [21]. Figure 3 shows DSC thermogram of all PU samples. A single glass transition temperature (T_g) was observed. The trend of T_gs is in the order of EG–PU > PD–PU > HCD–PU > CD–PU. Thus, introducing phenoxy side groups on EG molecules reduces the T_g of PUs. T_gs of HCD and CD are lower than those of PD–PU and EG–PU, resulting from the flexibility and the length of C15 alkyl chains [14]. Figure 4 displays the WAXD patterns of EG–PU, PD–CU, HCD–
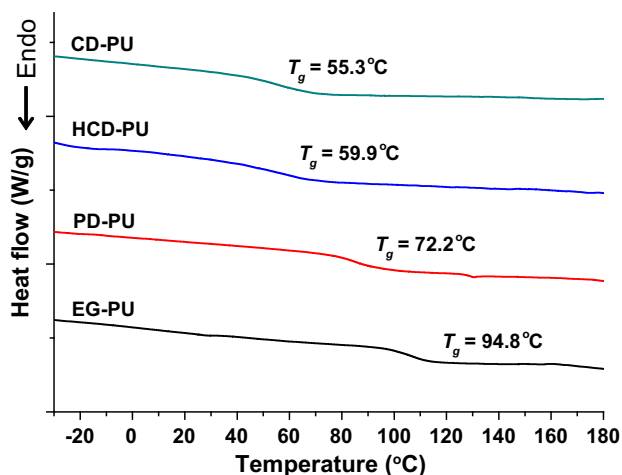

Fig. 3 DSC thermograms of EG–PU, PD–CU, HCD–PU and CD–PU

PU and CD–PU. Only amorphous halos were observed, indicating that all PU samples are amorphous.

Thermal Properties

Under practicable conditions, polymers are typically deteriorated by chemicals, light and heat, which cause them to turn yellowish and brittle. Typically, thermal and thermooxidative stabilities of polymers were determined by measuring the resistance to thermal degradation under N$_2$
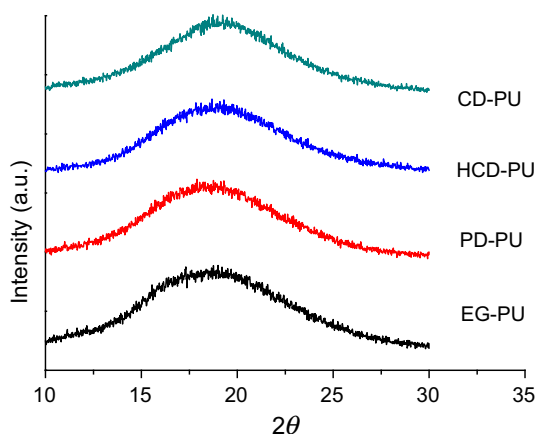
Fig. 4 WAXD patterns for EG–PU, PD–CU, HCD–PU and CD–PU

and O_2 or air, respectively by TGA. Figure 5 displays the plot of TGA results of all PU samples as a function of weight (%) and temperature under N_2 and O_2.

Thermal Degradation

The thermal degradation of all PU samples is analyzed at selected percentages of weight losses, which are 5 % (T5), 10 % (T10), 50 % (T50), 80 % (T80) and by the residue at 600 °C, as shown in Table 1. T5 corresponds to the dissociation of urethane bonds, which are known as thermally

unstable groups and typically start decomposing in a range of 150–200 °C [22]. The decomposition of urethane bonds involves three mechanisms: the dissociation to isocyanate and alcohol, the formation of primary amine and olefin, and the formation of secondary amine as displayed in Scheme 2 [23]. As seen in Scheme 2, the major volatile product is carbon dioxide (CO_2). As seen in Table 1, compared to EG–PU, T5 of PD–PU, HCD–PU and CD–PU increases by 41, 106 and 100 °C, respectively. This is due to the presence of phenyl rings alone for PD–PU and with long alkyl chains for HCD–PU and CD–PU. According to the mechanisms 2 and 3 in Scheme 2, the weight loss at T5 is due to the evaporation of CO_2, which mainly undergoes degradation through 6 and 4-membered ring transition states. Thus, side groups on PU chains are able to inhibit the rotation of chains to form the 6 and 4-membered ring transition states and retard the degradation. The thermal stability of CD–PU is slightly lower than that of HCD–PU because of the loose packing of unsaturated cardanol side chains, which helps promote the rotation of polymer chains and raises the free volume of CD–PU, supported by the observed T_g. The results of T10 are similar to those of T5. For T50, all samples decompose at nearly the same temperature, approximately 320–335 °C, respective to the characteristic degradation of IPDI based PUs [23]. HCD–PU and CD–PU show a higher T80 value compared to EG–PU and PD–PU, which comes from the thermal degradation of long alkyl side chains [24]. The superior thermal
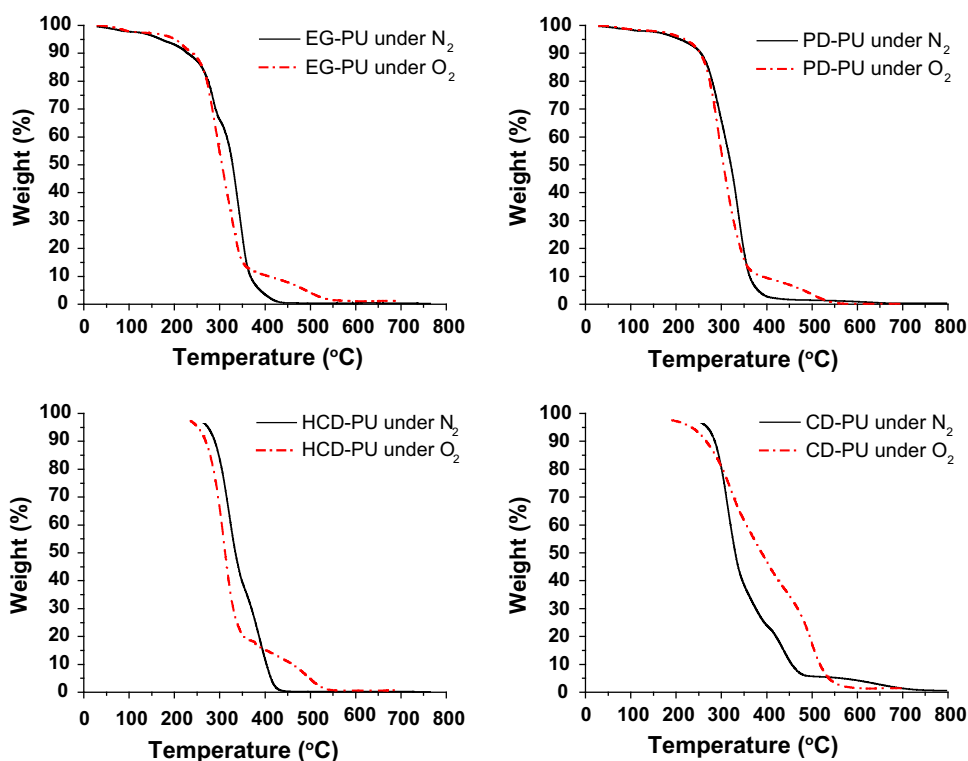

Fig. 5 TGA thermograms of PU samples under N_2 and O_2

Table 1 Thermal decomposition parameters of PU samples investigated under N₂ gas

Samples	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	T_{80} (°C)	Residue at 600 °C (wt%)
EG–PU	168	227	328	354	0.41
PD–PU	209	254	321	349	0.90
HCD–PU	274	289	335	387	0.23
CD–PU	268	285	330	420	4.26

stability (T80) of CD–PU (T > 400 °C) is possibly due to the crosslink of the unsaturation pendent side chains [25], which is difficult to evaporate as evidenced by the highest

amount of residue at 600 °C. Without the radical formation, the crosslink of unsaturation structures is formed via the ene reaction as presented in Scheme 3, which occurs at temperatures around 415–480 °C [26]. The ene reaction is a group transfer pericyclic reaction, which initiates the frontier orbitals interaction (HOMO/LUMO), a non-ionic and non-free radical mechanism. The reaction is preceded by a concerted pathway between allylic hydrogen (ene) and multiple-bond (enophile) compounds (called an activated intermediate complex), followed by a hydrogen transfer, causing a bond breaking and bond forming in a single step. The formation of crosslinks is created by the reaction between HOMO allyl groups (ene) and LUMO vinyl group
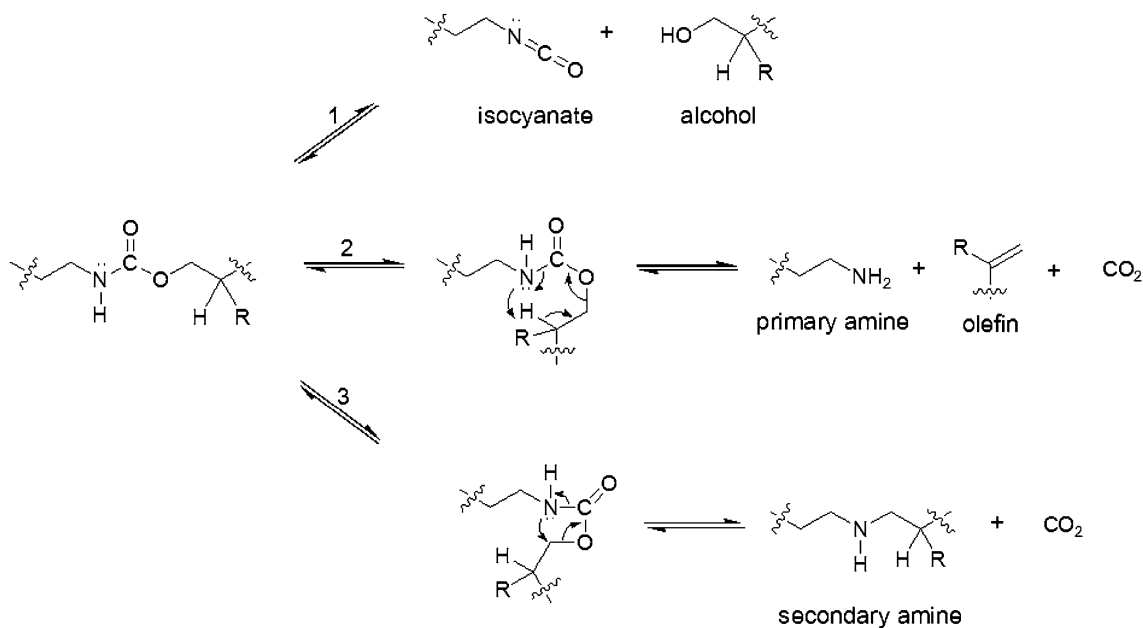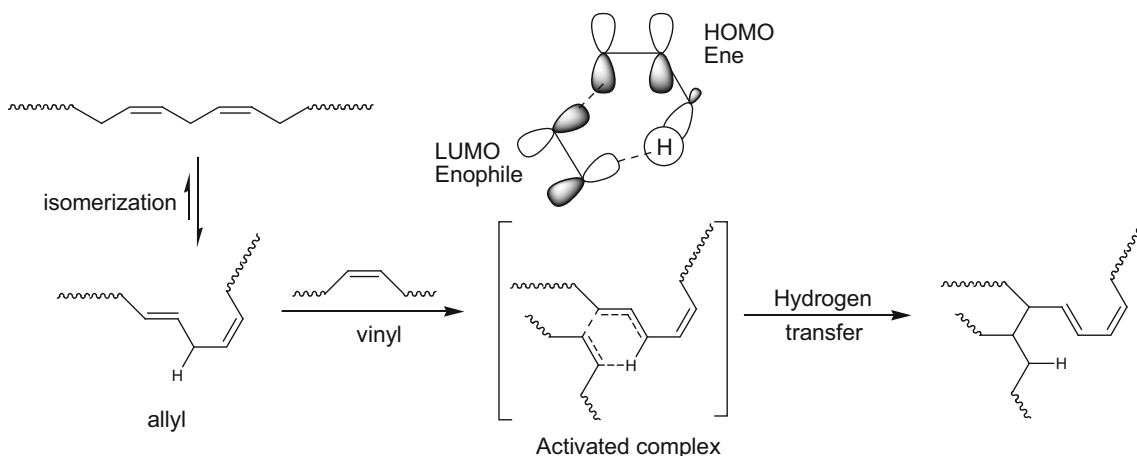

Scheme 2 Thermal decomposition mechanisms of urethane bonds [23]

Scheme 3 The ene reaction under N₂ gas

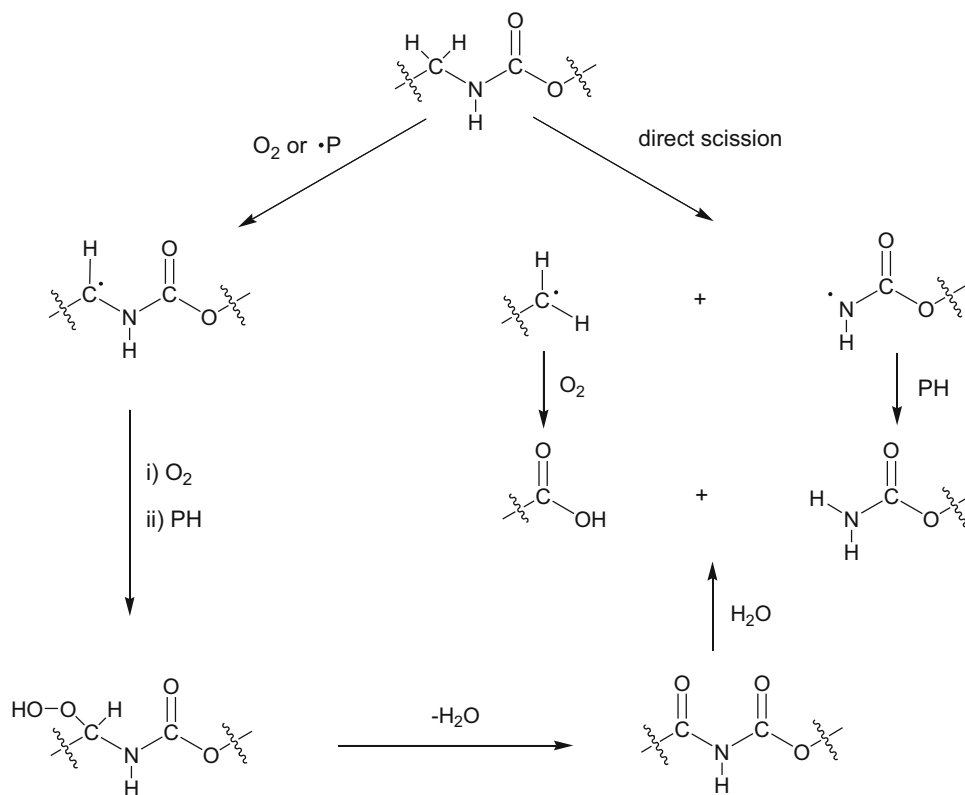**Table 2** Thermo-oxidative decomposition parameters of PU samples investigated under O_2 gas

Samples	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	T_{80} (°C)	Residue at 450 °C (wt%)	Residue at 600 °C (wt%)
EG–PU	202	240	305	340	7.83	1.07
PD–PU	219	253	304	342	6.95	0.08
HCD–PU	252	269	312	353	11.01	0.57
CD–PU	234	266	389	495	34.60	1.43

(enophile), followed by the rapid hydrogen transfer reaction (see Scheme 3).

Thermo-Oxidative Degradation

As shown in Table 2, under O_2, thermal stability of most PU samples decreases because of the autoxidation process. Oxygen molecules initiate free radicals on polymer backbones and form peroxy radicals (P–O–O) [27], which react further with another polymer chain to yield hydroperoxide (P–O–OH). Hydroperoxide easily either decomposes or forms crosslinks, called the thermo-oxidative degradation. The mechanism of thermo-oxidative degradation of urethane is based on the radical degradation and provides the carboxylic acid and carbamate as shown in Scheme 4 [28].

It is interesting that within a temperature range of 350–550 °C, there is another step of the thermo-oxidative degradation for all PU samples (see Fig. 5), which is probably due to the coupling of either main chain or side chain radicals as presented in Scheme 5 [29]. However, these free radical crosslinks are able to further degrade when the temperature reaches 600 °C, supported by the lower residue values compared to those at 450 °C (see Table 2). As shown in Table 2, the thermo-oxidative stability is in the order of CD–PU > EG–PU > HCD–PU > PD–PU. This indicates that phenyl rings in PD–PU structure are more effective to inhibit the coupling of polymer main chains than those of the saturated and unsaturated side chains of HCD–PU and CD–PU, respectively. In addition, this result indicates that the crosslinks of the unsaturated side chains are more stable than those of PU main chains and saturated side chains.

According to the thermo-oxidative degradation results, CD–PU is selected to study the oxidative induction time (OIT), compared to EG–PU. Figure 6a, b display the OIT behavior measured from DSC and TGA, respectively. Similar results were observed for both CD–PU and EG–PU in both techniques. To the authors' knowledge, there are no OIT reference standards for polyurethanes. Thus, we considered the OIT value based on the polyolefin standard. According to ASTM D3895, the test method for oxidative induction times of polyolefins by DSC, polymers having

Scheme 4 Radical degradation mechanisms of urethanes under O_2 gas [28]

Scheme 5 Possible crosslinks of PU samples under O₂ gas

Crosslink at PU backbones

Crosslink at side chains of HCD-PU
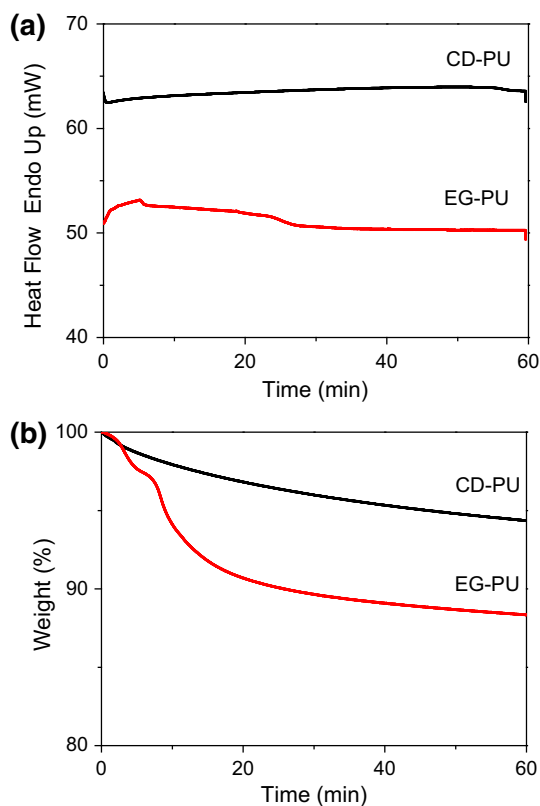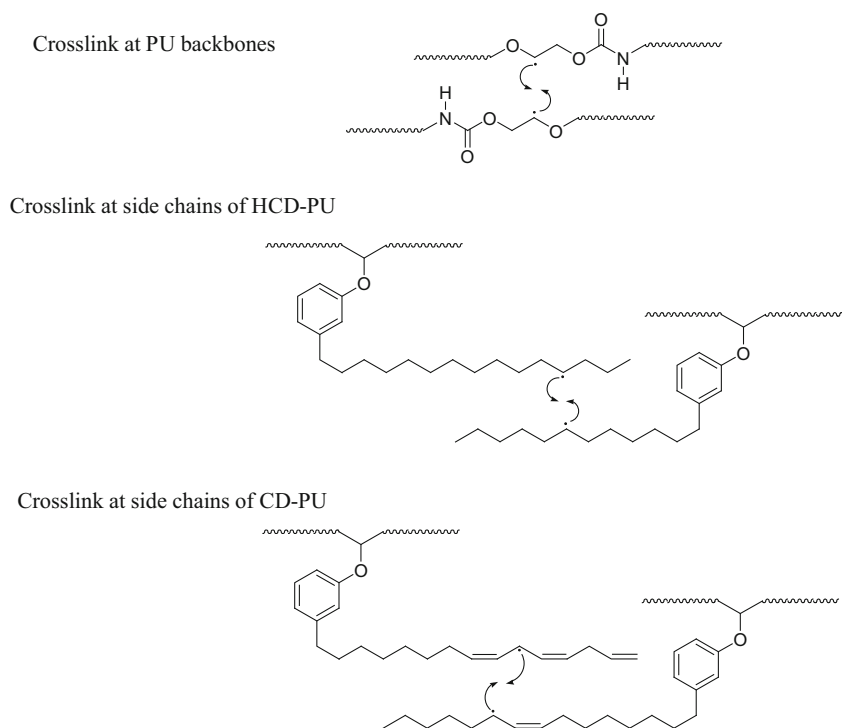

Crosslink at side chains of CD-PU

Fig. 6 OIT curves of EG–PU and CD–PU observed from **a** DSC and **b** TGA

OIT greater than 20 min are considered to have good oxidative stability. OIT values of reference polymers without adding antioxidant are 36.2, 17.9, 38.7 and 6.9 min for high density polyethylene, low density ethylene, polypropylene, and polybutylene, respectively [30]. Therefore, both CD–PU and EG–PU can be considered as good oxidative stable polymers since their OIT values are up to 60 min without the onset of oxidation (see Fig. 6). Furthermore OIT curves also confirm that CD–PU is more thermally oxidative stable than EG–PU, consistent with the thermo-oxidative degradation results.

Conclusions

Amorphous PU prepolymers were synthesized from IPDI and various diols based on ethylene glycol. The low molecular weight of PD–PU, HCD–PU and CD–PU, compared to EG–PU, was observed because an impurity, the secondary hydroxyl groups and the steric hindrance reduced the reactivity of the polymerization. The T_g of all PUs was in the order of EG–PU > PD–PU > HCD–PU > CD–PU. Long side groups on PU backbones decreased the T_g and enhanced the flexibility of PUs by acting as an internal plasticizer. All PU samples were thermally and oxidatively stable due to the possible crosslinks of either polymer main chains or cardanol side

chains. From T80 values, the unsaturation cardanol side chains of CD–PU significantly enhanced the thermal and thermo-oxidative stability by reducing the decomposition rate at high temperatures. PUs containing cardanol should be considered as good thermally oxidative stable polymers. These synthesized compounds could be applied as a naturally renewable chain extender for improving properties of PUs.

References

1. Woods G (1987) The ICI polyurethanes book. Wiley, Chicester
2. Krol P (2007) Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. Prog Mater Sci 52:915
3. Woebcken W (1995) Saechtling internation plastics handbook for the technologist, engineer. In: Haim J, Hyatt D (eds). Hanser, New York
4. Gandini A (2008) Polymers from renewable resources: a challenge for the future of macromolecular materials. Macromolecules 41:9491
5. Kumar PP, Paramashivappa R, Vithayathil PJ (2002) Process for isolation of cardanol from technical cashew (Anacardium occidentale L.) nut shell liquid. J Agric Food Chem 50:4705
6. Tyman JHP, Patel MS, Manzara AP (1982) Treatment of cashewnut shell liquid. US. Patent 4352944
7. Tyman JHP (1979) Practical liquid chromatographic separation of the phenols in technical cashew nutshell liquid from Anacardium occidentale. Chem Soc Rev 8:499
8. Mythili CV, Retna AM, Gopalakrishnan S (2004) Synthesis, mechanical, thermal and chemical properties of polyurethanes based on cardanol. Bull Mater Sci 27:235
9. Gopalakrishnan S, Fernando TL (2010) Processability and characteristics of novel polyurethanes from cardanol. Res J Pharm Bio Chem Sci 1:252
10. Suresh KI, Kishanprasad VS (2007) Process for preparing polyurethane polyol and rigid foams therefore. US. Patent 7244772 B2
11. Suresh KI, Kishanprasad VS (2005) Synthesis, structure and properties of novel polyols from cardanol and developed polyurethanes. Ind Eng Chem Res 44:4504
12. Rekha N, Asha SK (2008) Synthesis and FTIR spectroscopic investigation of the UV curing kinetics of telechelic urethane methacrylate crosslinkers based on the renewable resource-cardanol. J Appl Polym Sci 109:2781
13. Bhunia HP, Jana RN, Basak A, Lenka S, Nando GB (1998) Synthesis of polyurethane from cashew nut shell liquid (CNSL), a renewable resource. J Polym Sci A Polym Chem 36:391
14. Bhunia HP, Nando GB, Chaki TK, Basak A, Lenka S, Nayak PL (1999) Synthesis and characterization of polymers from cashew nut shell liquid (CNSL), a renewable resource II: synthesis of polyurethanes. Eur Polym J 35:1381
15. Risfaheri TT, Nur MA, Sailah I (2009) Isolation of cardanol from cashew nut shell liquid using the vacuum distillation method. Indones J Agric 2:11
16. Facanha MAR, Mazzetto SE, Carioca JOB, Barros GG (2007) Evaluation of antioxidant properties of a phosphorated cardanol compound on mineral oils (NH10 and NH20). Fuel 86:2416
17. Shahidi F (2005) Bailey's industrial oil and fat products. Wiley, New York
18. Coates J (2000) Interpretation of infrared spectra, a practical approach: encyclopedia of analytical chemistry. Wiley, Chichester
19. Young RJ, Lovell PA (2009) Introduction to polymers. CRC Press, Florida, CR
20. Ionescu M (2005) Chemistry and technology of polyols for polyurethanes. Rapra technology, Shropshire
21. Athawale V, Shetty N (2010) Synthesis and characterization of low-cost cardanol polyurethanes. Pigment Resin Technol 39:9
22. Chattopadhyay DK, Webster DC (2009) Thermal stability and flame retardancy of polyurethanes. Prog Polym Sci 34:1068
23. Zhang Y, Xia Z, Huang H, Chen H (2009) Thermal degradation of polyurethane based on IPDI. J Anal Appl Pyrol 84:89
24. Sinha BR, O'Connor D, Blum FD (1989) Characterization of substituted phenol-formaldehyde resins using solid-state carbon-13 NMR. J Appl Polym Sci 38:163
25. Zubarev ER, Pralle MU, Li L, Stupp SL (1999) Conversion of supramolecular clusters to macromolecular object. Science 283:523
26. Richard C, Scacchi G, Back MH (1978) Ene reactions of olefins. I. The addition of ethylene to 2-butene and the decomposition of 3-methylpentene-1. Int J Chem Kinet 10:307
27. Gryn'ova G, Hodgson JL, Coote ML (2011) Revising the mechanism of polymer autooxidation. Org Biomol Chem 9:480
28. Perrin FX, Irigoyen M, Aragon E, Vernet JL (2000) Artificial aging of acrylurethane and alkyd paints: a micro-ATR spectroscopic study. Polym Degrad Stab 70:469
29. Dannoux A, Esnouf S, Amekraz B, Dauvois V, Moulin C (2008) Degradation mechanism of poly(ether-urethane) Estane® Induced by high-energy radation. II. Oxidation effects. J Polym Sci B Polym Phys 46:861
30. Gopalakrishnan S, Fernado TL (2011) Studies on aging performance of some novel polyurethanes. J Chem Pharm Res 3:848