Functional Thermoplastics from Linear Diols and Diisocyanates Produced Entirely from Renewable Lipid Sources

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An unsaturated terminal diol, 1,18-octadec-9-endiol (ODEDO), and a saturated terminal diol, 1,9-nonanediol (NDO), were synthesized from oleic acid. The feasibility of utilizing these new diols for the production of thermoplastic polyurethanes (TPUs) was demonstrated by reacting them with a fatty acid-derived diisocyanate, 1,7-heptamethylene diisocyanate (HPMDI), and a commercially available petroleum-derived diisocyanate, 1,6-hexamethylene diisocyanate (HDI). One type of phase structure was obtained for both TPUs in this study, owing to the similarity between the ODEDO and NDO molecular structure. In addition, double yielding behavior (observed for the first time in polyurethanes) was observed in the stress-strain curves for both TPU systems. Compared to the TPUs prepared from HDI, the totally biobased TPUs (ODEDO-NDO-HPDMI) demonstrated comparable properties within acceptable tolerances, considering the impacts on physical properties due to the odd-even effect introduced by the HPDMI. This work is the first that establishes the production of linear thermoplastic polyurethanes entirely from lipid feedstock.

Introduction

Polyurethanes (PUs) are one of the most important and versatile classes of polymers and can vary from thermosetting plastics to rubbery materials to glassy thermoplastics. The industrial production of PU is normally accomplished through the polyaddition reaction between organic isocyanates and compounds containing active hydroxyl groups, such as polyols. Usually, both isocyanates and polyols are petroleum based. In recent years, natural oils, fatty acids, and their derivatives have attracted significant attention as raw materials for the preparation of monomers and polymeric materials to replace or augment the traditional petrochemical-based polymers and monomers due to uncertainty about the future cost of petroleum as well as the desire to move toward more environmentally friendly feedstocks.^{1–12} Vegetable oils are one of the cheapest and most abundant biological sources available in large quantities and they possess numerous advantages as starting materials, such as low toxicity, inherent biodegradability, and high purity.¹³ They are considered a readily available candidate for the production of biobased polymeric materials. For natural oils to be used as raw materials for PU production, multiple hydroxyl and isocyanate functionality are required. During the last several years, research has been focused on introducing hydroxyl functional groups at the double bonds on fatty acid chains of vegetable oils.^{3,5,7,8,12,14–16} Recently, our research group has successfully developed methodologies for the synthesis of isocyanates and polyols from vegetable oils and corresponding biobased PUs entirely from lipid feedstock.¹⁷ However, due to the nature of the triacylglycerol structure of vegetable oils, these types of PUs are mostly cross-linked materials (thermoset) and are therefore not reprocessable.

Thermoplastic polyurethanes (TPUs) are widely employed as a consequence of their flexibility, elasticity, strength, good abrasion resistance, and versatile melt processability.¹⁸ TPUs are typically formed as the reaction product of a diisocyanate with a hydroxyl-terminated polyether and polyester polyols and a low molecular weight glycol chain extender. The resulting TPUs have excellent mechanical properties but are rather hydrophilic, which can limit their utilization in moisturesensitive applications. Hydroxyl-terminated polyols with nonpolar backbones (e.g., hydroxyl functional polybutadiene) have been used to introduce hydrophobicity into polyurethane elastomers. Polyurethanes based on polybutadiene polyols are known for excellent hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties, and low-temperature elasticity.¹⁹ In addition, the fully hydrocarbon structure prevents the occurrence of intersegment hydrogen bonds, which are usually present in polyether or polyester polyurethanes and favors phase segregation.^{20,21}

In 1998, a novel \mbox{TPU}^{22} was prepared from cardanol, a renewable resource from the waste of the cashew industry, and diphenylmethane diisocyanate (MDI) from petroleum. Recently, Petrovic et al.^{23,24} examined the feasibility of the utilization of vegetable oils for the preparation of TPUs. In their work, polyester polyols were prepared by transesterification of ricinoleic acid, which resulted in dangling chains of six carbon atoms in the polyol structure. Furthermore, MDI and butane diol from petroleum resources were used in the reaction to produce TPUs. To the best of our knowledge, there is no literature reported on the preparation of aliphatic TPUs completely from renewable resources. Therefore, the primary purpose of this work was to synthesize suitable aliphatic diols and diisocyanates without dangling chains from fatty acids, so as to produce functional TPUs with fully hydrocarbon structure entirely from renewable lipid resources.

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Experimental Section

Materials. Oleic acid (90% purity), triethylamine, sodium azide, 1,3-bis-(2,4,6-trimethylphenyl)-2- (imidazolidinylidene)(dichlorophenylmethylene)-(tricyclohexylphosphine)ruthenium (Grubbs catalyst, second generation), ethyl vinyl ether, dibutyltin dilaurate (DBTDL), tin(II) 2-ethylhexanoate (Sn(OCT)₂), lithium aluminum hydride (Li-AlH₄), anhydrous DMF, and anhydrous THF were purchased from Sigma-Aldrich. Ethylchloroformate was obtained from BDH Ltd. Methanol, chloroform, ethyl acetate, and hexane were purchased from Fisher. Aliphatic 1,6-hexamethylene diisocyanate (HDI, Desmodur H) was sourced from Bayer Corporation. 1,7-Heptamethylene diisocyanate (HPMDI)¹⁷ was synthesized from oleic acid according to the reported procedure.

1,18-Octadec-9-enedioic acid **2.** Oleic acid [28.2 g (90%), 0.1 mol] was transferred into a 250 mL three-necked round-bottomed flask and stirred at 45 °C under nitrogen gas for 0.5 h. Grubbs catalyst, second generation (89 mg, 0.01 mmol), was then added. The reaction mixture was stirred with a stirrer bar and kept at 45 °C. After approximately 5 min, the diacid began to precipitate from the reaction mixture. The reaction was kept at this temperature for 24 h and then it was quenched with ethyl vinyl ether (6.5 mL), and excess ether was removed under reduced pressure. The residue was purified by column chromatography using a hexane/ethyl acetate eluting solvent (4:1, 3:1, 2:1, 1:1, 1:0) to give 10.0 g of pure 1,18-octadec-9-enedioic acid **2** as a white solid (64%).^{25 1}H NMR: δ 1.28–1.34 (m, 16H, 8CH₂), 1.61–1.66 (m, 4H, 2CH₂), 1.95–1.98 (m, 4H, 2CH₂), 2.35 (t, *J* = 7.2 Hz, 4H, 2 CH₂COO), 5.35–5.37 (m, 2H, CH=CH).

1,18-Octadec-9-endiol (ODEDO) 3. The diacid compound 2 (5 g, 16 mmol) was dissolved in 50 mL of anhydrous THF. The reaction flask was kept at 0 °C in an ice bath, and LiAlH₄ (1.5 g, 38.4 mmol) was added slowly over 30 min. The ice bath was removed, and the mixture was stirred at room temperature for 4 h, followed by refluxing for 0.5 h. Distilled water (40 mL) was added followed by 80 mL of 2 N HCl. The organic layer was extracted by 2×100 mL of ethyl acetate, washed with brine (2 \times 40 mL), and dried over MgSO₄. The solvent was evaporated by reduced pressure and residue was purified by flash chromatography to afford 4.1 g (90%) of diol 3 as a white solid. Purity of the compound (99%) was determined by GC-FID. ¹H NMR: δ 1.25-1.37 (m, 20H, 10CH₂), 1.41 (brS, 2OH), 1.53-1.59 (m, 4H, $2CH_2$), 1.94-1.98 (m, 4H, $2CH_2$), 3.63 (t, J = 6.5 Hz, 4H, $2OCH_2$), 5.36-5.38 (m, 2H, CH=CH); ¹³C NMR: δ 25.7 (CH₂), 29.0 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 32.6 (CH₂), 32.8 (CH₂), 63.0 (O-CH₂), 130.3 (CH=CH).

1,9-Nonanediol (NDO) **5.** The diacid compound **4** (9.4 g, 50 mmol) was dissolved in 200 mL of anhydrous THF. The reaction flask was kept at 0 °C in an ice bath, and LiAlH₄ (4.69 g, 120 mmol) was added slowly over 30 min. The ice bath was removed, and the mixture was stirred at room temperature for 3 h, followed by refluxing for 0.5 h. Distilled water (250 mL) was added, followed by 500 mL of 2 N HCl. The organic layer was extracted by 2×150 mL of ethyl acetate, washed with brine (2 × 20 mL), then dried over MgSO₄. The solvent was evaporated by reduced pressure, and the residue was purified by flash chromatography to afford 7.3 g (91%) of diol **5** as a white solid. Purity of the compound (99%) was determined by GC-FID. ¹H NMR: δ 1.29 (m, 10H, 5CH₂), 1.51–1.55 (m, 4H, 2CH₂), 3.58–3.61 (m, 4H, 2CH₂); ¹³C NMR: δ 25.7 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 32.7 (CH₂), 63.0 (O–CH₅).

Polymerization. An excess amount of HDI (12 mmol) or HPMDI (12 mmol) was dissolved in 4 mL of anhydrous DMF. The solution was added to a three-neck flask and stirred. ODEDO (1.14 g, 4 mmol) and four drops of $Sn(Oct)_2$ were dissolved in 20 mL of anhydrous DMF and added through an addition funnel fitted to the three-neck flask. ODEDO and catalyst solution was in this manner slowly (within 30 min) added to the diisocyanate solution. The reaction mixture was then stirred at 65 °C for 3 h to form the prepolymer. The prepolymer was then chain extended to form a high molecular weight polymer by adding NDO (1.28 g, 8 mmol) to the reaction mixture and stirring at 85 °C

for 20 h. The reaction mixture was precipitated into a large excess of warm distilled water. After removing water, the resulting polymer was dissolved in 70 mL of chloroform, then precipitated in 800 mL of methanol and stirred for 1 h at room temperature. The resulting white solid was filtered and washed in methanol. The samples were coded as ODEDO-HDI-NDO and ODEDO-HPMDI-NDO for TPUs produced from ODEDO with HDI and HPMDI, respectively, with NDO used as a chain extender. The yield for ODEDO-HDI-NDO was 83% and for ODEDO-HPMDI-NDO was 78%. The detailed reaction procedure for ODEDO-HPMDI-NDO system is illustrated in Scheme 2 as an example.

ODEDO-HDI-NDO. ¹H NMR: δ 1.27–1.32 (m, CH₂), 1.47–1.48 (m, CH₂), 1.57–1.58 (m, CH₂), 1.93–2.04 (m, CH₂), 3.14–3.15 (m, NCH₂), 4.01–4.03 (m, OCH₂), 4.76 (bs, NH), 5.36–5.38 (m, CH=CH); ¹³C NMR: δ 25.81 (CH₂), 25.87 (CH₂), 26.30 (CH₂), 29.08 (CH₂), 29.14 (CH₂), 29.28 (CH₂), 29.39 (CH₂), 29.61 (CH₂), 29.94 (CH₂), 32.57 (CH₂), 40.77 (N–CH₂), 64.84 (O–CH₂), 130.32 (CH=CH), 156.84 (C=O); IR (cm⁻¹): 1258, 1535, 1682 (C=O), 2853, 2921 (C–H), 3057(=C–H), 3315 (NH).

ODEDO-HPMDI-NDO. ¹H NMR: δ 1.23–1.30 (m, CH₂), 1.46–1.49 (m, CH₂), 1.57–1.59 (m, CH₂), 1.93–2.04 (m, CH₂), 3.13–3.15 (m, NCH₂), 4.01–4.05 (m, OCH₂), 4.73 (bs, NH), 5.36–5.37 (m, CH=CH); ¹³C NMR: δ 25.86 (CH₂), 25.92 (CH₂), 26.66 (CH₂), 28.92 (CH₂), 29.12 (CH₂), 29.19 (CH₂), 29.32 (CH₂), 29.44 (CH₂), 29.65 (CH₂), 29.98 (CH₂), 32.62 (CH₂), 40.94 (N–CH₂), 64.88 (O–CH₂), 130.38 (CH=CH), 156.89 (C=O); IR (cm⁻¹): 1253, 1536, 1684 (C=O), 2852, 2921 (C–H), 3067 (=C–H), 3328 (NH).

Gas Chromatograph-Flame Ionization Detector (GC-FID) System. Gas chromatograms were obtained on an Agilent 6890N capillary GC (Santa Clara, CA) equipped with a flame ionization detector and Agilent 7683B auto sampler. A 30 m \times 0.32 mm \times 0.1 μ m DB-5HT column was used for the determination of diisocyanate compound purity. The temperature of the column was initially set at 85 °C then increased to 250 °C at a rate of 10 °C/min and held for 5 min.

FTIR and NMR. FTIR spectrum of diisocyanate was measured with a Mattson Galaxy series 3000 FTIR spectrophotometer. The analysis of polymer specimens was performed using a Bruker Vertex 70 FTIR main bench with an attached Hyperion FTIR microscope using OPUS software. The spectra were obtained using a micro-ATR objective with an analysis area approximately 100 μ m in diameter. The spectra were acquired using 128 scans at a resolution of 4 wavenumbers. ¹H and ¹³C NMR were recorded at larmor frequencies of 500 and 125 MHz, respectively, using a Varian UNITY 500 NMR spectrometer (Varian, Inc., CA). Deuterated chloroform (CDCl₃) was used as solvent.

Molecular Weight Measurements by Gel Permeation Chromatography (GPC). The number and weight-average molecular weights (M_n and M_w , respectively) were determined by GPC (Santa Clara, CA). The tests were carried out using a GPC with an Agilent G1311A quaternary pump, G1362A refractive index detector, and a PL gel column (5 μ m mixed-D). Chloroform and DMSO (1:1) was used as the eluent at a flow rate of 0.8 mL/min. Sample concentrations of 0.4% (w/v) and injection volumes of 10 μ L were used. Polystyrene standards were used to generate a calibration curve.

Wide Angle X-ray Diffraction (WAXD). A Bruker AXS X-ray diffractometer (Madison U.S.A.) equipped with a filtered Cu K α radiation source ($\lambda = 0.1542$ nm) and a 2D detector was used to record the WAXD patterns. The procedure was automated and controlled by the Bruker AXS's "GADDs V 4.1.08" software. The frames were processed using GADDS software and the resulting spectra were analyzed using Bruker AXS's "Topas V 2.1" software.

Thermal Properties. MDSC measurements were carried out on a DSC Q100 (TA Instruments, DE, U.S.A.), equipped with a refrigerated cooling system. The samples were heated at a rate of 10 °C/min from 25 to 160 °C to erase thermal history, then cooled down to -50 °C at a cooling rate of 5 °C/min. MDSC measurements were performed with a modulation amplitude of 1 °C/min and a modulation period of 60 s at a heating rate of 3 °C/min to 160 °C. The second heating stage was selected for the analysis of heating data. All the DSC measurements







Table 1. Average Molecular Weight Determined by GPC and Thermal Properties of Thermoplastic Polyurethane Made from Different Raw Materials, Determined by MDSC and DMA

	<i>M</i> _n	M _w	PDI	T_{g} (°C) by DMA	T_{g} (°C) by DSC	$T_{\rm m}$ (°C) by DSC
ODEDO-HDI-NDO ODEDO-HPMDI-NDO	$\begin{array}{c} 4.1 \times 10^4 \\ 3.8 \times 10^4 \end{array}$	$\begin{array}{c} 6.3\times10^4\\ 5.8\times10^4\end{array}$	1.5 1.5	$\begin{array}{c} 12.2\pm0.1\\ 6.7\pm0.2\end{array}$	$\begin{array}{c} 0.3\pm0.2\\-5.6\pm0.1\end{array}$	$\begin{array}{c} 126.7 \pm 0.2 \\ 101.9 \pm 0.1 \end{array}$

were performed following the ASTM E1356-03 standard procedure under a dry nitrogen gas atmosphere.

DMA measurements were carried out on a DMA Q800 (TA Instruments, DE, USA) equipped with a liquid nitrogen cooling apparatus in the single cantilever mode, over a temperature range of -60 to 80 °C with a constant heating rate of 1 °C/min and a fixed frequency of 1 Hz. The dimension of the samples was $18 \times 7 \times 2$ mm. The measurements were performed following ASTM E1640-99 standard at a fixed oscillation displacement of 0.015 mm.

Mechanical Properties. Mechanical properties were tested using an Instron (MA, U.S.A.) tensile testing machine (model 4202) equipped with a 50 Kgf load cell and activated grips that prevented slippage of the sample before break. Specimens were cut out from the PU sheets using an ASTM D638 Type V cutter. The measurements were performed at room temperature with cross-head speed of 50 mm/min, as suggested by the above-mentioned ASTM standard. The data presented are an average of five different measurements. The reported errors are the associated standard deviations.

Results and Discussion

Recently, diisocyanates derived from fatty acids were successfully synthesized by our group. Azelaic acid (compound 4, Scheme 1), as the precursor of HPMDI, was synthesized by ozonolysis and oxidation of oleic acid.¹⁷ The diacid was then converted to the corresponding diisocyanate via Curtius rearrangement with purities up to 97% before polymerization. Unsaturated dicarboxylicacid was produced by using Grubbs catalyst and the self-metathesis procedure. In this case, the

double bond on the alkyl chain of the diacid has a *trans* geometry, which was determined by IR spectrum.²⁵ These diacids are also able to be reduced to corresponding diols by using LiAlH₄ (Scheme 1). The achieved 1,18-octadec-9-endiol and 1,9-nonanediol were characterized by ¹H and ¹³C NMR. The structures were in accordance with reported compounds with the same structures.^{26,27} In the case of 1,18-octadec-9-endiol, ¹H NMR showed a triplet at δ 3.63 ppm that is related to methylene groups attached to a hydroxyl group, which was further confirmed by the presence of a signal at δ 63.0 ppm in ¹³C NMR.

Preliminary experiments were performed to synthesize aliphatic polyurethanes by reacting 1,18-octadec-9-endiol with HPMDI at higher temperature (over 110 °C). However, the number molecular weights (M_n) of the resulted polymers were low (\sim 20000), and a yellow color resulted. To solve this problem, two-step polymerization procedures were applied. A longer chain diol (ODEDO) was first reacted with an excess amount of diisocyanate at low temperature (65 °C) to form prepolymers with M_n around 8000, and then the shorter chain diol (NDO) was added as a chain extender (Scheme 2). The $M_{\rm p}$ s of the obtained polyurethanes were around 40000, and the PDIs were 1.5, as determined by GPC, listed in Table 1. The structures of the polyurethanes were characterized by ¹H NMR, ¹³C NMR, and FTIR. The assignments of protons in the polymers are provided in Figures 1 and 2. It is obvious that peaks "a" in two figures have different integrals because different diisocyanates have been utilized in polymerization.



Figure 2. ¹H NMR of ODEDO-HPMDI-NDO thermoplastic polyurethane.

Note that ODEDO-HPMDI-NDO is a linear aliphatic TPU, which were produced entirely from renewable resources. OD-EDO-HDI-NDO TPU, where HDI is a petroleum-based diisocyanate, was prepared as a control. It is interesting that the structure of the TPUs synthesized in this work has only one phase structure, owing to the similarity between the molecular structure of ODEDO and NDO. This was confirmed by both DSC and DMA results where only one glass transition temperature ($T_{\rm g}$) was observed, as will be discussed in detail below.

The phase behavior of the synthesized TPUs was assessed using MDSC. Figure 3 shows the reversing heat flow versus temperature curves of both TPU samples, showing the glass transition temperature and the melting processes. Both TPUs have only one T_g value located at low temperatures, and the



Figure 3. MDSC curves of ODEDO-HPMDI-NDO and ODEDO-HDI-NDO thermoplastic polyurethane.

melting temperature (T_m) occurs over 100 °C. Single values of $T_{\rm g}$ indicate excellent phase mixing in both cases. This is due to the fact that the chain length of diol (ODEDO) in the current study is shorter than the conventional available diol, which, therefore, results in a small domain size containing ODEDO chains and increases the amount of exposed surface area per unit volume in the continuous domain (for a given weight fraction of each compound), thereby inducing a lower degree of phase separation. However, it is worth mentioning that the determination of phase separation is limited to the techniques applied as well. It is well-known that DMA and DSC are the two common techniques to determine T_g and, therefore, polymer-polymer miscibility of polymer blends. However, the broadness of the transition interval, the position of T_{o} and even the very possibility of detecting the existence of T_{g} experimentally are affected by the domains size. It was reported²⁸ that the domain dimensions, at which the glass transition is detectable by the two methods mentioned above, should be no less than 15 nm.

It should be noted that the $T_{\rm m}$ of ODEDO-HDI-NDO TPU is 126.7 °C, while that of ODEDO-HPMDI-NDO TPU is 101.9 °C (Table 1). It decreased 15 °C even though the chain length of HPMDI is only one carbon longer than HDI. This demonstrates a marked odd—even effect on crystal packing because chains with an odd numbers of carbon atoms pack less effectively compared to even-numbered chains.²⁹ This result is in agreement with thermal studies on PU, which indicate higher $T_{\rm m}$ for even—even PUs than for odd—even ones.²⁹

The FTIR spectra for ODEDO-HDI-NDO and ODEDO-HPMDI-NDO TPUs are shown in Figure 4. Most of the attention has been given to the characterization of the band intensity and shift of the vibrations associated with specific functional groups, that is, C=O or N-H. In the C=O region, stretching vibration bands characteristic of hydrogen-bonded urethane C=O groups in ordered (crystalline) domains (ca. 1684 cm^{-1}) were present in the FTIR spectra of both samples. In the N-H region, the distribution of the N-H stretching band for both TPUs is very narrow, which is due to the crystallization of the samples. Additionally, hydrogen-bonded N-H stretching of the ODEDO-HDI-NDO and ODEDO-HPMDI-NDO TPUs was observed at 3315 and 3328 cm^{-1} . respectively. This suggests that the hydrogen bond strength for the ODEDO-HDI-NDO specimen is higher than that for the ODEDO-HPMDI-NDO specimen. Generally speaking, higher bond strength is usually characterized by lower wave



Figure 4. FTIR spectra of (a) ODEDO-HPMDI-NDO and (b) ODEDO-HDI-NDO thermoplastic polyurethane.

numbers,³⁰ and the bond strength strongly depends on the local geometry, such as the linearity of the bonds involved and the distance between the groups.³¹ For example, in the case of ODEDO-HDI segments in ODEDO-HDI-NDO TPUs, an extended zigzag conformation could be generated, with fully saturated intermolecular hydrogen bonds between neighboring molecular chains, as illustrated in Scheme 3a. On the contrary, in the case of ODEDO-HPMDI segments in ODEDO-HPMDI-NDO TPUs, where both neighboring C=O dipoles are oriented in the same direction, the hydrogen bonding structure could only be established by rotating the N-H and C=O groups in the opposite direction relative to the alkane chains, as illustrated in Scheme 3b. In such a case, the overall hydrogen bond strength will be significantly lower. The same principle is applicable to HDI-NDO and HPMDI-NDO segments as well.

The WAXD data, presented in Figure 5, for both TPUs reveal a series of prominent peaks in the region $2\theta = 5-25^{\circ}$. However, the intensity distribution of the diffraction profile for ODEDO-HPMDI-NDO and ODEDO-HDI-NDO TPUs are different. For the ODEDO-HPMDI-NDO specimen, the pattern becomes less resolved and the intensity at d = 3.9 decreases compared to that of ODEDO-HDI-NDO. Again, we can attribute this to the disturbance to the crystal packing introduced by the odd-number HPMDI. Indeed, by comparing the WAXD patterns of both TPUs and their corresponding segments containing ODEDO or NDO profiles (not shown), it was found that the main peaks in TPUs arises from overall segments contributions, however, the pattern of the WAXD was dominated by those segments only containing NDO because they are the major component.

The dynamic mechanical behavior, illustrated in Figure 6, was also investigated as a function of temperature, starting in the glassy state through glass transition and well into the rubbery plateau of each material at a frequency of 1 Hz. The storage modulus drops significantly during the transition from glassy to rubbery states, indicating only one transition, that is, glass transition occurred for both TPUs. This result further confirmed that the extent of phase mixing in both TPUs is high. Obviously, the nonpolar nature of ODEDO precludes hydrogen bonding between segments. Therefore, the hydrogen bonding balance between those chains containing only ODEDO molecules and those chains containing both ODEDO and NDO molecules exert a secondary effect by modulating the degree of phase separation between different segments. Additionally, in the glassy state, stiffness is related to changes in the stored elastic energy upon

Scheme 3. Hydrogen Bonding Structure of Soft-Segment in Both Polyurethanes: (a) Saturated Hydrogen Bonding Structure Based on the All Trans Conformation for ODEDO-HDI-NDO TPUs; (b) Saturated Hydrogen Bonding Structure Established by Rotating the NH and CO Groups in the Opposite Direction for ODEDO-HPMDI-NDO TPUs



small deformations as the molecular segments resist motion. In the ODEDO-HDI-NDO TPU system, the shift in T_g to a higher temperature and the high modulus in the low-temperature region suggest that a more ordered crystal structure was obtained for the polymers containing the even-numbered methylene sequence



Figure 5. Wide angle X-ray diffraction patterns of ODEDO ODEDO-HPMDI-NDO and ODEDO-HDI-NDO thermoplastic polyurethane.



Figure 6. Storage moduli vs temperature, obtained from DMA of ODEDO-HPMDI-NDO and ODEDO-HDI-NDO thermoplastic polyure thane.



Figure 7. Nominal stress vs strain curves of ODEDO-HPMDI-NDO and ODEDO-HDI-NDO thermoplastic polyurethane.

HDI. It could also be due to the higher hydrogen bonding in this system, which hindered or restricted mobility of molecules, although hydrogen bonding probably does not directly influence mechanical properties to any great extent, as previously noted. $^{32-34}$

The tensile behavior of both TPUs are shown in Figure 7. The ODEDO-HDI-NDO sample demonstrated a significantly higher tensile strength and elongation at break than the ODEDO-HPMDI-NDO sample. One explanation for this enhanced extensibility and toughness is due to the higher hydrogen bonding density in the former. As discussed previously, the number of hydrogen bonds that could be formed for each repeating unit was two for even-numbered HDI and one for odd-numbered HPMDI. It may also be due to the presence of small crystallites within each domain, which appear to serve as an effective stress-bearing phase during deformation without sacrificing extensibility. In the case of the ODEDO-HDI-NDO system, the more ordered crystals might be able to absorb more strain energy upon deformation through an unfolding of the crystalline lamellae or break up of crystalline segments, as indicated by its overall toughness.

What is more notable about the mechanical property behavior is the observation of two yield points rather than a single yield point as normally observed for tough plastics. This phenomenon has not been found with other TPUs, which might be attributed

Thermoplastics from Linear Diols and Diisocyanates

to the unique structure of the polymers in this study. Most studies of the double yielding behavior of polymers have been focused on polyethylene systems,^{35–41} although this behavior was also observed in polyamide 6 systems.^{42–46} However, to the best of our knowledge, no literature has been reported concerning this special phenomenon in polyurethanes. To interpret the double yielding behavior, Gaucher-Miri and Séguéla³⁶ proposed a so-called heterogeneous slip and homogeneous slip model. According to Gaucher-Miri and Séguéla's model, two plastic deformation processes operate competitively, but having different activation parameters relative to both temperature and strain rate during the elongation after the first yield point. The amorphous regions between the crystal blocks are assumed to be the loci of the deformation in heterogeneous slip, while the folded chains in the lamella tend to undergo a uniform shear in the homogeneous slip process. The latter process will lead to the breakdown of the lamella. It is conceivable that the former process requires lower activation energy than that of the latter process. However, both processes can occur simultaneously after the first yield point but before the second yield point because crystallites with less-ordered structures require a much lower activation energy. Later, Shan and coauthors⁴⁴ reported that the double yielding behavior of polyamide 6 was not only the combination of two thermally activated rate processes depending on temperature and strain rate, but also intimately associated with the initial structure of samples, as well as the role of the inter- and intramolecular links. These two interpretations should be applicable to the TPU systems in this study, however, further adequate experimentation is required to investigate the root structural causes of the double yielding behavior.

This work suggests that acceptable TPUs were successfully synthesized entirely from vegetable oil sources with comparable properties, which increases significantly the amount of renewable carbon in such materials and provides an opportunity to replace or partially replace TPUs produced from petroleum derivatives. Nevertheless, there are still some limitations attributed to the inherent structure of fatty acid, for example, odd number of methylene groups, in this case, before this endeavor could be considered as an industrial solution.

Conclusion

Unsaturated terminal diol and saturated terminal diol have been successfully synthesized from oleic acid. Their chemical structures were in accordance with reported compounds with the same structures.^{26,27} These diols were used as a starting material for the preparation of entirely biobased TPUs by reacting them with fatty acid-derived diisocyanate, HPMDI. The physical properties and phase behavior of the TPUs prepared from these diols were compared to their counterparts prepared from similar but petroleum-based diisocyanate, HDI. In both TPUs in this study, only one phase structure was obtained, owing to the similarity between the ODEDO and NDO molecular structure. Additionally, the double yielding behavior was observed for the first time in TPU systems. However, in the case of TPU prepared from HPMDI, the strength of hydrogen bonding was weaker, the melting temperature was lower, the crystal structure was less ordered, and the tensile strength and elongation at break were less compared to that prepared from HDI, which is due to the effect of odd-numbered methylene groups in the former system.

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