Green Polyurethane from Dimer Acid Based Polyether Polyols: Synthesis and Characterization

Feng Yu, Prosenjit Saha, Pyoung Won Suh, Jin Kuk Kim

Department of Materials Engineering and Convergence Technology, Gyeongsang National University, Gyeongnam, Jinju 660–701, South Korea
Correspondence to: J. K. Kim (E-mail: rubber@gnu.ac.kr)

ABSTRACT: In this study, dimer acid (DA) obtained from waste soybean oil was used together with propylene oxide (PO) to obtain novel polyether polyols [prepolymers for polyurethanes (PUs)] through ring-opening polymerization reaction. The average molecular weight of polyols was estimated by gel permeation chromatography and titration method. The substantial reaction between DA and PO was evident from FTIR and nuclear magnetic resonance spectroscopy. Subsequently, the polyols were reacted with chain extender [ethylene glycol, (EG)] and 4, 4 - Diphenylmethane diisocyanate (MDI) to prepare green PUs. The effect of molar ratio variation of EG and MDI with a fixed amount of polyols was estimated by measuring hydrophobicity and mechanical strength of PUs. The molar ratio such as 1 : 4 : 5.7 of polyol : EG : MDI was found to exhibit maximum hydrophobicity and improved mechanical strength that were comparable with typical PU sample prepared from commercially available polyol, such as polypropylene glycol. FTIR spectroscopic analysis confirmed the chemical changes and possible crosslinking in PUs. Thermalgravimetric analysis and differential scanning calorimetry analysis also showed substantial thermal stability of the green PUs. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41410.

INTRODUCTION

Polyurethanes (PUs) are generally considered to be segmented polymers formed by the polyaddition reaction between polyols and isocyanates to make urethane bonds that consist of thermodynamically incompatible segments.[1,2] A single PU unit is made of an amorphous component known as soft segment that includes polyol, and a hard crystalline segment consist of isocyanate and a chain extender.[2] Several multidimensional uses of PUs as elastomer, thermoplastic, and thermoset materials can be seen depending on their segmental and domain structures, relative proportions of raw materials, and the processing conditions.[1] Hard segment of PUs has been found to impart dimensional and mechanical stability of a thermoset through crosslinking,[3] whereas the soft segments impart elastomeric as well as thermoplastic characteristics.[4] Owing to such unique characters, PUs have found extensive applications as coating, adhesive, sealent in construction, automotive, medical, and other chemical industry.[5–8] Substantial reports have shown that PUs can also be used as basic materials for roof construction due to their lightweight, hydrophobicity, and rigidity.[9–11] PUs are extensively used in building and construction sectors, however, global scientists are looking for the PUs that can be derived from low cost, renewable resources for construction to mitigate the issues originated from climate change and depletion of petroleum based energy resources.* Manufacturing of PUs is potentially related to impart possible adverse effect to environment due to use of synthetic raw materials, such as polyester or polyether polyols.[12] Therefore, an alternative route to prepare green PUs using renewable plant based polyols needs to be explored. One of the most frequently used renewable raw materials are cashew nut shell liquid for getting polyols.[12,13] Vegetable oil has also been blended to prepared polyols as a starting material for Pus.[14,15] Petrovic et al. have reported the preparation of rigid type PUs from soybean oil.[16] There are several reports available on the PUs based on soybean oil, castor oil, nahar seed oil, rape seed oil, and plam oil.[17–23] However, most of the materials have shown inferior hydrophobicity, and mechanical property that would hardly meet the required parameters for roof construction with resulted PUs.

To overcome these issues, an effective method is provided in this study to prepare green PUs from novel polyether polyols. Polyether based polyols were selected for their higher

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*Guidelines 2010/31/EU of the European Parliament and the Rates on May 19, 2010 on the total energy efficiency of buildings.

hydrophobicity and low cost compared to polyester based polyols. Novel polyols were synthesized from dimer acid (DA) that was derived from waste soybean oil. To the best of our knowledge, this unique route for obtaining PU from waste vegetable oil based DA is reported for the first time. DA together with propylene oxide (PO) was initially polymerized to synthesize polyether polyols of different molecular weights. PUs were then synthesized by reacting polyols with chain extender [ethylene glycol, (EG)] and isocyanate with different molar quantity. At the same time, a typical PU sample with commercial standard was also synthesized following similar method from commercial grade polypropylene glycol ($POLY_{com}$) for a comparative study. The basic objective of this study was to develop plant based water repellent, mechanically strong green PUs that can be used as roofing materials.

MATERIALS AND METHODS

Materials

DA from waste soybean oil (Gardner color ≤5, with dimmers % ≥80, monomers % ≤5%, and trimers % ≤15%, acid value: 190–195 mg KOH/g, and viscosity at 25°C: 9900 mPa-s) used in this study without any further modification was provided by GNO Co. South Korea. Propylene glycol as commercial grade polyol was also obtained from GNO Co. Oxide (PO) was purchased from Across Organics Co. (New Jersey, USA). 4, 4 - Diphenylmethane diisocyanate (MDI) was purchased from Uunsei Chemical Co. (Tokyo, Japan). Phthalic anhydride (PA), phenolphthalein, and sodium hydroxide from Sigma-Aldrich Co. were used. LLC potassium hydroxide, pyridine, EG, N,N-dimethylformamide (DMF) obtained from DaeJung Chemicals and Metals Co. were also used as required. However, DMF and toluene were dried for about 7 days at room temperature using 4 angstrom molecular sieves prior to their use.

Experimental

The experimental section includes the synthesis of polyols, followed by preparation of PU specimens. The details of these methods are given in the following subsections,

Synthesis of Polyols. Poly(dimeric acid) glycol was synthesized using DA as a starting material along with potassium hydroxide catalyst (0.3% by weight of total reaction mixture) following the method reported by de Lucas et al.[24] The temperature of the mixture of DA and potassium hydroxide loaded in a reactor (1 L capacity) under nitrogen atmosphere was initially increased and maintained at 100°C followed by continuous stirring for about 30 min. A vacuum system to remove excess water was also attached to the reactor throughout the reaction. A prepolymerization reaction takes place between alkaline DA in the reactor on slow addition of PO under the pressure below 3.5 bar and reaction temperature between 90° and 120°C. Finally, the reaction temperature was increased and maintained at 130°C for 1 h to complete the reaction at the pressure less than 1 bar. The temperature of the reactor was allowed to cool down up to 80°C once the reaction completed and the valve of the reactor was opened to collect the polymer samples. To prevent the unwanted reaction of —NCO and —OH groups with remaining KOH catalyst, it was essential to remove the excess KOH. Excess K-ions after polymerization were adsorbed by acidic clay added

to the polymer mixtures through vacuum suction. Total removal of excess ions was indicated by polyol discoloration at neutralization point. The details of the reaction steps are presented in Scheme 1. Polyols, with two different preassumed molecular weights (1000 and 2000), were prepared by adjusting the side-chain length of PO in reaction mixture. That was done to compare the variation of PO characteristics with molecular weight.

Preparation of Polyurethanes. In a four-necked round bottom flask of 1 L equipped with a mechanical stirrer, thermometer, condenser, and nitrogen inlet, calculated amount of polyol was charged for vacuum dehydration under mechanical stirring at 100°C for 2 h. While stirring, the prepolymers were cooled down to 50°C to add a mixture of chain extender EG, and DMF (70 wt %). Stirring was continued up to 30 min until a homogenous mixture was obtained. Thereafter, 80% (by wt) MDI was fed into the reactor. The temperature was found to increase due to exothermic character of the polyaddition reaction. However, the reaction was continued for 2 h by controlling the temperature that did not exceed 80°C. The rest of MDI was fed into the reactor and stirring was continued for another 10 min, and then the reaction was stopped. The resultant PUs had the solid content of about 30% by weight. The molar ratio of polyol, EG, and MDI was maintained as 1 : 3 : 4. PU samples were casted on a glass molds and dried at 80°C in a heating oven for 24 h to prepare the PUs specimens. Thereafter, the specimens were stored in desiccators at room temperature for further analysis. A typical standard for commercial PU sample was also prepared from propylene glycol ($POLY_{com}$) following the similar method. The crosslinking structure of PU was expected to form by the successive reaction between terminal isocyanate group of unreacted MDI and PU group in hard segment as shown in Scheme 1.

Characterization Techniques

Titration Method. The hydroxyl numbers and acid value of the polyols were determined using titration technique. The details of the technique for estimating hydroxyl numbers and acid values are given as follows,

Hydroxyl Numbers

About 25 mL of a reaction mixture consist of 255 mL of anhydrous pyridine, and 40 g of PA was added to a round bottom along with weighted amount of polyol sample for refluxing at 115°C for 60 min. After the esterification reaction, the solution was kept to cool down up to room temperature and then the acid was titrated with 0.5N sodium hydroxide (NaOH) solution (V_1) that was required for neutralization. A blank titration without using polyol sample was also carried out with 25 mL of same mixture with 0.5N NaOH to give the blank volume V_2. Each polyol and blank test was repeated at least for three consecutive occasions. During the titration, the pyridine mixture was replaced with fresh solution if the color of the used solution was found to change into yellow. It is to be noted, that the hydroxyl value (OHV) represents the amount of milligrams of KOH that are equivalent to one gram of polyol sample. OHV was then calculated by the following eq. (1):
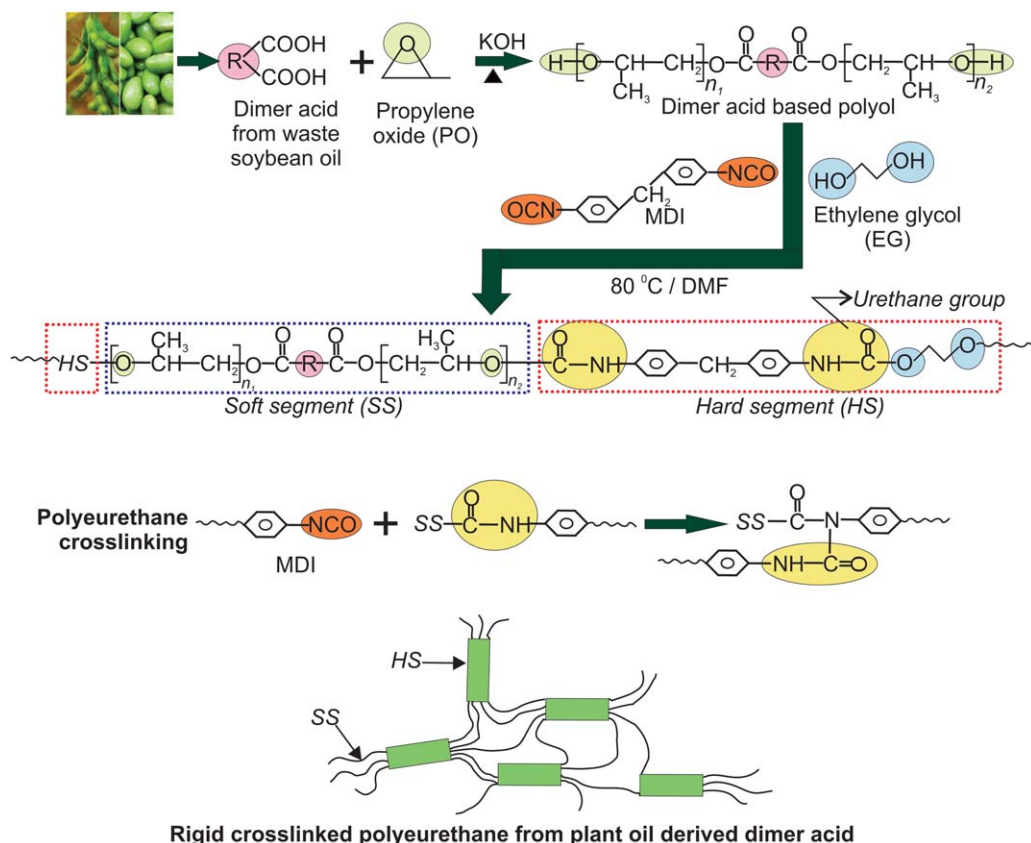
Scheme 1. Overview of chemical reaction method for PUs synthesis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$OHV = \frac{(V_2 - V_1) \times 0.5 \times 56.1}{m_1} \quad (1)$$

The number average molecular weight (M_n) was calculated using the OHV obtained from the titration method following another eq. (2) as reported elsewhere[25]

$$M_n = \frac{56100n}{OHV}$$

where, $n = 2$ as the functionality of DA, and OHV as calculated.

Acid Value

A polyol sample of a mass of m_2 was stirred with the mixture of equal volume of pyridine and water (50 mL each) for 10 min and titrated with 0.025N NaOH solution to get the required volume V_3. Similarly, a blank determination was also carried out with a similar procedure to get the required volume V_4.

The Acid value was estimated following eq. (2):

$$AV = \frac{(V_3 - V_4) \times 0.025 \times 56.1}{m_2} \quad (2)$$

Gel Permeation Chromatography. Samples of the Poly(dimeric acid) glycol, DAP, were characterized in terms of their molecular weights and molecular weight distributions using gel permeation chromatography (GPC). The sample was dissolved in tetrahydrofuran (THF) to prepare 3% (by weight) sample solution. GPC chromatogram was calibrated using monodisperse polystyrene solution using as a standard. It was working at room temperature with tetrahydrofuran as eluent with a flow rate of

1 mL/min. Polydispersity index (PDI) was also obtained from the GPC analysis as the values were provided by the analytical software of GPC instrument.

Hydrophobicity. Hydrophobicity or water repellency of the PU samples was estimated in terms of the water absorption of the sample. Water absorption of PU samples was measured by the method provided by ASTM D570.[26] The test specimens of $12.5 \times 4.0 \times 0.145 \, \text{mm}^3$ dimension were dried in an air-circulating oven at 100°C and weighted to the nearest 0.0001 g to get the initial weight ($W_{initial}$). Totally dried specimens were immersed in water at room temperature (23°C) for 7 days. After that, the samples were taken out from water, and the surface water was removed with a dry paper towel. The specimens were weighted immediately to get the final weight (W_{final}). The % of water absorption was then estimated by the following equation:[27]

$$\text{Water absorption (\%)} = \frac{W_{final} - W_{initial}}{W_{initial}} \times 100\% \quad (3)$$

Lower value of water absorption (%) represents the higher extent hydrophobicity or water repellency of the PU specimens.

FTIR Spectroscopy. A Nicolet iS5 FTIR spectrometer was used to record the FTIR spectra of the polyol as well as PU samples. The samples were prepared by casting the sample on KBr disks from dissolved sample solutions with subsequent drying to remove the solvent. Spectra are taken in the range of 4000–400 cm^{-1} in transmittance mode.

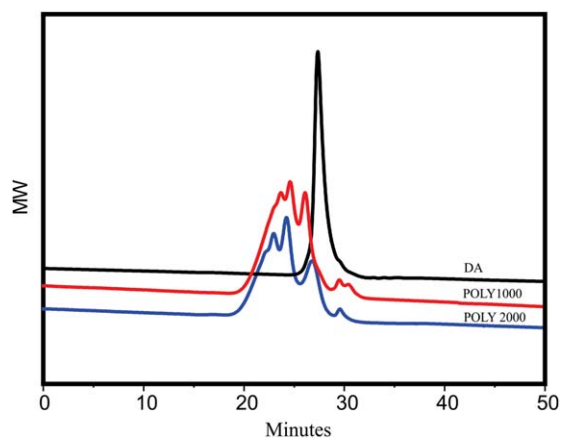**Figure 1.** GPC curve for DA, POLY 1000 (polyol with molecular wt ∼1000) and POLY 2000 (polyol with molecular wt ∼2000). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Proton Nuclear Magnetic Resonance Spectroscopy. Nuclear magnetic resonance spectroscopy (NMR) (Avance Bruker) was used to analyze the molecular structure of Polyol samples within a frequency range of 500 MHz. The NMR spectroscopy was equipped with ultrashield magnets. $CDCl_3$ was used as the solvent for sample used for NMR, whereas calibration was performed using the signal from residual protonated ($CHCl_3$) solvent (peak at 7.26 ppm). The composition of copolymer was determined from the 1H-NMR spectra.

Tensile and Hardness. The dumb-bell shaped specimens were cut out from a molded sheet of PUs, to test the mechanical properties of the PUs using a universal tensile testing machine (Lloyd LR10 K) under ambient condition with crosshead speed of 500 mm/min.

The moduli at 100% and 200% elongation, tensile strength and elongation at break (%) were measured at room temperature. Presented test result is the average of 10 test specimens at the same elongation rate. The values of the tensile strength, modulus at 100% elongation, 300% elongation, and elongation at break are averaged. The hardness of sheets was measured using a Shore A durometer.

Thermalgravimetric Analysis. Thermal stability of polyols and PUs was investigated using a SDT Q600 V8.3 Build 101thermogravimetric analyzer with a heating rate of 10°C /min from room temperature to 600°C under nitrogen atmosphere.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) measurement of PUs was carried out on a DSC

Q200 V24.2 Build 107, equipped with a refrigerated cooling system. The samples were heated at a rate of 10°C /min from −80 to 150°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization of Polyols

The polyols synthesized from the ring-opening polymerization of DA were characterized for their molecular weight, acid and OHVs, and chemical compositions. Thermal stability of synthesized polyols (POLY1000 and POLY2000) and commercial grade polyol such as polypropylene glycol (POLY com) was also evaluated by thermogravimetric analysis. The details of those observations are presented and discussed in the following subsections:

Molecular Weight

The chromatographic responses in GPC of two DA based polyols (POLY 1000 and POLY 2000) along with starting DA are shown in Figure 1. It can be noted that the average molecular weight of two polyol samples was calculated from GPC as well as from titration method. The estimated values from both procedures are presented in Table I. The chromatographic curve clearly indicates a single intense peak for DA, and several small peaks for polyol samples, respectively. Although, DA was eventually a mixture of mainly dibasic acids with insignificant fractions of monobasic and tribasic molecules, however, the detection of those monobasic and tribasic fractions was not evident by corresponding peaks in GPC. Several small peaks for polyols were observed due to presence of substantial extent of tribasic and monobasic acid fractions with different molecular weight produced during polymerization. This type of side reaction such as self-condensation of epoxy groups during synthesis was not unusual and also reported elsewhere.[13] It was again found from Table I, that the molecular weights of polyols estimated from titration method are 1140 and 1798 that fitted more closely to the targeted molecular weight values such as 1000 and 2000, compared to molecular weight of 1838, and 2470 as calculated from GPC. The substantial differences in the molecular weight obtained from titration and GPC methods can be explained on the basis of extent of side reactions during polymerization of DA with PO. Estimation of molecular weight of polyols with GPC curve was based on the inclusion of additional contribution from monobasic, and tribasic fractions present in DA, whereas the conventional titration method only considered the amount of active OH groups from dibasic fraction. The functionality was estimated about 2 for titration method. Theoretically the titration method was based on the assumption that no monomers or trimers were formed during

Table I. Polyols Synthesized from DA and PO

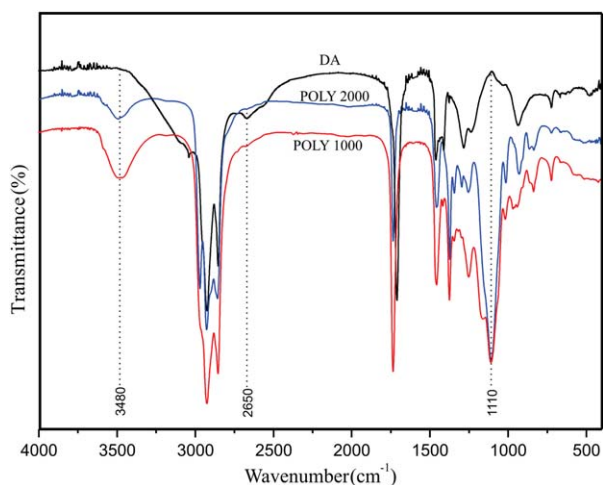| Sample	Molecular wt. (from titration method)	Molecular wt. (from GPC method)	Hydroxyl number (mg KOH/g)	Acid number (mg KOH/g)	Polydispersity from GPC
POLY 1000	1140	1838	97	1.40	1.09
POLY 2000	1798	2470	61	1.40	1.08

Figure 2. FTIR spectra of DA, and the polyols obtained from DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization. This extraordinary phenomenon is quite expected for such instances.[25]

Other typical properties of polyols, such as OHVs, acid numbers, PDI are also presented in Table I. The acid number of polyols was found 1.4 mg KOH/g, whereas the initial acid number of DA (starting material) was observed between 190 and 195 mg KOH/g. Substantial decrease of the acid number indicates the completion of reaction. However, the acid number was never found to decrease below 1, due to presence of trace tribasic or monobasic acid with polyol mixture. This observation is also supported by the presence of multipeaks in GPC for polyols.

Chemical Nature

The chemical nature of polyols was investigated by FTIR spectroscopy. The characteristic peaks of plyols and DA observed in FTIR spectra are presented in Figure 2. A broad absorption band observed at around 3480 cm^{-1} for polyols (POLY 1000 and POLY 2000) prepared from DA confirms the presence of secondary hydroxyl groups in the molecular structure of polyols.[12] Moreover, a newly formed sharp peak around 1110 cm^{-1} attributed to C—O—H stretching vibration for secondary alcohol of polyols also indicates successful ring-opening reaction of epoxy group of PO.[13] The completion of reaction can be confirmed by the disappearance of peak in polyol samples around 2650 cm^{-1} representing the free carboxylic (—COOH) groups in DA.

NMR spectroscopy was also used to confirm the successful formation of polyols. The NMR spectra for DA, and newly formed polyols are presented in Figure 3. The primary peaks observed due to corresponding functional groups for DA have been shown, respectively, in Figure 3. Spectra of polyols obtained from ^{1}H-MNR indicate four newly formed peaks after polymerization. It can be assumed that the peaks at 3.9 and 3.7 ppm were appeared due to hydroxyl protons in polyol chain, and methane proton bearing OH group that is CH—OH.[28] In addition, the other two peaks at 3.5 and 1.1 ppm were appeared due proton from newly formed methylene, and methyl groups,

respectively.[29] The observation strongly supports the hydroxylation of DA was progressed to yield the required polyol samples. Similar observation for polyols was also reported by some other researchers.[12]

TGA Analysis

TGA and DTG curves of both synthesized polyols (POLY1000 and POLY2000) and commercially available polyol (POLY$_{com}$) along with DA are given in Figure 4. The starting material of
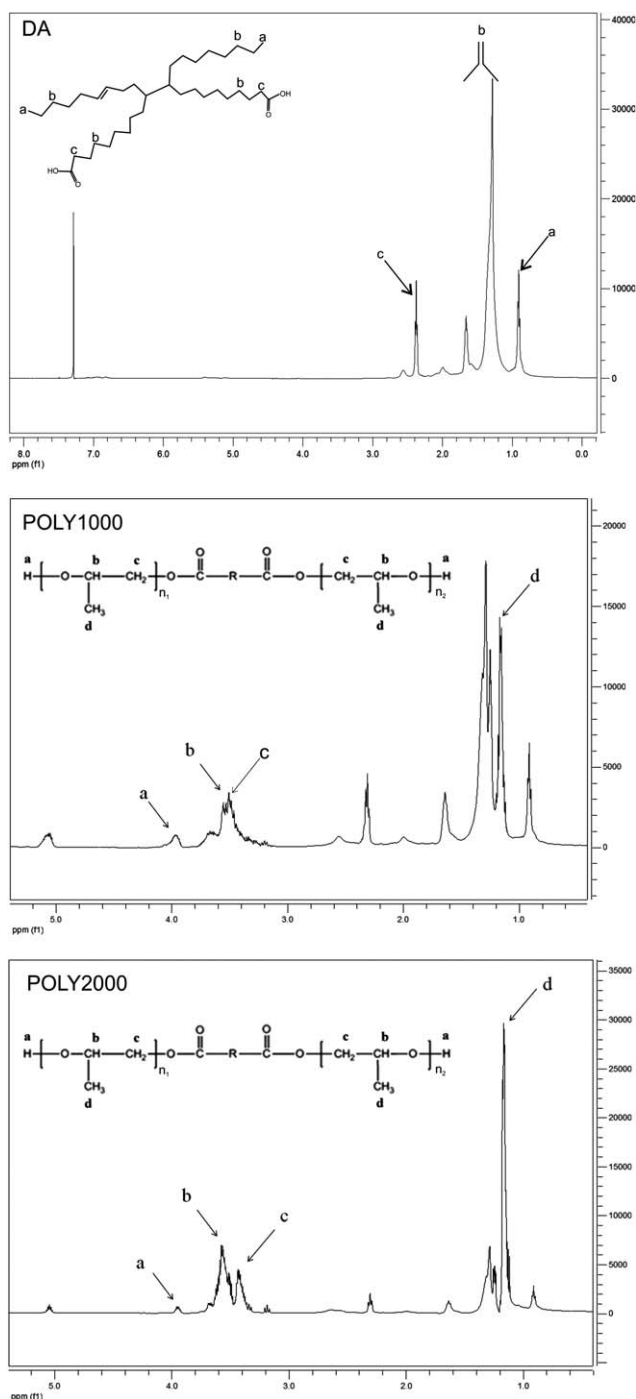

Figure 3. ^{1}H NMR spectra of DA, and polyols (POLY1000 and POLY2000) obtained from DA.
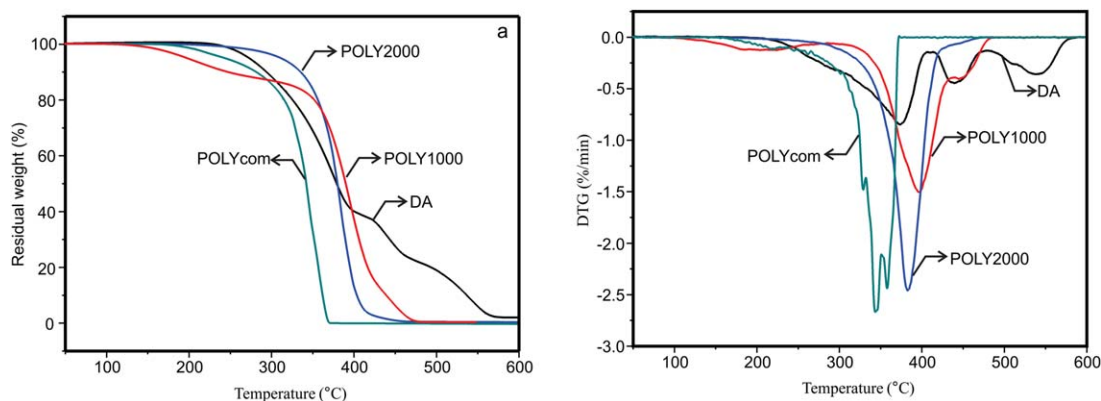
Figure 4. (a) TGA and (b) DTG curves of the DA, commercial grade polyols (POLY$_{com}$), and synthesized polyether polyols (POLY 1000 and POLY 2000). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polyols, that is, DA shows three distinct stages of thermal decomposition which is found consistent with the estimated chemical composition of DA. Generally, DA includes dibasic acid up to 80% of the total chemical component, therefore, it can be expected that dibasic acid must be involved mostly in first thermal decomposition in between 380–400°C. Whereas, the second and third degradation peaks around 450 and 550°C were formed due to degradation of stable monobasic and most stable tribasic acid fraction present in DA. POLY 1000 exhibited maximum thermal stability after DA, followed by POLY 2000, and one of the commercial grade polyols, such as polypropylene glycol (POLY$_{com}$). It can be clearly observed that polyether polyols (POLY 1000 and POLY 2000) prepared in this study exhibit greater thermal stability compared to POLY$_{com}$ as the decomposition temperature for polyether polyols were quite high than that of commercial POLY$_{com}$.

Characterization of Polyuethane

Selection of Polyol. The objective of this study was to prepare hydrophobic, mechanically strong sheets of PUs for desired end-use. The prepared PUs must show comparable physico-mechanical characteristics with a typical PU made from commercial grade polyether polyol, such as polypropylene glycol. Therefore, the first task was to find out the suitable polyol between POLY 1000 and POLY 2000 that can be used further as base materials for hydrophobic and rigid PUs that would be comparable to typical commercial grade PUs. The initial evaluation as presented in Table II shows that hydrophobicity and hardness of PU obtained from POLY1000 were found to increase about 70% and 8% compared to PU sample from POLY2000. Moreover, both the PUs synthesized from waste vegetable oil based DA, showed superior hydrophobicity and mechanical hardness compared to PU sample that has been

prepared from POLY$_{com}$. Furthermore, the water absorption (%) of a few other representative commercial PU samples with the trade name of Elastollan$^®$, and Irogran$^®$ was also measured to have a better idea on the material hydrophobicity comparison. The waster absorption of those commercial PU samples was found to lie between 0.3–1%. That indicates a comparable hydrophobicity of PU samples prepared in this study with other commercial PUs. The primary observation of the results presented in Table II, clearly indicate that POLY 1000 was the significantly better material to be used as pre-polymers for hydrophobic, mechanically strong PUs for roof construction.

The next step was to identify the most desirable quantity of POLY1000 to form strong and hydrophobic PU. For this reason, a series of four PU sheets (PU 1 to PU 4) were molded with altering molar ratio of POLY 1000, EG, and MDI. A systematic evaluation of physico-mechanical properties of all PU samples was performed and the results are presented in Table III. It should be noted that a PU sample (PU$_{com}$) from POLY$_{com}$ was also prepared in this study and a subsequent characterization was performed for PU$_{com}$ to present a comparative study outlining the properties of the commercial grade PU and the PUs prepared in this study.

Physico-Mechanical Property. PUs prepared from vegetable oil based DA were found to have more hydrophobic than that of PUs$_{com}$ from commercial polyol. This may be due to incorporation of hydrophobic alkyl chains of DA within the soft segment of PUs during polyol synthesis.[13] Variation of water absorption with increasing EG content is presented in Table III. Lowering of the water absorption of DA based PUs with increasing addition of chain extender (EG) is observed up to PU 3. That could be resulted from the increased incorporation of hydrophobic alkyl chains of DA into PUs with increasing EG content.

Table II. Physico-Mechanical Property of PUs from Polyether Polyols and Commercial Grade Polyol

Sample	Polyol / EG /MDI molar ratio	Hard segment (%)	Water absorption (%)	Hardness (Shore A)
PU from POLY 2000	1 : 3 : 4.6	42.60	0.869	72
PU from POLY 1000	1 : 3 : 4.6	54.80	0.256	78
PU from POLY$_{com}$	1 : 3 : 4.6	40.00	1.640	64

Table III. Physico-Mechanical Properties of Polyurethanes (PU1 to PU4)) Synthesized from Polyether Polyol and PU Prepared from Commercial Grade Polyol

Sample	POLY 1000 / EG / MDI molar ratio	Water absorption (%)	Hardness (Shore A)	Tensile strength (MPa)	Elong. at break (%)
PU 1	1 : 2 : 3.5	0.327	73	11	101
PU 2	1 : 3 : 4.6	0.256	78	18	310
PU 3	1 : 4 : 5.7	0.208	83	20	297
PU 4	1 : 5 : 6.9	0.386	86	28	202
PU$_{com}$	1 : 3 : 4.6	1.640	64	32	269

However, further increasing of molar ratio of EG imparts the reduction of hydrophobicity of PU sample (PU4). The enhanced hydrophobicity of PU 4 might be possibly due to formation of hydrogen bond between excess urethane groups and water molecules.

Both hardness and tensile strength of PUs were found to increase with increasing amount of EG as shown in Table III. Increase of EG has imparted the enhanced mechanical strength and flexibility in PUs by chain mobility initiated from subsequent chain extension during reaction with polyols . Elongation at break PU sample with minimum molar content of EG, was found 101%. However, the elongation was steadily increased for PUs (PU 2 and PU 3) with increasing EG content. The observed remarkable decrease of elongation at break for PU 4 was not unlikely due to higher crosslink density of with higher amount of isocyanates (MDI). Higher crosslink density of PU 4 might impart the reduced flexibility. Moreover, the high crosslink density of PU 4 also imparted a significant improvement of tensile strength and hardness.

Results obtained from physico-mechanical study of PUs reveal a direct effect of EG content on their water absorption and mechanical property. Based on this observation, PU 3 was found to exhibit the highest hydrophobicity and flexibility, although the tensile strength, flexibility, and hardness were found little less compared to PU 4.

FTIR Spectra. In the FTIR spectrum of PU samples in Figure 5, the observed broad peak around 3350 cm^{-1} indicates N—H stretching of urethane groups. This specific peak could not be found in FTIR spectra of polyols as well as MDI. In case of POLY 1000 and all PUs, the peaks at 2850 cm^{-1} and at 2920 cm^{-1} indicate the presence of —CH$_2$- and —CH$_3$- groups of long chains of DA. Strong peaks at 1230 cm^{-1} due to C—O stretching vibration, 1540 cm^{-1} for N—H bending, and 1730 cm^{-1} for C═O stretching confirms the formation of urethane group in PUs. The sharp peak at 2250 cm^{-1} was the characteristic peak for isocyanate groups in MDI. However, the disappearance of this peak for PUs clearly indicates the complete reaction of all isocyanate groups with polyols during PU synthesis.

Thermal Property. The TGA scans of all PU samples are presented in Figure 6(a). Initial decomposition for PUs observed at around 250–260°C due to thermal degradation of urethane linkages and formation of isocyanates, amines, and alcohols.

However, subsequent rapid weight loss observed around 420–470°C was resulted from the dehydrogenation and alkyl group decomposition. For each PU sample, the TGA curve showed no significant difference with variation of molar ratio of polyols to EG and MDI. That could be indicated to identical chemical composition and functionalities of all PUs. However, the temperatures for maximum weight loss (T_{max}) of PU chain were found 459, 462, 453, and 465°C for PU 1, PU 2, PU 3, and PU 4 sample, respectively [Figure 6(b)]. The slightly higher T_{max} value for PU 4 indicates the marginally higher thermal stability due to higher extent of crosslinking density. The observation supports the reduction of elongation at break of PU 4 that has already been explained in section "physico-mechanical property" earlier.

The DSC thermograms of PU samples are shown in Figure 7. PUs prepared in this study consisting of hard and soft segments belong to the thermoplastic elastomer category. Therefore, they are expected to exhibit two-phase microstructure resulting from thermodynamically incompatible hard and soft segments based on polyether and isocyanate, respectively. Each phase of PUs chain can be characterized by its glass transition (T_g) endotherm as seen in Figure 7, where two distinct endotherms for each PU sample in the range of around 65–75°C and −80 to −85°C.
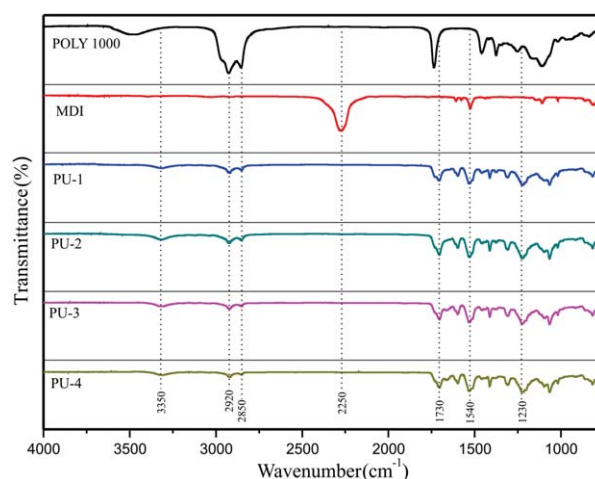
Figure 5. Comparison of FTIR spectral responses of different PU samples (PU, PU 2, PU 3, and PU 4) with polyol (POLY1000) and isocynates (MDI). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
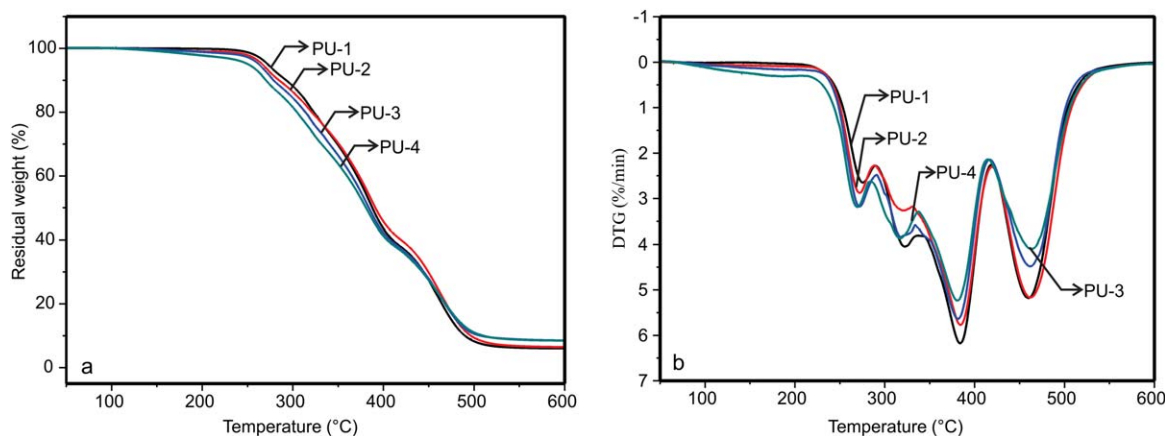
Figure 6. (a) TGA and (b) DTG curve of PU samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Similar observation was also reported by Chem and coworkers, where the PUs were found to retain their phase separated morphology between two different glass transition temperatures (from 80°C to −120°C).[30] The hard segments are found to consist of relatively less flexible and rigid short chains. As a result, the glass transition temperature exhibited higher value than that of room temperature. On the other side, the T_g that found to belong much lower value than that of room temperature was due to the presence of soft segments of polyether polyols. The interaction between these two segments, along with the formation of hydrogen bonds between two PU chains instigates a phase separation that in turn forms few hard aggregates of several PU sequences within soft segment of PU matrix.[31] The hard aggregates serve as the crosslinking points to form subsequent PU network structure that eventually provides an increased elasticity as well as elongation property to PUs. Furthermore, the presence of long fatty chain acids from DA might also impart en enhanced flexibility to PUs. High elongation as observed in Table III can also be explained from this phenomenon.

Moreover, it can be noted that the glass transition temperatures (T_g) mainly for hard segments were found to decrease from 75 to 65°C for PU 1 to PU 4 with increasing amount of EG and
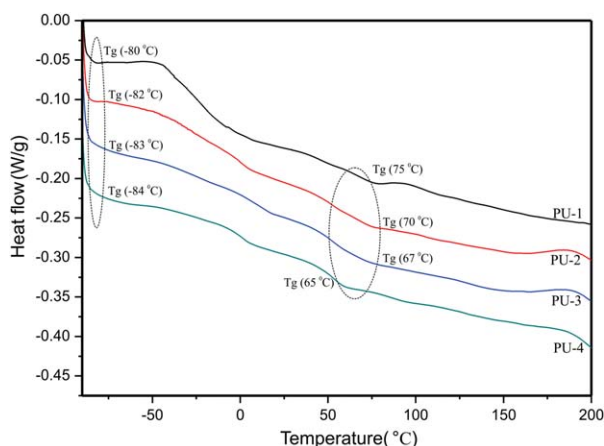
MDI addition. In general, it has been expected that the T_g would increase with increase of crosslink density. However, interestingly, in this study, the glass transition temperatures followed the reverse trend. Crystallinity of PU in context to such situation could play a significant role to determine the thermal stability.[23] All PU samples are expected to show mostly semicrystalline structure with crystalline hard segments and amorphous soft segments. In this study, long alkyl chains from DA within soft segment of PU backbone can impart a significant intermolecular disorder at the time of crosslinking. More the chain was found to extend more would be the loss of arrangement of PU molecules. As a result the crystallinity of highly crosslinked PU may found to be less compared to its less crosslinked counterparts. Lowering of T_g of PUs hence can be explained with the decrease of crystallinity with increased crosslinking.

CONCLUSION

Novel polyether polyols were prepared from DA available from waste soybean oil. The polyols with molecular weight ∼1000 was found preferable to be used as starting material for making hydrophobic and mechanically strong green PU specimens. The effect of molar ratio of EG and MDI used during reaction with polyols was evaluated by estimating hydrophobicity and mechanical strength of PUs. The molar ratio 1 : 4 : 5.7 of polyol : EG : MDI was found to exhibit maximum hydrophobicity and improved mechanical strength. However, all the PU samples showed a comparable or even better hydrophobicity and mechanical property compared to PU prepared from polyol of commercial standard. The chemical alteration and crosslinking within PUs have been evident from FTIR spectroscopy. Moreover, TGA and DSC analysis also showed substantial thermal stability of all PUs.

Figure 7. DSC curve of PU samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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