Rational design of sustainable polyurethanes from castor oil: towards simultaneous reinforcement and toughening

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ABSTRACT Sustainable polyurethanes prepared from castor oil and diisocyanates show very low strength and toughness, due to the highly cross-linked and flexible structure. Herein, we report a new strategy to simultaneously reinforce and toughen castor oil-based polyurethane *via* incorporating a stiff component (isosorbide, IS) to enhance network stiffness and reduce crosslink density. The crosslinking degree decreases while the strength, moduli, ductility and heat resistance significantly increase accordingly with increasing IS content. The tensile behaviors are tunable over a broad range (either as elastomers or as plastics) depending on the compositions. The polyurethanes show excellent thermal stability with onset decomposition temperature higher than 280°C. The investigation provides a new hint for future design and fabrication of high performance sustainable polymers from other vegetable oils.

Keywords: sustainable polyurethane, castor oil, isosorbide, crosslink density, mechanical property

INTRODUCTION

Exploitation of sustainable polymers from renewable feedstocks has attracted increasing attention, due to the continuously increased environmental concerns and resource crisis related to traditional fossil-based polymers [1–6]. Inexpensive vegetable oils, with various functional groups such as C=C double bond, ester, hydroxyl and epoxy groups depending on the origins, are thought as the ideal alternatives to fossil resources in production of novel sustainable polymers [7–9]. It is noted that the sustainable polymers synthesized directly from vegetable oils usually show poor mechanical performance leading to limited application [10–12]. Although high performance polymers such as polyamides, polyesters and

epoxy thermosets can be prepared from monomers derived from vegetable oils through well-designed chemistry techniques, the conversion of vegetable oils to monomers increases the cost of the resultant materials inevitably [3,7,13]. If high performance sustainable polymers can be prepared from vegetable oils directly without undergoing monomer conversion step, they would be much more commercially competitive due to the increased cost-efficiency. However, it remains a challenge to convert vegetable oils to high performance polymers directly.

Castor oil (CO) with naturally occurring hydroxyl groups is a good choice for polyurethane production [14–16]. In fact, it had played an important role in the early stage of polyurethane industry before the commercial availability of synthetic polyols [15]. CO-based polyurethanes exhibit some appealing properties such as water resistance and flexibility [15]. However, they were usually used in non-structural applications such as coatings and adhesives [17–19]. The poor mechanical properties hindered their use in structural applications, which is probably responsible for abandonment of castor oil in the modern polyurethane industry. The requirement for sustainable development has triggered renewed interest in fabrication of polyurethanes from castor oil in recent years [20–25].

The chemical structures of vegetable oils derived polymer networks such as castor oil-based polyurethane and dicarboxylic acid cured epoxidized soybean oil are characterized by the high crosslink density and the high flexible backbones, which endow the polymer networks with poor mechanical properties [11,26–28]. Although crosslinking would enhance mechanical strength [29], it would meanwhile reduce the ductility of polymer networks if the degree of crosslinking were excessively high.

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Table 1 Feeding contents and the contents of soft segment (SS) and hard segment (HS) of the samples

Sample	CO (wt%)	IS (wt%)	HDI (wt%)	SS (wt%)	HS (wt%)
COPU	80.50	0	19.50	–	–
C9I1PU	67.52	7.50	24.98	83.95	16.05
C8I2PU	56.14	14.03	29.82	69.82	30.18
C7I3PU	46.20	19.80	34.00	57.43	42.57
C6I4PU	38.81	25.87	35.32	48.25	51.75
C5I5PU	29.45	29.45	41.10	36.63	63.36
C4I6PU	22.37	33.56	44.07	27.80	72.20

The flexible backbones result in low strength and modulus while the high crosslink density leads to brittleness. For example, the tensile strength and Young's modulus of the polyurethane prepared from CO and hexamethylene diisocyanate are only 0.8 and 3.59 MPa, respectively, meanwhile the elongation at break is 31.6% [11]. Some studies have combined polymeric diols such as poly(ethylene glycol) and poly(ϵ -caprolactone) with castor oil to prepare polyurethanes [30,31]. Such a technique is useful to improve the toughness of CO-based polyurethanes. However, the enhancement in strength and modulus is limited, due to that the polymeric diols are flexible as well. In addition, the polymeric diols are derived from fossil-based resources, which would reduce the sustainability of the resultant materials.

The poor ductility of CO-based polyurethane results from the high crosslink density but not from poor flexibility of the network backbone. In fact, the network backbone is flexible enough. We don't need to incorporate flexible chains to improve the ductility. What we need to do is to reduce the crosslink density of the CO-based polyurethanes to improve the toughness. Therefore, it is not a good option to improve the mechanical properties of CO-based polyurethanes through combination of flexible polymeric diols. It is anticipated that simultaneous enhancement in both strength and ductility may be achieved if stiff structures were incorporated into the CO-based polyurethane to reduce crosslink density. The presence of stiff structures, on the one hand, increases the chain length between crosslinking sites, thus reduces the crosslink density and improves the ductility. On the other hand, the stiff structures enhance the stiffness of the resultant polyurethanes to reinforce the strength and modulus [32].

Renewable compounds with rigid structures are preferred as structure modifier for castor oil-based polyurethane from the viewpoint of sustainability. Isosorbide [33–35], a commercially available compound with double aliphatic rings, may be the good modifier for castor oil-based polyurethane. Besides the stiff nature, the hydroxyl

of isosorbide is also secondary hydroxyl group, and thus has comparable activity with castor oil when reacting with diisocyanate. Herein, we report the fabrication of sustainable polyurethanes containing castor oil and isosorbide as well as the composition dependence of gel fraction, swelling ratio, mechanical properties and thermal stability of the polyurethanes in detail.

EXPERIMENTAL SECTION

Materials

Castor oil (CO, AR grade) was procured from the Micxy Chemical Co., Ltd. (Chengdu, China). Hexamethylene diisocyanate (HDI, 99%) was obtained from the Aladdin Biochemical Technology Co. Ltd. (Shanghai, China). Isosorbide (IS, 98%) was purchased from the Adamas Reagent Ltd. (Shanghai, China).

Preparation of the sustainable polyurethanes

The biobased polyurethanes were prepared *via* a two-step procedure, i.e., pre-curing and post curing. The pre-curing process was performed in a three-necked round-bottomed flask at 160°C for 20 min. Predetermined amounts of CO and IS were added into the flask, which was then vacuumed and purged with N₂ three times. Thereafter, predetermined amount of HDI was added into the flask and the reactants were stirred with a magnetic stirring bar for 20 min to complete pre-curing. In the post curing process, the pre-cured homogeneous mixture was further cured in a mold (100 × 100 × 0.5 mm³) between two plates of a flat vulcanizing machine at 160°C under 10 MPa for two hours. The molar ratio of –NCO to the total –OH was fixed at 1:1.

Six samples with CO/IS weight ratio of 9:1, 8:2, 7:3, 6:4, 5:5 and 4:6 were prepared and designated as C9I1PU, C8I2PU, C7I3PU, C6I4PU, C5I5PU and C4I6PU, respectively. For property comparison, the polyurethane consisting of CO and HDI was also prepared with the same procedures and was abbreviated as COPU. Table 1 lists the feeding contents of CO, IS and HDI during

preparation of the samples.

Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra were recorded on a RF-5301PC spectrophotometer (Shimadzu, Japan) from 4,000 to 400 cm^{-1} with the resolution and scanning number of 4 cm^{-1} and 32 times, respectively. The as-prepared sample sheets after curing under compression molding were used for FT-IR measurement.

Gel fraction and swelling ratio

The gel fraction and swelling ratio of the samples were measured through solvent swelling experiment. The sample with dimension of $10 \times 10 \times 0.5 \text{ mm}^3$ and weight of W_0 was immersed in 25 mL *N,N*-dimethylformamide for two days to reach swelling equilibrium. The swollen sample was weighed as W_1 after removing the surface solvent with filter paper. The swollen sample was then vacuum dried at 60°C for two days to obtain deswollen sample with weight of W_2 . The gel fraction (G_f) was calculated by

$$G_f = \frac{W_2}{W_0} \times 100\%. \quad (1)$$

The swelling ratio (S_r) was calculated by

$$S_r = \frac{W_1 - W_0}{W_0} \times 100\%. \quad (2)$$

Tensile properties

Tensile properties were measured on a MTS E44 universal testing machine at room temperature ($\sim 25^\circ\text{C}$) with a crosshead speed of 10 mm min^{-1} in general accordance with ISO 527-3. The standard dumbbell-shaped testing bars with width and thickness of 4.0 and 0.5 mm were cut from the sample sheet. The gauge length between the two pneumatic grips was 25 mm. Averaged results were reported from five measurements for all the samples.

Dynamic mechanical analysis (DMA)

The dynamic mechanical properties were measured on a TA Instruments DMA Q800 analyzer using a tensile mode from -50 to 120°C at a heating rate of 3°C min^{-1} and an oscillation frequency of 1 Hz. The samples with dimension of 35 mm (length) $\times$ 6 mm (width) $\times$ 0.5 mm (thickness) were used for the measurement.

Thermogravimetric analysis (TGA)

Thermal stability of the biobased polyurethanes was studied by a TA Instruments TGA Q500 from room temperature to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$

under N_2 atmosphere.

RESULTS AND DISCUSSION

Preparation and characterization of the polyurethanes

The castor oil based polyurethanes were prepared *via* a two-step procedure. The first step was performed in a flask at 160°C for 20 min to produce homogeneous precursors. In the second step, the precursors were cured in a mold at 160°C under 10 MPa for 2 h to generate the polyurethane. Fig. 1 shows the reaction for the preparation of the polyurethane network from CO, IS and HDI and the digital photo of the typical sample sheet. The sample is almost colorless and translucent.

The chemical structures of the polyurethanes were characterized by FT-IR, as shown in Fig. 2. No absorption was observed at 2,200–2,300 cm^{-1} for all the samples, indicating that HDI was consumed completely during the two-step procedure curing process [36–38]. The two absorptions occurring at 1,745 and 1,695 cm^{-1} for COPU were attributed to the stretching vibration of carbonyls of ester and urethane groups, respectively [15,39]. The absorption of ester carbonyl becomes less prominent and that of urethane carbonyl becomes more prominent with increasing the IS content. The characteristic stretching vibration of C–O–C in ether group was observed at $\sim 1,100 \text{ cm}^{-1}$ for all CIPUs [40,41]. The results indicated that the polyurethane containing IS unit was successfully synthesized.

The gel fraction and swelling behavior were investigated by a solution method to demonstrate the effect of IS content on the crosslink structure of the polyurethane networks, as shown in Fig. 3. The gel fraction of the control COPU was 97.5 wt%, and the values were 98.4, 96.3, 94.5, 95.7, 94.6 and 93.8 wt% for C9I1PU, C8I2PU, C7I3PU, C6I4PU, C5I5PU and C4I6PU, respectively, which indicates that all the samples have crosslinked structure. Swelling ratio can be used to describe the crosslink density of network polymer qualitatively or semi-quantitatively, since the swelling ratio usually decreases with increasing crosslink density [42]. The crosslink density of CIPU should decrease with increasing IS content, due to the bi-functional structure of IS. The swelling ratio of COPU is 129%. In accordance with the expectation, the swelling ratio increased apparently with increasing IS content and the values are 183%, 190%, 228%, 300%, 350% and 420% for C9I1PU, C8I2PU, C7I3PU, C6I4PU, C5I5PU and C4I6PU, respectively, indicating reduced crosslink density with increasing IS content.

Figure 1 Reaction between CO and IS with HDI to fabricate the CO-based polyurethane (a) and the photo of the prepared typical sample sheet (b).

Figure 2 FTIR spectra of COPU and CIPUs with different compositions.

Figure 3 Gel fraction and swelling ratio as functions of weight ratio of CO/IS.

Mechanical properties

We studied the effect of composition on mechanical properties of the polyurethane network through tensile testing. Fig. 4 shows the stress-strain curves of COPU and CIPUs with different compositions. It is obvious that the

control COPU with high crosslink density and flexible structure shows tensile behavior of soft and weak material with tensile stress (σ) and elongation at break (ϵ) of only 0.76 ± 0.06 MPa and $37\% \pm 3\%$, respectively. Interestingly, both σ and ϵ increased with increasing isosorbide content when the feed weight ratio of CO/IS is less than 5/5. C9I1PU, C8I2PU, C7I3PC and C6I4PU exhibited elastomer-like tensile behavior with σ increased to 0.80 ± 0.05 , 2.07 ± 0.12 , 4.96 ± 0.35 and 12.89 ± 0.63 MPa and ϵ increased to $42\% \pm 4\%$, $71\% \pm 8\%$, $200\% \pm 15\%$, $363\% \pm 20\%$, respectively. The improvement in the σ and the ϵ was 16.9 and 10 times for C6I4PU compared to the control COPU. The results are in good agreement with our design principles to improve the strength and toughness of the polyurethane through incorporation of stiff unit to reduce the crosslink density. The stiffness of the sample can be described by Young's modulus (E). The control COPU shows E of 4.68 ± 0.33 MPa. E increases to 5.02 ± 0.25 , 13.91 ± 1.47 , 16.82 ± 2.01 and 19.01 ± 3.43 MPa for C9I1PU, C8I2PU, C7I3PC and C6I4PU, respectively, indicating gradually increased stiffness with increasing IS content. Surprisingly, C5I5PU and C4I6PU show a plastic-like tensile behavior especially for C4I6PU, with yielding appeared during stretching. ϵ of C5I5PU and C4I6PU decrease to $214\% \pm 15\%$ and $198\% \pm 17\%$ while σ of both increase to ~ 34 MPa, which are 2.6 times that of C6I4PU. The significantly enhanced tensile strength should be attributed to the transformation of the network structure from flexibility to stiffness with CO/IS feed ratio changed from 6/4 to 5/5 and 4/6. The polyurethanes are usually thought as segmented copolymers consisting of hard and soft segments. In this study, the soft segment (SS) is the moiety formed by reaction of CO with HDI and the hard segment (HS) is the moiety formed by reaction of IS with HDI. Table 1 lists the contents of both SS and HS calculated according to the feed ratio. For the samples with CO/IS feed ratio of higher than 6/4, the samples behave like elastomers due to that SS is the main component. With the CO/IS feed ratio decreased to less than 6/4, the content of HS increased to much higher than that of SS, thus the samples changes to plastic-like tensile behavior with high Young's modulus. The E value increased significantly from 54.15 ± 11.45 MPa for C5I5PU to 366.13 ± 51.24 MPa for C4I6PU, also indicating a drastic enhancement in stiffness with CO/IS feed ratio changed from 5/5 to 4/6.

The dynamic mechanical properties of COPU and CIPUs were investigated by DMA. Fig. 5 shows the dependence of storage modulus and $\tan\delta$ with temperature of COPU and CIPUs. COPU exhibits a single drop in the

Figure 4 Stress-strain curves of COPU and CIPUs with different compositions.

Figure 5 Storage modulus (a) and $\tan\delta$ (b) versus temperature of COPU and CIPUs.

storage modulus plot (Fig. 5a) and a sharp peak in the $\tan\delta$ plot (Fig. 5b), corresponding to the α -relaxation (glass transition) of COPU. The relaxation peak temperature was defined as the glass transition temperature (T_g). The T_g of COPU is -20.5°C . All CIPUs show two drops in the storage modulus plots, corresponding to the glass transition of the soft segment and hard segment, respectively, which indicates that phase separation occurred for the CIPUs. The T_g of SS with increasing HS content shifted to higher temperature range, while the T_g of the HS with increasing SS content shifted to lower temperature range, which suggests that the SS and the HS are partially miscible. The storage moduli of CIPUs are higher than that of COPU and increase with increasing HS content in the full temperature range, indicating reinforced mechanical performance due to the enhanced stiffness. The storage modulus at high temperature can be used to evaluate the heat resistance of a material, because higher storage modulus demonstrates better tolerance to external loading [5,27,28]. The storage modulus of COPU is only 1.59 MPa and the value increases to 2.69, 3.29, 3.54, 13.67, 21.29 and 94.8 MPa for C9I1PU, C8I2PU,

Figure 6 TGA (a) and DTG (b) curves of the control COPU and CIPUs with different compositions.

C7I3PU, C6I4PU, C5I5PU and C4I6PU, respectively, indicating enhanced heat resistance by incorporation of IS moiety. The damping peak height of the polyurethanes at low temperature range reduces gradually with increasing IS content (Fig. 5b), again relating to the enhanced stiffness, which restricts the molecular movement thus lowers the damping in transition zone.

Thermal stability

The thermal stability of the control COPU and CIPUs with different compositions was studied by TGA. Fig. 6 shows the TGA and DTG curves of the samples from room temperature to 600°C under N_2 atmosphere. The control COPU showed two weight loss stages with the maximum decomposition temperatures ($T_{\max}$) of 358 and 419°C , corresponding to the thermal degradation of HID and CO moieties, respectively. CIPUs with different compositions also showed two weight loss stages with the two $T_{\max}$ s at ~ 330 and 420 – 460°C . The weight loss of the first stage increased while that of the second stage decreased with increase in IS content. Therefore, the first stage should be ascribed to the thermal degradation of IS and HDI moieties as their decomposition temperatures may overlap with each other and the second stage is the thermal degradation of CO moiety. The onset decomposition temperature, T_5 (5% weight loss temperature), is more commonly used to describe the thermal stability of materials. The T_5 of the control COPU is 320°C and the value decreases to 298, 294, 288, 288, 284 and 285°C for C9I1PU, C8I2PU, C7I3PU, C6I4PU, C5I5PU and C4I6PU, respectively, which indicates that incorporation of IS moiety reduces the thermal stability of the polyurethane due to its low thermal decomposition temperature. Although the onset decomposition temperature reduced, the thermal stability of all CIPUs is still not too bad as the T_5 values are higher than 280°C for all the samples.

CONCLUSIONS

In summary, we designed and fabricated a series of castor oil-based polyurethanes with stiff isosorbide as a structure modifier. All the polyurethanes with different compositions show gel fraction of higher than 93 wt%. The crosslink density of the samples decreases with increasing IS content, as evidenced by the increasing swelling ratio. Meanwhile, the stiffness of the samples increases with increasing the IS content since all the tensile strength, Young's modulus and storage modulus increase with the IS content. Furthermore, the elongation at break of the polyurethanes containing IS units is also improved significantly compared to the control polyurethane without IS unit, which is attributed to the reduced crosslink density. The polyurethanes with tensile properties varied from elastomer to tough plastic were fabricated by controlling the compositions. The soft segment is partially miscible with the hard segment for the polyurethanes. The heat resistance of the polyurethanes also increases with increasing the IS content due to the increasing stiffness. All the polyurethanes exhibit good thermal stability with onset decomposition temperature of higher than 280°C. The investigation demonstrates that incorporation of a stiff component to reinforce the stiffness and reduce crosslink density is a very efficient approach to improve the overall mechanical properties of flexible and highly crosslinked polymer networks.

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Conflict of interest The authors declare no conflict of interest.

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可持续蓖麻油基聚氨酯的设计合成: 同时实现增强与增韧

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摘要 蓖麻油基聚氨酯(COPU)链柔顺性大且交联密度高, 导致其力学强度与韧性俱差. 本文将双官能度刚性物质引入COPU, 一方面, 利用其刚性增强COPU的力学强度与模量; 另一方面, 利用双官能度结构, 降低COPU的交联密度, 提升其韧性, 同时实现COPU的增韧与增强. 我们将生物基异山梨醇(IS)用作COPU的结构调节单元, 设计合成了一系列生物基聚氨酯(CIPU). 研究发现: 当IS含量较少时, CIPU表现出弹性体的拉伸行为, 其拉伸强度与断裂伸长率均随IS含量增加而大幅增加; 当IS含量高于蓖麻油时, CIPU表现出塑料的拉伸行为, 拉伸强度与断裂伸长率分别可达~34 MPa与~200%, 为COPU的44与5倍. 此外, 该CIPU还表现出优异的热稳定性与耐热性. 该研究可为植物油基高分子新材料的设计合成提供借鉴.