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Research Article

Isosorbide-Based Thermoplastic Polyurethane with Different Polyols and Soft/Hard Ratios

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A series of isosorbide-based thermoplastic polyurethanes (ISB-TPUs) with different soft/hard ratios have been successfully step polymerized using individual two types of polycaprolactone diol (PCL) or poly (tetramethylene glycol) (PTMG) for soft segment and bio-based isosorbide (ISB) or methylene diphenyl diisocyanate (MDI) for hard segment, based on the similar molecular weight. The effect of the molecular structure on the mechanical and thermal properties has been evaluated in terms of the types of soft/hard and polyol, ranging from 6/4 to 9/1 ratio values. With the increasing of PCL content, the thermal properties of the ISB-TPU have enhanced gradually. When the range from PCL was 6/4, the tensile strength has achieved the maximum value in comparison with that of the PTMG block. Elongation at break has increased with the increase of hard segment concentration, due to the superior interaction between ester groups and urethane groups. The obtained ISB-TPUs can be a promising resin for soft, flexible, and biocompatible application fields.

1. Introduction

Since thermoplastic polyurethanes (TPUs) have been widely utilized as a dispensable resin in our life, their supply and demand have continuously extended in various applications [1]. The increasing demand of TPUs has been resulted in a large amount of atmospheric carbon dioxide concentration and unexpected wastes. As these issues have been dramatically covered in international area, sustainability and environmental friendliness have become a main challenge in the development of TPU [2, 3].

Recently, environmental eco-friendly TPUs have become a key opportunity in the development of polymer technology in the 21st century. With increasing environmental concerns in both academia and industry, the replacement of petroleum-based TPU with greener alternatives has become increasingly important. Eco-friendly TPUs possess a linear block copolymer structure composed of a soft segment for elastic properties and a hard segment acting like a physical crosslinker [4–6]. The environmental friendliness of the molecular structure could be imparted by replacing the constituents of polyol, diisocyanate, and chain extender [7]. Alternatives to replace the use of petroleum-based chemicals in the segmented structures could also be one of the main challenges of modern-day polyurethane chemistry [8]. Eco-friendly TPU could be used in a wide range of the practical applications in industrials such as automobile parts, coating, molded articles, foams, and film fields [9].

Isosorbide (ISB) derivatives are diols or polyols that could be used in TPU technologies, either directly or indirectly in the formulations of TPU [10]. ISB derivatives could be introduced as a chain extender in order to prepare a rigid block in eco-friendly TPU applications [11]. Replacement of petroleum-based chain extender by using biomass-based diol could significantly provide fascinating properties such as biocompatibility, biodegradability, and mechanical properties [12]. The incorporating ISB derivatives as the chain extender could also lead to a reduced environmental impact [13].

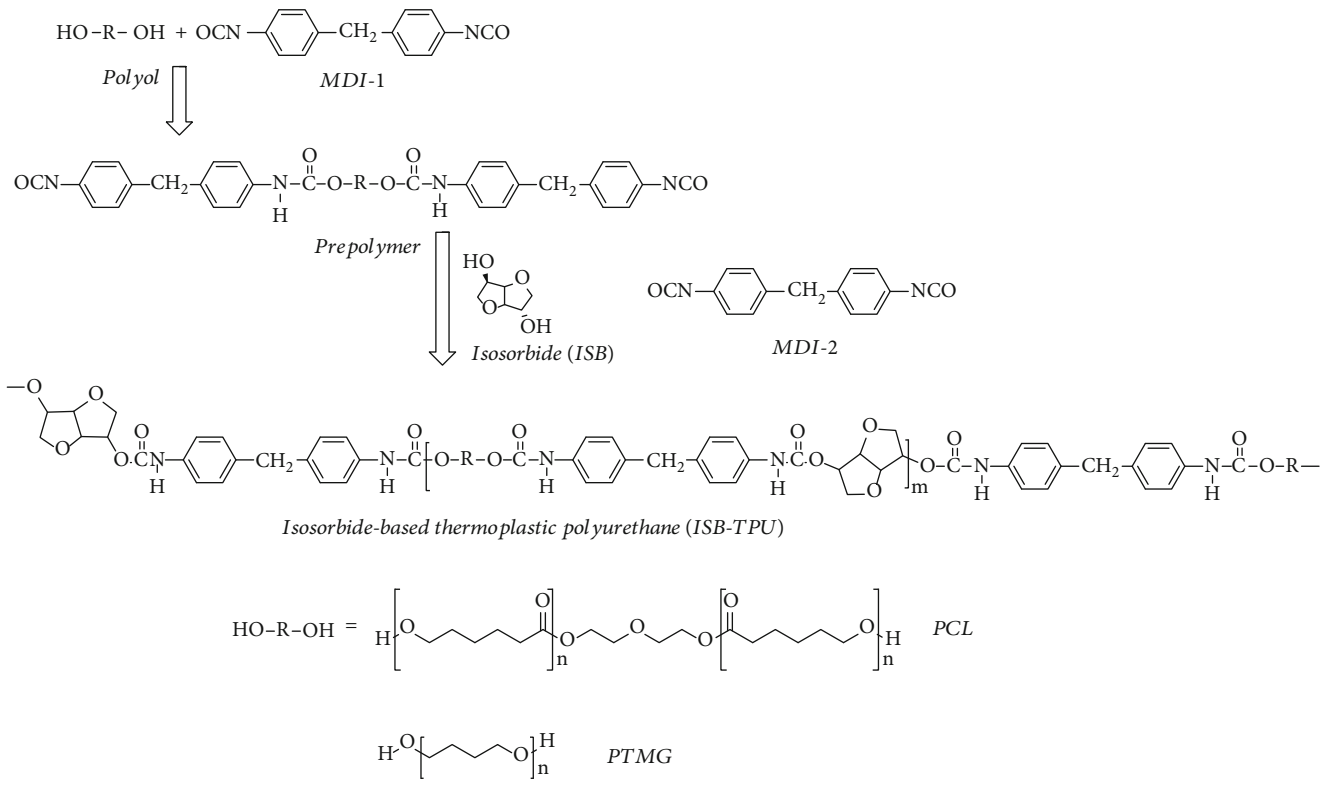

Figure 1: A schematic procedure to synthesize an ISB-TPU series.

Table 1: Specific amounts of an ISB-TPU series.

Sample code	Specific amounts (g)			
	Polyol	MDI-1	ISB	MDI-2
ISB-PTMG-TPU 6/4	26.11	3.8923	7.3735	12.6265
ISB-PCL-TPU 6/4	26.11	3.8923	7.3735	12.6265
ISB-PTMG-TPU 9/1	39.44	5.5605	1.843	3.1566
ISB-PCL-TPU 9/1	39.44	5.5605	1.843	3.1566

In this study, a novel isosorbide-based thermoplastic polyurethane (ISB-TPU) series was synthesized by altering the molecular structure of the hard segment in the backbone of ISB-TPU, based on the different soft segments [14]. ISB could be incorporated alongside hard segment to modify the properties of TPU [15]. The molecular structure, molecular weight, glass transition temperature (Tg), and mechanical properties of ISB-TPUs with different soft blocks were characterized using Fourier transform infrared (FT-IR), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and universe testing machine (UTM).

2. Experimental

2.1. Materials. Polycaprolactone diol (PCL, Mn = 2000 g/mol) and poly (tetramethylene glycol) (PTMG, Mn = 2000 g/mol) and methylene diphenyl diisocyanate (MDI) were purchased from Sigma-Aldrich and used after vacuum dry. Isosorbide (ISB) was obtained from Samyang Corporation and dehydrated with a molecular sieve before being used. N,N-Dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Duksan Chemical and distilled over CaH_2 prior to use. Deionized water was used to rinse any residual reactants.

2.2. Synthesis of an ISB-TPU Series. ISB-TPUs with different polyols were synthesized through two steps as shown in Figure 1. The materials and amounts used in the synthesis are shown in Table 1. Firstly, MDI-1 was added to PCL or PTMG diols in a 250 mL four-necked reactor equipped with a condenser, a mechanical stirrer, a temperature-controlled heating mantle, and nitrogen purge. The mixture was reacted at 70°C for 2 h to form NCO-terminated prepolymer. ISB was served as a chain extender to form ISB-TPU at 60°C for 2 h. Finally, MDI-2 was introduced slowly in ISB-TPU to terminate as NCO group and reacted continually for 2 h at 70°C. MDI-1 and MDI-2, which have an aromatic ring structure, form urethane bonds capable of hydrogen bonding, and these rigid segments are called hard segments. Deionized water was used to terminate ISB-TPUs and remove residual reactants.

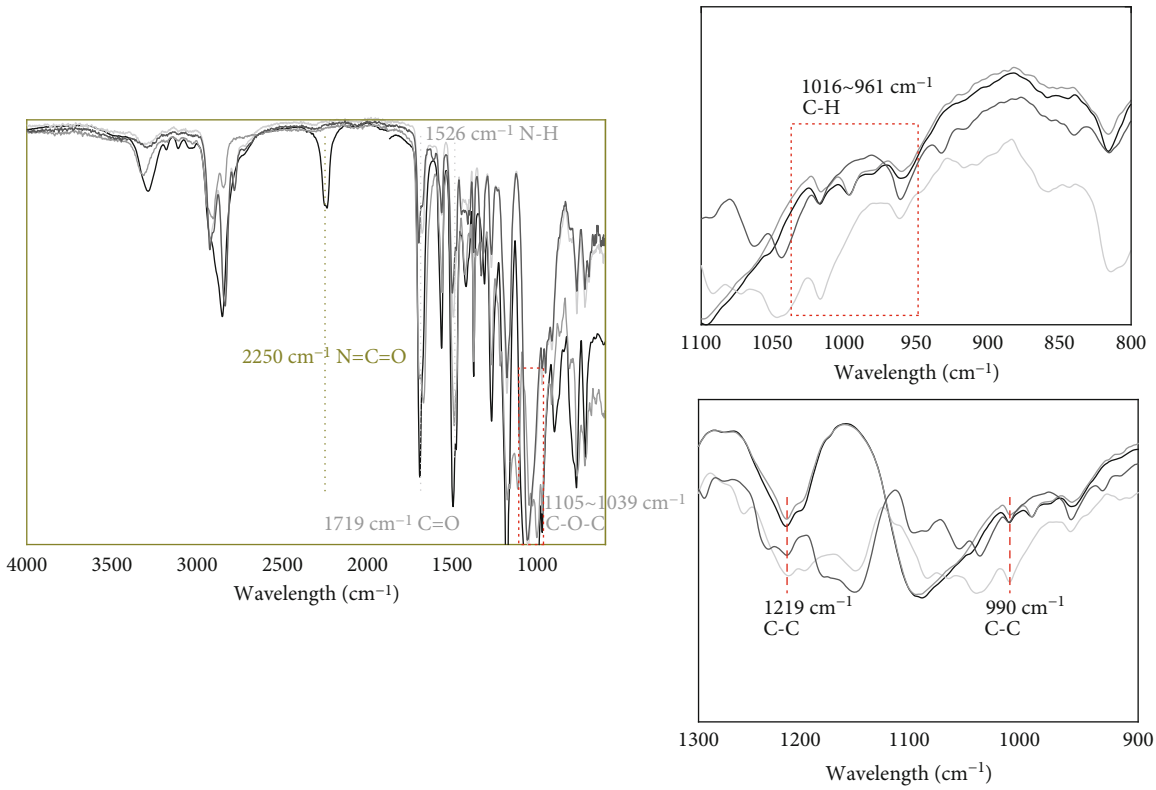

Figure 2: FT-IR spectra of an ISB-TPU series with different polyols.

2.3. Characterization. All Fourier transform infrared (FT-IR) measurements were analyzed on CARY-640 spectrometer in the range from 650 to 4000 cm^{-1}. All molecular weights and polydispersity indexes (PDI) of ISB-TPUs with different polyols were measured by gel permeation chromatography (GPC, Waters) with a refractive index detector and polystyrene as the standard. Thermal properties were measured using differential scanning calorimetry (DSC, DSC-Q20, TA instruments) and thermogravimetric analysis (TGA, TGA-Q50, TA instruments). DSC analyses were performed under heating and cooling scans at a rate of 10°C/min from -80°C to 250°C under a nitrogen atmosphere. TGA analyses were carried out under air and nitrogen flow (25 ml/min) from 30°C to 700°C at a heating rate of 10°C/min. The mechanical properties were analyzed using a universal testing machine (UTM, LLOYD INSTRUMENT) under conditions of 20 mm gauge length and 500 mm/min crosshead speed (ASTM D638).

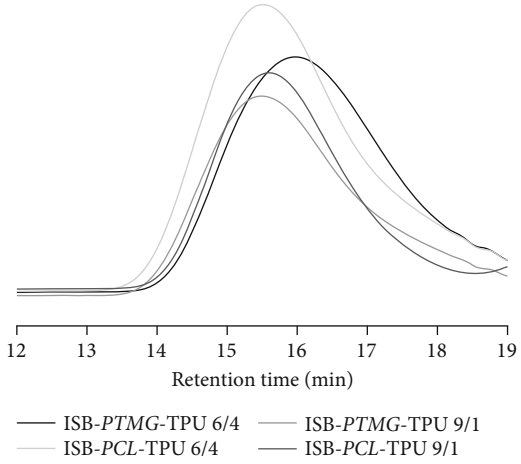

Figure 3: GPC curves of ISB-TPUs with different polyols and OH/NCO ratios.

3. Results and Discussion

The successful synthesis of an ISB-TPU series could be verified by the formation of urethane groups and the dissipation of –NCO groups. The FT-IR spectra of ISB-TPUs with different soft blocks are illustrated in Figure 2. All FT-IR spectra showed the successful formation of an ISB-TPU series with the five characteristic peaks of urethane function. Three characteristic bands at 1719 cm^{-1}, 1526 cm^{-1}, and 1105~1039 cm^{-1} could be assigned to ester C=O stretching vibration, N-H bending bonds, and C–O–C stretching of ether oxygen for urethane linkage [16]. The IR peak at 1016~961 cm^{-1} might be ascribed to C–H stretching in the isosorbide [17]. The bands observed at 1219~990 cm^{-1} might also be assigned to C–C stretching vibration [18]. The result indicated that the characteristic peaks of ISB were observed significantly because of the presence of ISB in both ISB-PTMG-TPU and ISB-PCL-TPU.

The effects of isosorbide on the thermal and mechanical properties of ISB-TPU were studied in terms of the independent condition of molecular weight (MW). The MW and

Table 2: Average MW parameters of an ISB-TPU series determined by GPC.

Sample code	Average molecular weight		
	M_n (g/mol)	M_w (g/mol)	PDI
ISB-PTMG-TPU 6/4	15,800	31,300	1.98
ISB-PCL-TPU 6/4	17,900	41,900	2.34
ISB-PTMG-TPU 9/1	20,700	42,700	2.06
ISB-PCL-TPU 9/1	20,700	38,800	1.87

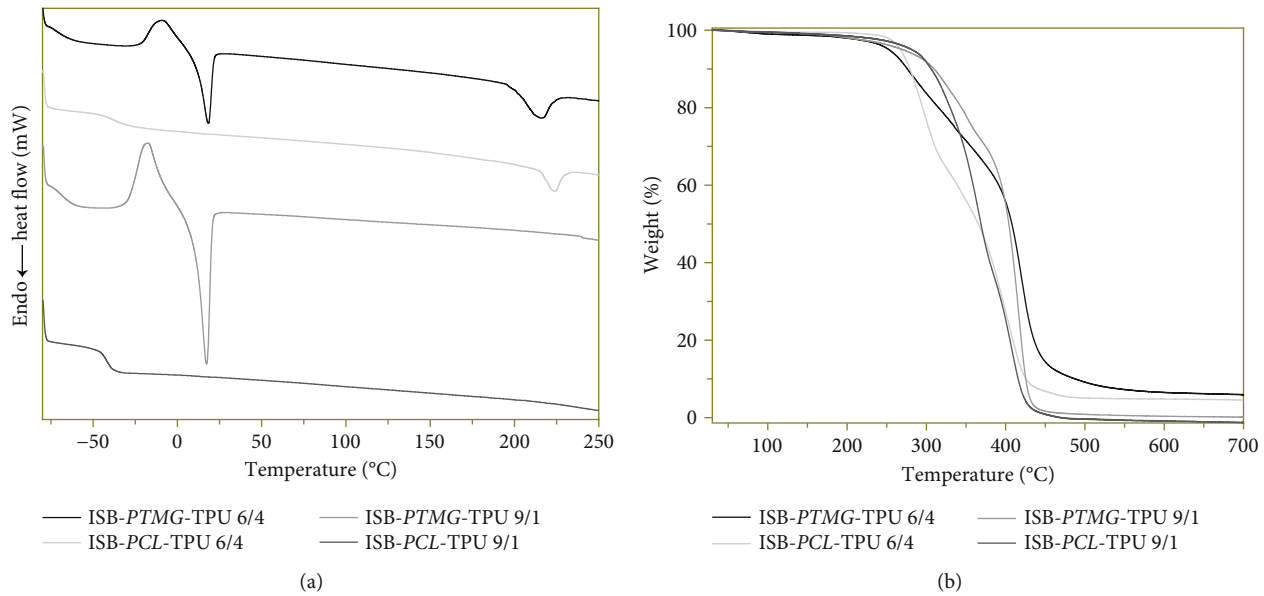

Figure 4: (a) DSC thermograms of an ISB-TPU series. (b) TGA curves of an ISB-TPU series.

Table 3: Thermal stability of ISB-TPUs with different polyols and soft/hard ratios.

Sample code	A	B			
	Tg (°C)	Onset$_{d-r}$ (°C)	T_{d-r} (°C)	Onset$_{d-f}$ (°C)	T_{d-f} (°C)
ISB-PTMG-TPU 6/4	-71.34	252.50	276.08	276.66	419.91
ISB-PCL-TPU 6/4	-38.16	267.29	279.20	296.90	400.41
ISB-PTMG-TPU 9/1	-77.41	269.75	309.83	352.16	416.33
ISB-PCL-TPU 9/1	-42.42	281.33	306.24	365.66	407.16

polydispersity of an ISB-TPU series with different polyols were measured to verify the successful formation of almost the same MW and determine the polyol dependence of physical properties. Figure 3 illustrates the GPC curves of an ISB-TPU series obtained by size exclusion chromatography (SEC), and the MW parameters are summarized in Table 2. An ISB-TPU series containing different polyols analyzed in this study showed MWs ranging from 15000 to 21000 and similar MW distributions between 1.87 and 2.34. The result indicated that the formation of an ISB-TPU series is a little bit different.

DSC and TGA analyses were performed to characterize the thermal behaviors of an ISB-TPU series based on the different polyols, and their curves are displayed in Figure 4. The Tg values for ISB-PCL-TPUs were higher than those of ISB-PTMG-TPUs, due to the relatively rigid structure of PCL blocks as shown in Figure 4(a). PTMG might be a long polyether polyol which can confer good flexibility and toughness to ISB-PTMG-TPUs, and their Tgs are lowered by about -78°C. Melting peaks of the hard segment in an ISB-TPU series were clearly observed only for polyol/isocyanate = 6/4 while the melting temperatures for polyol/isocyanate = 9/1 disappeared with the increase in the mass fraction of the soft segment. An acceptable first thermal behavior of 250~400°C was observed by the degradation of hard or rigid segments on an ISB-TPU series, as shown in Figure 4(b). With increasing the soft segment content, the first and second ranges of degradation were shifted to a higher temperature and are summarized in Table 3. The second thermal behavior related to the degradation of elastic or soft segments occurred in the range of 350~420°C. It may be considered that the hard segment could provide an abundance of rigid urethane linkages and ISB rings for an ISB-TPU series, which

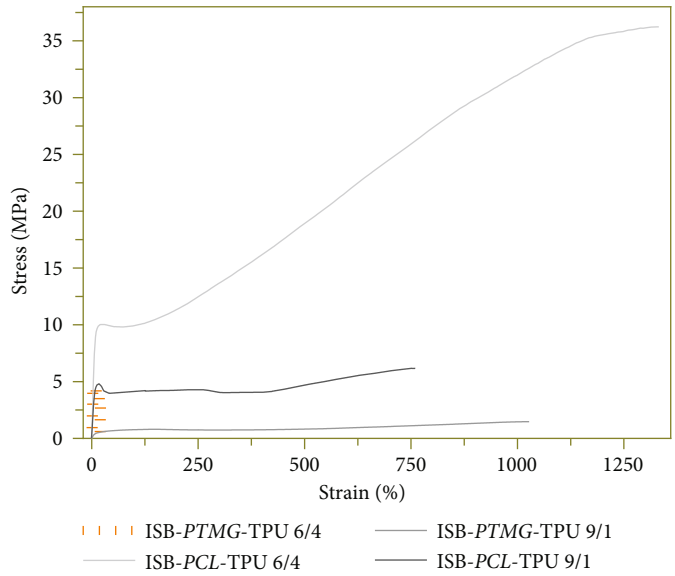

Figure 5: Stress-strain curves of an ISB-TPU series with different polyols and soft/hard ratios.

restricted the rotation of soft segments. Thermal stability could further improve with incorporating ISB as a hard domain or chain extender.

The tensile properties were evaluated to provide a large range of mechanical properties of an ISB-TPU series, based on the different polyol blocks. Figure 5 shows the stress-strain curves of an ISB-TPU series. The ISB-PCL-TPU with soft/hard = 6/4 exhibited superior tensile strength and toughness compared to those of other ISB-TPU series. It achieved a higher tensile strength of 36 MPa and a remarkable toughness value of 8.7 MJ m^{-3}. When soft/hard = 9/1 was incorporated into ISB-PTMG-TPU, a slight decrease of tensile strength and a sufficient increase of elongation were observed, which might be attributed to increasing chain entanglements. It might be inferred that the incorporation of ISB as a chain extender could confer more reversible mechanical properties to an ISB-TPU series, which might also be dependent upon the polyol structure used in soft segments.

4. Conclusion

The synthesis of an ISB-TPU series in the presence of different polyols was successfully performed using two-step polymerization. The ISB-TPUs are composed of two different reactive polyols such as PTMG and PCL. This work studied whether ISB as a chain extender was significantly affected to achieve an ISB-TPU series with desirable thermal properties or good mechanical properties. The obtained ISB-TPUs exhibited some limits of thermal and mechanical properties when switching the polyol of soft segments. In order to achieve the specific properties required in industrial applications, it is necessary to study the in-depth research, such as the increase or the decrease of ISB content in the resulting ISB-TPU. Consequently, an ISB-TPU series could be considered as a viable candidate for practical applications where potential adhesives, coatings, and biocompatibility have been required.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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