Elevation of Modulus and Elongation of Semicrystalline Polyurethanes

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ABSTRACT: Polyurethanes were synthesized based on an amorphous polyester polyol, and different chain extenders, comparing the universally accepted symmetric chain extender (1,4-butanediol) with an asymmetric (1,2-propanediol) chain extender. The effect of incorporating a crystalline polyester polyol polyhexamethylene adipate (PHMA) was investigated. The resulting morphologies and tensile properties are dramatically different. Based on the thermal and infrared data obtained, the sample with the symmetric chain extender exhibits a phase-separated morphology, which can change as a function of time and temperature. Conversely, the polyurethane with the asymmetric chain extender has a phase mixed morphology that remains stable under the same experimental conditions. Incorporating crystalline PHMA resulted in a substantial change in the mechanical properties of the materials, especially for the copolymer comprising asymmetric chain extender. The rate of crystallization and the degree of crystallization achieved depended on the type of chain extender used. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. **2018**

KEYWORDS: polyurethane; chain extender; mechanical properties; crystallization

INTRODUCTION Polyurethanes (PUs) are one of the most versatile polymer classes available. A diverse range of physical properties is achievable resulting in extensive applications including foams, fibers, coatings, sealants, adhesives, elastomers, engineering plastics, and others.[1,2] PUs are relatively easy to synthesize and a broad range of polymers can be made via a judicious choice of polyols, isocyanates, and chain extenders.[1,3,4] In many cases, the resulting structure possesses interesting features composed of relatively flexible soft segments (SSs) and relatively rigid hard segments (HGs). The SSs comprise flexible macrodiols with glass transition temperatures below ambient temperature and provide the elastic deformation needed. The HSs originating from the reaction of diisocyanates with low molecular chain extenders possess T_g's well above ambient temperature. Due to the chemical–physical difference between the SS and HG, the resultant PU typically exhibits a phase-separated structure. In fact, PUs are often referred to as physically crosslinked systems because the HG domains are held together by strong hydrogen bonds.[5–7] This type of phase-separated structure is accountable for the resilient yet robust physical properties realized for PUs.

In this study, we focus on the role of the chain extender in determining PU multiblock structure. This area is important but has not been comprehensively studied. Chain extenders are typically low molecular weight diols, which are used to not only increase the molecular weight of the PUs but can also control morphological and physical properties.[2,4,8–20] We seek to understand how changing the symmetry of the chain extender from the traditional linear diols can influence the morphological development and the physical properties achieved. We elected to modify the symmetry of the chain extender by using 1,2-propanediol (1,2 PDO), thereby introducing asymmetry into the structure by incorporating a pendant group on the backbone of the chain extender. We have shown that because of this structural asymmetry, the segmental mobility in PU comprising 1,2 PDO is decreased as compared to the universally accepted symmetrical chain extender 1,4-butanediol (1,4 BDO).[21] The degree of self-association in the HS structure comprising 1,2 PDO is also much lower than in the former 1,4 BDO because of the steric hindrance of the pendant group.[21] Here, we compare the effect of the asymmetry of the chain extender on the mechanical properties of the materials. Other recent studies have indicated that different chain extenders can affect the PU physical properties such as hardness, density, elongation, glass transition temperature, softening temperature, and others.[19,20,22]

In addition to changing the chain extender used, we also elected to incorporate a crystallizable polyester polyol

TABLE 1 Molecular Constitution of the Two Types of PU Samples

Sample	M_n (g/mol)	PDI	HS%	%SC
I	10,600	1.5	42	
I + SC	13,400	1.7	38	18
II	11,000	1.5	42	
II + SC	14,700	1.6	38	19

segment in addition to an amorphous polyester polyol. This modification is grounded on the fundamental elasticity theory and the merit shown in recent reports.[23,24] Specific analysis based on the Halpin–Tsai and percolation models have also shown the effects of the crystalline regions on the elastomeric properties of the polymers.[25–27] Furthermore, the size and aspect ratio of the crystallites formed have also proved to be important in determining the sample tensile and elastic properties. The crystalline component not only can improve the ultimate physical properties but also the dynamics of the crystallization process and how quickly the desired physical properties are obtained. In this study, infrared spectroscopy was used to assess the change of conformational order achieved during crystallization. The differences in the crystallization kinetics and the degree of crystallinity obtained were correlated to the moduli and elongation measured. The intent of this communication is to shed some understanding on the relationship between the structure of the chain extender on the crystallization kinetics and the degree of crystallinity achieved, thus providing an explanation of the different mechanical properties measured.

RESULTS AND DISCUSSIONS

PU compositions comprising asymmetric 1,2 PDO chain extender are designated I, whereas compositions with symmetric 1,4 BDO chain extender are designated II. The addition of SC designates compositions which *also* comprise the crystallizable polyhexamethylene adipate (PHMA) polyester component (designated as the semi-crystallizable or SC component) in addition to the amorphous polyester component. The two types of samples (with or without PHMA) exhibit two sets of similar molecular weight and distribution. Based on the GPC data shown in Table 1, I and II have molecular weights (M_n) of 10,600 and 11,000 g/mol, respectively. I + SC and II + SC have a M_n of 13,400 and 14,700 g/mol, respectively. The higher molecular weights of the semi-crystalline PU compositions reflect the incorporation of semi-crystalline polyester polyol with a higher molecular weight (M_n = 3500 g per mole) as compared to the amorphous polyester polyol (M_n = 830 g per mole). The compositions correspond to approximately eight monomer units, essentially reflecting the values predicted by Carother's equation and the 1:2:1.2 (OH:MDI:chain extender). Based on the NMR data obtained, the molecular compositions measured are also listed in Table 1. The molecular composition of each sample is as expected and is very similar to the PU samples prepared previously.[28–30]
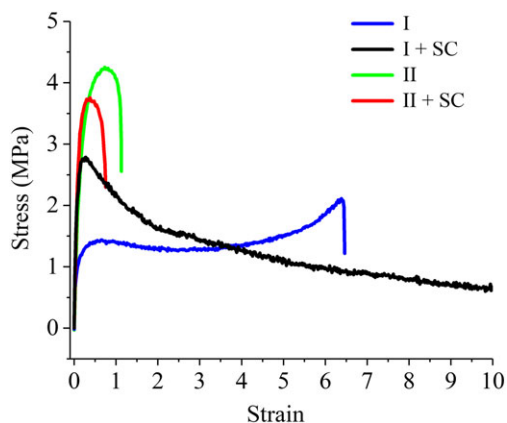
FIGURE 1 Mechanical behavior of the two types of PUs after the incorporation of crystallizable polyester (PHMA) units. [Color figure can be viewed at wileyonlinelibrary.com]

The mechanical properties of materials at room temperature exhibit considerable differences as shown in Figure 1. The moduli and elongation measured are tabulated in Table 2. The materials comprising 1,2 PDO (I, I + SC) have a much higher elongation as compared to the materials comprising 1,4 BDO (II, II + SC) at this molecular weight. The incorporation of crystallizable PHMA polyols clearly raised the modulus of both types of PUs but the enhancement of mechanical properties is especially dramatic for the material with the asymmetric chain extender. As shown in Table 2, the incorporation of crystallizable units raised the modulus of sample I (with 1,2 PDO) by a factor of 6. In contrast, for sample II (with 1,4 BDO), the modulus increased by only 75%.

As hypothesized in various theoretical developments and demonstrated in previous studies, the incorporation of crystallizable PHMA units should improve the mechanical properties of the PUs being studied here.[23–27] The introduction of crystallites acting as rigid fillers to the amorphous matrix is responsible for the increase in the sample modulus.[23] The degree of crystallinity, size of crystallites, and the aspect ratios of the crystallites formed should be important in determining the sample tensile and elastic properties. The dramatic increase of mechanical properties in I + SC may be related to the crystallinity of the crystallizable PHMA segments. The thermograms of the materials are shown in Figure 2.

The glass transition temperatures measured for PU I and I + SC are at ~14 and 9 °C, respectively. The T_g of PU II and

TABLE 2 Changes in Modulus and Elongation by the Introduction of PHMA Units

Sample	Tensile Strength (MPa)	Modulus (MPa)	Percent Elongation
I	1	4	640
I + SC	3	26	1100
II	4	16	128
II + SC	4	28	71
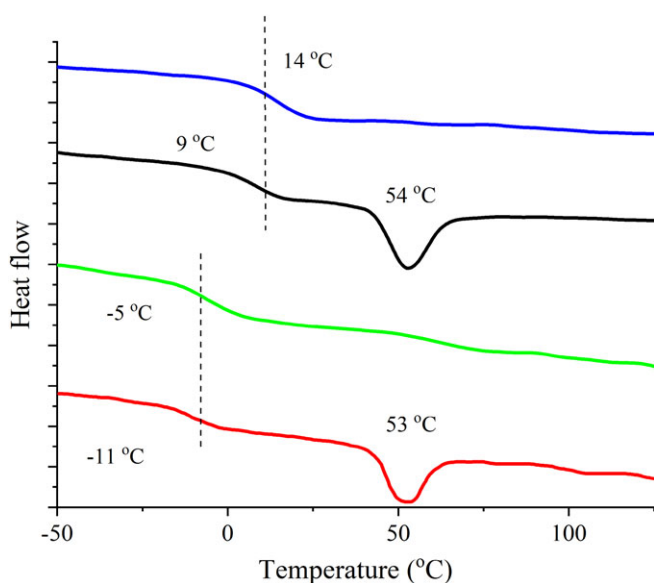
FIGURE 2 Thermograms of the PUs. Materials with 1,2 PDO chain extender are shown in blue (I) and black (I + SC). Materials with 1,4 BDO chain extender are shown in green (II) and red (II + SC). [Color figure can be viewed at wileyonlinelibrary.com]

PU II + SC are observed at approximately −5 and −11 °C, respectively. In each case, the T_g is much higher than the T_g of the pure SS (T_g = −51 °C). The increase in the T_g as compared to the polyol itself is due to the formation of HS in each sample. The difference between samples I and II is attributed to the inherent rigidity in the asymmetric chain extender structure.[21] It is clear that by incorporating the crystallizable PHMA, the glass transition temperature of each sample decreased by approximately 5°.

The endotherms observed for the PU comprising the semi-crystalline component (I + SC and II + SC) are assigned to the melting transition of the PHMA units incorporated into the PU structure. For neat PHMA, the T_m and ΔH are measured at 56 °C and 87 J/g, respectively. For sample I + SC, there is an obvious depression in melting enthalpy (ΔH = 62 J/g normalized to the percentage of PHMA) and melting temperature (T_m, 54 °C) as compared to neat PHMA. Similarly, for sample II + SC, the T_m and ΔH of the crystallizable PHMA were observed at 53 °C and 50 J/g, respectively. Under similar experimental conditions, the melting temperatures measured for the two types of PUs are similar. However, based on their melting enthalpies, sample I + SC (with 1,2 PDO) clearly achieved ∼25% higher degree of crystallinity as compared to the PU with the more flexible 1,4 BDO chain extender.

As mentioned earlier, a number of studies have demonstrated that morphological changes due to the incorporation and manipulation of crystallizable segments can affect the mechanical properties of PUs significantly.[23,24,31] The technique that we employed to follow the crystallization process was *in situ* infrared spectroscopy. Each sample was heated

above the melting temperature then quenched to a specific temperature (15, 25, 35 or 50 °C) above each T_g allowing structural reorganization, including crystallization of PHMA, to occur. The infrared spectra obtained for the two types of PUs revealed that different structural units in each sample type are organized at very different rates as shown in Figure 3.

The carbonyl stretching vibration in the 1700 cm^{-1} region exhibits differences for the two types of PUs as shown in Figure 3. Sample I [Fig. 3(a)] shows a predominant peak at 1732 cm^{-1} with an insignificant shoulder at ∼1710 cm^{-1} This band remains unchanged as a function of time and at all temperatures that measurements were taken, even at 50 °C. In contrast, for sample II [Fig. 3(b)], a distinct doublet at frequencies of 1703 and 1732 cm^{-1} was observed as in most PUs.[32,33] The higher frequency component is generally associated with C=O free from hydrogen bonding. The lower frequency component is assigned to the hydrogen-bonded component. The difference in frequency is characteristic of the strength of hydrogen bond formed.[34,35] Their relative intensity as a function of time (once the contributions of the ester C=O stretching are removed) can be used to characterize the kinetics of morphology formation (phase separation) of various PUs.[32,33] Based on the relative intensities of the two components in this region for the two types of samples, it can be concluded that PU I remains as a phase mixed state. However, PU II is less stable and its morphology changes as function of time and temperature. The presence of the asymmetrical chain extender 1,2 PDO with a methyl group extending away from the main chain in sample I evidently hinders the possibility for forming intermolecular hydrogen bonding interactions as compared to the symmetrical 1,4 BDO system.

There are also a series of skeletal deformation bands assignable to PHMA in the 900 to 1300 cm^{-1} region.[36–38] These bands in both types of PU samples changed as a function of time at specific temperatures [e.g., Fig. 3(c)]. These changes reflect the conformational distribution when crystallization occurs. Although a number of vibrations can be used for analysis, we elected to use the 971 cm^{-1} skeletal deformation (mainly C—C stretching) vibration. Even though this band is weak in intensity, it is clearly unique and separate from other vibrations associated with the amorphous polyester, chain extender, and reacted urethane derivatives for intensity analysis. It should be noted that the infrared measurements are different as compared to the long-range coherence found with X-ray diffraction.[39,40] There can be changes in the amorphous regions that are not accounted for in diffraction studies. Nevertheless, the measurements using infrared are easy to carry out and the temporal changes of these skeletal deformation bands are of great interest in explaining the differences of the mechanical properties measured.

Once the intensities are normalized to the final intensity, the data can be summarized as shown in Figure 4. Even after taking into account the differences in the T_g's of the two types of PUs, it is clear that the crystallization kinetics of PHMA in sample I + SC are slower than sample II + SC. Using Avrami
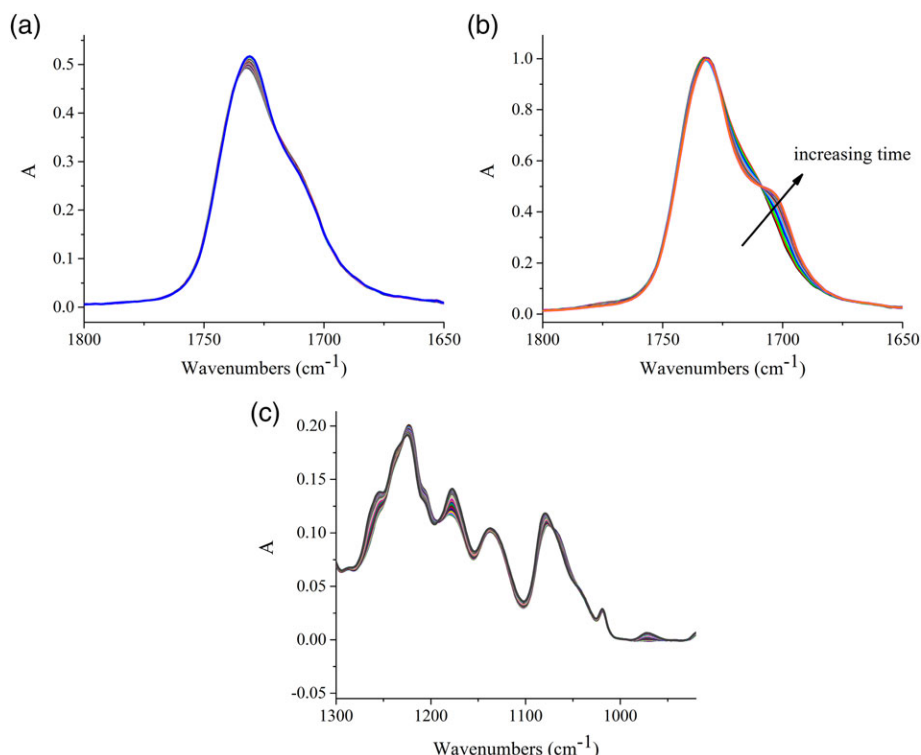
FIGURE 3 Infrared spectra obtained for two types of PUs; (a) C=O stretching for the PU with 1,2 PDO chain extender (I); (b) C=O region for the PU sample with 1,4 BDO as chain extender (II); and (c) the skeletal region for the PU sample with 1,4 BDO as chain extender (II + SC). All spectra were obtained at 25 °C. [Color figure can be viewed at wileyonlinelibrary.com]

type analysis, the rate of crystallization growth is 6–8 times faster in sample II containing 1,4 BDO as compared to sample I containing 1,2 PDO at the same measurement temperatures.

Clearly, the different types of chain extender have induced different crystallization kinetics *and* different degrees of crystallization. The PU with the traditional symmetric flexible 1,4
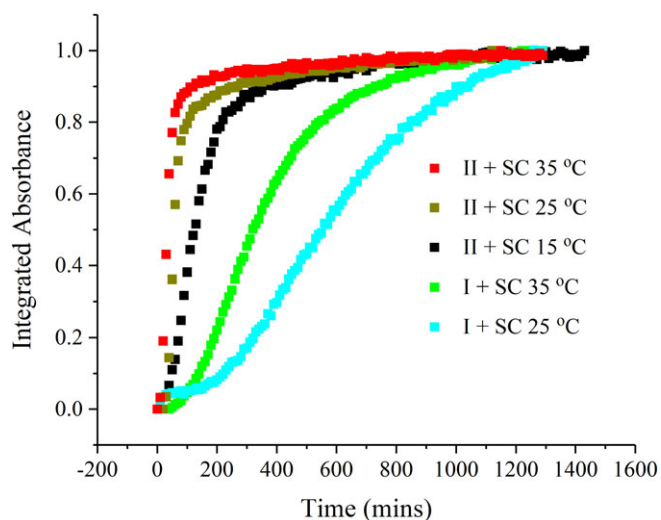
FIGURE 4 Crystallization kinetics of two types of PUs with different chain extenders at different temperatures. [Color figure can be viewed at wileyonlinelibrary.com]

BDO enables faster crystallization of the crystalline phase but produces a phase separated amorphous morphology that results in an ultimately lower degree of crystallinity. In contrast, the rigid asymmetric 1,2 PDO chain extender hinders the crystallite growth kinetics but produces a phase mixed amorphous morphology resulting in an ultimately higher degree of crystallinity. This interplay of amorphous phase structure, degree of crystallinity, and crystallization kinetics are important considerations in designing PU mechanical properties. The incorporation of semicrystalline PHMA has a much greater effect on the mechanical properties of the PU comprised of the asymmetric chain extender because originally, the amorphous PU is not phase separated and after incorporation of the PHMA, the ultimate degree of crystallization obtained is higher.

CONCLUSIONS

This study was carried out to determine the influence of the symmetry of chain extender on the crystallization behavior of PUs to which some degree of crystallizable PHMA had been incorporated. Using *in situ* infrared spectroscopy, the effect of the symmetry of the chain extender on the dynamics of crystallization was found to be significant. It was observed that the higher segmental mobility of the symmetric chain extenders led to a comparatively faster crystallization speed for all temperatures examined than with the asymmetric chain extender showing relatively slower speeds for all temperatures studied. The higher T_g (~10 °C) of the asymmetric system narrows the range accessible for crystallization whereas

the symmetric chain extender, with a lower T_g ($\sim -10\ ^\circ$C) has a broader range accessible for crystallization to proceed. Thermal properties, particularly the enthalpy of crystallization, at equilibrium morphologies revealed a greater degree of crystallinities for the asymmetric system. This was attributed to the absence of amorphous phase separation in the PU comprising asymmetric 1,2 PDO. In contrast, the ordered nature of the HS from the symmetric 1,4 BDO leads to the presence of phase separated domains that inhibits the crystallization of the PHMA.

EXPERIMENTAL

An amorphous polyester polyol was provided by Henkel and used in the synthesis of the PU, comprising isophthalic acid, adipic acid, neopentyl glycol, and dipropylene glycol with a molecular weight of 830 g/mol. In addition, 20% of PHMA polyol with a molecular weight of 3500 g/mol, previously used in our laboratory, was incorporated into the amorphous polyester polyol structure and the PUs containing different chain extenders were synthesized as follows. These polyols and a hindered phenol-based antioxidant used to prevent degradation were added to a flask and heated to 80 $^\circ$C under nitrogen and vacuum for approximately 1 hour to remove any moisture present in the polyol. Vacuum was removed, nitrogen reapplied, and MDI (purchased from Sigma Aldrich, St. Louis, Missouri) added to the mixture after which the resultant mixture was stirred at 300 rpm for 30 min. NCO content was measured via titration until the experimental value obtained was close to the theoretical value calculated. The chain extension step was subsequently carried out at 120 $^\circ$C using different chain extenders. The chain extenders employed were 1,4 BDO (purchased from Sigma Aldrich) and the 1,2 PDO (purchased from Alfa Aesar, Haverhill, Massachusetts).

Molecular weight and polydispersity index (PDI) measurements of the polymers were measured using a GPC 50 integrated GPC system that was calibrated against polystyrene standards in THF at a flow rate of 1.0 mL/min using a refractive index detector. The molecular weight of the two types of PUs has been shown to be virtually identical as tabulated in Table 1. A 400 MHz Bruker instrument was employed in determining the compositions of the two types of PUs. The samples were dissolved in deuterated DMSO. A TA instrument Q100 DSC equipped with a nitrogen-purged refrigerated cooling system was employed in determining the thermal transitions present in the polymer structures. The heating rate was maintained at 20 $^\circ$C/min for all DSC measurements. Calibration was carried out using Indium (T_m = 156.6 $^\circ$C; equilibrium heat of fusion = 28.6 J/g). All infrared data were obtained by using the transmission mode. A PerkinElmer 100 FTIR spectrometer was utilized in both types of infrared spectroscopy. For all infrared data, 32 scans of 4 cm^{-1} resolution were co-added. A home-built heating and cooling cell was used for variable-temperature crystallization studies. Tensile testing was performed at room temperature using an Instron universal testing machine. Dog bone specimens having a thickness of approximately 300 microns were employed. Testing was performed at a crosshead speed of 250 mm/min with a 5 kN load cell. For each sample, at least three individual specimens were tested in separate analyses.

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