Thermoplastic polyurethanes with controlled morphology based on methylenediphenyldiisocyanate/isosorbide/butanediol hard segments

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Abstract

Isosorbide, a cyclic, rigid and renewable diol, was used as a chain extender in two series of thermoplastic polyurethanes (PUs). Isosorbide was used alone or in combination with butanediol to examine the effects on the morphology of PU. Two series of materials were prepared – one with dispersed hard domains in a matrix of polytetramethylene ether glycol soft segments of molecular weight 1400 g mol⁻¹ (at 70 wt% soft segment concentration, SSC) and the other with co-continuous soft and hard phases at 50 wt% SSC. We investigated the detailed morphology of these materials with optical and atomic force microscopy, as well as ultra-small-angle X-ray scattering. The atomic force microscopy measurements confirmed the different morphologies in PUs with 50 wt% SSC and with 70 wt% SSC. Small-angle X-ray scattering data showed that in PU with 70 wt% SSC, the hard domain size varied between 2.4 and 2.9 nm, and decreased with increasing isosorbide content. In PU with 70 wt% SSC, we found that the correlation length and average repeat distances became smaller with increasing isosorbide content. We estimated the thickness of the diffuse phase boundary for PU with 70 wt% SSC to be ca 0.5 nm, decreasing slightly with increasing isosorbide content.

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Keywords: morphology; segmented polyurethanes; isosorbide; chain extender

INTRODUCTION

Thermoplastic polyurethanes (TPUs) are a class of polymers with many useful properties, including elasticity, transparency and resistance to oil, grease and abrasion.1–3 TPUs are block copolymers composed of alternating flexible soft segments and rigid, often crystallizable, hard segments. The properties of TPUs depend on the structure of the soft and hard building blocks, their molecular weights, soft segment concentration (SSC) and microstructural morphology of the final product.4–6 From a structural point of view, immiscibility of the soft and hard segments leads to phase separation. When the contents of the soft and hard phases are about equal, TPUs normally exhibit a co-continuous morphology.7 When the concentration of the hard segments is low, the hard segments tend to form globules that are dispersed in the soft matrix.8 These two different morphologies are illustrated in Fig. 1. In TPUs, the crystalline or pseudo-crystalline hard domains act as physical crosslinks, which account for the high strength, whereas the flexible chains impart high elongation and elastic recovery to the polymer.

Typical hard segments of TPUs are made from methylenediphenyldiisocyanate (MDI) and butanediol (BD). During recent years, growing interest and efforts have been devoted to the utilization of natural products in both academic research and industrial applications because of important issues associated with environmental protection, waste disposal and depletion of non-renewable resources. Materials derived from renewable resources can provide a sustainable and eco-friendly platform to partially, and to some extent totally, substitute petroleum-based polymers through the design of bio-based polymers. With the availability of new bio-based diols of rigid structure, it would be interesting to systematically examine the properties of the hard phase in polyurethanes when BD is replaced by a bicyclic diol obtained from renewable raw materials, such as isosorbide (ISO).

ISO is derived from starch by hydrolysis to glucose, followed by hydrogenation to sorbitol and double dehydration to the final product. The value of ISO arises from its attractive price, rigidity of its molecule, high degree of thermal stability, biodegradability,
renewability, solubility in water and non-toxicity. To investigate the
effect of ISO on the structure and properties of TPU, we prepared
two series of TPU with different concentrations of ISO with SSCs
of 50 and 70 wt%, respectively.

We used MDI/BD, MDI/ISO and their mixtures as hard segments.
These hard segments are crystallizable and likely to separate into
domains with a recognizable melting point if the hard segment
concentration (HSC) is high enough. Here, the calculation of the
HSC takes into account the mass of all MDI and BD and/or ISO units.
When HSC is low, hard segments may be short and unable to crys-
tallize. We selected polytetramethylene ether glycol (PTMEG) with
a molecular weight of 1400 g mol$^{-1}$ as the soft segment because
it does not crystallize and yields strong elastomers. The molecular
weight of the soft segment also determines the molecular weight of
the hard segment at a given SSC.$^{5,9}$

ISO is a diol with two secondary hydroxyls, one of which is reactive
(exo-hydroxyl) and the other, internal and hydrogen bonded
(endo-hydroxyl), is less reactive in the absence of catalysts.$^{18}$ The
ISO structure contains two fused furan rings forming an angle of
120° which impart a certain rigidity to the molecule. ISO is water
soluble and more hydrophilic than BD, which would affect phase
separation, and thus morphology, of segmented polyurethanes.
Replacing linear aliphatic diols in polyurethanes with ISO was
found to increase the glass transition temperature and melting
point of the hard segment.$^{11}$ In the work reported here, we systematically varied the molar ratio of BD to ISO in the hard segment of
polyurethane in these steps: 100:0; 75:25; 50:50; 25:75; and 0:100.

Cognet-Georjon and co-workers investigated a series of polyurethanes
with ISO/MDI hard segments and a range of PTMEG polyls of different molecular weights and varying SSCs.$^{12,13}$ In
these works, those authors did not attempt to control the mor-
phology. Instead, they varied the molecular weights of polyls and
kept the molar ratio of components fixed.

MDI/BD and MDI/ISO hard segments of sufficient length have a
tendency to crystallize, which yields blocks with melting
points that depend on their molecular weight. The morphol-
ogy is also affected by the preparation protocol. Standard

durotane elastomers are prepared using either a prepolymer
or a one-shot method. We used the prepolymer method in the
work reported here. This method consists of reacting polyls with
a molar excess of isocyanate to obtain an isocyanate-terminated

EXPERIMENTAL

Materials
Terathane 1400, obtained from Invista, Wilmington, DE, USA,*
is a PTMEG of nominal molecular weight of 1400 g mol$^{-1}$ and
hydroxyl number of 80.2 mg KOH g$^{-1}$. Rubinate 44 MDI, having iso-
cyanate (NCO) content of 33.5 wt%, was kindly supplied by Hunts-
man. 1,4-BD (99 wt%) and ISO (assay > 98 wt%) were purchased
from Aldrich.

Synthesis of polyurethanes
The synthesis of polyurethanes was carried out in bulk using a
two-step, prepolymer method as described in a separate paper.$^{11}$
Briefly, Terathane was reacted with excess MDI at 75 °C for 1 h
to obtain a quasi-prepolymer. Then, the chain extender was added
and the reaction continued with stirring for an additional 2 h to
secure completion. Polyurethanes in both series are soluble in
dimethylformamide but 70 wt% SSC samples were also soluble at
hot tetrahydrofuran.

The TPU samples are named using the following convention:
PUAA-BBB. Here, PU refers to polyurethane; AA indicates the SSC
of the sample; and BBB indicates the molar percentage of ISO in
the BD/ISO mixture. For example, PU50-100 means that the sample
has 50 wt% SSC and 100% ISO in the BD/ISO mixture.

*Certain trade names and company products are mentioned in the text or identified in illustrations in order to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.
Polydispersity index is close to 2 in all polymers. Generally, the number-average molecular weight of 1.06 g cm\(^{-3}\) and vary little with hard segment composition. Densities of TPUs with 70 wt\% SSC are around 1.06 g cm\(^{-3}\) and vary within experimental error. All samples with 50 wt\% SSC are opaque, while samples with 70 wt\% SSC are clear and transparent with mixed BD/ISO hard segments and hazy (translucent) with pure BD or pure ISO. Low transparency suggests the presence of large morphological objects with sizes comparable to or greater than the wavelength of visible light.

Polyurethanes with 50 wt\% SSC having soft segments of molecular weight of 1400 g mol\(^{-1}\) must have hard segments of the same number-average molecular weight, i.e. 1400 g mol\(^{-1}\). The repeat unit in PU50-0 consists of MDI and BD and has a molecular weight of 14000 g mol\(^{-1}\). Therefore, for this sample, on average, the hard segment has about four repeat units. We note that it has been found that one repeat unit is sufficient to observe phase separation. On the other hand, number-average molecular weight of hard segments in polyurethanes with 70 wt\% SSC is 1400 × 30/70 = 600, i.e. hard segments, on average, consist of less than two repeat units, which makes it difficult to form crystalline hard domains within the hard segments. The existence of blocks of chain extenders in mixed hard segments is possible but it is considered inconsequential because of very limited numbers of repeat units.

We analyzed the morphology of TPUs of various SSCs using both SAXS and AFM. Figures 2 and 3 show the slit-smeared SAXS data for 70 and 50 wt\% SSC TPU samples, respectively.

The line shapes of these scattering profiles for 70 wt\% SSC TPU samples and 50 wt\% SSC TPU samples exhibit much resemblance – both show a low-\(q\) (\(q < 0.001\) Å\(^{-1}\)) scattering feature dominated by a power-law slope and a high-\(q\) peak (near 0.05 Å\(^{-1}\)) characteristic of phase-separated domains. Despite these general similarities, we elected to analyze the SAXS data of 70 wt\% SSC samples and 50 wt\% SSC samples using different models, due to the different underlying morphologies of the phase-separated domains. Here, 70 wt\% SSC samples show dispersed hard domains in the soft matrix and 50 wt\% SSC samples show continuous network morphology. These assumptions involving the underlying morphologies are further validated by mechanical testing results using dynamic mechanical analysis, stress–strain testing and elastic recovery testing. We performed the data reduction and analysis using the Irena SAXS analysis package, as well as user-defined MATLAB functions. We describe our detailed approach and analysis in the sections below.

**SAXS analysis of 70 wt\% SSC samples**
We examined the low-\(q\) scattering intensity for its dependence of \(q\). The presence of low-\(q\) scattering suggests that structural inhomogeneities exist at sizes greater than 1 μm. Detailed characterization of these large inhomogeneities is limited by the accessible scattering \(q\) range, and quantification of their size is not possible. However, we were able to establish the power-law slope of these low-\(q\) scattering profiles (analysis conducted on desmeared scattering data), and find that the slopes range between −3.12 and −3.15.
and $-3.95$ (Table 1). In other words, the power-law slope falls between $-3$ and $-4$ for all 70 wt% SSC samples. This behavior is consistent with scattering from objects having rough surfaces or interfaces.\textsuperscript{18,19}

Interestingly, for the 70 wt% SSC samples with BD-to-ISO molar ratios of 25:75 and 0:100, we also identified that a hump emerges on top of the low-$q$ power-law slope. We analyzed the Guinier radius for this feature in these two samples, and find it to be 2425 and 3946 Å, respectively. An example of this analysis is shown in Fig. 2 (solid line denoted ‘low $q$ Guinier, BD/Isosorb. = 0:100’). While this hump is not prominent, it cannot appear in completely homogeneous systems. This result unequivocally shows that by increasing ISO components in the hard segments, domains form on the scale of hundreds of nanometers.

We analyzed the high-$q$ scattering peak following a procedure reported elsewhere.\textsuperscript{20} In this analysis, we assume that the hard domains are spherical in shape, and are spatially well dispersed. We also assume that the size distribution of the spherical hard domains follow a Gaussian size distribution. A single spherical particle scattering intensity is as follows:

$$I_1(q) = (\Delta \rho)^2 V^2 \left[ 3 \sin qr - qr \cos qr \right] / (qr)^3]$$

where $V$ is the volume of a sphere, $r$ is the radius of a sphere and $\Delta \rho$ is the relative scattering length density. At high particle concentration, the cumulative scattering intensity can be written as $I(q) = N \times I_1(q) \times S(q)$, where $N$ is the total number of particles and $S(q)$ is a structure factor defined as

$$S(q) = \frac{1}{1 + 8\varphi \left[ 3 \sin (q\xi) - q\xi \cos (q\xi) \right] / (q\xi)^3}$$

where $\xi$ is the mean separation distance between domains and $\varphi$ is the volume fraction of the minority phase. This model well describes the scattering feature at high $q$. An example of the fit is shown in Fig. 2 (solid line denoted ‘fit of high $q$ peak, BD/Isosorb. = 0:100’). The fitting parameters are listed in Table 1.

Table 1 shows that the nominal radius of the hard segment domain is between 2.4 and 2.9 nm, which is similar to the domain size reported for other TPU systems.\textsuperscript{5,20-24} We also find that with increasing ISO content in the hard segments, the radius of the spherical hard segment domains decreases. With the SSC kept constant in the PU70 series, this result suggests that the addition of ISO leads to more globular domains. At the same time, the mean separation distance between these hard segment domains also decreases with increasing ISO. This behavior is expected given that, in all samples, we maintained the weight content of hard segments constant at 30%.

### Table 1. SAXS morphological parameters for 70 wt% SSC samples

<table>
<thead>
<tr>
<th>Sample\textsuperscript{a}</th>
<th>Sphere radius (Å)</th>
<th>Gaussian width (Å)</th>
<th>Mean separation distance (Å)</th>
<th>$R_g$ (Å)</th>
<th>Power-law slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU70-0</td>
<td>28.8</td>
<td>8.5</td>
<td>123.9</td>
<td>84.7</td>
<td>$-3.95 \pm 0.08$</td>
</tr>
<tr>
<td>PU70-25</td>
<td>27.0</td>
<td>6.2</td>
<td>110.7</td>
<td>110.6</td>
<td>$-3.19 \pm 0.10$</td>
</tr>
<tr>
<td>PU70-50</td>
<td>26.1</td>
<td>5.5</td>
<td>110.6</td>
<td>2425 ± 51</td>
<td>$-3.12 \pm 0.27$</td>
</tr>
<tr>
<td>PU70-75</td>
<td>25.0</td>
<td>8.0</td>
<td>90.2</td>
<td>3946 ± 33</td>
<td>$-3.51 \pm 0.11$</td>
</tr>
<tr>
<td>PU70-100</td>
<td>23.8</td>
<td>6.4</td>
<td>84.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Sample identification consists of two numbers indicating wt% SSC and molar ratio of ISO in the BD/ISO mixture, respectively.

### Table 2. SAXS morphological parameters for 50 wt% SSC samples

<table>
<thead>
<tr>
<th>Sample\textsuperscript{a}</th>
<th>Correlation length (Å)</th>
<th>Average repeat distance (Å)</th>
<th>$R_g$ (Å)</th>
<th>Power-law slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU50-0</td>
<td>62.2</td>
<td>152.5</td>
<td>708 ± 29</td>
<td>$-3.84 \pm 0.11$</td>
</tr>
<tr>
<td>PU50-25</td>
<td>54.1</td>
<td>126.1</td>
<td>5379 ± 32</td>
<td>$-3.96 \pm 0.09$</td>
</tr>
<tr>
<td>PU50-50</td>
<td>44.7</td>
<td>133.6</td>
<td>7080 ± 29</td>
<td>$-3.69 \pm 0.07$</td>
</tr>
<tr>
<td>PU50-75</td>
<td>50.2</td>
<td>118.9</td>
<td>5966 ± 15</td>
<td>$-4.18 \pm 0.04$</td>
</tr>
<tr>
<td>PU50-100</td>
<td>49.1</td>
<td>109.8</td>
<td>7080 ± 29</td>
<td>$-3.84 \pm 0.11$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Sample identification consists of two numbers indicating wt% SSC and molar ratio of ISO in the BD/ISO mixture, respectively.

### Figure 4. Dependence of diffuse layer thickness at the interface of hard segments and soft segments on the molar ratio of isosorbide for 50 wt% SSC samples.

SAXS analysis of 50 wt% SSC samples

Figure 3 shows the scattering profiles of 50 wt% SSC samples with various BD-to-ISO ratios. The low-$q$ scattering again suggests that structural inhomogeneities exist at length scales larger than 1 μm. We analyzed the power-law behavior of the low-$q$ scattering of these samples. The power-law slopes are given in Table 2. Here, the power-law slopes range between $-3.69$ and $-4.18$. These values in general are lower than those found for 70 wt% SSC samples, which suggests that the interfaces/surfaces are less rough, or, in the cases where the values of the slopes are less than $-4$, domains may contain diffused interfaces. For some of these samples, we again observe a hump on top of the low-$q$ power-law slope. Guinier radii related to these features are also reported in Table 2.
We assume that the 50 wt% SSC samples have a co-continuous morphology based on previous studies and mechanical testing results. Such an assumption invalidates the isolated-scatterer model described for 70 wt% SSC samples. Instead, we elected to analyze the high-q scattering peak using the Teubner–Strey model. This model is based on the Landau–Ginzburg free-energy theory, describes a two-component structure when particle shape is not well defined and has been successfully applied to a range of two-phase non-particulate systems ranging from microemulsions to polymeric composite membranes. This model predicts a scattering intensity as follows:

$$I(q) = A \times \frac{1}{a_2 + c_1 q^2 + c_2 q^4}$$

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**Figure 5.** Optical micrographs acquired using reflected light of the cryo-faced surface of (a) sample PU50-0 and (b) sample PU50-100.

**Figure 6.** Tapping mode height and phase images of PU50-0. (a) Area 1, 10 μm scan size. (b) Area 2, 2.5 μm scan size.
where $a_2$, $c_1$, and $c_2$ are coefficients from an order parameter expansion of the free energy density and $A$ is a normalization parameter that is related to the volume fraction of a given phase and its scattering contrast.

The scattering intensity described in Eqn (3) is related to the correlation function of the Teubner–Strey model following a direct Fourier transform. Here, the correlation function is as follows:

$$\gamma(r) = \frac{d}{2\pi r} \exp\left(-\frac{r}{\xi}\right) \sin\left(\frac{2\pi r}{d}\right)$$

where $r$ is the real-space distance, $\xi$ is the correlation length and $d$ is the $d$-spacing related to an average repeat distance. Parameters $\xi$ and $d$ are related to $a_2$, $c_1$, and $c_2$ following complicated relationships. These relationships can be found elsewhere.25

Our analysis shows that the Teubner–Strey model describes well the high-$q$ scattering peak. An example of the fit is shown in Fig. 3 (solid line denoted ‘fit of high $q$ peak, BD/Isosorb. = 0:100′). The correlation lengths and average repeat distances are listed in Table 2. We find that as more ISO is added to the hard segments, both the correlation length and the average repeat distance become smaller. Similar to the PU70 series, this suggests that with increasing ISO, more domains form, which may be related to the fact that ISO is bent and therefore more compact than BD from a molecular structure point of view.

For the 50 wt% SSC samples, we also estimated the influence of the diffuse phase boundaries between the phase-separated domains. It has been shown by Ruland28 that diffuse phase boundaries contribute to the measured scattering intensity as follows:

$$\lim_{q \to \infty} \left[ I_M(q) - I_B(q) \right] = I_{\text{Porod}}(q) \times H^2(q)$$

where $I_{\text{Porod}}(q)$ is the Porod scattering intensity from a perfect interface and $H(q)$ is related to the Fourier transform of the integral of the electron density profile over the diffuse phase boundary. We assume a sigmoidal-gradient model for the electron density profile over the phase boundary, i.e. the smoothing function in Eqn (5) has a Gaussian form. This model is supported by thermodynamic arguments and has been suggested to occur more likely in nature.29

The characteristic value of the sigmoidal-gradient model, $\sigma$, is the...
standard deviation of the Gaussian function. It is related to $H(q)$ as follows:

$$H^2(q) = \exp\left(-4\pi^2\sigma^2 q^2\right)$$  \hspace{1cm} (6)

The diffuse layer thickness is defined by $E = \sigma \times 12^{1/2}$.  

Following this approach, we have estimated the diffuse layer thickness for the 50 wt% SSC samples. These thicknesses, as well as their uncertainties, are shown in Fig. 4. The relatively large uncertainty of the diffuse layer thickness originates from the challenges in the determination of the background intensity due to the relatively high level of noise in the scattering background. For the samples with various BD-to-ISO ratios, we find that the values of diffuse layer thickness are similar. Nonetheless, there appears to be a slight dependence of the diffuse layer thickness on the molar ratio of ISO – the more ISO, the thinner the diffuse layer. This result suggests that with the addition of more ISO, the intermixing energies between soft and hard segments become slightly greater and the degree of phase separation is slightly improved.

**AFM and optical microscopy of 50 wt% SSC samples**

We used AFM and optical microscopy to image cross-sections of the polyurethane samples.

For optical measurements, a small piece of polymer sample was mounted in a cross-section holder for cryo-facing. We identified large domains that were optically observable in all samples in the PU50 series. These large domains display a brighter phase signal than their surrounding material, indicating that they are on average harder/stiffer. However, as AFM data will show later, these micrometer-scaled bright domains and darker regions contain finer structures of hard and soft segments. To demonstrate, we show two representative optical micrographs of PU50 samples (PU50-0 and PU50-100) in Fig. 5. The micrometer-sized granular structures are clearly visible, which are indicative of the presence of spherulites in these samples. These large structures may account for the low-$q$ power-law scattering identified in the SAXS data. Additionally, there appears to be a size dependence of the spherulites on the amount of ISO – the more ISO, the smaller the average size of the spherulites.
These optical observations of samples in the PU50 series are further verified by AFM results, which are shown in Figs 6 and 7. These AFM measurements were conducted in tapping mode, and we acquired both height and phase images.

Figure 6 shows AFM images of the PU50-0 sample. In the lower magnification images in Fig. 6(a), we clearly observe spherulites with dimensions greater than 10 μm. A certain degree of branching is also observed. At a higher magnification, we observe the finer structures of the spherulites, which demonstrate characteristics of a co-continuous morphology at length scales under 50 nm. This result is consistent with the SAXS findings.

Figure 7 shows AFM images of the PU50-100 sample. Here, at lower magnification (Fig. 7(a)), we again observe micrometer-sized spherical spherulites which on average are notably smaller than their counterparts in the PU50-0 sample. Results acquired at higher magnification (Fig. 7(b)) show a co-continuous morphology that is qualitatively very similar to that of the PU50-0 sample. This observation suggests that the addition of ISO in the hard segments may modify the details of the nanometer-scale microstructure but does not change the nature of it.

AFM and optical microscopy of 70 wt% SSC samples
Our optical microscopy measurements show that for the PU70 series samples, only PU70-0 exhibits a discernable globular structures with diameters of ca 5 μm (images not shown), which suggests that the formation of such structures is unfavorable with the addition of ISO.

The optical microscopy observations are further supported by the AFM results. Figure 8(a) shows that PU70-0 has low-contrast micrometer-scale agglomerates, whose size and shape resemble that identified from optical micrographs. At a submicrometer scale (Fig. 8(b)), both in height mode and phase mode of AFM measurements, a granular structure characteristic of isolated hard domains is observed. In fact, all samples in the PU70 series show very similar, poorly defined globule-like submicrometer structures through AFM, a result consistent with the SAXS findings.

Interestingly, the sample with the pure ISO chain extender (PU70-100) also shows spherulite-like structures in AFM (Fig. 9(a)). However, the sizes of these structures are below 1 μm. This size also coincides with the structural inhomogeneities on the scale of hundreds of nanometers identified in the SAXS analysis and illustrated...
Segmented polyurethanes with ISO chain extender hard segments, and two morphologies, were prepared and compared with those with BD or BD/ISO mixed chain extender. TPU s with 50 wt% SSC displayed co-continuous morphology, which was established from AFM and optical microscopy and confirmed by previous dynamic mechanical tests, while the series with 70 wt% SSC resulted in globules of hard phase dispersed in the soft phase. Increasing ISO content led to smaller domains.

The radius of spherical hard domains in the 70 wt% SSC series measured using SAXS varied between 2.4 and 2.9 nm, decreasing in size with increasing ISO content. Also the mean separation distance decreased from 12.4 to 8 nm with increasing ISO content in the chain extender mixture from zero to 100 wt%.

In the 50 wt% SSC series, correlation length and average repeat distances became smaller with increasing ISO content, implying that the number of domains increased. Boundary layer thickness was estimated to be around 0.5 nm, decreasing slightly with increasing ISO content.

Spherulitic structures of micrometer size were found in all samples using optical microscopy in the 50 wt% SSC series and in PU70-0. AFM gave evidence of spherulites of submicrometer size in all samples with 70 wt% SSC and hard domains of around 20 nm.

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