Study on Mechanical Properties and Viscoelastic Properties of Bio-polyurethanes

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Abstract: The bio-polyester polyol has been prepared by azelaic acid and 1,3-propanediol (1,3-PD) from biomass with esterification synthesis method, and MDI (4,4'-methylenebis (phenyl isocyanate)), H₂MDI and IPDI (isophorone diisocyanate) were used as isocyanates, 1,4-butanediol (1,4-BD) was used as chain extender. It also had been set the general polyurethane with SS-106 polyol, and bio-polyurethane without chain extender as control groups. The viscoelastic behaviors of the bio-polyurethanes were explored using a rubber processing analyzer (RPA) in the mode of strain sweep. And the mechanical properties (tensile strength, hardness value, resilience, abrasion resistance) were characterized by UTM, shore A, ball rebound and taber abrasion resistance tester. From the results above, the bio-polyurethane which synthesized in this research with bio-polyester polyol showed better abrasion resistance, elongation rate and viscoelastic properties compared to the general polyurethane material as elastomers.

Keywords: bio-polyurethane, bio-polyester polyol, viscoelastic properties, abrasion resistance, mechanical properties.
types and amounts of polyols, isocyanates, and chain extenders in the precursor mixture. PU is segmented block copolymer composed of a soft domain (polyols) and a hard domain (isocyanate and the chain extender). The polyol in the soft domain gives the PU its elastic quality, while the hard domain (depending on its nature) confers hardness and rigidity. Thus, micro-phase separations and the contents of the soft and hard domains significantly affect the mechanical properties of PU.

Biodegradable elastomers are expected to be suited for any application requiring the use of a flexible, elastic material such as soft tissue engineering, the work reported herein involves the synthesis and characterization of a series of biodegradable linear PU elastomers.

In this research, the azelaic acid which is extracted from castor beans\(^6\) which was synthesized with 1,3-propanediol (1,3-PD) which prepared from fermentation process of biomass to make the bio-polyester polyols as the bio-based polyol. And polyols of that type offer lower viscosity than oligoesters derived from dicarboxylic acids and glycols\(^7\) which could provide superior mechanical properties for PU materials as elastomers.

**Experimental**

**Raw Materials.** The raw materials in this research were shown in Table 1. And diisocyanates were used with industrial class, other materials were used with chemical pure class. The nitrogen gas which used as protect gas in polyester synthesis process was from Daesung Co.

**The Polymerization of Polyester Polyol:** The mechanism for polymerization of polyester polyol was shown in Scheme 1. A typical polymerization reaction was carried out as following: azelaic acid powder and 1,3-PD were poured into the reaction system. The mixture was stirred by a magnetic stirrer at 400 rpm. And first 4 h, it was controlled below 180 °C with atmosphere of nitrogen, and next 4 h, raised the temperature of 200 °C and dropped 50 ppm stannous octoate\(^8\) as catalyst, and last 4 h, removed the nitrogen atmosphere and set the vacuum system (2 torr)\(^9\) with the temperature of 160 °C, then cooled down the system temperature below 60 °C, and the polyester polyol in this research had been synthesized.

**Polymerization of Polyurethane Materials:** The PU polymerization raw materials ratios were shown in Table 2. Polyols, diisocyanates and chain extender had been poured into reaction system by one-step synthesis method, stirred with 200 rpm at room temperature, aged at 80 °C for 2 weeks.

**Characterization.** Acid Number Characterization of Polyester Polyol:

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbr.</th>
<th>Structure</th>
<th>(M_n) (g)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azelaic acid</td>
<td>Emeox 1144</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>188.22</td>
<td>Emery Oleochemicals</td>
</tr>
<tr>
<td>Diphenyl-methane diisocyanate</td>
<td>MDI</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>250.25</td>
<td>Kumho Co.</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>1,3-PD</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>76.10</td>
<td>Daejung Co.</td>
</tr>
<tr>
<td>1,4-Butanediol</td>
<td>1,4-BD</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>90.12</td>
<td>Daejung Co.</td>
</tr>
<tr>
<td>Poly(1, 4-butylene adipate)</td>
<td>SS-106</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>1000</td>
<td>Songwon Industrial</td>
</tr>
<tr>
<td>4,4'-dicyclohexyl methane diisocyanate</td>
<td>H(_2)MDI</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>262.3</td>
<td>Songwon Industrial</td>
</tr>
<tr>
<td>Isophorone diisocyanate</td>
<td>IPDI</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>222.3</td>
<td>Covestro Chemical</td>
</tr>
</tbody>
</table>

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Acid Number and Hydroxyl Number. Table 3 showed the results of acid number, hydroxyl number and $M_n$ of bio-polyol and SS-106, from this table, it can be found that the acid number of bio-polyol is small, which means the degree of esterification reaction is high. And compare to SS-106, the results of hydroxyl number and $M_n$ of bio-polyol are almost similar to polyols from petrochemical industry, which means bio-polyol...
could be a good raw material for PU synthesis process.

**Viscoelastic Properties.** As the dynamic strain sweep mode, it is always used for explaining Payne effect of rubber materials to describe the dispersion state of fillers. The more uniform dispersion state, the more homogeneous matrix, and then, the larger storage/loss modulus and also higher regular elastic/viscous torque of the materials. But as bio-TPUs in this research, due to without any other filler in matrix, so when discussed with “Payne Effect” of TPU matrix, it is mainly about the regularity of block (soft segments and hard segments) arrangement distribution (shown in Figure 3), thus, the more homogeneous block arrangement distribution, the larger storage/loss modulus and higher elastic/viscous torque of TPU materials. Otherwise, it also could be known whether the array distribution of TPU matrix is through the dynamic strain sweep mode results.

The viscoelastic results of PU samples were shown in Figure 1. From the figures, it can be found that compared to the SS-106 (the feedstock for petroleum cracking), although there is a disparity, the bio-polyester polyol also showed good performance for mechanical properties when reacted with MDI and 1,4-BD. The higher storage modulus value, the better segments distribution, the higher loss modulus value, the more anti destructive property. In TPU 2, 3, and 4, it can be found that MDI could provide higher storage modulus and loss modulus compare to IPDI and H$_2$MDI. And in TPU 2 and 5, it can be found

<table>
<thead>
<tr>
<th></th>
<th>Acid number (mg KOH/g)</th>
<th>Hydroxyl number (mg KOH/g)</th>
<th>$M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-polyol</td>
<td>0.70</td>
<td>125.7</td>
<td>892.46</td>
</tr>
<tr>
<td>SS-106</td>
<td>1.40</td>
<td>112.2</td>
<td>996.35</td>
</tr>
</tbody>
</table>

**Figure 1.** Dynamic strain sweep of $G'$, $G''$ for samples at a frequency of 60 cpm and at a temperature of 60 °C.

**Figure 2.** Dynamic strain sweep of $S'$, $S''$ for samples at a frequency of 60 cpm and at a temperature of 60 °C.
when 1,4-BD had been added as chain extender, the viscoelastic property had increased with the segments distribution regularity.

Figure 2 showed the results of elastic torque and viscos torque, from the curves of elastic toque, it could be found at low strain amplitudes, TPU 1 showed smaller value of $S'$, but when at high strain amplitudes, TPU 1 presented a great increase and always on the top of others, which means TPU 1 had the best elastic restore performance in this research, as for TPU 2, it showed relatively stable trend compared to other samples during all the strain amplitudes stage, and also presented great elastic performance. And from the curves of viscos torque, it was found that TPU 1 and TPU 2 showed high strain amplitudes, which means these two TPU materials had great viscous property.

**Mechanical Properties.** The tensile strength and elongation rate results were shown in Table 4. From this table, it can be found that the SS-106(TPU 1) could provide the best tensile strength in this research, and in TPU 2, 3 and 4, with the same ratio of disocyanate, MDI provided the best tensile strength in TPU synthesis process.

Also, compared with TPU 5, TPU 2 showed the better modulus, but as strain, which also said as elongation rate, the TPU without chain extender showed larger strain value than other TPU samples, the reason is chain extender could increase the reaction rate\(^\text{16}\) of PU synthesis, and also could reduce the ratio of carboxyl end group,\(^\text{17}\) which could improve the mechanical properties of TPU materials, such as hardness and tensile strength.

The resilience result (percentage rebound value $R$) can be calculated from the equation below:\(^\text{18}\)

\[
R(\%) = \frac{h}{h_{\text{max}}} \times 100
\]

where $h$ is the ball rebound height, expressed in mm; $h_{\text{max}}$ is the height of the drop (500 mm).

The results of resilience were shown in Figure 4, it could be found TPU 2 showed the largest rebound value, which means this material had the best resilience. It could be found TPU synthesized by bio-polyester polyol also showed the same hardness properties with traditional TPU material, which is an important mechanical property in TPU industry (Figure 5). Also, from the Figure 6, TPU 2 showed the smallest mass loss per 1000 cycles, which means this material has the best abrasion resistance in this research. The probable reason for the results is: the soft segment in bio-polyester polyol has longer carbon chain and lower glass state temperature,\(^\text{19}\) which could provide better molecular flexibility and increase the hysteresis characteristic of polymer,\(^\text{20}\) thus the bio-PU showed these great performance.

![Figure 3. Viscoelastic illustration of TPUs.](image)

![Figure 4. Resilience results of TPUs.](image)

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**Table 4. The Tensile Strength and Elongation Rate of TPUs**

<table>
<thead>
<tr>
<th>Samples</th>
<th>100% modulus (MPa)</th>
<th>300% modulus (MPa)</th>
<th>Final modulus (MPa)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU 1</td>
<td>9.24</td>
<td>10.47</td>
<td>10.56</td>
<td>325</td>
</tr>
<tr>
<td>TPU 2</td>
<td>5.21</td>
<td>7.26</td>
<td>7.58</td>
<td>402</td>
</tr>
<tr>
<td>TPU 3</td>
<td>2.98</td>
<td>X</td>
<td>3.15</td>
<td>127</td>
</tr>
<tr>
<td>TPU 4</td>
<td>3.57</td>
<td>4.98</td>
<td>5.29</td>
<td>347</td>
</tr>
<tr>
<td>TPU 5</td>
<td>3.05</td>
<td>5.76</td>
<td>6.92</td>
<td>550</td>
</tr>
</tbody>
</table>

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\(^{16}\) L. L. Li et al., *Polymer*, 43, 5, 2019, 678.
Conclusions

In this research, the synthesis and properties analysis (mechanical and viscoelastic) of bio-PU materials had been studied. The bio-polyester polyol was prepared by azelaic acid and 1,3-PD with esterification synthesis method, and MDI, H₁₂MDI and IPDI were used as isocyanates, 1,4-BD was used as chain extender, and from the characterization process, it can be found the bio-polyester polyol could provide good viscoelastic and mechanical properties when combined with diisocyanates, especially with MDI, such as storage modulus, loss modulus, tensile strength, elongation rate, resilience, hardness and abrasion resistance, the probable reason is due to the regularity of block (soft segments and hard segments) arrangement distribution. The more homogeneous block arrangement distribution, the larger storage/loss modulus and higher elastic/viscous torque of TPU materials. As an important elastomer material in polymer industry, the bio-PU materials will attract great attention in the near future.

References