High Performance TPU’s based on Polycarbonate Soft Segments

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Abstract:
Polycarbonate soft segments provide an improved balance of oil resistance and resistance to hydrolytic type degradation. Ester type polyurethanes are often selected over ether types for hydraulic sealing applications because ester types are more resistant to oil swell. Ester types, however, are not resistant to chemical degradation by hydrolytic type mechanisms and often fail prematurely not just in hot humid environments but also in contact with acidic or alkaline additives and degradation products which may be found in some hydraulic fluids.

The work presented herein compares 85-90 Shore A polycarbonate, polyether, and polyester type TPU seal compounds demonstrating a polycarbonate type TPU with low compression set, high strength, and an improved balance of oil resistance and hydrolytic stability.

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A. Background:
Thermoplastic polyurethanes are random segmented copolymers formed by the reaction of a diisocyanate, a short chain diol or chain extender, and either a polyether type or polyester type macro diol (a.k.a. polyol) as shown in figure 1 below. The polyol forms a soft elastomeric block and the diisocyanate and the chain extender come together to form a hard block.

Figure 1: TPU Random Segmented Structure

<table>
<thead>
<tr>
<th>Soft Block</th>
<th>Hard Block</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO---OH</td>
<td>+</td>
</tr>
<tr>
<td>Polyol</td>
<td>NCO------NCO + HO------OH</td>
</tr>
<tr>
<td></td>
<td>Diisocyanate</td>
</tr>
</tbody>
</table>

Random Segmented Copolymer TPU

The most common high performance automotive grades of TPU are based on 4,4’ methylene bis diphenylene diisocyanate (MDI), 1,4 butanediol (BDO) and either polytetramethylene ether (PTMEG) or polycaprolactone ester (PCL) type polyols. Other industrial grades may be based upon ether polyols such as EO capped polypropylene ether (EO-PPG) polyols or adipate ester polyols such as polybutylene adipate (PBA) or polyethylene adipate (PEA) types.

High performance diisocyanates such as para-phenylene diisocyanate (PPDI) or 3,3’ toluidine diisocyananate (TODI) replace MDI to gain the highest performance in applications where high temperature resistance or superior dynamic properties are critical. For similar performance advantages, BDO may be replaced with hydroquinone bis hydroxyl ethyl ether (HQEE) or hydroxy ethyl ether of resorcinol (HER).
Figure 2a: Typical Diisocyanates used in TPUs

**MDI:**
\[
\text{NCO} \quad \begin{array}{c}
\text{CH}_3 \\
\text{NCO}
\end{array} 
\text{CH}_3
\]

**TODI:**
\[
\text{NCO} \quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{NCO}
\end{array} 
\]

**PPDI:**
\[
\text{NCO} \quad \begin{array}{c}
\text{NCO}
\end{array} 
\]

Figure 2a: Typical Chain Extenders used in TPUs

**BDO:**
\[
\text{HO-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-OH}
\]

**HQEE:**
\[
\text{HO-CH}_2\text{CH}_2\text{O} \quad \begin{array}{c}
\text{O-CH}_2\text{CH}_2\text{-OH}
\end{array} 
\]

**HER:**
\[
\text{HO-CH}_2\text{CH}_2\text{O} \quad \begin{array}{c}
\text{O-CH}_2\text{CH}_2\text{-OH}
\end{array} 
\]
Figure 2c: Typical Polyols used in TPUs

**PTMEG Ether:**  \( \text{HO-}[\text{(CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{)}\text{-0}]_n\text{-H} \)

**PBA Ester:**  \( \text{H(-O-(CH}_2\text{)}_4\text{-}[\text{O-C-(CH}_2\text{)}_4\text{-C-O(CH}_2\text{)}_4\text{O}]-\text{H}} \)

**PCL Ester:**  \( \text{HO-}[\text{(CH}_2\text{)}_5\text{-C-O-}]_x\text{(CH}_2\text{)}_4\text{[-OC-(CH}_2\text{)}_5]_y\text{-OH}} \)

**Poly Carbonate:**  \( \text{H(-O-(CH}_2\text{)}_6\text{-}[\text{O-C-O-(CH}_2\text{)}_6\text{-O-C-O(CH}_2\text{)}_6\text{O}]-\text{H}} \)

**EO/PPG Ether:**  \( \text{HO-}[\text{(CH}_2\text{CH}_2\text{CH}_2\text{-O})_x\text{-}(\text{CH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{-O})_y\text{-}(\text{CH}_2\text{CH}_2\text{O})_z\text{-H}} \)

**B. Structure-Property Relationships:**

TPU chemistry provides remarkable versatility allowing one to mix and match diisocyanate, chain extender, and polyol components to optimize one or more key properties such as temperature resistance, oil resistance, low temperature flexibility, resilience, abrasion resistance all over a broad range of hardnesses from less than 60 ShoreA to greater than 70 Shore D.

Elastomeric TPUs exist in a two phase state where the polyol based soft segment forms a continuous rubbery phase which is held together by dispersed hard segment domains forming in a “virtually crosslinked network” at normal use temperatures. See figure 3 below. The hard segments however melt at elevated temperatures and allow thermoplastic melt processing. When cooled the hard segment domains and “virtual crosslinks” re-form.
The ability of the hard segments to segregate into discrete domains is critical to the development of many critical properties such as high resilience, low glass transition temperature (Tg), and high softening points. The dominant factors influencing the ability to phase separate are the relative solubilities of the hard and soft segments and the ability or tendency of either to crystallize. Polyol soft segments with lower polarity, higher molecular weight, and reduced ability to hydrogen bond or electrostatically interact with the hard segment favor higher phase separation. The hard segments being derived from the combination of diisocyanate and chain extender depends on both ingredients for high symmetry and the ability to fit into highly ordered, densely packed extended arrays of hydrogen bonded and preferably crystalline structures.

The urethane hard segment is generally very thermally and chemically stable compared to the soft segment so it is primarily the nature of the soft segment that determines oil resistance, hydrolytic stability and chemical resistance. And of course the elastomeric properties such as resilience and low temperature flexibility are dominated by the soft segment character.

Toughness, tear resistance and fatigue/crack growth resistance are derived from both phases. Hard segment domains with a crystalline nature which can yield somewhat and/or undergo strain induced crystallization and soft segments with sufficient symmetry to undergo strain induced crystallization generally have superior toughness and resistance to crack growth. These characteristics are usually enhanced by a high degree of phase separation.
C. Polycarbonate Polyols:
Polycarbonate polyols first appeared in the market place in the 1970’s. Based on patent literature, technical publications and commercializations one finds that interest focused on optical properties such as clarity, non-yellowing, and UV resistance. The magnetic media binder industry also found that the carbonate polyols provided the high polarity and specific adhesion character of the polyester polyols but did not degrade rapidly in warm humid environments as did the polyesters. Through the 1980’s the leather and fabric coating industries seemed to be the only industries who recognized polycarbonate polyol’s unique ability to provide a soft polyurethane with excellent hydrolysis resistance, resistance to body oils, and excellent UV stability.

The medical device industry recognizing that polyester type TPUs were rapidly hydrolyzed in the body and that polyether types were vulnerable to metal ion catalyzed oxidation has recently moved to polycarbonate type TPU elastomers for implantable devices such as drug delivery catheters and implantables, vein grafts, and orthopedic implants.

The common polycarbonate polyol used in elastomers is poly hexamethylene carbonate diol. Comparing the polyhexamethylene carbonate structure to a typical polyester polyol like a polycaprolactone one can see great similarity. Both have a long polymethylene sequences connected by a very polar carbonyl structure. This carbonyl structure is what gives high resistance to oils. The big improvement, as will be shown in the next section, is that the carbonate structure unlike the ester structure is not subject to rapid hydrolysis.

D. Recent Developments:
We found that polycarbonate polyols can provide TPUs which demonstrate a unique combination of excellent oil resistance and excellent hydrolytic stability not available in either an ether based TPU or an ester based TPU. The polycarbonate backbone is also well known to have excellent UV and oxidation resistance. Heretofore in order to obtain the required oil resistance, hydraulic seals for demanding automotive, truck, or construction machinery designers specified polyester type TPUs. These provide the toughness and oil resistance required but degrade rapidly in hot humid environments. Often what is hoped or expected is that the application is sufficiently rigorous mechanically that the part will wear out so rapidly that hydrolytic failure is not often encountered.
E. Experimental:

a. TPU Synthesis:
A series of TPU s was synthesized based upon soft segments derived from either polycaprolactone ester (PCL), polytetramethylene ether (PTMEG), or polyhexamethylene carbonate (PC) polyols. The hard segment was comprised of methylene bis diphenyl diisocyanate (MDI) or 3, 3’ toluidine diisocyanate (TODI) combined with either 1,4 butanediol (BDO) or hydroquinone bis hydroxyether ether (HQEE). Synthesis was conducted by one shot hand cast method where the chain extender, polyol, and then diisocyanate were weighed into a mixing vessel at 100C, stirred vigorously, and then poured into a preheated Teflon lined tray. The tray was placed in a 150C oven for 1.5 hrs then 110C oven for 16hr. The resulting solid polyurethane was granulated, dried at 80C overnite, and then molded at 200-210C.

b. Test Result:

Table 2: Comparative Hydrolysis Resistance of 85A TPU s – PTMEG vs PCL vs PC

![Tensile Strength Change Aged in Water](image-url)
Table 3: Comparative Properties of 85A TPUs - PTMEG vs PCL vs PC

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Ester Type</th>
<th>Ether Type</th>
<th>Polycarbonate Type</th>
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<tbody>
<tr>
<td>Polyol MW</td>
<td>MDI/BDO/PCL 2000</td>
<td>MDI/BDO/PTMEG 1000</td>
<td>MDI/BDO/PC 2000</td>
</tr>
<tr>
<td>Test Data:</td>
<td>Shore A 84</td>
<td>84</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>Tensile St (psi) 7322</td>
<td>6440</td>
<td>6044</td>
</tr>
<tr>
<td></td>
<td>%UE 500</td>
<td>480</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>Die C Tear (ppi) 480</td>
<td>420</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td>Fuel C Swell/23C (%) 20.1</td>
<td>36.2</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>IRM Oil Swell/100C (%) 3.3</td>
<td>12.2</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>H20 Swell/120C (%) 2.5</td>
<td>3.2</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>% Comp Set B, 22hr/100C 42</td>
<td>49</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Bashore Resilience (%) 34</td>
<td>48</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>DMTA Tg (C) -42</td>
<td>-34</td>
<td>-17</td>
</tr>
</tbody>
</table>

Table 4: TODI, BDO, and HQEE based TPUs

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>TODI/BDO</th>
<th>MDI/HQEE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol MW</td>
<td>TODI/BDO/PC 3000</td>
<td>MDI/HQEE/PC 3000</td>
</tr>
<tr>
<td></td>
<td>TODI/BDO/PCL 2000</td>
<td>MDI/HQEE/PCL 2000</td>
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<tr>
<td>Test Data:</td>
<td>Shore A 90</td>
<td>88</td>
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<tr>
<td></td>
<td>Tensile St (psi) 5160</td>
<td>5800</td>
</tr>
<tr>
<td></td>
<td>%UE 450</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td>Die C Tear (ppi) 495</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>% Comp Set B, 22hr/100C 55</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Bashore Resilience (%) 41</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>DMTA Tg (C) -27</td>
<td>-28</td>
</tr>
<tr>
<td></td>
<td>#903 Oil Swell 22hr/70C 6.8</td>
<td>6.4</td>
</tr>
</tbody>
</table>
F. Discussion and Conclusions:

Tables 2 and 3 demonstrate, in a direct comparison, a polycarbonate based TPU with superior (ether-like) hydrolytic stability and superior (ester-like) oil resistance. One sees that the PC TPU has high tensile strength and tear resistance. As is often the case however, the oil resistant PC has reduced resilience and higher Tg compared to the ether type. This is mitigated by using higher molecular weight polycarbonate, see table 4, but only at the expense of oil resistance. Compression set resistance of the PC was similar to either the ether and slightly reduced compared to the ester.

Table 4 demonstrates a higher molecular weight PC based TPUs where HQEE is substituted for BDO and TODI is substituted for MDI. One sees that HQEE significantly improves compression set resistance and the PC seem to give higher tear strength. Compared to the 2000 molecular weight based PC TPU of table 3, resilience and Tg are improved.