Rheological Characterization of Medical Thermoplastic Polyurethanes

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Abstract

The use of thermoplastic polyurethanes (TPUs) in the medical device industry is widespread due to the unique combination of biological properties, abrasion resistance, and processability that they provide. Phase separation at the microscopic level within the morphology of TPUs results in the presence of hard and soft polymer block segments, creating these desirable characteristics. However, the microphase separation also complicates the understanding of TPU structural properties, particularly their flow properties, and creates difficulties during melt processing. Properties of several TPUs were characterized with a novel rheological method to quantify the effects of time dependence and are reported in this study.

Introduction

Thermoplastic polyurethanes (TPUs) are widely used in many medical devices due to their unique combination of biological and mechanical properties [1-4]. TPUs are segmented copolymers, consisting of micro-phase separated hard and soft domains. The stiffer hard segment typically consists of an aromatic diisocyanate and a low molecular weight diol called a chain extender. The relatively flexible soft segment typically consists of a higher molecular weight macrodiol.

The polymerization reaction in TPUs can proceed through either a one-step process or a two-step process [4]. The difference between the processes is essentially the addition sequence of the raw materials for synthesis. In a one-step process, all the raw materials for the synthesis are added at once, whereas, in a two-step process, the polyl is first reacted with an excess of isocyanate to produce an isocyanate end-capped pre-polymer. The pre-polymer is then reacted with a stoichiometric quantity of the short chain diol or the chain extender. The pre-polymer can also be seen as the soft segment and the reaction of the pre-polymer with the chain extender as the formation of the hard segment.

Due to the high degree of thermodynamic incompatibility between hard and soft segments, a complex morphology arises within the material. Hard segments separate from the soft segments, aggregating into larger hard domains, but the separation is not complete. Generally, some soft segments remain included in the hard microphase, and some hard segments remain dissolved in the soft microphase. The degree of phase separation can be influenced by the choice of macrodiol for the soft segment, thus creating differences in segment interaction and the polymer properties that depend on it. The chemical composition and relative amounts of both the soft and hard segments can be varied in TPUs to produce widely different final polymer properties.

Many of the desirable properties possible in TPUs are a direct result of the phase separated morphology and the resulting interaction between the hard and soft segments. Soft segment composition tends to have a greater impact on the long term biostability of the polymer, with polysiloxane based soft segments being the most stable [5, 6].

Time Dependence of TPU Rheology

During melt processing, the TPU becomes completely molten and the phase separated structure gives way to a single phase, homogeneous melt. The rheology of TPUs is complex and shows effects not commonly observable in melt rheology of other polymers. Two factors are seen to play a role in this complex behavior, depolymerization and allophanates. During TPU synthesis, the reaction between isocyanate and hydroxyl end groups forms a urethane bond. The urethane bond is itself reversible at high temperatures, and this reversal can lead to a complex rheological behavior. Several studies have looked into the effects of this depolymerization reaction on the TPU melt rheology [7-9]. Allophanates are linkages formed due to the reaction between an isocyanate group and an already formed urethane bond. The allophanate reaction occurs as depicted in Figure 1.

![Allophanate Reaction](image)

Figure 1: The reversible allophanate reaction, a side reaction between isocyanate and urethane.

Allophanates dissociate at TPU melt temperatures [10] and this dissociation occurs over a period of time, giving rise to the time dependence of TPU viscosity. Time dependence is a factor of the amount of allophanates present in the system, the kinetics of allophanate dissociation and residence time of the melt in the
processing equipment. It has been observed that TPU systems with higher incompatibility between the soft and the hard phases show a greater amount of allophanates, such as in siloxane based TPUs [10]. The presence of allophanates also creates effects in the molecular weight of the TPU, as allophane crosslinks can significantly increase the higher molecular weight component of the TPU. Upon dissociation of the allophanates this component has been seen to reduce [10].

In this study, we examine the time dependence of the melt rheology in TPUs and evaluate the role of allophanates and their dissociation on TPU rheology and processing.

Materials

Five medical TPUs with varying silicone content were studied in this work. Two thermoplastic silicone-polycarbonate-urethanes (TSPCUs), and three thermoplastic silicone-polyether-urethanes (TSPUs) were evaluated; these materials and their relevant properties are included in Table 1. All materials are manufactured by DSM, with the exception of Elast-Eon 2A™ which is manufactured by Abbott.

<table>
<thead>
<tr>
<th>Material Name</th>
<th>Reference Name</th>
<th>Silicone Content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CarboSil™ 20 80A</td>
<td>TSPCU20-80A</td>
<td>20</td>
</tr>
<tr>
<td>CarboSil™ 20 55D</td>
<td>TSPCU20-55D</td>
<td>20</td>
</tr>
<tr>
<td>PurSil™ 20 80A</td>
<td>TSPU20</td>
<td>20</td>
</tr>
<tr>
<td>PurSil™ 35 80A</td>
<td>TSPU35</td>
<td>35</td>
</tr>
<tr>
<td>Elast-Eon 2A™</td>
<td>TSPU48</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 1: Materials evaluated in this study.

TSPCUs are formulated with a mixture of polycarbonate based and polysiloxane based macrodiols as the soft segment. TSPUs are formulated with a mixture of polyether based and polysiloxane based macrodiols as the soft segment. The numerical prefix after each material name indicates the amount by weight percentage of the silicone present in the TPU, whereas the hardness value is an indication of the ratio of soft to hard segments in the material. The hard segment for all materials is made up of methyl diphenylene isocyanate (MDI) and butanediol (BDO).

Experimental

Capillary Rheometry

Capillary rheometry was performed for each of the materials previously described. All samples were evaluated using a Rosand RH2200 twin bore benchtop capillary rheometer with 15 mm diameter barrel. All testing was performed with a 1 mm capillary die with a length-diameter (L/D) ratio of 32, and a 138 MPa (20,000 psi) pressure transducer. Rheometer parameters, including barrel temperature and applied shear rate, were set using the rheometer’s included Flowmaster™ software program, with shear rate controlled for each run by changing the movement speed of the piston through the barrel. Barrel temperatures were set based on recommended extrusion conditions provided by the manufacturer for each material. All materials were dried under vacuum at 60 °C until moisture content was measured below 200 ppm by Karl Fischer Coulometry.

In order to accurately characterize the rheology of TPUs across a range of shear rates, a new method was developed to account for the time dependence observed in some of the materials. Prior to initiation of shearing, to start from a point of thermal equilibrium, all materials were compressed to a pressure of at least 0.5 MPa and preheated at the melt temperatures for a total time of 300 seconds. Then, a constant shear rate test was performed, with the shear rate held at a given value for up to 1800 seconds after the preheating phase. Following the collection of shear viscosity data through time for each shear rate, data points at intervals of 100 seconds for each shear rate were compiled into new data sets. These new data sets then showed the shear rate vs. viscosity graph typical of rheological evaluation, but only for the specified time point since the initiation of melting. The set melting time specified by this method ensures that the time dependence of each TPU is captured consistently and can be compared to the rest of the TPUs. The transformation of data sets is demonstrated in Figure 2.

Following the transformation of data into the more typical shear rate vs. viscosity format, a simple power law model was fitted to the data for each material at each timepoint. The data was converted to a log-log plot of shear rate and viscosity, and the slope of the resulting plot used to determine the flow behavior index of each material. Equation 1 gives the basic power law model, and equation 2 shows the logarithmically transformed power law used with a log-log plot,

\[ \eta = m \gamma^{n-1} \]  

(1)

\[ \ln(\eta) = \ln(m) + (n - 1)\ln(\gamma) \]  

(2)

where \( \eta \) is the shear viscosity, \( m \) is the flow consistency index, \( n \) is the flow behavior index, and \( \gamma \) is the shear rate. From equation 2, the slope of the log-log plot is equal to the flow behavior index minus 1.
Figure 2: (a) Example TPU melt viscosity data for constant shear rates from 50 s$^{-1}$ to 250 s$^{-1}$; black line indicates 500s timepoint used to create new data set of shear rate vs. shear viscosity. (b) Log-log plot of shear rate vs. shear viscosity used to determine flow behavior index of TPU at 500s.

**Allophanate Titration**

Quantification of allophanates was performed on each material by titration of the allophanate bond with dibutylamine (DBA), an established method for allophanate content determination in polymers [11]. 4 grams of the materials was dissolved in 50 mL of dimethyl formamide (DMF) and 5 mL of 2.0 M DBA in toluene. The sample was stirred at 75 °C for 72 hours to allow all allophanates to react, then 20 g of the sample was transferred to a titration flask and diluted with an additional 70 grams of DMF. The samples, and a blank containing no polymer, were titrated with a Mettler Toledo T5 autotitrator using 0.3 M HCl in methanol as the titrant. The allophanate concentration was calculated from the result of the titration, and each material was tested in duplicate.

**Results and Discussion**

The time dependent rheological profile of TPUs is apparent when measured with constant shear rate capillary rheometry. Figure 3 shows the viscosity data obtained over a period of 2000 seconds at a constant shear rate of 50/s for all TPUs evaluated in this study. This shear rate was chosen because it is a typical shear rate seen during extrusion, a common processing method for TPUs. As demonstrated in Figure 3, a constant shear rate method does not give a constant viscosity value that would be expected for a typical polymer melt. The observed decrease in viscosity is due to the degradation of allophanate crosslinks at the elevated temperatures of the polymer melt. However, Figure 3 also demonstrates that not all TPUs exhibit the same degree of time dependence; all materials show a decrease in viscosity with time, but each material decreases by a different amount.

For each material, the change in viscosity was calculated as the percent difference between the initial and equilibrium viscosity. These values are available in Table 2. Due to slight fluctuations produced by small temperature variations within the rheometer, the equilibrium viscosity was defined as the average of the final 5 viscosity values measured.
Material | $\eta_0$, Pa s | $\eta_{equilibrium}$, Pa s | $\Delta \eta$, %
--- | --- | --- | ---
TSPCU20-80A | 2066 | 1163 | 43.7
TSPCU20-55D | 2360 | 1350 | 42.8
TSPU20 | 3080 | 2667 | 13.4
TSPU35 | 3488 | 2177 | 37.6
TSPU48 | 3744 | 1709 | 54.4

Table 2: Table of measured initial and equilibrium viscosity values for different TPUs, with calculated difference between the two values.

Furthermore, the change in viscosity was correlated to the silicone content of each TPU and plotted in Figure 4. For the TSPUs, there is a strong correlation between silicone content and difference between initial and equilibrium viscosity. However, the TSPCUs do not follow the trend of the TSPUs. This is likely due to the difference in soft segment caused by the polycarbonate backbone in the TSPCUs. Moreover, both types of TSPCUs contain 20% silicone and had similar changes in viscosity, suggesting that the silicone content in these materials still influences the time dependence of the viscosity.

Quantification of allophanate content was performed on each material to determine the impact of allophanate crosslinks on rheology. The results of the testing demonstrate that allophanate crosslinks are present in pellets of each material in a measurable amount. In addition, the amount of allophanates has an impact on the amount of time dependence seen in a given polymer’s rheological profile. As the amount of silicone in the material increase, the amount of allophanates measured appears to show a general increasing trend, with the highest silicone material, TPSU48, clearly having a much higher allophanate content than any other material. Table 3 shows the measured allophanate content of each polymer.

<table>
<thead>
<tr>
<th>Material</th>
<th>Allophanate Content (wt. %) ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSPCU20-80A</td>
<td>0.0451 ± 0.015</td>
</tr>
<tr>
<td>TSPCU20-55D</td>
<td>0.0471 ± 0.007</td>
</tr>
<tr>
<td>TSPU20</td>
<td>0.0672 ± 0.017</td>
</tr>
<tr>
<td>TSPU35</td>
<td>0.0731 ± 0.032</td>
</tr>
<tr>
<td>TSPU48</td>
<td>0.135 ± 0.009</td>
</tr>
</tbody>
</table>

Table 3: Measured allophanate content for each TPU tested.

An additional consequence of the time dependent rheology of TPUs is the variable value of the flow behavior index. Using the method outlined in the experimental section, the flow behavior index was calculated for each material at 100 second intervals, starting at 400 seconds and ending at 1000 seconds. Calculation was ended at 1000 seconds due to limitations imposed by the size of the rheometer; at higher shear rates, the rheometer could only hold enough material for approximately 1000 seconds of shearing. The calculated values for each material were plotted against time in Figure 5. For all tested TPUs, the flow behavior index increased throughout time as allophanate crosslinks broke, lowering the apparent molecular weight of the polymer. With less interaction between polymer chains, the polymer melt exhibits less shear thinning and becomes more Newtonian, as observed in Figure 5.

Figure 4: Silicone content vs. viscosity change for all measured TPUs.

Figure 5: Plot of flow behavior index through time for all materials evaluated.
Conclusions

In this study, we demonstrated and analyzed the time dependent rheology of several TPUs. Data was collected across a range of typical processing shear rates and transformed using a new method into data sets that could be used to accurately describe the polymer melt behavior at a given time and shear rate. In addition, allophanate crosslink content of each TPU was measured to quantify the effect of silicone content on allophanate formation.

It was observed that rheological time dependence is directly related to silicone content in TPUs. As silicone content increases, the soft segment becomes more incompatible with the hard segment, resulting in greater separation between the micro-phases. The direct relationship between silicone content and time dependent rheology was apparent for TSPUs, but was also consistent between multiple TSPCUs with identical silicone content. In the case of the TSPCUs, a direct comparison to TSPUs based on silicone content alone is not possible due to the presence of polycarbonate macrodiol in the soft segment changing the interactions between soft and hard segments. Overall, the increased separation between microphases caused by additional silicone increases the ability of allophanates to form, as measured through quantification of allophanate content by titration.

The quantification of TPU melt rheology using this unique method provides several benefits. This method allows for increased accuracy in the modeling of melt processing operations by taking into account both the shear rate the material experiences and the time the material has been melted. By accurately measuring the time dependence of a given material, a model can more accurately determine the process conditions at a given point and produce a model that more closely mirrors reality.

References