Effect of the chemical structure and processing conditions on the morphology and electrical conductivity TPU/EG composites

Beate Krause, Francesco Piana, Jürgen Pionteck
Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany
pionteck@ipfdd.de

Abstract
With the aim to produce electrically conductive composites, we analysed the influence of the processing conditions and chemical structure of thermoplastic poly(urethane) (TPU) on the electrical percolation threshold concentration in thermoplastic poly(urethane)/expanded graphite (TPU/EG) composites. For that, TPU with varying hard segment (HS) structure and HS content have been synthesized (Table 1). Commercial products (Elastollan series of Elastogran, BASF group) with same HS structure but different soft segments (SS) and varying composition – and therefore different hardness - have been used (S60A15 (hardness: 63 Shore A), 1185A (87 shore A, 36 shore D), and C74D50 (73 Shore D). Conductivities σ have been determined on compression moulded plates.

Table 1: Structure and composition of self-made TPU

<table>
<thead>
<tr>
<th>Name</th>
<th>Isocyanate</th>
<th>Molar composition (DI / BD / PTHF)</th>
<th>HS content (wt.%)</th>
<th>γ (mN/m)</th>
<th>PC wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDI-2</td>
<td>MDI</td>
<td>2 / 1 / 1</td>
<td>17</td>
<td>41</td>
<td>&lt;10</td>
</tr>
<tr>
<td>MDI-5</td>
<td>MDI</td>
<td>5 / 4 / 1</td>
<td>45</td>
<td>45</td>
<td>&lt;8</td>
</tr>
<tr>
<td>H12-MDI-2</td>
<td>H12-MDI</td>
<td>2 / 1 / 1</td>
<td>17</td>
<td>39</td>
<td>8</td>
</tr>
<tr>
<td>H12-MDI-5</td>
<td>H12-MDI</td>
<td>5 / 4 / 1</td>
<td>46</td>
<td>42</td>
<td>&lt;8</td>
</tr>
<tr>
<td>IPDI-5</td>
<td>IPDI</td>
<td>5 / 4 / 1</td>
<td>44</td>
<td>41</td>
<td>6</td>
</tr>
</tbody>
</table>

Monomers: MDI: 4,4’-methylenebis(phenyl isocyanate); H12-MDI: methylenebis(cyclohexyl isocyanate); IPDI: isophorone diisocyanate; BD: 1,4-butanediol; PTHF: poly(tetrahydrofuran) (Mn = 1400 g/mol)

Melt mixing, solution casting and in-situ polymerization have been compared. The in-situ polymerization is limited in regard to the filler amount which can be incorporated into the polymer matrix. At the maximum filler concentration of 2 % only MDI-2 and IPDI-5 showed some electrical conductivity. The observed percolation concentrations (PC) of composites prepared by melt mixing of synthesized TPU are in between 6 and 10 wt.%. In both cases no correlation between chemical structure, composition, physical properties, e.g. surface tension γ (estimated from Parachor method [1]), to the electrical behavior could be found.

Solution blending resulted in composites with more than 10 wt.% filler contents. The use of these materials as masterbatch for melt mixing with pure TPU was not beneficial in regard to conductivity and percolation concentration when compared to direct melt mixing of TPU with EG. Melt mixing of the commercial products at processing conditions where a homogeneous composites is obtained resulted in different PC with the lowest one of < 2 wt.% for TPU C74D50, the hardest polymer with the highest HS content and highest degree of crystallinity (Figure 1). However, when changing the processing conditions (melt mixing temperature, compression moulding temperature, and rotational speed of the mixer) of the TPU 1185A/EG composites the primary observed PC of ca. 4 wt.% could be shifted to < 2 wt.% (Figure 2, [2], the same which was observed for TPU C74D50 composites without optimization the processing conditions. Thus, again no correlation between structure and electrical properties can be proven till now.

It should be mentioned, that at the conditions optimized in regard to electrical conductivity a very inhomogeneous material was obtained. Furthermore, the conductivities determined with two different electrode systems revealed increased resistance in the surface near regions. Overall, the conductivities of the composites are rather small if compared to that of EG.

Acknowledgements
We are grateful for the support of the project by the Deutsche Forschungsgemeinschaft (DFG) and to SGL Carbon for providing the expanded graphite.
References


**Figure 1:** Electrical conductivity of TPU/EG composites prepared by melt mixing at standard conditions in dependence on EG content.

**Figure 2:** Successive shift of electrical percolation concentration of TPU 1185A/EG composites prepared at standard conditions (black squares) by optimizing the processing conditions melt mixing temperature (red circles), compression moulding temperature (blue uptriangles) and rotational speed (pink downtriangles).