The stabilisation of recycled polyethylene terephthalate with phosphorus-containing compounds in continuous processes of extrusion

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SUMMARY

An examination is made of the process of introducing a mixture of stabilisers – sterically hindered phenols and phosphites – to stabilise recycled polyethylene terephthalate (RPET) with an initial moisture content of ~0.5 wt% during continuous extrusion. It is shown that, using a mixture of stabilisers of optimum composition, it is possible to increase the molecular weight of the RPET and to achieve effective thermal stabilisation of the extruded polymeric material.

The extrusion of recycled polyethylene terephthalate (RPET) with a high moisture content leads to the degradation and to a reduction in the molecular weight characteristics of the polymer, which makes it impossible to manufacture extruded products with high physicomechanical characteristics [1].

The modification of RPET with a moisture content of ~0.5 wt% under conditions of continuous extrusion using a concentrate of pyromellitic dianhydride (PMDA) and phenylenebisoxazoline is an effective way to increase the molecular weight (MW) of the polymer; however, in this case the thermal stability of the obtained composites remains at a low level [1, 2].

It is well known [3-10] that phosphorus-containing compounds, such as phosphates and phosphites, have been widely used not only as thermal stabilisers for RPET but also as modifiers/chain extenders during its extrusion [for example, triphenylphosphate and bis-(2,4-ditetrabutylpheno) pentaerythritol diphosphite]. The process of chemical modification of RPET with triphenyl phosphate has been fairly well studied [5–8].

It has been demonstrated experimentally that cyclic, sterically hindered phosphites are characterised by high resistance to hydrolysis [11]. In Bimestre [12], a mechanism is proposed for the reaction of diphosphite with terminal hydroxyl groups of RPET, and it is also shown that its introduction into the recycled polymer is more effective by comparison with PMDA.

Earlier investigations into the modification of RPET with the above stabilisers were conducted on the recycled polymer having passed through a stage of preliminary drying to a residual moisture content not exceeding 0.02 wt%.

It was of interest to study the effect of thermal stabilisers (phosphates and phosphites) on the process of chain extension (increase in MW) and thermal stabilisation of RPET under conditions of an increased moisture content (up to 0.5 wt%) directly during extrusion, and also on the rheological and physicomechanical properties of the polymer obtained.

MATERIALS AND METHODS

The investigation was conducted on RPET in the form of flakes (OOO ZPP PLARUS, Russia) produced by the mechanical crushing of bottles, with an intrinsic viscosity [η] = 64–78 mL/g, and on virgin PET of PAPET grade (KP Chemical Corporation, South Korea) with [η] = 81–83 mL/g.

The stabilisers employed were as follows: bis-(2,4-ditetrabutylpheno) pentaerythritol diposphite – SZDiFt (Irgafos 126, Ciba, Switzerland); triphenyl phosphate (TPhP) (Disflamoll TP, Lanxess, Germany), and pentaerythritol tetrabis[3-(3,5-di-tert-butyl-4-
RESULTS AND DISCUSSION

The processing of RPET with a moisture content of over 0.02 wt% has a considerable effect on its processing and service properties (MW, viscosity, physicomechanical characteristics) [1]. In this connection, the properties of thermally stabilised RPET were compared with the properties of polymeric material having passed through a stage of processing under the corresponding regime.

At the first stage of the work, an investigation was made of the process of chain extension of RPET with an initial viscosity of 0.5 wt% in the presence of phosphate and phosphite stabilisers of different structure, and of the change in MW during continuous extrusion. The MW data are given in Table 1. It was established that the introduction of SZDiFt (from 0.5 to 1.5 wt%) into RPET does not lead to any increase in MW, while the introduction of TPhP (from 0.5 to 2.0 wt%) leads to a small increase in MW (4–6% in total).

The obtained data correlate well with the intrinsic viscosity and MFI. The small increase in the MFI for RPET with TPhP is evidently connected with its plasticising effect.

It was shown that the introduction only of phosphorus-containing thermal stabilisers into RPET with a moisture content of 0.5 wt% during continuous extrusion does not provide a significant effect in terms of chain extension and MW increase.

In Kirpichikov [13] it was shown that phosphites are widely used in combination with stabilisers of the phenol type, as they are capable of suppressing the process of their oxidation.

Below, data are given on the modification of RPET with a moisture content of 0.5 wt% with a mixture of stabilisers (SZDiFt + SZFl) taken in a mass ratio of 4:1 and a range of concentrations of 0.5–1.5 wt% in the process of continuous extrusion.

Figure 1 gives MWD curves for PET, for RPET, and for RPET stabilised with an SZDiFt + SZFl mixture.

It was shown that the MWD curve for RPET with 0.5 wt% SZDiFt + SZFl is shifted towards higher molecular weights. From the data in Table 1 it follows that the MW of stabilised RPET increases by ~15%, the \([\eta]\) increases from 65 to 75 mL/g, and the MFI decreases from 14 to 8 g/10 min.

However, the MW and rheological characteristics of RPET containing an SZDiFt + SZFl mixture do not reach the level of those of the virgin PET (\(M_h = 51 600, M_z = 25 200, M_w = 83 500, [\eta] = 83 \text{ mg/mL, MFI} = 5 \text{ g/10 min}\)).

Figures 2 and 3 give the results of investigating the thermal stability of virgin PET, of RPET after extrusion, and of RPET stabilised with an SZDiFt + SZFl mixture. The values of the intrinsic viscosity and MW of the stabilised RPET approach those of the PET.

Thus, for RPET with 0.5 wt% SZDiFt + SZFl, \(M_h\) decreases by ~3% after 5 min heating at 270°C, by...
For PET, \( M_h \) changes respectively by \(-4\%\), \(-8\%\), and \(-11\%\), and for unstabilised RPET by \(\sim 10\%\) after 5 min and by \(15\%\) after more than 10 min. Similar data were obtained for the intrinsic viscosity.

In Kalinchev and Sakovtseva [14] it was shown that a 3–5% change in the MW of the polymer does not lead to any significant changes in the physicomechanical characteristics of the products and does not disrupt the stability of processing with the force and speed parameters that are realised in the production equipment. Thus, RPET stabilised with a 0.5 wt% SZDiFt + SZFl mixture with continuous extrusion under conditions of an increased

Table 1. Molecular weight characteristics and MFI of virgin PET and of recycled PET with stabiliser before and after extrusion

<table>
<thead>
<tr>
<th>Polymer with stabiliser</th>
<th>Stabiliser content, wt%</th>
<th>Moisture content, wt%</th>
<th>( M_w )</th>
<th>( M_h )</th>
<th>( M_w/M_n )</th>
<th>( M_z )</th>
<th>[h], mL/g</th>
<th>MFI, g/10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0</td>
<td>0.2</td>
<td>51 600</td>
<td>25 200</td>
<td>2.1</td>
<td>83 500</td>
<td>83</td>
<td>5</td>
</tr>
<tr>
<td>PET (after extrusion)</td>
<td>0</td>
<td>0.2</td>
<td>39 600</td>
<td>18 900</td>
<td>2.1</td>
<td>65 600</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>RPET (after extrusion)</td>
<td>0</td>
<td>0.5</td>
<td>36 100</td>
<td>17 000</td>
<td>2.1</td>
<td>60 300</td>
<td>65</td>
<td>14</td>
</tr>
<tr>
<td>RPET with TPhP</td>
<td>0.5</td>
<td>0.5</td>
<td>37 800</td>
<td>18 200</td>
<td>2.1</td>
<td>62 900</td>
<td>69</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.5</td>
<td>34 900</td>
<td>16 800</td>
<td>2.1</td>
<td>58 400</td>
<td>66</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.5</td>
<td>36 900</td>
<td>17 900</td>
<td>2.1</td>
<td>61 400</td>
<td>67</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.5</td>
<td>38 400</td>
<td>18 300</td>
<td>2.1</td>
<td>64 100</td>
<td>66</td>
<td>22</td>
</tr>
<tr>
<td>RPET with SZDiFt</td>
<td>0.5</td>
<td>0.5</td>
<td>35 900</td>
<td>16 900</td>
<td>2.1</td>
<td>60 300</td>
<td>65</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.5</td>
<td>36 000</td>
<td>17 100</td>
<td>2.1</td>
<td>60 200</td>
<td>65</td>
<td>14</td>
</tr>
<tr>
<td>RPET with SZDiFt + SZFl</td>
<td>0.5</td>
<td>0.5</td>
<td>40 500</td>
<td>19 300</td>
<td>2.1</td>
<td>67 200</td>
<td>75</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.5</td>
<td>40 100</td>
<td>19 200</td>
<td>2.1</td>
<td>66 300</td>
<td>75</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 1. MWD curves: 1 – RPET after extrusion; 2 – RPET with 0.5 wt% SZDiFt + SZFl; 3 – PET

Figure 2. The dependence of the intrinsic viscosity of PET (1), of RPET after extrusion (2), and of RPET with 0.5 wt% SZDiFt + SZFl (3) on the heating time at 270°C

Figure 3. The dependence of \( M_h \) of PET (1), of RPET after extrusion (2), and of RPET with 0.5 wt% SZDiFt + SZFl (3) on the heating time at 270°C
moisture content (up to 0.5 wt%) possesses necessary and adequate properties for its processing by extrusion.

Data are given from assessing the physicomechanical properties of the materials obtained. From the data in Table 2 it follows that the introduction into the RPET of a small quantity (up to 0.5 wt%) of the stabiliser mixture has practically no effect on the combination of deformation and strength properties of the RPET, and they remain at the level of the RPET after extrusion. However, RPET containing the mixture of stabilisers, by comparison with PET, is characterised by a lower strain (about a twofold reduction) and impact strength.

The practical application of stabilised RPET showed that, for many products, such a level of physicomechanical properties is entirely satisfactory for consumers.

CONCLUSIONS

Thus, as a result of the investigations conducted under conditions of a high moisture content and continuous extrusion, from recycled feedstock (flakes of RPET), a new polymeric material stabilised with an SZDiFt + SZFl mixture has been obtained that in its combination of processing and physicomechanical properties is entirely satisfactory for the processing industry.

REFERENCES


