Reaction modification of recycled polyethylene terephthalate with 1,3-phenylene-bis-oxazoline

E.V. Veselova, T.I. Andreeva, and M.V. Strelkova
Institute of Plastics, Moscow, Russia

SUMMARY

The introduction into recycled polyethylene terephthalate of 0.5% 1,3-phenylene-bis-oxazoline in the process of extrusion without preliminary drying makes it possible to increase the intrinsic viscosity of the material to 75 mL/g, without any change in its thermophysical properties. The existence of an induction period, during which the additive is less effective, is shown.

An analysis of the scientific technical and patent literature showed that bi- and polyfunctional compounds, capable of reacting with the terminal groups of polyethylene terephthalate (PET), are used as polymer chain modifiers. Dianhydrides, bis-oxazolines, diepoxides, etc., are used as chain extenders [1-8].

Earlier, investigations were carried out on the modification of recycled polyethylene terephthalate (RPET) with pyromellitic dianhydride (PMDA). It was shown that the use of a PMDA concentrate based on PET ensures an increase in the molecular weight and viscosity of the melt during the processing of RPET without its preliminary drying [9].

Bis-oxazolines are likewise effective chain extenders capable of reacting with the terminal carboxyl groups of PET [10] (Scheme 1).

It was of interest to investigate the effect of bis-oxazoline on the molecular weight, viscosity, and thermophysical characteristics of recycled polyethylene terephthalate in the process of processing without preliminary drying.

MATERIALS AND METHODS

The investigation was conducted on RPET in the form of flakes with an intrinsic viscosity of 0.82 dL/g, with a content of COOH groups of 3.0 mg KOH/g, and on 1,3-phenylene-bis-oxazoline (PBO) ($T_{meh} = 145-147^\circ$C).

The introduction of modifier was done on a complex line based on a Labtech Scientific twin-screw extruder of

The melt flow index (MFI) and the heat stability were assessed according to the GOST 11645-73 standard on an MeP laboratory extrusion plastometer (ATS FAAR S.p.A) under the following conditions: temperature 265, 270, and 275°C, heating time 10, 20, 30, 40, and 60 min, load 0.75 kgf. Prior to analysis, the specimen was dried in a vacuum oven at a temperature of 150°C to a residual moisture content in the specimen of no more than 0.02%. The moisture content was determined by the thermogravimetric method on an MA 100 moisture meter (Startorius) at a temperature of 150°C.

The intrinsic viscosity was determined according to the GOST 18249-72 standard. Dichloroacetic acid was used as the solvent. The data obtained were converted by means of the formula (ISO 1628-5):

$$[\eta] = 1.20 \cdot y_1 - 18.07$$

where $[\eta]$ is the limiting viscosity number in a mixture of phenol and 1,2-dichlorobenzene (50:50) (mL/g), and $y_1$ is the limiting viscosity number in dichloroacetic acid (mL/g).

Investigations of the molecular weight (MW) characteristics were carried out on an Alliance GPCV-2000 high-temperature, high-pressure chromatograph (Waters) with a refractometric detector at 100°C, a Styragel HT 6 E 300 x 7.8 mm column, m-cresol as the eluent, and a flow rate of 1 mL/min. The chromatographic system was calibrated to finely disperse polystyrene specimens.

Thermophysical investigations were carried out on a DSC-20 instrument (Mettler Toledo) in a dynamic heating/cooling regime at a rate of 10°C/min (temperature range 50-300°C) in nitrogen. The glass transition temperature ($T_g$), the temperature of the start and maximum rate of crystallisation ($T_{cryst}$), and the temperature of the maximum of the melting peak ($T_p$) were determined from thermograms. The heat effects (heats) of the processes of crystallisation ($\Delta H_{cryst}$) and melting ($\Delta H_{melt}$) were recorded. The specimen was amorphised before testing.

The magnitude of the relative residual crystallinity was calculated by means of the formula:

$$\alpha = 100 \times (\Delta H_{melt} - \Delta H_{cryst})/\Delta H_{melt}$$

where $\alpha$ is the relative residual crystallinity (%).

TGA investigations were carried out on an STA 503 instrument (BÄHR Thermoanalyse GmbH, Germany) in air. The change in weight during heating at a rate of 7°C/min to 650°C in corundum crucibles was recorded. The temperature of 5% weight loss was used as the criterion of the heat resistance of the specimens.

**RESULTS AND DISCUSSION**
Taking into account that processing without preliminary drying has a considerable effect on the properties of RPET [9], the properties of the investigated composites were compared with the properties of the initial material processed under identical conditions.

Figure 1 presents gel chromatograms of RPET after extrusion and of composites with PBO (concentration range 0.1-0.5%).

From the obtained gel chromatograms, the molecular weight characteristics of the investigated composites were calculated (Table 1).

**Figure 1. Gel chromatograms of RPET with additive PBO**

<table>
<thead>
<tr>
<th>Table 1. The molecular weight characteristics of RPET</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formulation</strong></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Initial PET</td>
</tr>
<tr>
<td>PET after extrusion</td>
</tr>
<tr>
<td>PET + 0.1% PBO</td>
</tr>
<tr>
<td>PET + 0.25% PBO</td>
</tr>
<tr>
<td>PET + 0.5% PBO</td>
</tr>
</tbody>
</table>
The results show that, when PBO is introduced in the given concentration range, there is an increase in the molecular weight of the RPET. With increase in the additive concentration there is no significant increase in molecular weight (Table 1). The polydispersity does not change and remains at a level of 2.0. The obtained results are confirmed by intrinsic viscosity data.

Figure 2 presents concentration dependences of the MFI with different heating times of the composites.

As can be seen from the data obtained, the introduction of PBO lowers the MFI of RPET. With increase in concentration, the MFI likewise changes little and remains roughly at a level of ~14 g/10 min. All the composites were heat stable.

In the next experiment, a study was made of the effect of the temperature of determination of the MFI on the heat stability and intrinsic viscosity of a composite containing 0.5% PBO. Figures 3 and 4 present values of the MFI and intrinsic viscosity for different temperatures and different heating times.

At a temperature of 265°C, the MFI of the composite amounted to 9 g/10 min. With increase in the heating time to 60 min, the MFI increased little (11 g/10 min). At a temperature of 270°C, the MFI was 13 g/10 min, and its magnitude did not change with time. At a temperature of 275°C, the MFI became equal to 17 g/10 min, and at 60 min it was 18 g/10 min. Here, the intrinsic viscosity of the composite after holding at temperatures of 265-270°C fell to ~65 dL/g.

From Figure 4 it can be seen that during processing of the composite in the temperature range 265-270°C and with an exposure time of less than 10 min there is a reduction in the molecular weight characteristics of the composite, but with increase in the residence time, stabilisation of the viscosity properties is observed. This effect is probably due to the induction period of action of the additive.

The modification of RPET with additives of the dianhydride class was studied earlier [9]. The best result was obtained by using additive PMDA. In this work it was shown that, during processing of a composite containing additive PMDA, an induction period is also observed, as a result of which there is a reduction in the intrinsic viscosity of the RPET (Figure 5).

An investigation was made of the effect of bisoxazoline on the thermophysical characteristics of RPET. As can be seen from Table 2, during the processing of RPET with PBO there are no changes in the thermophysical properties. The temperature of the start of crystallisation of the composites amounts to 114-119°C, and maximum

Table 2. Thermophysical properties

<table>
<thead>
<tr>
<th>Formulation</th>
<th>( T_g ) (°C)</th>
<th>( T_{melt} ) (°C)</th>
<th>( \Delta H_{melt} ) (J/g)</th>
<th>( T_{cryst} ) (°C)</th>
<th>( \Delta H_{cryst} ) (J/g)</th>
<th>( a ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial PET</td>
<td>78</td>
<td>248</td>
<td>45</td>
<td>123</td>
<td>143</td>
<td>36</td>
</tr>
<tr>
<td>PET after extrusion</td>
<td>75</td>
<td>248</td>
<td>57</td>
<td>118</td>
<td>126</td>
<td>35</td>
</tr>
<tr>
<td>PET + 0.1% PBO</td>
<td>78</td>
<td>247</td>
<td>49</td>
<td>117</td>
<td>127</td>
<td>35</td>
</tr>
<tr>
<td>PET + 0.25% PBO</td>
<td>77</td>
<td>247</td>
<td>49</td>
<td>114</td>
<td>128</td>
<td>35</td>
</tr>
<tr>
<td>PET + 0.5% PBO</td>
<td>78</td>
<td>247</td>
<td>44</td>
<td>119</td>
<td>129</td>
<td>34</td>
</tr>
</tbody>
</table>

Figure 2. The dependence of the MFI (270°C, 0.75 kgf) on the content of additive with different heating times

Figure 3. The dependence of the MFI on the temperature and time of heating for a composite containing 0.5% PBO

Figure 4. The dependence of the intrinsic viscosity on the holding time at different temperatures
crystallisation remains at the 127-129°C level, with an enthalpy of crystallisation of 34-35 J/g. The melting temperature amounts to 247°C, with an enthalpy of melting of 44-49 J/g. The glass transition temperature is 77-78°C.

Thermogravimetric investigations of specimens showed that the introduction of a chain extender has no effect on the heat resistance of RPET. The temperature of 5% weight loss for all the composites was 390°C.

CONCLUSIONS

Thus, the use of an additive of the bis-oxazoline class makes it possible to increase the molecular weight of RPET during reaction extrusion without preliminary drying of the material. However, during subsequent processing of RPET with polymer chain modifiers, an induction period is observed, during which the viscosity properties of RPET decrease.

REFERENCES