The modification of radiation-crosslinked composites based on high-density polyethylene and ternary ethylene–propylene rubber with AP-U alkylresorcinol resin

S.V. Chagaev, I.N. Musin, and V.I. Kimel’blat
Kazan’ State Technological University

SUMMARY
An investigation was made of the modifying effect of alkylresorcinol resin on filled radiation-crosslinked composites based on high-density polyethylene. The limits of action of the modifier and also the optimum radiation doses ensuring the most satisfactory combination of properties were determined.

Polyolefin plastics based on high-density polyethylene (HDPE) possess a favourable combination of mechanical properties and chemical resistance. At the same time, the developers of new polymer composites based on polyolefins strive to raise the level of a number of mechanical properties by modification and even to replace structural plastics and engineering plastics with special polyolefin grades [1].

The aim of this work was to raise the combination of properties of composites based on HDPE to the level of requirements laid down for a number of critical articles of the cable and automotive industry by means of different modification methods.

In order to ensure that the polymeric material meets the requirements of the many users, the material must possess a high yield point and increased heat resistance, retaining its elastic strength properties and deformation properties at low temperatures.

In order to realise most fully the mechanical properties of the material, it is expedient to search for a combination of effective formulation and processing factors making it possible to improve the properties of the composites. One of the strategies for optimising the properties is to find a synergism of the components of the composites. Earlier, synergistic effects from using polymer components were shown in composites based on low-density polyethylene [2]. In the present work, an attempt was made to improve the properties of composites of HDPE 276-73 with ethylene–propylene rubbers and modified fillers, with the achievement of synergistic effects in terms of elastic and strength properties. The investigated composites were also subjected to radiation crosslinking.

Composites were obtained by mixing in a Brabender plasticorder at a temperature of 150°C. Test specimens were cut from strips produced by extrusion on a Brabender extrusion attachment. The temperatures in the different zones were as follows: $T_1 = 140°C$, $T_2 = 160°C$, $T_3 = 180°C$, $T_{head} = 180°C$. Specimens were tested on an Inspekt Mini tensile testing machine (Hegewald & Peshke). The precision of the equipment and the computer interface ensure reliability of the mechanical test data. The flow temperature of the composites was determined from thermomechanical curves obtained on a penetrometer. The cold resistance of the composites was estimated during the bending of specimens cooled to $-50°C$. The heat resistance of articles was estimated from the retention of the geometric shape of specimens at a temperature of 150°C.

In the work, use was made of two rubbers: No. 1 – of West European production; No. 2 – of Russian production.
Table 1. Properties of the ethylene–propylene rubbers used

<table>
<thead>
<tr>
<th>Rubber HDPE 276-73</th>
<th>Rubber No. 1</th>
<th>Rubber No. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass proportion of ethylene units, %</td>
<td>69</td>
<td>68–71</td>
</tr>
<tr>
<td>Content of ENB units, %</td>
<td>4.6</td>
<td>4.3–5.7</td>
</tr>
<tr>
<td>Viscosity, kPa s (150°C)</td>
<td>47</td>
<td>50</td>
</tr>
</tbody>
</table>

As can be seen from Figure 1, with a dose of rubber No. 2 of 2 parts, the highest yield point is observed.

The achieved effects of increasing the elastic strength properties are important, but they are small, and therefore it is expedient to attempt to use additional agents for improving the combination of properties. To this end, a silica filler BS-100 modified with AP-U resin was introduced into the composites.

Modifier AP-U is a piperylene-alkenylation alkylresorcinol resin. Resin AP-U was synthesised by the alkenylation of Alkirez-1 (alkylresorcinol fraction with a boiling point of 275–290°C, containing roughly 55% 5-methylresorcinol) with piperylene in the presence of an acidic catalyst and with subsequent condensation of the reaction resin with urotropin [3].

The formula of resin AP-U is given in Figure 2.

In order to study the simultaneous introduction of several modifying additives, a multifactorial experiment was used, where the filler and rubber doses were varied from 0 to 10 parts, and the polyethylene dose was varied from 90 to 100 parts. The ratio of filler and modifier AP-U was selected from the results of previous studies and amounted to 15:1 [2]. The results of investigation are presented in Figure 3.

From the diagram presented it follows that the maximum yield point is observed in the region of the following concentrations: 2–3 parts rubber, 2–4 parts filler. Compared with the properties of HDPE 276-73, the increase in elongation at break was 15%, and the increase in yield point was 7.3%. The increases achieved in the properties make a considerable contribution to optimising the properties of the composite.

To increase the long-term strength, and also the physicomechanical properties, the polyethylene-based composite can be crosslinked. Normally, organosilanes, peroxide systems, sulphur systems, and radiation (β- and γ-radiation) are used for crosslinking. Earlier [4] it was shown that the service properties of composites based on HDPE and SKEPT can be improved. The radiation crosslinking of polyolefin composites consists in the formation, under ionising radiation, of chemical crosslinks
between macromolecules, leading to the emergence in the polymer of a three-dimensional network. It was of interest to investigate the effect of modifier AP-U on the properties of radiation-crosslinked composites. For radiation crosslinking, a composite with the greatest yield point was chosen. Table 2 presents the formulation of the given composite. β-Radiation was conducted on an RV-1200 unit.

Modifier AP-U was introduced in a ratio to BS-100 of 1:15.

Figure 4 presents the flow temperature and crosslink density of composites as a function of the radiation dose.

With increase in the radiation dose to 5 Mrad, a network appears whose density increases with further increase in the radiation dose. Likewise, with increase in the radiation dose there is an increase in the flow temperature of the composite, which is an important indicator of the heat resistance of the material.

The elastic strength properties of radiation-crosslinked composites are presented in Figure 5 as a function of the radiation dose.

### Table 2. Formulation of the crosslinked composite

<table>
<thead>
<tr>
<th>Component of composite</th>
<th>Content, parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE 276-73</td>
<td>93</td>
</tr>
<tr>
<td>Rubber No. 1</td>
<td>3</td>
</tr>
<tr>
<td>BS-100</td>
<td>3</td>
</tr>
</tbody>
</table>

**Figure 4.** Flow temperature (a) and molecular weight between crosslinked points (b) of composites as a function of the radiation dose.

**Figure 5.** Yield point in elongation (a), elongation at break (b), and nominal tensile strength (c) of composites as a function of the radiation dose.
With increase in the radiation dose, the yield point consistently increases, while the elongation at break falls. Here, specimens modified with AP-U resin have higher elastic and strength properties. The given effect can be attributed to the formation of the product of interaction of the modifier, the filler, and the rubber, which possesses a reinforcing action, and here an increase in the elastic strength properties is observed.

During radiation with doses exceeding 5 Mrad there is a sharp reduction in elongation at break. The fall in the elastic properties means that, at a radiation dose greater than 10 Mrad, specimens do not withstand cold resistance tests. Specimens do withstand heat resistance tests at radiation doses of 5 Mrad and above.

Modified composites lose cold resistance at a radiation dose of 15 Mrad. As follows from Figure 6, there is a certain range of radiation doses that satisfies the heat and cold resistance requirements, and here, when a modifier is introduced, the range is widened.

Increase in the optimum range of properties during radiation crosslinking facilitates the radiation treatment of the material.

Thus, the results of the conducted investigations showed the effectiveness of the methods used for improving the combination of properties of composites based on HDPE. In a number of cases it is possible to recommend the given composites instead of expensive engineering plastics.

ACKNOWLEDGEMENT

This study was supported by a grant of the President of the Russian Federation (No. MK-4519.2009.3).

REFERENCES


Figure 6. Radiation dose range according to the heat and cold resistance requirements