Modification of the structural and mechanical properties of highly filled polyolefin composites

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Summary
The effect of additions of ethylene copolymers on the mechanical properties of filled polyolefin composites based on polyethylene 10803-020 and whiting was investigated. It was established that the best deformation properties are ensured by introducing copolymers of ethylene with propylene with an ethylene content of 50–70%. It was shown that the increase in elongation at break when the copolymers are introduced is connected with amorphisation of the polymer base.

The use of highly filled polyethylene composites encounters a number of difficulties owing to the inadequate level of their mechanical and, above all, deformation properties. Meanwhile, the volumes of polyethylene waste (secondary PE) that could be processed into structural materials of low-duty designation by filling with readily available fillers, in particular calcium carbonate, are increasing [1]. In this context, the problem of improving the processing and mechanical properties of highly filled polyethylene composites is of particular interest.

It is assumed that, because of its high degree of crystallinity, polyethylene is, by and large, little suited to filling. Crystallites in such systems can per se be regarded as filler particles [2]. Even the concept of ‘interstructural filling’ has been introduced, where filler particles are located between crystallites, which leads to an increase in the local degree of filling in amorphous regions in relation to the total degree of filling and causes a deterioration in the mechanical and, above all, in the deformation properties.

To improve the mechanical properties of filled polyolefins, it has been proposed additionally to introduce a small amount of solid plasticisers (5–10 wt%), in particular ethylene copolymers [2, 3].

In this connection, of particular interest is the study of the influence of the nature of the ethylene copolymers on the mechanical properties of highly filled polyethylene composites.

As the base, use was made of a composite based on low-density polyethylene 10803-020 (PE-108) and whiting (M-60). With increase in the whiting content in the mixture with PE-108 to 60% there is a reduction in the strength and a sharp decrease in the tensile strain (Figure 1).

Here, satisfactory raw material costs are ensured if 50–60% whiting is used, but in this case the tensile strain amounts to 22–9%, which comes short of the service requirements.

Figure 1. The dependences of the tensile strength (a) and tensile strain (b) on the whiting content in the composite with PE-108
The following were used as modifying additions (solid plasticisers):

- a copolymer of ethylene with vinyl acetate (CEVA-113) with a vinyl acetate content of 10–14%;
- a ternary copolymer of ethylene, vinyl acetate, and maleic anhydride (grade 2113);
- paraffin wax;
- copolymers of ethylene with propylene (SKEPT) with different ethylene contents, produced in Russia and the foreign grades Vistalon and Suprene, differing in Mooney viscosity.

The characteristics of the initial additions, DSC data, and the mechanical properties of filled composites of PE-108 and whiting (50:50) with 10% ethylene copolymers are given in Table 1.

At present there is the hypothesis that polyethylene must be amorphised for use as the polymer base of filled composites with the aim of improving their mechanical and, above all, their deformation properties. The enthalpy of melting of the copolymers used (Table 1) is considerably lower than that of polyethylene, and their introduction may lead to its amorphisation.

In fact (Figure 2), with decrease in the enthalpy of melting ($\Delta H$) of the copolymers there is a tendency for $\Delta H$ of the polymer matrix of the filled composite to decrease. However, this decrease is not so significant, from 60 J/g for the individual PE to 45–50 J/g for a composite with 10% copolymer.

For SKEPT rubbers, minimum values of $\Delta H$ are observed with an ethylene content in the 50–70% range (Figure 3). It is for this reason that these rubbers are best used for the modification of filled PE composites.

In the general case, with reduction in the enthalpy of melting there is an increase in the elongation at break of the filled composite (Figure 4).

However, for composites based on PE–SKEPT (O) there is a considerable spread of data. This may be due to differences in SKEPT rubbers in terms of their Mooney viscosity ($M$), which is proportional to their molecular weight. In the general case, increase in the molecular weight of the polymer should lead to an increase in the elongation at break. Therefore, to characterise

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Mass fraction of ethylene, %</th>
<th>Mooney viscosity at 125°C</th>
<th>$\Delta H$, J/g</th>
<th>$\sigma_t$, MPa</th>
<th>$\varepsilon_{br}$, %</th>
<th>$T_m$, °C</th>
<th>$\Delta H$, J/g</th>
<th>$\sigma_t$, MPa</th>
<th>$\varepsilon_{br}$, %</th>
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<tbody>
<tr>
<td>Without additive</td>
<td>130.6</td>
<td>15</td>
<td>860</td>
<td>107</td>
<td>60.0</td>
<td>8.0</td>
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<tr>
<td>CEVA-113</td>
<td>42.3</td>
<td>15.8</td>
<td>1200</td>
<td>108</td>
<td>57.7</td>
<td>8.5</td>
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<tr>
<td>2113</td>
<td>14.2</td>
<td>15.7</td>
<td>1670</td>
<td>107</td>
<td>48.8</td>
<td>10.8</td>
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<tr>
<td>Paraffin wax</td>
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<td></td>
<td></td>
<td>108</td>
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<td>25</td>
<td>42.4</td>
<td>107</td>
<td>53.4</td>
<td>6.5</td>
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<td>26.9</td>
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<td>49.4</td>
<td>6.4</td>
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composites based on SKEPT rubbers, a combined index – the ratio $M/\Delta H$ – is used (Figure 5).

Thus, to modify filled PE–SKEPT composites, it is necessary to use rubbers with the lowest enthalpy of melting value and the maximum molecular weight (Mooney viscosity).

Thus, in the course of the investigation it was shown that the mechanical properties of highly filled polyolefin composites can be improved by adding copolymers of ethylene with a lower degree of crystallinity by comparison with pure ethylene. Amorphisation of the composites leads to an increase in their elongation at break. The best effect from the viewpoint of the amorphisation of polyethylene and increase in the elongation at break is possessed by copolymers of ethylene with propylene (SKEPT) with the lowest enthalpy of melting and the maximum molecular weight (Mooney viscosity).

REFERENCES
