INTRODUCTION

In the past decade, increasing attention has been paid to natural, ecologically clean materials, so-called “green polymers”.

One of the most promising materials is poly-3-oxybutyrate (POB), which can be synthesised by different microorganisms. This polymer is one of the poly-3-oxyalkanoates, has high biocompatibility with the human body, and is capable of biodecomposition and self-degradation. However, the use of POB in pure form as packaging material in the food and pharmaceutical industries is inexpedient on account of its high cost and brittleness. At present, in order to produce a less expensive material with prescribed physicomechanical characteristics, POB is mixed with polymers of different classes: cellulose, polyethylene (PE), and oligoethers (ref. 1).

In the present work, a new material – a blend of POB and SKEP ethylene–propylene copolymer – has been produced and investigated.

EXPERIMENTAL

Use was made of grade SO-059 SKEP, produced by the Italian company “Dutral”, in the form of granules with comonomer contents of 67.4 mol.% ethylene and 32.6 mol.% propylene, and POB of the German company “Biomer” with a viscosity-average molecular weight $M_n = 2.5 \times 10^5$ in the form of finely dispersed powder. The ratio of the components POB/SKEP was as follows: 100:0, 80:20, 70:30, 50:50, 30:70, 20:80, 0:100 %.

Preliminary mixing of the components was carried out on laboratory VK-6 mixing micromills with heating: roll diameter 80 mm, friction coefficient 1.4, rotational speed of low-speed roll 8 rpm, roll gap 0.05 mm. Mixing was carried out at a temperature of 150°C for 5 min.

The films were manufactured by pressing using a manual heated press at 190°C with a cooling time of 3 min and a pressure of 5 MPa.

The thermophysical characteristics of the films were obtained using a DSM-2M differential scanning calorimeter (scanning rate 16 deg/min) with a specimen weight of 8–15 mg, and calibration was carried out with respect to indium with $T_m = 156.6^\circ C$. To determine the degree of crystallinity, use was made of a heat of melting of crystalline POB of 90 J/g (ref. 2). The accuracy of determining $T_m$ and $T_c$ was 1 K, and the calculated degree of crystallinity is given with an error of up to ±10%. The polymer chain structure was determined by means of IR spectroscopy on a Specord-M80 instrument with an accuracy of ±3 cm$^{-1}$. Use was made of structurally sensitive 720 and 620 cm$^{-1}$ bands belonging to SKEP and POB respectively (ref. 4).

The mechanical properties of all specimens (the breaking elongation, the tensile strength, and the tensile elastic modulus) were determined in accordance with GOST 11262–80.

RESULTS AND DISCUSSION

The thermophysical characteristics of blends of different composition are presented in Table 1, from which it can
be seen that the melting temperature changes little compared with pure POB. During melting, as during cooling, only a single peak appears, belonging to the crystallising fraction of POB. It must be noted that, on transition from a POB-rich composition to a composition with a predominance of SKEP, a significant change is observed in the enthalpy of melting: with a high SKEP content, the heat of melting is much lower. These results make it possible to assume that, in SKEP-rich blends, a fall in the heat of melting and in the degree of crystallinity of POB may be the result of the mutual segmental solubility of polymers (ref. 6), which seems to lead to the appearance of an extensive interphase layer. It must also be pointed out that the reduction in the degree of crystallinity is further due to the low rates of structural relaxation of rigid-chain POB, which in turn has to affect the nature of interaction of components of the blend.

The absence of significant changes in the magnitudes of $T_m$ and $T_c$, indicates that the fall in the enthalpy of melting is due to the significant amorphisation of POB, and that SKEP most likely takes no part in the process of nucleation during crystallisation, while the fall in the degree of crystallinity seems to be connected more with the presence of an interphase layer. It is obvious that the differences in structure have to affect the physicomechanical properties of the blends.

Figure 1 presents the dependence of the breaking elongation on the blend composition, which indicates that the addition even of 20 wt.% POB to SKEP leads to a sharp fall in the breaking elongation from 1500 to 160%. This can be attributed to the fact that rigid-chain POB prevents the appearance of elasticity of SKEP and lowers sharply the breaking elongation.

An analysis of the graph of the dependence of tensile strength (Figure 2) indicates that the strength of blends with a higher SKEP content is determined by the strength of the phase of the latter, and with increase in the POB content of the blend the strength increases to 13 MPa. The absence of additivity for the given dependence may be due to change in the structure of the components and to the presence of an extensive interphase layer in specimens with a predominance of SKEP (ref. 3).

<table>
<thead>
<tr>
<th>Specimen POB/SKEP ratio, wt.%</th>
<th>$T_m$, °C</th>
<th>$\Delta H_m^1$, J/g</th>
<th>$\Delta H_m^2$, J/g</th>
<th>$T_c$, °C</th>
<th>Degree of crystallinity α, %</th>
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</thead>
<tbody>
<tr>
<td>100:0</td>
<td>174</td>
<td>89.8</td>
<td>90.8</td>
<td>64</td>
<td>98.1</td>
</tr>
<tr>
<td>80:20</td>
<td>173</td>
<td>94.7</td>
<td>98.1</td>
<td>64</td>
<td>84.2</td>
</tr>
<tr>
<td>70:30</td>
<td>172</td>
<td>80.5</td>
<td>82.7</td>
<td>60</td>
<td>66.1</td>
</tr>
<tr>
<td>50:50</td>
<td>172</td>
<td>98.0</td>
<td>95.2</td>
<td>62</td>
<td>52.6</td>
</tr>
<tr>
<td>30:70</td>
<td>172</td>
<td>97.7</td>
<td>71.9</td>
<td>60</td>
<td>32.6</td>
</tr>
<tr>
<td>20:80</td>
<td>171</td>
<td>81.7</td>
<td>66.9</td>
<td>—</td>
<td>24.8</td>
</tr>
<tr>
<td>0:100</td>
<td>—</td>
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</tbody>
</table>

Table 1. Thermophysical properties of POB–SKEP blends

Figure 1. Dependence of breaking elongation on blend composition

Figure 2. Dependence of tensile strength on blend composition
From a comparison of Figures 1 and 2 for the specimen with a POB/SKEP ratio of 20:80 wt.% it can be seen that the strength of the blend is determined by the SKEP phase, while the breaking elongation is much lower than anticipated, which may be the result of loosening of the structure of the SKEP by small amounts of POB.

The monotonic increase in the tensile elastic modulus $E_t$ is due to the contribution of the high-modulus phase POB, but the given parameter does not reach its theoretical value ($E_t = 990$ MPa) (Figure 3). Here, as in the case with the tensile strength, there is an absence of additivity (curves 1 and 2). It must be pointed out that a considerable increase in $E_t$ is observed at a ratio of 70:30; with a lower POB content the $E_t$ is determined by the SKEP phase, and only with the 50:50 specimen is there any marked increase in the elastic modulus.

Analysing the above dependences, it is possible to speak of the existence of phase inversion, which is borne out by the data of IR spectroscopy.

For the present work, use was made of the 620 cm$^{-1}$ band of POB and the 720 cm$^{-1}$ band of SKEP (ref. 5), responsible for vibrations of the $\text{-C-C-}$ bonds in the methylene sequences ($\text{CH}_2$)$_n$, where $n > 5$ in trans-zigzag conformation. The given optical density ratios of the 720/620 cm$^{-1}$ bands are transformed in coordinates of the equation

$$W = \lg\left[\frac{D_{720}}{D_{620}} \times \beta + 1 - \beta\right] + 2$$

where $\beta$ is the proportion of SKEP.

Figure 4 presents the dependence of $W$ on the composition of the blend. As can be seen, the dependence is linearised in the given coordinates but has an inflection, which indicates the existence of phase inversion and a change in the nature of intermolecular interactions (ref. 6).

CONCLUSIONS

It can be seen that, in blends with a 50:50 ratio, phase inversion is observed, and here specimens with a predominance of SKEP seem to have an extensive interphase layer, on account of which a fall in the degree of crystallinity of POB and the absence of additivity for the mechanical properties are observed.

It has been established that the physicomechanical properties are determined largely by the predominant phase of the blend.

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(No date given)