The effect of metal-containing nanofillers on the properties of blended and dynamically vulcanised thermoplastic elastomers based on isotactic polypropylene and ternary ethylenepropylene diene elastomer

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SUMMARY

New thermoplastic elastomers based on isotactic polypropylene and a ternary ethylenepropylene-diene elastomer of different composition (with and without oil) with the use of nanofillers containing nanoparticles of oxides of different metals have been developed. It is shown that a small addition of nanofiller has practically no effect on the crystallinity and dielectric permittivity of the thermoplastic elastomers, but lowers their elastic modulus. The size of the nanoparticles has a considerable effect on the mechanical properties of the materials. The introduction of nanofillers into blends based on oil-extended elastomer does not affect their properties.

This stage of development of the chemistry and technology of composite materials in many ways is determined by the search for ways to create materials with improved properties. The intense development of the petrochemical industry worldwide presupposes a constant search for new materials that possess high user properties, are environmentally friendly, and are easy to process. Thermoplastic elastomers (TPEs), with reason, are materials of this kind. The creation of TPEs is a priority in the field of polymer materials science [1, 2].

The most promising way to produce new types of TPE is to mix elastomers with plastics with the simultaneous vulcanisation of the elastomer, which leads to a high degree of dispersion of the rubber phase in the materials. The TPEs produced in this way have been called ‘thermoplastic vulcanisates’ (TPVs). A distinguishing feature of TPVs is a combination of the properties of vulcanised rubbers during service and of thermoplastics during processing. Owing to their high physicomechanical properties, the wide temperature range in which they can operate, and the lower cost of the end products, TPVs are considered to be among the most promising classes of polymer composite materials. The areas of their application are extremely varied [3, 4].

A large number of studies of TPEs and TPVs have been carried out using polypropylene as the thermoplastic and SKEPT ternary ethylenepropylene diene copolymer, natural rubber, nitrile butadiene rubber, etc., as the elastomers, with the use of different fillers or compatibilisers to improve the compatibility and the physicomechanical properties of the composites [5–8].

The use of solid nanoparticles of different form and chemical nature as fillers of polymeric materials opens up possibilities of modification of the latter, as the surface properties of a nanosized substance are noted for high surface energy and adsorption activity.
Composite materials containing nanoparticles possess high adhesion strength of the polymer matrix with the nanoparticles [9].

The development of research on nanosized and cluster metal-containing particles in polymer matrices is promoted in many ways by the creation of metal–polymer composite materials possessing specific physico-mechanical and service properties: increased thermal and electrical conductivity, high magnetic susceptibility, the ability to screen ionising radiation, etc. [10, 11].

Earlier, we produced new TPEs based on PP/SKEPT with the use of a nanofiller containing nanoparticles of copper oxide [12]. It was shown that the introduction of nanoparticles into the TPE has practically no effect on the melting point of the blends, but leads to an increase in the temperature of the start of thermo-oxidative degradation by 30–50°C, with retention of the mechanical characteristics of the TPE.

In this work, we studied the effect of small additions of nanofillers containing nanoparticles of oxides of different metals on the properties of blended TPEs and dynamically vulcanised TPVs based on isotactic PP and SKEPT of different composition.

EXPERIMENTAL

In this work, we used: isotactic PP of grade 21030-16 (Russia) with \( M_n = 7.7 \times 10^4 \) and \( M_w = 3.4 \times 10^5 \), with a density of 0.907 g/cm\(^3\), a degree of crystallinity of 55%, a melting point, \( T_m = 165°C \), and a melt flow index (MFI) of 2.3 g/10 min at \( T = 190°C \) and under a load of 2.16 kg; SKEPT of grade Dutral TER 4044 (Italy) (SKEPT-4044) with a quantity of propylene units of 35% and a Mooney viscosity of 44 (at 100°C); SKEPT of grade Dutral TER 4535 (Italy) (SKEPT-4535) containing 50% oil introduced during synthesis, 32% propylene units, and a Mooney viscosity of 32 (at 125°C). In the SKEPT, the diene component was 5-ethylidene-2-norbornene and a Mooney viscosity of 32 (at 125°C). In the SKEPT, the diene component was 5-ethylidene-2-norbornene and a Mooney viscosity of 32 (at 125°C). In the SKEPT, the diene component was 5-ethylidene-2-norbornene and a Mooney viscosity of 32 (at 125°C). In the SKEPT, the diene component was 5-ethylidene-2-norbornene and a Mooney viscosity of 32 (at 125°C).

To investigate the mechanical characteristics of the polymer blends, specimens were cut out of the pressed sheets in the form of dumb-bell testpieces with dimensions of 35.50 \( \times \) 5.00 \( \times \) 0.35 mm. Uniaxial elongation of the specimens was carried out on an Instron-1122 testing machine (UK) at room temperature and with a constant speed of the upper crosspiece of 50 mm/min. From the strain diagrams, the elastic modulus \( E \), the tensile strength \( \sigma_t \), and the elongation at break \( \epsilon_b \) were determined. The results were averaged for 10–14 specimens. The error in measuring the elastic modulus and tensile strength did not exceed 10%, and the error in measuring the elongation at break did not exceed 20%.

The MFI was determined using an IIRT-5 instrument (Russia) at a temperature of 190°C and under loads of 2.16, 5.00, and 10.6 kg.

RESULTS AND DISCUSSION

The effect of nanofillers containing nanoparticles of metal oxides on the structure of blended TPEs based on SKEPT-4044 was investigated by the X-ray phase method. Figure 1 presents a diffraction pattern of PP/SKEPT-4044, on which reflexes corresponding to PP can be seen: \( d_{40k}\) 4.11616, 3.73572, 2.97165, 2.48033, 2.34787, 2.25572, 2.22098, 2.17096, 2.10536, 2.06313,
1.93822, 1.71736, and 1.66867 Å. Amorphous SKEPT yielded a halo image. On the diffraction pattern of the PP/SKEPT-4044/NFCuPE specimen (Figure 2) there are also reflexes characteristic of copper-containing nanoparticles: $d_{hkl} = 3.02053, 2.46466, 2.13683, 1.74331, 1.51025, \text{and} 1.28812 \text{Å}$, which corresponds according to the ASTM catalogue to the $d_{hkl}$ series of copper(I) oxide (Cu$_2$O). Note that, irrespective of the polymer matrix on which the copper-containing nanoparticles are stabilised, they indicate identical reflexes. On the diffraction patterns of TPEs with the addition of the remaining nanofillers, likewise, reflexes are observed that correspond to nickel oxide (NiO) or iron oxide (Fe$_3$O$_4$).

The properties of blended TPEs and dynamically vulcanised TPVs based on PP/SKEPT containing nanofillers with nanoparticles of oxides of different metals are presented in Tables 1 and 2. It can be seen that the dynamic vulcanisation of the PP/SKEPT-4044 blend lowers its crystallinity, $K$, slightly from 54 to 49%. Note that the introduction of nanofillers of different nature has practically no effect on the crystallinity of the investigated TPEs and TPVs.

It is known that for the initial PP the dielectric permittivity $\varepsilon'$ is 2.2–2.4 [15]. As shown by our investigations (Tables 1 and 2), for TPEs and dynamically vulcanised TPV based on SKEPT-4044 not containing nanofillers, $\varepsilon' = 2.0$, and with increase in the frequency of investigations from $10^{-2}$ to $10^7$ Hz this quantity does not change. When a nanofiller containing different nanoparticles is introduced into the blends, then $\varepsilon'$ hardly changes and is constant in the entire investigated range of frequencies. The obtained values of $\varepsilon'$ for the investigated blended and dynamically vulcanised TPEs correspond to those given for normal dielectrics.

The use of nanofillers in blended TPEs based on SKEPT-4044 leads to a certain reduction in the elastic modulus, tensile strength, and elongation at break (Table 1). The dynamic vulcanisation of the PP/SKEPT-4044 blend leads to a considerable fall in its elastic modulus and to an increase in its limiting mechanical properties (Table 2). The introduction of nanofillers of different composition into TPVs leads to a further reduction in the elastic modulus of the blends, with retention of their tensile strength and elongation at break. Reduction in the elastic modulus of materials is probably due to aggregation of the nanoparticles, which leads to the formation of microdefects within the polymer matrix.

Note that the use of a nanofiller containing NPFeSKS significantly reduces the mechanical characteristics of the TPEs and TPVs. This is probably due to the fact that the size of nanoparticles of the given type is fairly great, and they introduce additional defects into the structure of the blends.

Table 1. The properties of TPEs (crystallinity $K$, dielectric permittivity $\varepsilon'$, elastic modulus $E$, tensile strength $\sigma_s$, elongation at break $\varepsilon_{br}$, MFI)$^*$

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$K$, %</th>
<th>$\varepsilon'$</th>
<th>$E$, MPa</th>
<th>$\sigma_s$, MPa</th>
<th>$\varepsilon_{br}$, %</th>
<th>MFI, g/10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/SKEPT4044</td>
<td>54</td>
<td>2.0</td>
<td>395</td>
<td>11.0</td>
<td>170</td>
<td>0.9</td>
</tr>
<tr>
<td>PP/SKEPT4044/NPCuPE</td>
<td>50</td>
<td>2.2</td>
<td>260</td>
<td>9.3</td>
<td>150</td>
<td>1.1</td>
</tr>
<tr>
<td>PP/SKEPT4044/NPNiPE</td>
<td>50</td>
<td>2.2</td>
<td>263</td>
<td>8.7</td>
<td>110</td>
<td>1.1</td>
</tr>
<tr>
<td>PP/SKEPT4044/NPCuABS</td>
<td>51</td>
<td>1.7</td>
<td>270</td>
<td>8.6</td>
<td>110</td>
<td>1.0</td>
</tr>
<tr>
<td>PP/SKEPT4044/NPFeSKS</td>
<td>50</td>
<td>2.4</td>
<td>200</td>
<td>7.6</td>
<td>40</td>
<td>1.2</td>
</tr>
<tr>
<td>PP/SKEPT4535</td>
<td>—*</td>
<td>—*</td>
<td>35</td>
<td>3.4</td>
<td>155</td>
<td>1.0</td>
</tr>
<tr>
<td>PP/SKEPT4535/NPCuPE</td>
<td>—*</td>
<td>—*</td>
<td>38</td>
<td>2.6</td>
<td>140</td>
<td>0.9</td>
</tr>
</tbody>
</table>

$^*$ A dash (—) denotes that flow was not observed; a dash with an asterisk (—*) denotes that measurements were not conducted.
The MFI of a TPE with a nanofiller hardly differs from that of the PP/SKEPT-4044 thermoplastic elastomer (Table 1). However, the MFI values of blends under a maximum load of 10.6 kg are little higher than the MFI values of a TPE not containing a nanofiller. Dynamically vulcanised TPVs do not possess flow under any of the loads investigated (Table 2). The exception is the blend with an addition of NPCuPE, for which weak flow appears under maximum load.

The mechanical parameters of TPEs based on oil-extended SKEPT-4535 are lower and the MFI is higher (with the exception of the values obtained under a load of 2.16 kg) than for blends containing SKEPT-4044 (Table 1). Dynamic vulcanisation increases the mechanical properties of the oil-extended TPEs but adversely affects their flow. The addition of a nanofiller into TPEs and TPVs based on SKEPT-4535 does not alter their mechanical characteristics or MFI. The nanofiller seems to be localised in the oil-extended elastomer phase and has no effect on the properties of the blend.

CONCLUSIONS

The effect of nanofillers containing nanoparticles of oxides of different metals on features of the properties of blended and dynamically vulcanised TPEs based on isotactic PP and SKEPT of different composition have been investigated. XPA diffraction patterns confirm the presence of nanoparticles of metal oxides in the TPEs.

It has been shown that a small addition of nanofiller in a quantity of 1 part hardly affects the crystallinity and dielectric permittivity of TPEs and TPVs. The data obtained on the electrical properties of TPEs correspond to the indices of normal dielectrics. The introduction of nanofillers of different nature reduces the elastic modulus of the investigated TPEs and TPVs. The size of the nanoparticles has a considerable influence on the mechanical properties of the materials.

The properties of blends based on an oil-extended elastomer are not dependent on the introduction of small additions of nanofillers.

Further investigations of the influence of the amount and nature of nanofiller on the properties of materials of this kind are required.

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