The effect of a peroxide modification coagent on the viscous properties of binary blends of polypropylene and ethylene propylene rubber

I.G. Ryzhikova,¹ N.A. Bauman,¹ A.M. Volkov,¹ Yu.M. Kazakov,¹ S.I. Vol’fson,² A.A. Nikiforov,² and R.S. Yarullin²

¹OOO NIOST, Tomsk
²Kazan National Research Technological University, Kazan

In the motor industry, with each passing year the number of components and assemblies based on polymer compounds is increasing, and accordingly the market demand for them is growing. The lion’s share in this case is taken by high-impact polypropylene compounds, which can be used at temperatures ranging from −60 to +135°C [1, 2].

The first attempts to blend polypropylene (PP) and ethylene propylene rubbers (SKEPT) in order to increase the impact strength of PP date back to the 1970s. Since then, the production of high-impact polypropylene (PP) has developed at exceptionally high rates. However, in spite of structural similarity, PP and SKEPT are incompatible polymers, and the rubber exists as individual particles in the polypropylene matrix, while poor dispersion of these particles and their large size may work against any increase in the impact strength of the composites obtained [3].

The introduction of rubber into PP leads to a reduction in the rigidity and to an increase in the viscosity of the composites, which has an unfavourable effect on the technological effectiveness and service characteristics of such materials. Improvement in the properties of the PP/SKEPT binary blend can be achieved by increasing the energy of interaction at the phase boundaries of the given components.

A well-known approach to solving the problem is the use of compatibilisers — polymer products containing structural regions (blocks) that are compatible in nature with both polymer components [4, 5]. Furthermore, solutions exist that are associated with processes of “reaction mixing” of polymers, in which use is made of the chemical modification of the polymer matrices in the process of their mixing in a melt [6].

We conducted research [7–9] to study the possibilities of improving the user and processing properties of propylene compounds based on several grades of ethylene propylene diene rubbers, differing in molecular weights, monomer composition, degree of crystallinity, and degree of branching of macromolecules, and grades of polypropylene, differing chiefly in melt flow index. It was shown that the modification of a binary PP/SKEPT blend in the process of reaction mixing in the presence of 1,4-bis-(2-tertbutylperoxyisopropyl)benzene peroxide enables high-impact composites to be obtained.

In this work an examination is made of the results of investigating the influence of peroxide modification coagents on the viscous properties of PP/SKEPT binary blends.

Investigations were conducted on blends prepared with a propylene/rubber ratio of 80:20 and enjoying wide application in the motor industry. Use was made of SKEPT rubbers differing in the content of ethylene, propylene, and ethylenenorbornene (ENB), in molecular weight, and in Mooney viscosity, and polypropylene of grade 21030-16N with a melt flow index (MFI) of 3 g/10 min. The characteristics of rubbers Royalene 563, Royalene 521, Royalene 509 (Lion copolymer), Buna 3850, Buna 3950 (Lanxess), and saturated rubber SKEP Keltan 3200 A (DSM Elastomers Europe) are presented in Table 1.
As modifying agents, use was made of 1,4-bis(2-tert-butyleroxyisopropyl)benzene peroxide supported by CaCO3 and the following modification coagents: trifunctional triallyl isocyanurate \((\text{N}_3\text{O}_3)(\text{CH}_2–\text{CH}=\text{CH}_2)_3\) (TAIC) and trimethylolpropane trialkylate \(\text{H}_2\text{C}=\text{CH}–\text{C(O)}–\text{O}–(\text{CH}_2)\text{4}–\text{O}–\text{C(O)}–(\text{CH}_3)\text{C}=\text{CH}_2\) (TMPTA), bifunctional 1,4-butanediol dimethacrylate \(\text{H}_2\text{C}=\text{CH}–\text{C(O)}–\text{O}–\text{CH}_2–\text{CH}–[\text{CH}_2–\text{CH}_2–\text{O}–\text{C(O)}–\text{CH}=\text{CH}_2\text{2}]\) (BDDMA), and monofunctional butyl acrylate \(\text{CH}_3–\text{O}–\text{C(O)}–\text{CH}=\text{CH}_2\) (BA).

The composites were prepared in a Brabender batch mixer with electric heating at a temperature of 180°C and a rotor speed of 100 rpm. After mixing for 2 min, PP was introduced into the rubbers, and mixing of the melt continued for 5 min. Then the peroxide and coagent were introduced, and after 3 min the blend was discharged. The viscous properties of thermoplastics are characterised most simply by their melt flow index (MFI), i.e. the amount of melt flowing through a calibrated capillary at a temperature of 230°C under a load of 21.6 N over the course of 10 min (Zwick plastometer, ASTM D 1238-04C).

Thermomechanical action in the melt causes different chemical processes both in plastics and in rubbers that affect the viscosity of blends. These processes are the degradation of PP and SKEPT, promoting a reduction in the viscosity of the blends (increase in the MFI), the crosslinking of the SKEPT rubber both by the main chain and with the participation of reactive ENB units, and the formation in situ of block or graft copolymers of PP and SKEPT of very complex structure, which may promote a reduction in the MFI [6, 10].

In the presence of peroxide, many processes are initiated, which ultimately leads to an increase in the compatibility of the components of the system and to an improvement in the properties of the composites. When a polar coagent is introduced into the system, new reactions are possible between the radical particles formed as a result of thermomechanical and peroxide modification.

By virtue of their chemical activity, the modification coagents may react with radicals of the PP and rubber, promoting their crosslinking or the formation of block and/or graft copolymers. On account of the difference in functionality in the radical reactions, the coagents may have different effects on the viscous properties of the composites. The results of investigating the influence of the concentration of peroxide and coagent on the melt flow index of the composites are presented in Figures 1 and 2.

Figure 1 shows the change in the MFI of PP/SKEPT blends of different types, modified with a system containing peroxide (0.1 wt%) and trifunctional coagents – TAIC and TMPTA, as a function of their dosage (ranging from 0.1 to 0.8 wt%).

<table>
<thead>
<tr>
<th>Table 1. The characteristics of the ethylenepropylene rubbers</th>
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<td>Royalene 521</td>
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<td>Royalene 509</td>
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<td>Buna 3850</td>
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<td>&lt;sup&gt;a&lt;/sup&gt; M&lt;sub&gt;n&lt;/sub&gt; – number-average molecular weight; M&lt;sub&gt;w&lt;/sub&gt; – weight-average molecular weight; M&lt;sub&gt;z&lt;/sub&gt; – z-average molecular weight</td>
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From Figure 1a it can be seen that, for coagent TAIC, the MFI of the blends changes little in the investigated range of concentrations, and here the degree of change in the MFI hardly depends on the type of rubber. This may be attributed to the low activity of the allyl radicals formed by the interaction of TAIC with active peroxide radicals. Inactive radicals may, in some measure, inhibit the subsequent reactions of grafting and recombination responsible for the crosslinking of macromolecules. For this reason, as shown earlier [7, 8], there is also an increase in the value of the MFI with increase in the peroxide concentration: in the presence of 0.1 wt% coagent TAIC with a peroxide concentration of 0.02 wt% the MFI lies in the range 6–10 g/10 min, with a content of 0.05 wt% the MFI is raised to 10–15 g/10 min, and with 0.1 wt% the MFI is raised to 16–30 g/10 min.

The trifunctional coagent TMPTA (Figure 1b) containing acrylate groups active in radical reactions seems to accelerate processes of crosslinking of PP and SKEPT chains both between each other and in the “cross” variant, which consistently leads to an increase in viscosity (a reduction in the MFI) for all PP/SKEPT blends in the process of modification.

Figure 2 shows the influence of the functionality of the coagents as a function of the number of terminal double bonds on the degree of change in the MFI during peroxide modification (0.1 wt% peroxide) for the case of blends of PP and rubber Royalene 521.

In the presence of monofunctional coagent butyl acrylate, the MFI of the composite begins to decrease slightly only at a coagent concentration of 0.8 wt%. Such behaviour of the composites may be due to the small likelihood of reactions of crosslinking of the rubber and the formation of block and/or graft copolymers, and also to the predominance of the process of degradation of polypropylene in the presence of peroxide and butyl acrylate.

In the presence of the bi- and trifunctional coagents, processes of crosslinking and the formation of copolymers of the PP/BDDMA (TMPTA)/SKEPT type predominate, which leads to a reduction in the MFI. The bifunctional coagent BDDMA forms less branched block and/or graft copolymers, in contrast to TMPTA with three functional groups, and therefore the MFI level of blends modified using coagent BDDMA lies between the MFI levels of composites modified with BA and TMPTA.

For blends modified with coagents TMPTA and BA and having the most diverse MFI values, an assessment was made of the rheological characteristics in tests on a Smart Rheo rheometer at 200°C in the shear rate range 50–2000 s⁻¹. By way of example, Figure 3 presents the results of tests of blends of polypropylene with rubber Royalene 563, not modified and modified with peroxide/coagent systems (peroxide 0.1 wt%, coagent 0.5 wt%). Similar dependences were also obtained for other rubber grades. The obtained dependences of viscosity on shear rate correlate with data on the effect of the modifying system on the MFI of melts of composites.

Thus, the viscous properties of binary blends of polypropylene and ethylenepropylene/ ethylpropylenediene rubbers of different molecular weight can be varied in a wide range both by changing the peroxide content and by appropriate selection of the peroxide modification coagent.

ACKNOWLEDGEMENTS

This study was supported financially by the Russian Ministry of Education and Science within the project framework of the State Programme in the Sphere of Scientific Activity (10.863.2014/K).
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Received 25.10.2014