Processing to increase the structural activity of zeolite in polymer–elastomer composites

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Recently, a promising direction in the development of new elastomeric materials has been the creation of polymer blends (rubbers) that can combine the properties of the individual polymers and entirely new properties.

However, the stability of polymer blends and their capacity for long-term service are determined by the interaction at the phase interface, as the vast majority of blends of this kind are thermodynamically incompatible [1]. Dispersed fillers with high surface activity can act as agents intensifying the interaction of polymers at the phase interface, with the formation of a developed transition layer [2, 3].

Mechanical activation is a promising method for converting substances into the active state by physical action. This method is characterised by low-power-requirement and low-metal-content equipment, simplicity, and safety of the process. It is well known that, during mechanical activation, besides dispersion, breakdown of the degree of ordering of the crystalline structure of substances occurs, defects appear, and transition occurs to a metastable, non-equilibrium state of the particles [4]. Undoubtedly, the application of such substances as polymer blend modifiers may have a considerable positive effect by increasing activity in relation to the polymer binder.

Dispersed fillers are generally unevenly distributed between the polymer phases in heterophase blends. They cannot diffuse in quiescent or agitated blends. Therefore, the spontaneous redistribution of fillers between the phases of the blend is impossible, in contrast to plasticisers capable of being redistributed between the phases in accordance with their thermodynamic affinity for the polymer components of the blend [1].

The transfer of fillers from phase to phase and their transition from freely dispersed state to the state of a dispersion in viscous polymer occur during mechanical mixing, on account of which the mixing conditions and the order of introduction of the filler have a key effect on its distribution between the phases. This influence is occasionally more substantial than the influence of differences in the affinity of polymers of the blend for the surface of the given filler [1, 3].

In connection with the above, in this work a natural aluminosilicate – natural zeolite from the Khonguruu field in the Sakha Republic (Yakutia) – was subjected to mechanical activation. Furthermore, an investigation was made of different schemes for producing polymer–elastomer composites consisting of vulcanisate V-14 based on butadiene–acrylonitrile rubber (NKS-18) and a composite of ultrahigh-molecular-weight polyethylene (UHMWPE) with a modifying mechanically activated natural zeolite.

The choice of polymers is based on the promise of using such a blend as material for the manufacture of cold-resistant seals. Butadiene–acrylonitrile rubber is the only industrially produced rubber in Russia for the manufacture of oil- and petrol-resistant rubbers [5], and UHMWPE possesses high cold resistance and wear resistance [6].

There are hundreds of different zeolite structures of both natural and synthetic origin. Zeolites are widely used minerals, and, in terms of the given property, they occupy sixth place worldwide [7]. In industry, zeolites are used as adsorbents, molecular sieves, catalysts, fillers, and so on. As noted by the nanotechnology pioneer M. Ratner [8], “The secret behind the potential...
of zeolites lies in their special nanoporous structure, and they represent one of the first full-scale, very profitable applications of nanotechnologies”.

In the Sakha Republic (Yakutia) there are rich zeolite fields. An analysis of data indicates that, in terms of the clinoptilolite content, Yakut zeolites of the Khonguruu field are inferior only to zeolites from the Dzeg field in Georgia [9]. The relatively low content of impurities and the high heat resistance of Yakut zeolite-bearing rock (the most developed formation Khongurin-III has a mainly sodium composition, and zeolites with monovalent cations are more heat resistant than zeolites with bivalent cations) in combination with their low cost make natural zeolites a promising modifier of various polymeric materials. The possibility of using them in polymer blends is due to their considerable adsorption capacity, high adsorption potential, and strict selectivity to different compounds.

Experience of using natural zeolites in rubber mix formulations has shown that their introduction leads to an improvement in the service properties of rubbers [10, 11]. The modification of a vulcanisate based on butadiene–acrylonitrile rubber with activated zeolites makes it possible to increase the stability of the service parameters during holding in petroleum at ambient temperatures through the participation of zeolites in the process of crosslinking of the vulcanisates, increase in the density of the three-dimensional network, and also possible adsorption of the plasticiser by the zeolites [10, 11].

In the present work, natural zeolites were used with the aim of improving the interaction at the interface of the polymer phases.

The mechanical activation of natural zeolite was conducted in an AGO-2 planetary mill. Activating mills of this type ensure a very high level of energetic action on the material (up to 600 N). The mechanical activation regime was as follows: number of drums – 2; drum capacity – 150 mL; average diameter of steel milling bodies – 8 mm; loading of drums – with milling bodies (200 g) and with material being treated (15 g); rotational speed of carrier – 890 r/min; rotational speed of drums – 1820 r/min; duration – 2 min.

Mechanically activated zeolite was introduced into a blend of polymers consisting of vulcanisate V-14 based on BNKS-18 and UHMWPE, with the production of a polymer–elastomer composite by the following schemes:

1. The introduction of filler in a quantity of 2 wt% into crystalline polymer UHMWPE and mixing of the composite in a paddle mixer. The subsequent introduction of the obtained composite in a quantity of 10 wt% into the elastomer matrix on a mill or in an internal mixer.
2. The successive introduction of UHMWPE and activated zeolite into the elastomer matrix on a mill or in an internal mixer.

The structural characteristics of dispersed fillers were studied on a specific surface analyser of the “Sorbomter TM” series by the BET method. Investigations of the elastic strength properties were conducted according to GOST 270-75; investigations of the resistance to hydrocarbon media according to GOST 9.030-74, investigations of the abrasive wear resistance according to GOST 23509-79, and determination of the cold resistance coefficient according to GOST 408-78. Investigations of the supermolecular structure were conducted on a scanning electron microscope of grade JSM-6460 (LV) (Jeol, Japan) with an X-ray spectral analyser attachment, an “Olympus BX-41” optical microscope, and an “NTEGRA” atomic force microscope.

Table 1 gives data on the textural characteristics of zeolites. It was established that the activated zeolite is characterised by an increased specific geometric surface. Mechanical activation led to an increase in the number of pores of smaller size, which can be judged from the increase in the specific volume of pores. It is assumed that dispersion leads to breakdown of particles by the large pores, and thus the proportion of pores of smaller size increases.

On the distribution curve (Figure 1) it is shown that the number of pores of smaller size in the activated zeolite is greater than in the non-activated zeolite: at the maximum, practically twice as great.

Thus, investigations of the structural characteristics of zeolites before and after mechanical activation showed that the mechanical activation of the zeolite leads to a reduction in the pore size, an increase in the pore number, and a higher degree of filling of the pore volume, and indicates an increase in adsorption capacity and selectivity.

The next stage of the work is to choose the sequence of introduction of the filler – mechanically activated

Table 1. Textural characteristics of zeolites

<table>
<thead>
<tr>
<th></th>
<th>Non-activated zeolite</th>
<th>Activated zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific pore volume, m³/kg</td>
<td>3.3 x 10⁻⁵</td>
<td>4.4 x 10⁻⁵</td>
</tr>
<tr>
<td>Specific geometric surface, m²/kg</td>
<td>1.1 x 10⁴</td>
<td>1.69 x 10⁻⁵</td>
</tr>
<tr>
<td>Average pore size, nm</td>
<td>4.1</td>
<td>3.5</td>
</tr>
</tbody>
</table>
zeolite – into a polymer blend consisting of a model blend based on butadiene–acrylonitrile rubber and ultrahigh-molecular-weight polyethylene.

Figure 2 shows the distribution of activated zeolite in model blends. By electron scanning microscopy with X-ray spectral analysis, the appearance of a peak of silicon, the main element in the composition of the zeolite, on UHMWPE particles and the absence of this peak in the elastomeric medium (Figures 2a and b) in composites obtained by the first production scheme were recorded.

When UHMWPE and zeolite are introduced by the second scheme, the presence of silicon in practically identical concentrations, lower than on UHMWPE particles (Figure 2b), is found in two phases – the elastomer and polyethylene phases (Figures 2c and d), which lowers the activity of the filler at the phase interface and consequently leads to a reduction in the level of properties of the composite by comparison with a composite manufactured by the first scheme. Similar behaviour was observed in composites based on industrial rubber mix V-14, produced by the first scheme (Figure 3, Table 2).

Electron scanning microscopy data established the advantage of the first production scheme, which makes it possible to ensure the formation of interphase layers in the multicomponent system with an increased filler concentration. Here, the introduction of filler into the polymer is substantiated by the fact that UHMWPE possesses lower surface tension by comparison with the rubber, and therefore the interphase tension at the “polymer–rubber” boundary increases, which is not conducive to a high resistance to loads – separation of the material by the interphase boundaries occurs. The filler is capable of reducing the surface tension of polyethylene, which reduces the difference in surface tension values and increases the stability of the material.

When UHMWPE is mixed with filler in a paddle mixer, in all likelihood the adsorption of some macromolecules...
on filler particles occurs. With subsequent introduction of this composite into the elastomer matrix, the filler, fixed on the UHMWPE particles, remains at the phase boundary and does not pass in large quantities into the elastomer matrix of lower viscosity, which promotes the formation of a developed transition layer.

Table 2. Interpretation of X-ray spectra of the scanning region

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Mass concentration, %</th>
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<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>Spectrum 1</td>
<td>2.66</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>1.18</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>3.78</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>—</td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>—</td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>2.99</td>
</tr>
<tr>
<td>Maximum</td>
<td>3.78</td>
</tr>
<tr>
<td>Minimum</td>
<td>1.18</td>
</tr>
</tbody>
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* Not found

Table 3. Main service characteristics of polymer–elastomer composites

<table>
<thead>
<tr>
<th>Material</th>
<th>( f_{100} ), MPa</th>
<th>( f_t ), MPa</th>
<th>( \varepsilon_b ), %</th>
<th>( Q ), %</th>
<th>( \Delta V ), m³</th>
<th>( K_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-14</td>
<td>4.7</td>
<td>11.6</td>
<td>215</td>
<td>5.27</td>
<td>( 2.18 \times 10^{-7} )</td>
<td>0.644</td>
</tr>
<tr>
<td>V-14 + 10% [UHMWPE + 2% activated zeolite]</td>
<td>7.3</td>
<td>10.5</td>
<td>250</td>
<td>2.08</td>
<td>( 1.51 \times 10^{-7} )</td>
<td>0.687</td>
</tr>
<tr>
<td>V-14 + 10% [UHMWPE + 2% non-activated zeolite]</td>
<td>7.2</td>
<td>9.8</td>
<td>223</td>
<td>2.57</td>
<td>( 1.83 \times 10^{-7} )</td>
<td>0.612</td>
</tr>
</tbody>
</table>

Note: \( f_{100} \) – nominal stress under 100% elongation; \( f_t \) – nominal tensile strength; \( \varepsilon_b \) – elongation at break; \( Q \) – degree of swelling in oil I-50A; \( \Delta V \) – volume wear; \( K_o \) – coefficient of oil resistance at \(-45^\circ C\).

Investigations of the main service characteristics of polymer–elastomer composites produced by the first scheme showed the correctness of using pre-mechanically activated zeolite as a modifying filler of the blended composite, because the physicomechanical characteristics and cold, wear, and oil resistance of a composite with activated zeolite have higher values than those of composites with non-activated zeolite (Table 3). The elongation at break is 27% higher, with comparable values of the nominal stress and nominal strength, the abrasive wear resistance is 21% higher, the oil resistance in I-50A oil is 19% higher, and the cold resistance is 11% higher.

Figure 3 presents electron micrographs of polymer–elastomer composites. It can be seen that the introduction of crystalline polymer leads to the appearance of fibrillar inclusions germinated from the zone of UHMWPE with the formation of different subparticles, protrusions, and cavities (thickness 15–25 µm) with smooth boundaries. Micrographs of a composite with activated zeolite by comparison with a composite with pure UHMWPE are characterised by more saturated, finely divided structural elements (protrusion thickness 10–15 µm) and developed (more extended) interphase transition boundaries, which confirms that UHMWPE is more actively separated into transition layers. The scanning of specimens by atomic force microscopy made it possible to obtain a three-dimensional image (Figures 4c and d). It can be seen that a polymer–elastomer composite with activated zeolite has a more homogeneous structure. That is, the introduction of mechanically activated zeolite undoubtedly promotes strengthening of the interaction of polymer blends at the “butadiene–acrylonitrile rubber/ultrahigh-molecular-weight polyethylene” phase boundary.

Thus, the results of the investigations conducted showed that, for structural activity of natural zeolite in a system of an incompatible pair of polymers based on butadiene–acrylonitrile rubber/ultrahigh-molecular-weight polyethylene, the use of production methods such as preliminary mechanical activation and a certain order of introduction of the filler lead to the production of polymer–elastomer composites with an increased level of service properties.
REFERENCES


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Figure 4. Electron micrographs of polymer–elastomer composites, obtained by electron scanning microscopy (a, b – 100x and 1000x magnification respectively) and atomic force microscopy (c, d – 15 x 15 µm): a, c – V-14 + 10% UHMWPE; b, d – V-14 + 10% (UHMWPE + 2% activated zeolite)