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Application of Nanofillers to Improve the Interaction at the Interface of Incompatible Polymers

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Abstract

The effect of nanofillers (nanocarbon, β-sialon and cobalt spinel) on the state of the interface of butadiene-nitrile caoutchouc (acrylonitrile content: 17–20 %) and ultrahigh-molecular polyethylene (UHMPE) is investigated. A set of physicomechanical tests was carried out, the characteristics of wear, oil and frost resistance of the investigated compositions were determined. It was shown that the use of additives allows one to improve the interaction and the interface of butadiene-nitrile caoutchouc and UHMPE and the performance characteristics of the materials based on these polymers.

INTRODUCTION

Mixtures of caoutchouc can be used as a basis not only to obtain rubber combining the characteristics of separate polymers but also to achieve the variety of characteristics that cannot be obtained with caoutchouc alone. A substantial difference between polymer systems and classical colloid ones is the formation of a transition (interface) layer between two components to be mixed, which has a loosened structure with increased segmental mobility of macromolecules [1, 2].

Because of this, the problem of improving the interaction at the interface was formulated as one of the important areas of the investigation of polymer mixtures. One of the methods to solve the problem is structural modification of the polymers to be combined or one of the polymers, with the help of additives that allow one to active the interaction at the interface thus providing the possibility to synthesize the mixtures with the necessary phase structure.

In the present work, to achieve improvement of the interaction at the interface of butadiene-nitrile caoutchouc with acrylonitrile content of 16–18 % (BNCA-18) and ultrahigh-molecular polyethylene (UHMPE) with the molecular mass of about 4 10^6, we chose activated natural zeolite and nanofillers (nanocarbon, β-sialon and cobalt spinel) possessing high structuring ability toward various polymer matrices. Chemical composition and characteristics of fillers are shown in Table 1 [3].

The choice of polymers was based on the promising character of the use of such a mixture as a material to manufacture frost-resistant sealings. Butadiene-nitrile caoutchouc is the only caoutchouc produced by Russian industry to manufacture gas and oil resistant rubber [4], while UHMPE possesses unique antifriction characteristics [5].

EXPERIMENTAL

The natural zeolite of the Yakutian deposit was preliminarily activated in a planetary mill; particle size reduced to 0.1–2 μm. The activated zeolite and nanofillers were introduced into the UHMPE phase in the amount of 2 mass %, then this composition was added to the rubber

TABLE 1

Chemical composition and characteristics of additives

Additive	Concentration, mass %	Particle size (*R*), mm	Specific geometric surface (*q*), m^2/g	Density, g/cm^3	Particle shape
Zeolite	SiO_2 63–68 Al_2O_3 11–13 Na_2O 2–5 CaO 0.67–1.77 TiO_2, Fe_2O_3, FeO Na_2O, K_2O – the rest	0.1–2	21	0.62–0.72*	Crystal with developed system of pores and channels of molecular size
Nanocarbon	Cubic diamond – 30, graphite and amorphous carbon – 58, solid oxides and carbide – 6, adsorbed water – 3, gas admixtures (N_2, CO_2, N_2O, NO, O_2 , CO) – 3	0.004–0.006	680	1.3	Plate-like, with irregular shape, elongated and angular
β-Sialon	Si 20.8–42 Al 14–36.7 N 24.8–27.5	0.025–0.1	35–40	3.34	Complex chains, aggregates
Cobalt spinel $CoAl_2O_4$	Co 26.5–30.0 Al 32.5–35.0 O – the rest	0.07	30–40	4.4	Chain

* Bulk density.

** Solid solutions of α-Al_2O_3 and AlN in β-Si_3N_4.

mixture in the amount of 10 mass %. Vulcanisation of samples for tests was carried out using standard regimes.

Mixtures prepared for experiments were:

1. Mixtures of UHMPE with nanofillers.
2. Model rubber mixtures based on butadiene-nitrile caoutchouc (vulcanizing group and a minimal set of technological ingredients) with UHMPE and nanofillers.
3. Rubber mixtures according to industrial formulas with UHMPE and nanofillers.

It is known [5] that polyethylene is characterized by high surface tension in comparison with caoutchouc, so the dispersed inorganic filler will get distributed mainly over the elastomer matrix [2]. The introduction of additives into the polyethylene phase and subsequent addition of the resulting polyethylene composition into the elastomer promote a decrease in the interfacial tension between the two polymers, which causes an improvement of compatibility and adhesion between phases. In this case, additives get distributed more uniformly. In addition, surface-active additives have a substantial effect on polyethylene crystallization; crystallization of UHMPE and vulcanisation of caoutchouc take place within the same temperature range (140–160 °C). Because of this, we made and investigated the mixtures of UHMPE with nanofillers.

The use of model mixtures is connected with the fact that they can simplify revelation of the effect of additives on the properties and structure of polymer mixtures and correction of industrial formulas on the basis of research results.

The phase arrangement and supramolecular structure of the compositions were investigated with the help of JEM-6A microscope (JEOL, Japan) with the guaranteed resolution of 2 Å. The accelerating voltage of 80 keV, transmission mode and replicas from low-temperature chips in liquid nitrogen were used.

Vitrification temperature was determined using the TMA procedure with the help of thermoanalytical system Du Pont 1090 in the scanning mode with temperature changing at a rate of 10 °C/min. The strength characteristics were examined in the stretching mode according to All-Union State Standard GOST 270–75, relative hysteresis on stretching according to GOST 125–75 with the test machine UTS-Testsysteme GmbH (Germany). Investigation of oil resistance of rubber was carried out according to GOST 9.030–74 in AMG-10 oil at a temperature of 70 °C in a SNOL oven. Resistance to wear with respect to abrasion was determined according to GOST 23509–79 (friction path 40 m, rotation frequency 40 min^{-1}) using the abrasion machine AP-40 (Germany). Frost resistance on stretching (GOST 408–78) was determined with UTS-Testsysteme GmbH test machine.

RESULTS AND DISCUSSION

The following confidence intervals were obtained in statistical processing of the results of investigations: vitrification temperature, ±0.5 °C, engineering strain at 100 % elongation and conventional strength on stretching ±0.3 MPa, relative elongation ±15 %, swelling index ±0.02 %, volumetric wear ±0.003 cm^3.

Photomicrographic images obtained with the electron microscope JEM-6A and characterising the morphology of UHMPE with a nanofiller (β-sialon) and without it, manufactured according to the hot pressing technology with the parameters close to those of rubber vulcanisation, are shown in Fig. 1. One can see that the compositions of UHMPE with β-sialon have a better-developed fibrillar structure in comparison with pure UHMPE. The basic structural unit of the composition is an extended fibril of different thickness (from 220 to 4500 Å) growing from the sample mass and then splitting into thinner ones (110 to 660 Å), branching, bending and interlacing as a net. It was shown in [6] that the intermediate layer between caoutchouc and polyethylene is formed as a result of the growth of polyethylene fibrils into the caoutchouc matrix. It may be assumed that the presence of a better developed fibrillar structure of polyethylene, with a set of the fibrils of different thickness, will allow one to intensify the interaction at the interface between UHMPE and caoutchouc.

Comparative investigation allowed us to follow changes in morphology accompanying the introduction of a composition of UHMPE with β-sialon and without it into the elastomer matrix of BNCA-18 (Fig. 2). The introduction of

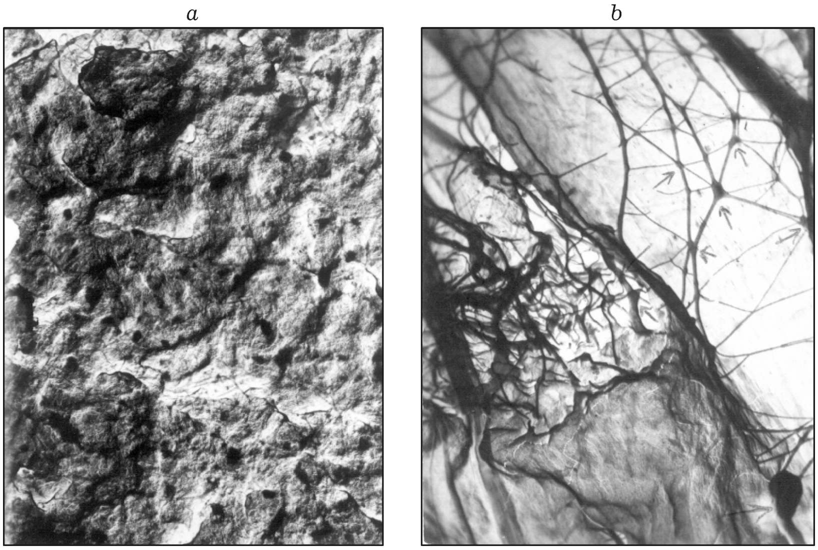

Fig. 1. Electron photomicrographs of UHMPE (*a*) and a composition of UHMPE with β-sialon (*b*). Magnification: 9000.

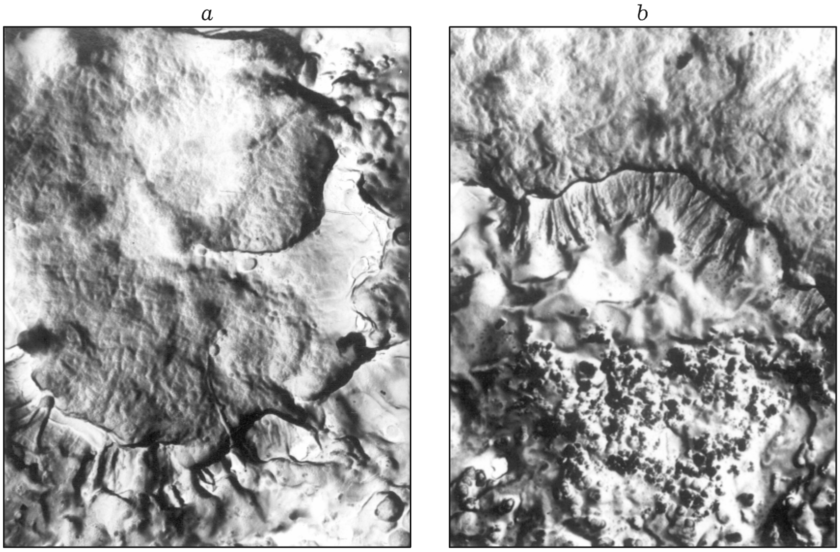

Fig. 2. Electron photomicrographs of the compositions BNCA-18 + UHMPE (*a*) and BNCA-18 + (UHMPE + β-sialon) (*b*). Magnification: 9000.

β-sialon conserves the internal structure of UHMPE regions; however, the shape and structure of its boundaries with BNCA-18 vary strongly in this process; the fibrils are observed to grow into the elastomer matrix. What is more important, in this case we observe a classical transition layer (see Fig. 2, *b*) described in [6]. It is composed of two boundary layers differing in morphology from the bulk regions of the components: fibrils 0.8–0.9 μm long grown from the UHMPE region into the matrix of the composition, and a matrix layer up to 1.9 μm deep depleted of the dispersed components.

Analysis of thermograms obtained by means of TMA showed that changes in vitrification temperature are observed for UHMPE compositions. Below we show the data on vitrification temperature of the modified commercial rubber of different composition, °C:

BNCA-18	−48
BNCA-18 + UHMPE	−49
BNCA-18 + UHMPE + β-sialon	−54
BNCA-18 + UHMPE + nanocarbon	−56
BNCA-18 + UHMPE + spinel	−53
V-14 + UHMPE + activated zeolite	−56

A shift of vitrification temperature to lower values is an evidence of the improvement of the interaction between incompatible polymers – BNCA-18 caoutchouc and UHMPE with nanofillers added, due to the formation of a better developed transition layer in which the segmental mobility of macromolecules increases and therefore vitrification temperature shifts to lower values [1, 4].

Investigation of the strength characteristics showed that the introduction of UHMPE into rubber causes a decrease in strength characteristics and relative elongation, which is natural since a harder polymer is introduced. However, such a decrease in strength characteristics should not affect the performance of sealings because strain and deformation provided by tests according to All-Union State Standards never occur under actual performance conditions. The introduction of nanofillers causes an increase in strength characteristics (tensile strength, relative extension strain for rupture, strain for 100 % elongation) in comparison with polymer mixtures BNCA-18/UHMPE without nanofillers (Table 2). An important result is the conservation of engineering stress values for 100 % elongation of modified rubber in comparison with the initial one, because this index provides the best correspondence with actual strain during the performance of rubber sealings.

In addition, the introduction of nanofillers allowed improving such performance characteristics as frost, wear and oil resistance in comparison not only with the BNCA-18/UHMPE without fillers but also with the rubber based only on butadiene-nitrile caoutchouc (see Table 2), both for model and for industrial formulas.

TABLE 2

Physicomechanical properties of modified rubber

Characteristics	Ratio of UHMPE to filler, % (type of filler)					
	0/0	10/0	10/2 (activated zeolite)	10/2 (β-sialon)	10/2 (nanocarbon)	10/2 (cobalt spinel)
			Model mixtures based on BNCA-18			
Conventional tensile strength, MPa	13.6	8	8.6	9.2	9.8	8.6
Engineering stress on 100 % elongation, MPa	7	6.9	7.1	6.9	7.4	6.5
Relative elongation, %	529	382	392	459	433	448
Frost resistance coefficient at −45 °C	0.496	0.569	0.673	0.623	0.734	0.712
Swelling index, %	4.87	3.65	3.34	3.35	3.12	3.22
Volume wear, cm^3	0.326	0.212	0.205	0.187	0.198	0.203
			Mixtures based on industrial formula V-14			
Conventional tensile strength, MPa	11.6	6.1	6.3	5.9	7.3	6.9
Engineering stress on 100 % elongation, MPa	4.9	2.8	3.0	3.1	3.2	3.1
Relative elongation, %	215	208	243	225	250	223
Frost resistance coefficient at −45 °C	0.564	0.644	0.687	0.675	0.754	0.718
Swelling index, %	5.27	2.93	2.43	2.14	2.08	2.18
Volume wear, cm^3	0.218	0.186	0.151	0.147	0.149	0.165

It should be noted that the effect of nanofillers on the characteristics of industrial compositions is less noticeable than that of model compositions. This fact is most likely connected with the high content of the active filler – technical carbon – in the former (about 150 mass parts per 100 of caoutchouc, against 50 : 100 in model mixtures). Investigation showed that the introduction of a small amount of structurally active additives will allow a substantial decrease in the content of technical carbon and at the same time improvement of performance characteristics. The most substantial effect is observed with nanocarbon, which is undoubtedly connected with its high surface activity in comparison with other studied additives. However, taking into account-increased requirements to storage and the high cost of this material, it seems reasonable to use β-sialon, cobalt spinel and zeolites as additives.

CONCLUSIONS

Preliminary mechanical activation of zeolites in a planetary mill causes a substantial increase in their surface activity and provides such a level of the characteristics of rubber based on butadiene-nitrile caoutchouc and UHMPE, modified with this additive, which is quite comparable with the level of the same rubber with nanofillers. It should be noted that the main role in the improvement of interaction at the interface in the investigated polymer mixture is played by the surface characteristics of additives.

So, it was demonstrated that the introduction of nanofillers allows one to improve the interaction at the interface of incompatible polymers and therefore to improve the performance characteristics of the materials for sealings made on this basis.

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