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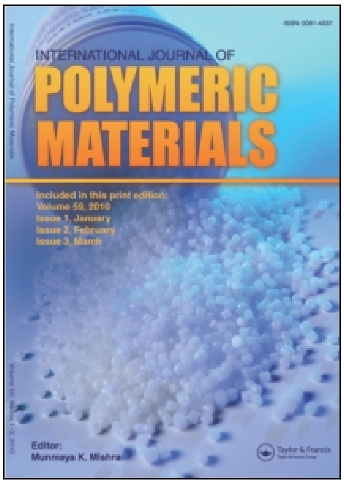

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The Shungite Effect on the Physico-Mechanical Properties of Elastomers and Polypropylene

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The Potential of shungite a microheterogeneous mineral complex as filler for polymers is explored.

Keywords: Shungite; composition; filler; polymers; applications; properties; elastomers; polypropylene

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INTRODUCTION

Shungite is a microheterogeneous natural mineral complex containing noncrystalline carbon, silicates, small amount of metal oxides and organic additives [1]. The unique property of shungite is the inseparability of carbon and mineral parts that are not connected chemically so that the carbon and mineral part can be isolated only by special heat treatment. Shungite carbon structure and physico-chemical properties are those of ungrafitable metastable noncrystalline carbon, whose main structure unit is globule. There are some references suggesting that powder shungite may be used as filler for elastomers and plastics replacing carbon black and silica. Unseparability of carbon and mineral parts is the cause for an easy incorporation of shungite into polymer polar and nonpolar macromolecules upto high degrees of filling [2–4].

There are three main types of shungite: I-total carbon content 98–99%; II-carbon content 28–32%; III–carbon content 3–5%. The most common type of shungite is type II. Its supply is about 2.10^4 min. ton. Supply of I type of shungite is less than 0,01% of total shungite supply.

Some physico-chemical characteristics and composition of shungite (type 2) are represented in the Table I.

This paper represents the investigation of some physico-mechanical properties of elastomers (nitriloacryl butadien rubber (NBR), ethylene-propylene rubber (EPR-50), butyl rubber (BR), isoprene-rubber (IR), fluorine-rubber (FR) as well as PP, filled with shungite powder.

EXPERIMENTAL

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Cured elastomeric compositions were made based on BNR-40, BNR-26, EPR-50, BR, IR, FR-26. Sulfur systems were used as curatives (for FR-26 bis-phenol system was used). PP (melt index-Shungite filled elastomers and PP were prepared using a laboratory roll at standard conditions (elastomers) or in a Brabender (PP, 170°C, rate and time of mixing 90 revolutions per minute and 10 min;). Shungite of I, II and III type was used.

The mechanical characteristics were measured by standard methods. The equilibrium swelling of cross-linked EPR was carried out in heptane vapor at the ambient temperature.

TABLE I Some physico-chemical properties of shungite (type II)

1. Carbon content, %	28–32
2. The mineral Part composition, %	
SiO_2	57–66, 2
Al_2O_3	3, 2–4, 45
TiO_2	0, 16–0, 3
$Fe_2O_3 + FeO$	1, 0–2, 3
MgO	0, 4–0, 8
CaO	0, 07–0, 3
K_2O	0, 8–1, 6
Na_2O	0, 11–0, 3
MnO	0, 01–0,02
3. Sulfur content, %	0, 2–0, 7
4. Particle diameter, mkm	10–50
5. pH of water suspension	4, 69–5, 20
6. Water content, %	0, 2–0, 5
7. Specific surface, m^2/g	30–50

Adhesive properties of modified PP were studied by measuring its adhesion to steel wire. The technique of samples preparing and measuring was described in [5]. The backing was high durable steel wire of diameter $d = 150\,\text{mkm}$. Initial and modificated PP were used for measuring adhesion characteristics. Steel wire fragment and some amount of polymer were put in the center of an aluminium container. The fixture with containers was placed into a heated thermostat. Samples were formed in isothermic conditions at $t = 210°C$ during 75 min. During that time the powder polymer was transformed into a homogeneous melt able to uniformly wet the wire. Heat treatment was carried out in air. After cooling the steel wire was imbedded into PP layer. The length of wire in polymer determines the length of adhesive connection L. The area of adhesive connection is $S = \pi dl$. That areas were from 0.1 to $1.4\,m^2$. The determination of breaking load F was made using the adhesiometers designed and constructed at the Institute of Chemical Physics (RAS). The measure of adhesion was the adhesive strength τ_{ad}, determined by pull-out the adhesive strength τ_{ad} was calculated using the formula $\tau_{ad} = F/S$. All the measurements were carried out at room temperature and constant load rate of 1 N/sec.

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RESULTS AND DISCUSSION

Shungite improves the mechanical and technological parameters of filled polymers, particularly technological viscosity of polymer blend, the relative elongation ($\Delta 1$) comparing to carbon black. For example, some base mechanical properties of BNR-40 containing shungite and carbon black are represented in Table II.

Usually, the addition of filler into rubber reduces the polymer chain mobility, increases the durability and decreases the elongation ability [6].

The specific feature of shungite in contrast to other fillers including technical carbon is that by increasing its content in filled rubbers improves both the durability and relative elongation. Figure 1 illustrates this effect for the example of polar and nonpolar rubbers.

This peculiarity may be caused by the fact that the shungite presence in polymer does not decrease molecular mobility but actually increases it. This can be observed by investigating the swelling of cross-linked shungite filled EPR-50 in heptane vapor. Usually, the filler presence in rubber leads to a reduction in swelling in solvents

TABLE II Some mechanical properties of BNR-40, containing shungite and carbon black are represented

Unaged Properties	*Sample carb. black*	*Sample with shungite*
1. Mooney viscosity (120C)	52,0	29,0
2. Tensile strength (MPa)	14,0	14,0
3. Elongation (%)	610	830
4. Hardness	58,0	62,0
5. Endurance under rotation:		
time till destruction, min	14,0	30,0
temperature inside		
sample, C	92,0	65,0

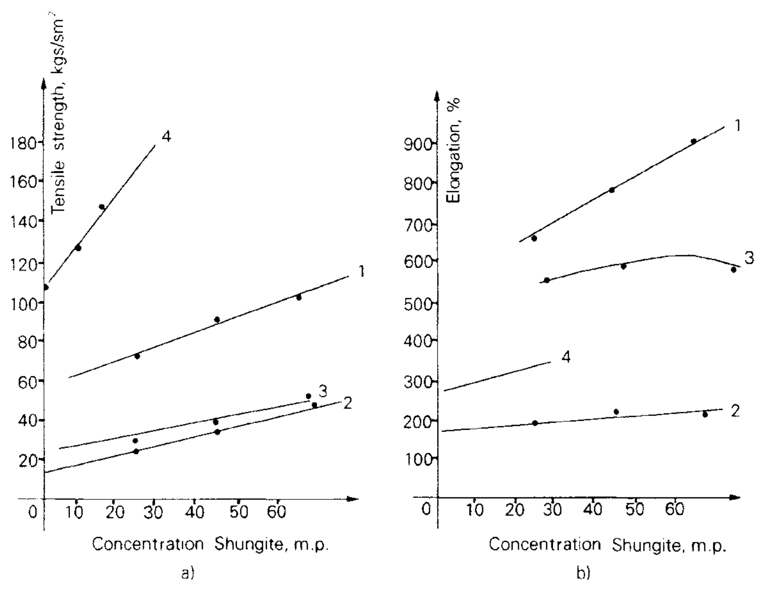

FIGURE 1 Dependence of strength 6 (a) and elongation Δl (b) at break on shungite content in standard rubber blends: 1- IR, 2- EPR-50, 3- BNR-26, 4- FR-26.

vapor [7]. Shungite effects the rubber in another way. Figure 2 shows the dependence of EPR-50 mass growth on shungite content after swelling in heptane vapour (equilibrium swelling). It can be seen that up 25% of shungite content in EPR-50, the rubber swelling increases*.

*These experiments were made by Ljapunova M. A.

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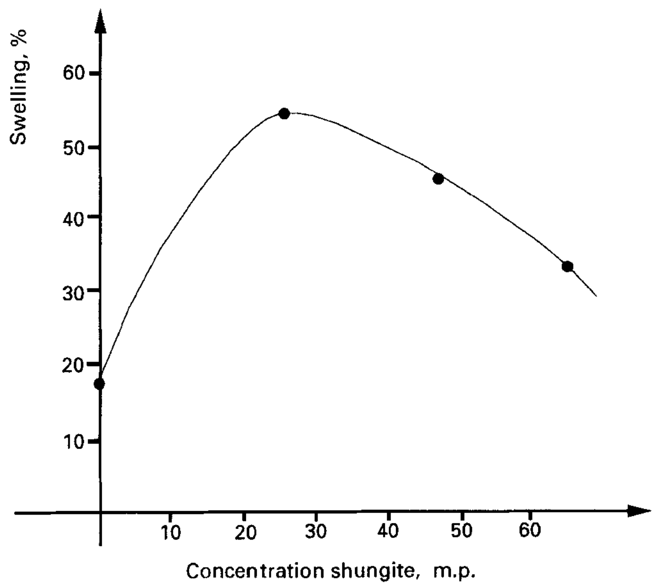

FIGURE 2 Dependence of equilibrium swelling (in%) in heptane vapour on shungite concentration in EPR-50 rubber.

It is known that the last factor may be one of the causes of the increase of adhesion of polymers to various surfaces.

In particular, the measuring of adhesion force of PP samples containing from 2 to 25% of shungite shows that the shungite addition can increase the strength (τ_{ad}) of PP-to-steel wire bond by 30–40%, depending on the amount of shungite admixtured and the shungite type. The dependence of τ_{ad} on shungite content is described by the curve having maximum at 6–13% of shungite contain (Fig. 3), whose position depends on shungite type, i.e. shungite carbon content in the rock. The extremal type of adhesion force dependence on shungite content is not yet clear.

Similarly, adhesion increase was observed for shungite mix with BR.

Table III shows the results of tests on destructive strength for butylrubber filled with powdered rubber wastes, tech. carbon and shungite (100 mass % relative to BR)*.

*These experiments were made by Nedel'kin W. I.

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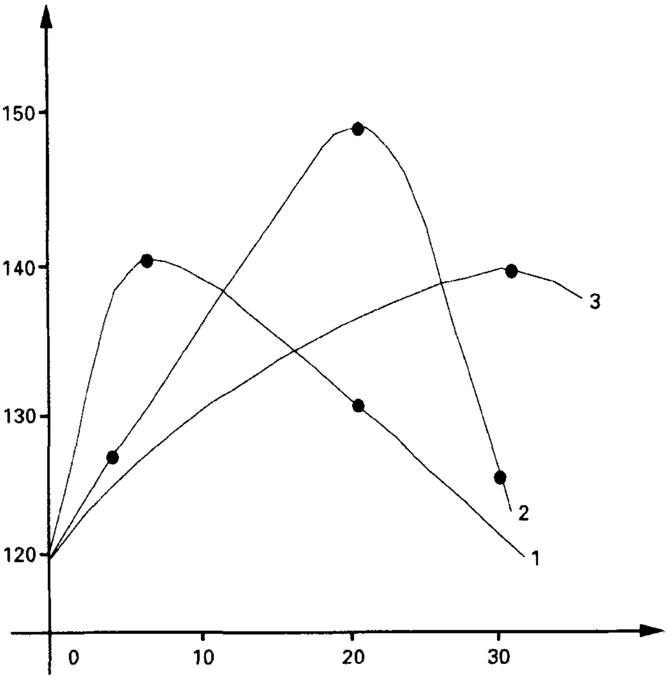

FIGURE 3 Dependence of adhesional strength of shungite containing PP to steel wire on shungite content. The type of shungite: Curve 1 - (I), curve 2 - (II), curve 3 - (III).

TABLE III Adhesion strength of butyl rubber containing shungite and some other fillers

Filler/ Properties	*Natural rubber powder*	*Nitril rubber powder*	*Shungite type I*	*Shungite type II*	*Shungite type III*	*Carbon black*	*Extrusion rubber powder*
1. Destructive shift strength kg/cm^2	0.42	0.77	0.7	0.89	0.5	0.94	1.1
2. Pulling-off strength kg/cm^2	1.5	2.1	3.6	4.25	3.2	2.0	3.5

Data show that shungite ability to increase adhesion exceeds those of both powdered rubbers and technical carbon. The best results were shown by shungite containing 30% carbon.

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CONCLUSIONS

The unusual shungite effect on physico-mechanical properties of shungite filled polymer compositions leads to simultaneous improvement of durability and elongation at break with the increase of shungite content in rubber. In addition, we noted an increase in swelling for shungite containing EPR-50 and the improvement of adhesive strength of PP after shungite addition.

The nature of these phenomena is not yet completely clear. The unexpected effects can possibly be explained by the presence of organic substance (OS) in shungite. OS can be isolated from shungite by some solvents extraction [8]. Its content in shungite is from 0,1 to 8 mass.%. The main part of OS are bituminous, polycyclic hydrocarbons and other complex organic compounds, that can act as plastic additives in shungite. Such "softeners" enhance the ability to stretch and the mobility of polymers in contact with shungite particles.

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Acknowledgements

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