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ATOMIC FORCE MICROSCOPY AND PHYSICAL - MECHANICAL PROPERTIES OF NEW ELASTOMER COMPOSITES

H.H. Valiev*, Yu.N. Karnet, N.L. Kochurov, M.S. Parshina, N.A. Semenov, O.B. Yumaschev, Yu.G. Yanovsky

Foundation Russian Academy of Sciences, Institute of Applied Mechanics RAS, Moscow, Russia

*e-mail: hhvlv@mail.ru

Abstract. The results of a comprehensive study of the new composites filled with modified micro and nanoscale shungit are presented. Correlation characteristics of the surface structure of elastomers and their physical - mechanical properties are deduced.

1. Introduction

The development advanced technologies for the production of nanostructured composite materials with improved physical - mechanical properties [1] require conducting modern fundamental and applied research in physics and chemistry of functional materials. The basic principles of the creation of composite materials using nano-structured fillers with the ultimate goal of the implementation of the best examples in the industry were laid down in Institute of Applied Mechanics Russian Academy of Sciences under the guidance of Professor Yu.G. Yanovsky [2-6]. One such area is the use of natural mineral shungit as filler in elastomers. Theoretically predicted and experimentally proved that nano shungit becomes essentially active in the elastomeric matrix butadiene - styrene and butadiene - methyl styrene rubbers [2-6]. The level of strength and values of the elastic module of the composites reached are not inferior and even superior characteristics provided by such well-known fillers as carbon black N 660. Theoretical calculation methods of quantum mechanics conducted by using the original software package, which includes a set of programs for structural, electronic, energy, deformation and spectroscopic characteristics of the atomic - molecular systems, predicted the prospect of functionalization the nanoshungit silicate component during milling in the presence of alcohol [6]. These findings were confirmed experimentally by atomic - force microscopy (AFM). The further development of these areas was carried out in this work by chemical functionalization of shungit silicate component by organosilanes. The research data were supported by AFM studies and investigation of physical - mechanical properties of synthesized rubbers.

2. Experimental procedure and materials

New model samples of rubbers based on butadiene - styrene rubber (BSC) were selected on the ratio of the components: SBR- 30ARK: 60 wt.%, schungit filler: 39 wt.%, and vulcanizing group: 1 wt.%. Nanoshungit fillers were produced by milling the initial powder ("Carbon - Schungit" Karelia, Russia) in a medium of isopropyl alcohol on a planetary ball mill RM -100 (Retsch, Germany). The functionalization of nano shungit by organic modifiers organosilanes was made directly during the grinding in the mill. Organosilanes used in parts 1,5 wt.% were:

- "TESPT" - Bis (3-Triethoxysilylpropyl) tetrasulfide ($C_{18}H_{42}O_6S_4Si_2$) STRUKTOL® SCA98;
- "Si-264" - 3-Thiocyanatopropyltriethoxysilane ($C_{10}H_{21}NO_3SSi$) STRUKTOL® SCA 984;

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• "Glymo" - gamma-Glycidoxypropyltrimethoxysilane ($C_9H_{20}O_5Si$) STRUKTOL® SCA 960;
• "Thiol" - 3-Mercaptopropyltriethoxysilane (($C_9H_{22}O_3SSi$) STRUKTOL® SCA 989

The introduction, dispersion of filler and blending all ingredients of elastomers was carried in a laboratory mixer HAAKE Rheomix (Germany). Kinetics of vulcanization was investigated by analyzer RPA 2000 (Alpha Technologies, England). The mixtures optimum curing was determined from obtained graphs. The surface structure of obtained rubber was studied using atomic - force microscope AFM easyScan (Nanosurf, Switzerland), who worked in tapping mode in air at room temperature using an additional mode of the phase contrast. AFM images processing was carried out using modern computer software SPIP ™ (Image Metrology, Denmark). Studies of physical and mechanical properties of the composites with these nanofillers were conducted on a universal tensile testing machine UTS - 10 (Ulm, Germany).

3. Experimental results

Surface AFM topography images and the phase contrast of the composite material allowed directly visualize the distribution of the fillers in the matrix rubber SBR- 30ARK (Figs. 1-4).
Analysis Fig. 1 revealed the uneven distribution of original micro shungit filler in the rubber matrix. Predominant size of the shungit aggregates remains in the micron region. The distribution of aggregates and agglomerates of milled nano shungit in the rubber (Fig. 2) is considerably more homogeneous with a primary particle size of the filler already in the nanometer range. Figure 3 shows that the use of organosilane Glymo as nanoshungit chemical modifier significantly improves the uniform distribution of the agglomerates and the aggregates in the matrix rubber. The aggregates and agglomerates nanoshungit modified by organosilane Thiol, (Fig. 4) distributed more uniformly at the rubber matrix even in comparison with modification by Glymo.

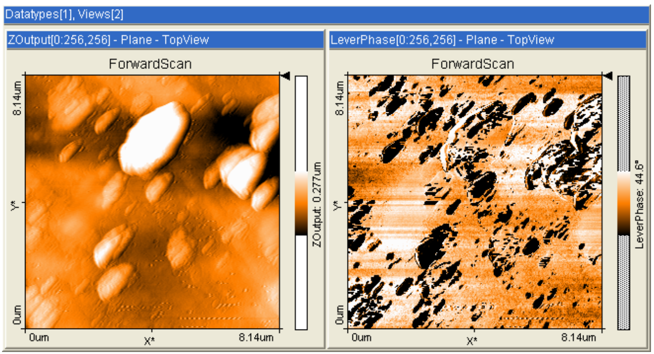

Fig. 1. AFM image of distribution in the rubber of original schungit.
Scan 8.14 x 8.14 mm^2. Left - topography, right - phase contrast.

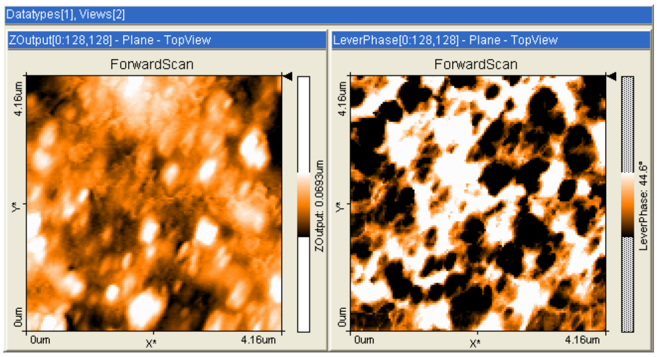

Fig. 2. AFM image of distribution in the rubber of milled nanoshungit.
Scan 4.16 x 4.16 mm^2. Left - topography, right - phase contrast.

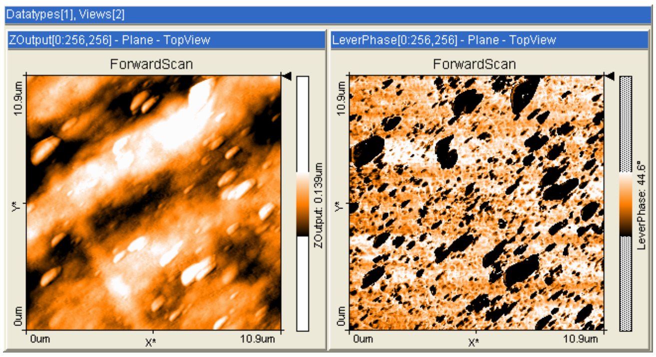

Fig. 3. AFM image of distribution in the rubber of milled nanoshungit, modified by organosilane Glymo.
Scan 10.9 x 10.9 mm^2. Left - topography, right - phase contrast.

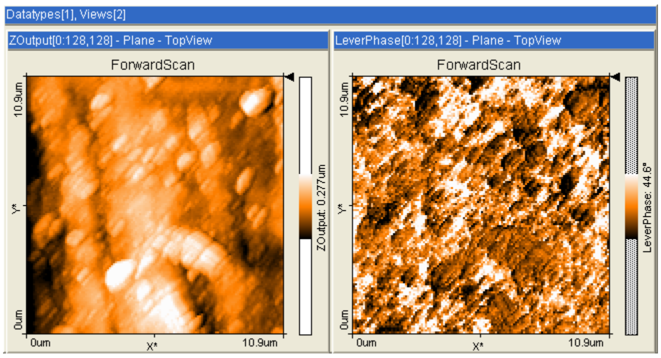

Fig. 4. AFM image of distribution in the rubber of milled nanoshungit, modified by organosilane Thiol.
Scan 10.9 x 10.9 mm ^{2}. Left - topography, right - phase contrast.

Determination of these composites deformation characteristics was carried out on the machine UTS-10. The graphs of conventional strain - strength properties of elastomers are shown in Fig. 5. Designations ШИКНИ and ШИКНМ means rubber filled by original and milled nanoshungit respectively, others by nanoshungit, modified by proper organosilanes.

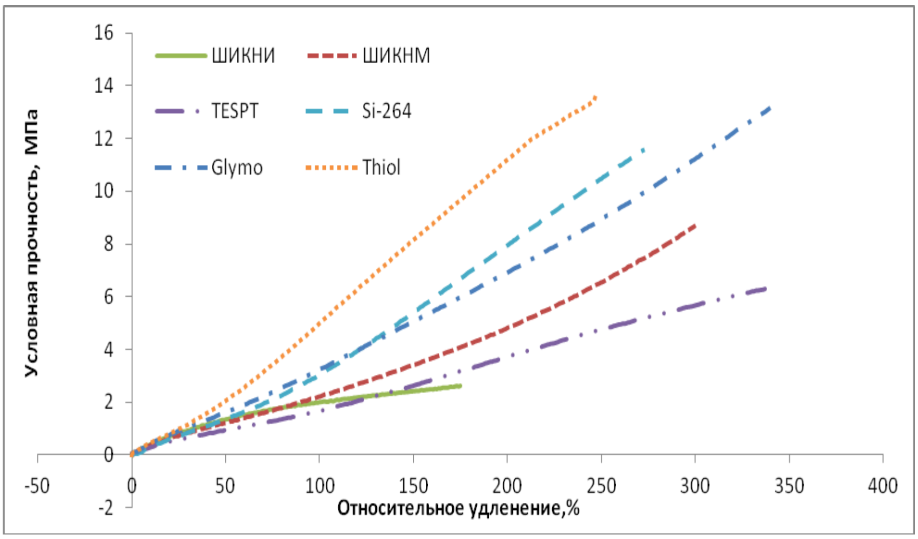

Fig. 5. The graphs of conventional strain - strength properties of studied composites. Engineering strain (%) are plotted in abscissa and engineering stress (MPa) in ordinates.

4. Discussion of the results

Analyses of the experimental data allow deducing certain conclusions.

Modification of nanoshungit filler by organosilanes significantly improves the quality of rubber compounds. Using the Thiol organosilane we obtained the highest tensile strength at 5 MPa more than rubber filled with nanoshungit without modification, with the extension not reached 300 %, which shows good mechanical properties of the vulcanizate. Organosilane Glymo sulfur-free showed an increase in rubber tensile strength, but its elongation was over 300 %. The use Si 264 as nanoshungit modifier also showed an increase in elastomer strength about 3 MPa relative to filled by nanoshungit without modification. This shows that the modification has been successfully completed. The sample with TESPT showed increased elastic - strength properties up to 330 %.

The obtained data reveal a correlation between characteristics of the surface structure as a function of changes in the size, composition, distribution shungit micro and nanofillers aggregates observed by the AFM and changes in deformation - strength characteristics of these investigated complex heterogeneous materials.

5. Conclusions

The comprehensive study of AFM and physical - mechanical tests of the new model samples of rubbers based on butadiene - styrene rubber SBR-30 ARK filled with micro and nanoshungit modified by organosilanes, yielded important data on the properties of the investigated objects. Comparison of the AFM data with the results of tensile testing machine on the characteristics of these composites has allowed them to conduct cross-correlation. These results are important for both the fundamentals of the theory of the reinforcement of composites, as well as practical applications in industry.

Acknowledgements

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