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APPLICATION OF QUANTUM-CHEMICAL MODELING RESULTS IN EXPERIMENTAL INVESTIGATIONS OF SILICONE COMPOSITES

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Abstract. The results of direct numerical simulation obtained earlier, within the cluster quantum-chemical approximation, are used in experimental investigations of polydimethylsiloxane composites with shungit. The surface structure of these composites by scanning electron and atomic force microscopy was studied. Correlation of the distribution of micro and nano - dimensional filler in the polymer matrix with the physical mechanical properties of the elastomers was established.

Keywords: polydimethylsiloxane composites, nanoshungit filler, scanning electron and atomic force microscopy.

1. Introduction

The problems of increasing the strength of polymer materials are important for both fundamental science and applied research. For example, the polydimethylsiloxanes as representative of organosilicon polymers are of the great importance in industry. However, they have low mechanical strength. Increasing the resistance to fracture of these polymers is usually achieved with fillers [1].Therefore, it is necessary to study new reinforcing substances from disperse fillers of various nature.

Of great interest in this respect is the use of schungit, natural composite, consisting of silica, dispersed in matrices of amorphous carbon [2]. There seems advisable preliminary to perform the molecular computational modeling, which is an effective method of a virtual analysis of the structural, energetic and micromechanical properties of micro and nanocomposites.

As reported in [3], the energetic and structural characteristics of elastomer complexes with shungit have been calculated quantum - chemically under developed NDDO / sp-spd semiempirical original program [4]. Numerical calculations on the supercomputer MBC-5000 in the Interdepartmental Supercomputer Center were performed. The microscopic characteristics of nanomechanical behavior, deformation and fracture characteristics of shungit adsorbates with polyisoprene during uniaxial tension based on this program in the cluster approximation were examined. It was deduced, that one can expect a substantial reinforcement for such composites.

As reported in [5], the quantum - chemical studies of deformation in polydimethylsiloxane oligomer molecules in contact with the particles of silicates predict strong interactions between these components.

The results of these calculations were used by us in the practical synthesis of siloxane composites with schungit. It has also been developed the multistage physical chemical

modification technology for obtaining the active nanostructured schungit filler for rubbers, based on these quantum chemical calculations.

According to the results of [6] there is an increase in the tear resistance and in the specific work of the deformation during fracture, with preservation of the increased strength properties of synthetic thermally stable low-molecular-weight silicone elastomers based on SCTN-A, filled with micro and nanoscale schungit.

To further elucidate the nature of the onset of strengthening effects, knowledge of the distribution of fillers in these elastomeric matrices is necessary. The surface structure of these composites, using electron and atomic force microscopy, in the present paper was studied.

2. Experimental procedures and materials

As a filler of elastomers, a natural shungit mineral was used (Zazhoginsky deposit, Carbon-Shungite Trade Ltd, Karelia, Russia). The rock is a natural composite, in the carbon matrix of which are distributed highly dispersed silicate particles and small amounts of other oxides. The chemical composition of schungit used in this work is shown in Table 1.

Table 1. Chemical composition of shungit (%) [2].

SiO_2	TiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	S	C	H_2O_{cryst}
57.0	0.2	4.0	2.5	1.2	0.3	0.2	1.5	1.2	29.0	4.2

As the basis of the composite matrix, silicone low-molecular rubbers SKTN-A were chosen. Filler was both the original shungit and the grounded one in a ball planetary mill PM100 (Retsch, Germany) under different environments. The introduction and dispersion of the filler and the mixing of all the ingredients were carried out in a laboratory mixer [6]. Table 2 shows the compositions of the samples studied.

Table 2. Composition of the synthesized samples.

Ingredients name	Code of mixture								
	C300	C301	C302	C303	C304	C305	C306	C307	C308
	%								
SKTN-A rubber	100	90	80	70	60	90	80	70	60
Shungit (original)		10	20	30	40				
Shungit (grounded)						10	20	30	40
Total	100	100	100	100	100	100	100	100	100

The fillers were added to the SKTN-A rubber according to the compositions given in Table. 2, kneaded by hand, and then passed through rolls. The resulting mixtures were evacuated for 15 minutes, and then a catalyst was introduced with a certain concentration for each composition and again evacuated. The samples were placed in teflon forms and cured.

The Scanning Electron Microscope (SEM) Merlin (Carl Zeiss, Germany) worked with an accelerating voltage of 5 kV and beam current of 300 pA.

The atomic-force microscope (AFM) easyScan (Nanosurf, Switzerland), operating in a contact mode at ambient conditions, using also the force modulation mode, or in the semi-contact mode with the phase contrast mode, were used. In a semi-contact mode, a SuperSharpSilicon probe (Nanosensors, Switzerland) with a tip radius of about 2 nm was used. Image processing was performed using the SPIP™ - advanced software package for processing and analyzing microscopy images at nano- and microscale (Image Metrology, Denmark).

Investigations of the physical mechanical properties of the composites were conducted [6] on universal testing machine UTS-10 (Ulm, Germany).

3. Experimental results

Initially shungit samples, after deposition on the surface of highly oriented pyrolytic graphite (HOPG) from a suspension in toluene, were tested by AFM. The AFM topography images of shungit powders on the HOPG surface and phase contrast images established the particle sizes of the original schungit in the range from 1 to 5 μm and the grounded powders in the range from 70 to 250 nm. Examples of AFM scans on the synthesized composites from the table 2 are shown in figure 1 - 2. The AFM surface images of pure SCTN-A rubber are presented in Fig. 1 and AFM surface images of C 308 composite - in Fig. 2. The distribution and sizes of shungit fillers, presented as bright dots in the background of polymeric matrix, clearly are visualized in right images of material contrast Fig. 2.

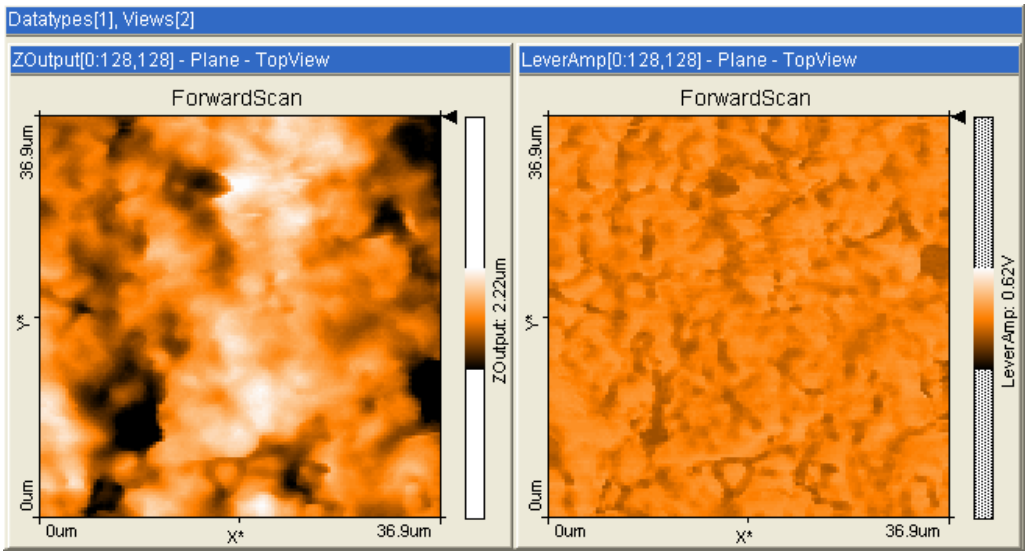


Fig. 1. AFM surface images of pure SCTN-A rubber
Scans 36.9 x 36.9 μm^2. Left - topography, right – material contrast.

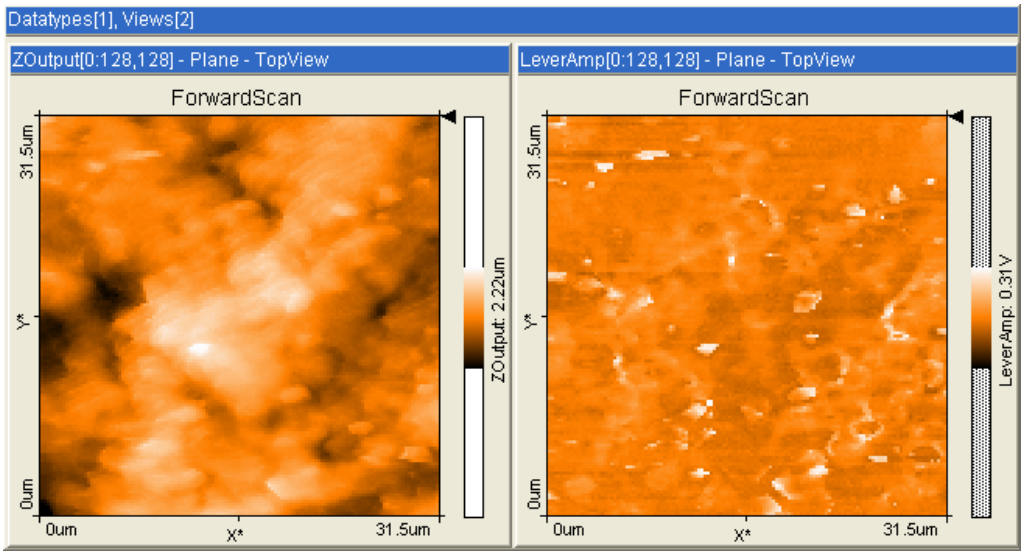
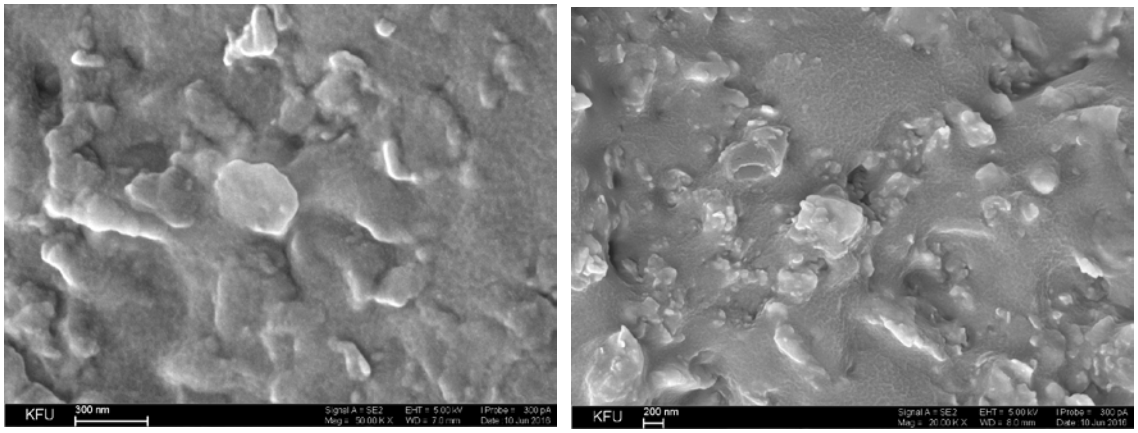


Fig. 2. AFM surface images of C 308 composite (b).
Scans 31.5 x 31.5 μm^2. Left - topography, right – material contrast.

The AFM images data processing showed that the aggregate sizes of these nanostructured schungit filler in composite C 308 are located in the range 50 nm to 2 μm, and the nearest distances between them on the average in 300 nm.

Electron microscopic photographs of the C 308 composite are shown in Fig. 3a, b. The SEM surface topography C 308 composite, prepared in the form of plate, is presented in Fig. 3a and SEM images of its perpendicular cross – section in Fig. 3b.



a) b)

Fig. 3. SEM images of the top surface topography plate C 308 composite (a) and of the plate perpendicular cross – section (b). Unite scales: 300 and 200 nm respectively.

These SEM images shows the same approximate values of filler aggregate sizes as deduced from AFM measurements, and additionally visualize the space arrangement of fillers in the elastomer matrix. The application of SEM and AFM methods to visualize topography of surfaces and sections of investigated silicone rubber composites with schungit fillers allowed direct observation of changes in the structure of composite elastomers on the micro and nanometer range with increasing concentrations of reinforcing fillers.

4. Discussions

Correlation these results with the physical mechanical properties of these materials, studied in [6], makes it possible to understand the cause of the enhancing ability of nanostructured schungit in organosilicon elastomers, as due to the formation of a spatial filler network in the polymer matrix. These data make it possible to understand the reasons for the shungit filler manifestation of the reinforcing properties in the SKTN-A rubber, as conditioned not only by the chemical affinity of the amorphous carbon and the silica with the polydimethylsiloxane matrix, but also by a fairly uniform spatial distribution of the filler in the composite. The role of polar hydroxyl groups (OH) bound to silica part of the shungit (silanol groups) interacting with siloxane segments (Si - O - Si) of matrix is also important, because the formed complex prevent the macroscopic agglomeration of initial schungit particles during introduction to the polymer. The resulting increase in the interaction surface of the nanostructured filler with the polymer macromolecules leads to an effective reinforcement of the initial polydimethylsiloxane matrix. As reported in [6] the tests of these composites on a machine UTS-10 showed an increase in the tensile strength from about 0.5 MPa in pure SCTN-A rubber to 3.6 MPa in C 308 composite and tear resistance from 1.3 kN / m to 7.0 kN / m, respectively. It was also showed that C 308 composite is comparable in the maximum value of the specific work deformation for destruction with well known silicon composite reinforced by silica. These results, when compared with traditional silicon dioxide filler [1, 6], show good effectiveness of the present nanostructured shungit as reinforcement filler in polydimethylsiloxane. The

experimental verifications about theoretical predictions that nano shungit may be active also in the reinforcement of butadiene - styrene rubbers was shown in [7].

5. Conclusions

The application of SEM and AFM methods to visualize topography of surfaces and sections of investigated silicone rubber composites with schungit fillers allowed direct observation of changes in the internal structure of composite elastomers in the micro and nanometer range. The correlation these results with the physical mechanical properties of the composites is important for the development the basic principles of reinforcement material strengths. The preliminary direct numerical calculations within the framework of the cluster quantum-chemical approximation [3 - 5] of the shungit nanostructure and its components, predicting the effectiveness of its use as filler in elastomers proved to be valuable for conducting these experiments. The presented experimental results show both theoretical and practical significance of the quantum - chemical approach proposed in [3 - 5] for computer selection of components in elastomeric composites and ways of modifying their fillers in order to predict the technologies for obtaining materials with improved strength characteristics. This developed computational technique can be applied in similar problems of designing new advanced materials.

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