Chapter 2

Atomic Force and Electron Scanning Microscopy of Silicone Composites

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Abstract

The conclusions of direct numerical simulation obtained earlier, within the cluster quantum-chemical approximation, are used in experimental investigations of polydimethylsiloxane composites with schungit or silica. The surface structure of these composites by atomic force and scanning electron microscopy was studied. Correlation of the distribution of micro- and nanodimensional fillers in the polymer matrix with the physical-mechanical properties of the composites was established.

Keywords: polydimethylsiloxane composites, schungit, silica, atomic force and scanning electron microscopy

1. Introduction

The problems of increasing the strength of polymer materials are important for both fundamental science and applied research. For example, the polydimethylsiloxane (PDMS) CKTH rubbers, as representative of organosilicon polymers, are of the great importance in industry. Materials made on the basis of such CKTH rubbers are resistant to temperatures from −90 to +300°C, as they possess high hydrophobicity, chemical inertness, dielectric properties, vibration resistance, resistance to fungi and microorganisms, and resistance to ozone, oxidizers, and ultraviolet rays. Also they are physiologically inert, tissue and hemocompatible, gas permeable (the highest permeability of all known polymers), selective for gas permeability, and easily sterilized. Unlike organic, CKTH silicone rubbers are more economical, reliable, and durable even under extreme conditions; and are also easy to process. However, they have low

mechanical strength. Reinforcement of these polymers is usually achieved with fillers. The nature of the interaction of matrix elastomers with fillers is determined by the chemical nature, dispersion, shape, activity of the filler particles, the possibility of chemical bonds between the components of composites, and the relationship between the processes of amplification and structuring. In the works of Mark and coworkers [1, 2], which generalize numerous studies, it is stated that the physical and mechanical properties of synthetic low-molecular-weight siloxane elastomers filled with silica are significantly enhanced. It is of great interest also for the search for new reinforcement fillers to PDMS. One of favorable proposals may be schungit [3]. In the development of advanced composites, it is 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 nanomaterials. As reported in [4–6], the energetic and structural characteristics of elastomer complexes with silica or schungit have been calculated quantum chemically under developed NDDO/sp-spd semiempirical original program [7]. Numerical calculations on the supercomputer MBC-5000 in the Interdepartmental Supercomputer Center were performed. The microscopic characteristics of nanomechanical behavior, deformation, and strength characteristics of silica or schungit adsorbates with polydimethylsiloxane oligomer molecules during uniaxial tension based on this program in the cluster approximation were examined. It was deduced that one could expect a substantial reinforcement of physical-mechanical properties for such composites.

We used the conclusions of these calculations in the practical synthesis of siloxane composites with schungit and silica. The multistage physical-chemical modification technology for obtaining the active nanostructured schungit filler for rubbers, based on these quantum-chemical calculations, has also been developed.

According to the results of [8], 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 CKTH-A, filled with micro- and nanoscale schungit and silica SIPERNAT 360.

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 atomic force and electron scanning microscopy, in the present chapter was studied as extension of the studies [8–11].

2. Examination procedures and materials

As the basis of the composite matrix, silicone low-molecular thermal shock resistant synthetic rubber CKTH brand A (silanol terminated polydimethylsiloxane, HO [–Si $(CH_3)_2$ O–] n H) was chosen. As a filler of CKTH-A rubber a natural schungit mineral was used (Zazhoginsky deposit, Carbon-Shungite Trade Ltd., Karelia, Russia) [3]. 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, according to [3], used in this work is shown in **Table 1**.

Fillers were both the original schungit from provider and the original schungit milled by us in a ball planetary mill PM100 (Retsch, Germany) under different environments. The fillers were added to the CKTN-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; then, a catalyst No 68 was introduced with a certain concentration for each composition and again evacuated. The samples were placed in Teflon forms and cured [8]. **Table 2** shows the ingredients of the samples used and corresponding code of synthesized composites.

CKTN-A composites with silica fillers, precipitated silicon dioxide, and SIPERNAT 360 (Evonik Industries AG, Germany), were prepared analogues to composites with schungit. **Table 3** shows the ingredients of the samples studied.

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, was used. In a semi-contact mode, a SuperSharpSilicon probe (Nanosensors, Switzerland) with a tip radius of about 2 nm was

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

Table 1. Chemical composition of schungit (weight percentage).

Composite ingredients name	Code of composites								
	C300	C301	C302	C303	C304	C305	C306	C307	C308
	Weight percentage								
CKTH-A rubber	100	90	80	70	60	90	80	70	60
Schungit (original)		10	20	30	40				
Schungit (milled)						10	20	30	40
Total	100	100	100	100	100	100	100	100	100

Table 2. Ingredients of the synthesized composites with schungit filler.

No	Composite ingredients name	Code of mixture					
		C 300	C 309	C 310	C 311	C 312	C 313
		Weight percentage					
1	CKTH-A rubber	100	80	90	80	70	60
2	SIPERNAT 360	—	20	10	20	30	40
3	Total	100	100	100	100	100	100

Table 3. Ingredients of the synthesized composites with silica filler.

used. Image processing was performed using the SPIP™—advanced software package for processing and analyzing microscopy images at nano- and microscale (Image Metrology, Denmark). The scanning electron microscope (SEM) Merlin (Carl Zeiss, Germany) worked with an accelerating voltage of 5 kV and beam current of 300 pA. Investigations of the physical-mechanical properties of the composites were conducted on universal testing machine UTS-10 (Ulm, Germany), and nanoscale mechanical properties were studied with NanoTest 600 (MicroMaterials, UK) [8].

3. Experimental results

Initially, schungit powder samples, after deposition on the surface of highly oriented pyrolytic graphite (HOPG) from a suspension in toluene, were tested by AFM. The AFM topography and phase contrast images established the particle sizes of the original schungit from provider in the range from 1 to 5 μm. AFM images of the schungit particles deposited on the HOPG after milling in a ball planetary mill PM100 are shown in **Figure 1**. The agglomerates of nanosized schungit in the range from 50 to 250 nm are clearly detected.

AFM images of surface of pure C 300 rubber CKTH-A are shown in **Figure 2**. The scans visualized typical nodular polymer structure.

In **Figure 3**, an example of AFM scan on sample C 308 from the synthesized composites listed in **Table 2** is displayed. The distribution and size of schungit fillers, presented as bright color in the background of polymeric matrix, clearly are visualized.

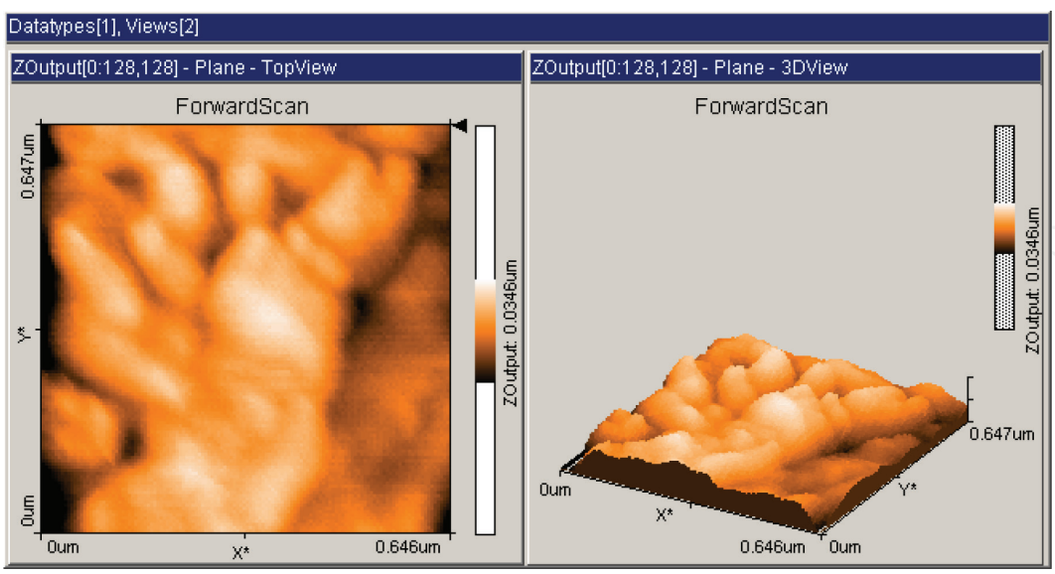

Figure 1. AFM images of the schungit agglomerates after milling, deposited on the HOPG surface. Scan XY = 0.646 × 0.646 microns. Left—topography and right—3D view.

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

Electron microscopic photographs of the C 308 composite are shown in **Figure 4a** and **b**. The SEM surface topography C 308 composite, prepared in the form of plate samples, is presented in **Figure 4a** and SEM images of its perpendicular cross section in **Figure 4b**. It is well known that the quality of many materials in particular of composites depends on a large extent on the homogeneity of the materials realized. Visualized by these methods

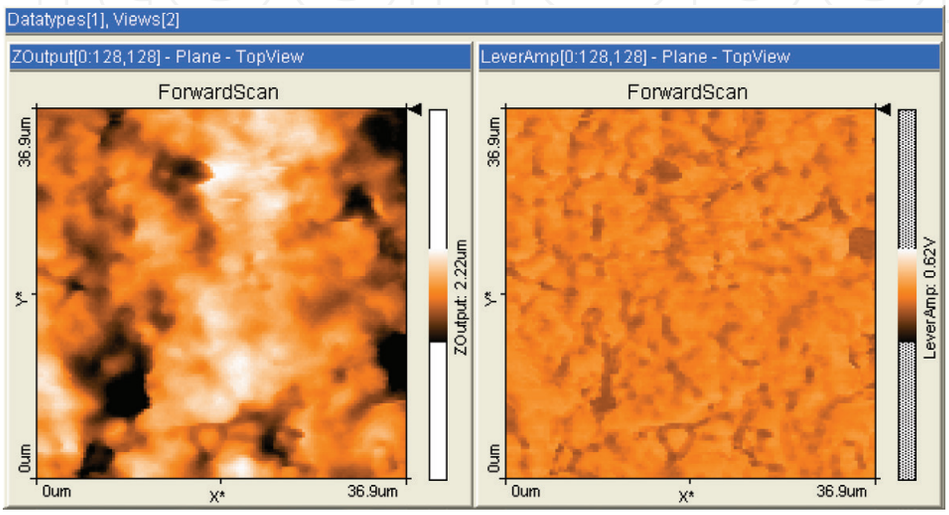


Figure 2. AFM images of the surface of the pure CKTH -A rubber C 300. Scans XY = 36.9 × 36.9 microns. Left—topography and right—phase contrast.

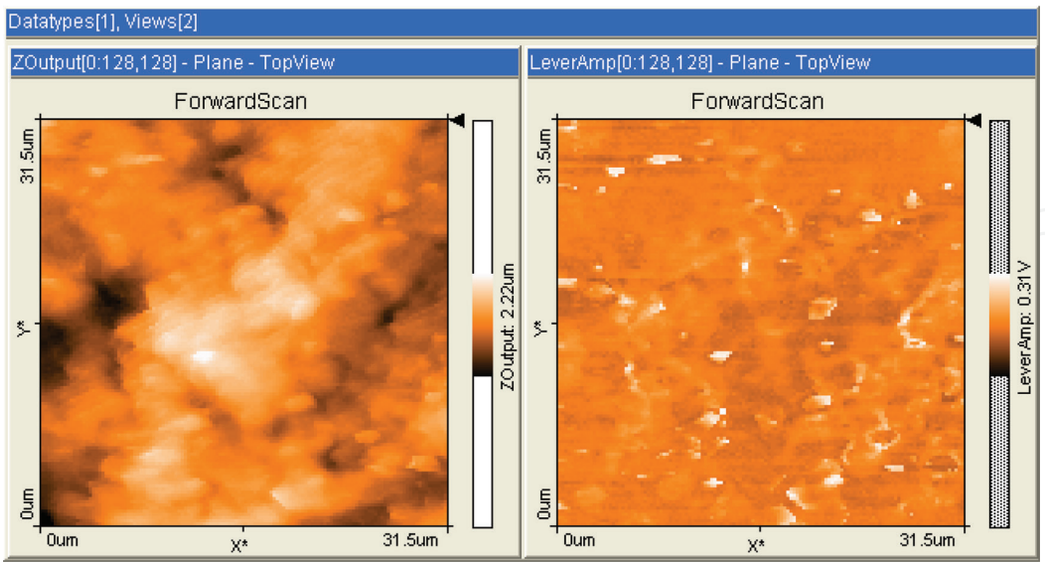
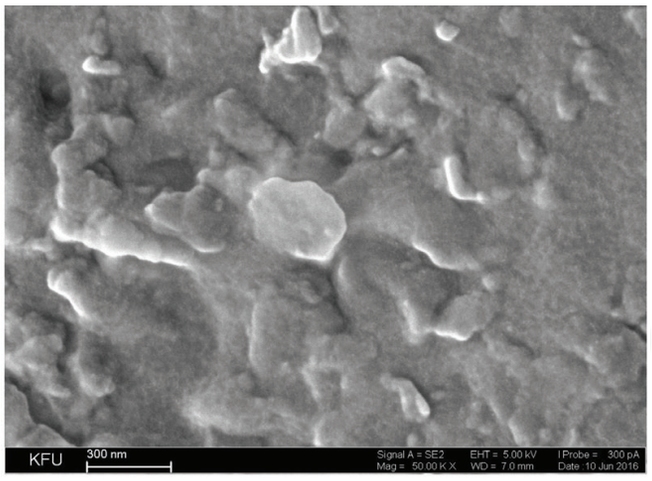
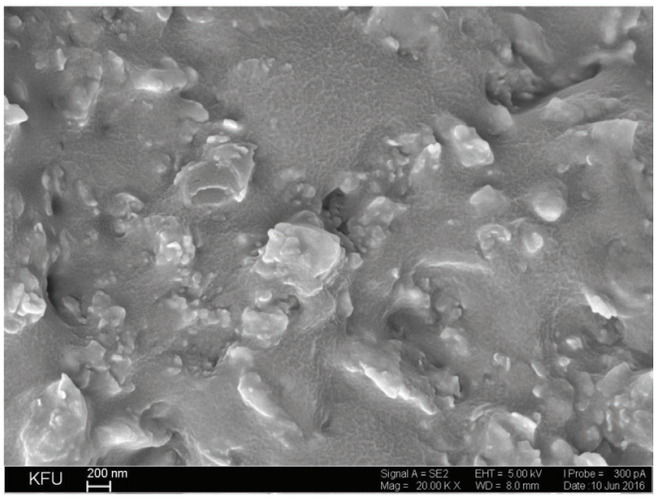


Figure 3. AFM surface images of C 308 composite. Scans 31.5 × 31.5 microns. Left—topography and right—phase contrast.



a)



b)

Figure 4. SEM images of the top surface topography plate C 308 composite (a) and of the plate perpendicular cross section (b). Unite scales: (a) 300 and (b) 200 nanometer, respectively.

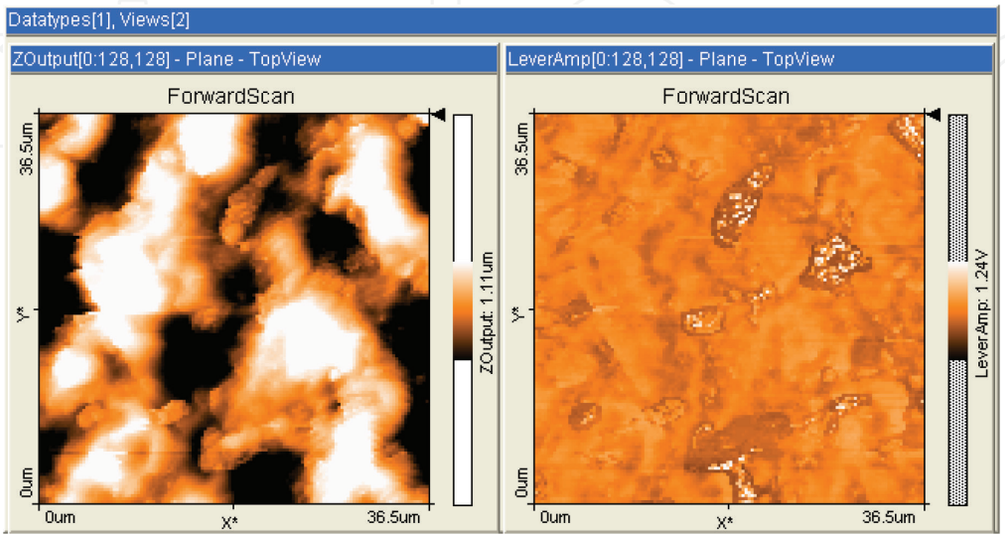


Figure 5. AFM images of the surface structure of composite C 311. Scans XY = 36.5 × 36.5 microns. Left—topography and right—phase contrast.

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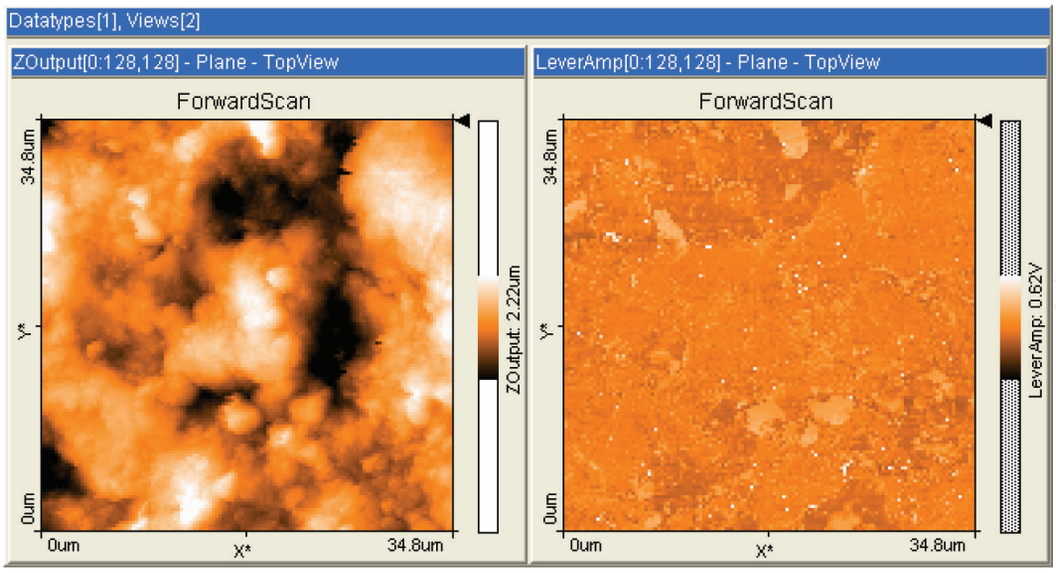
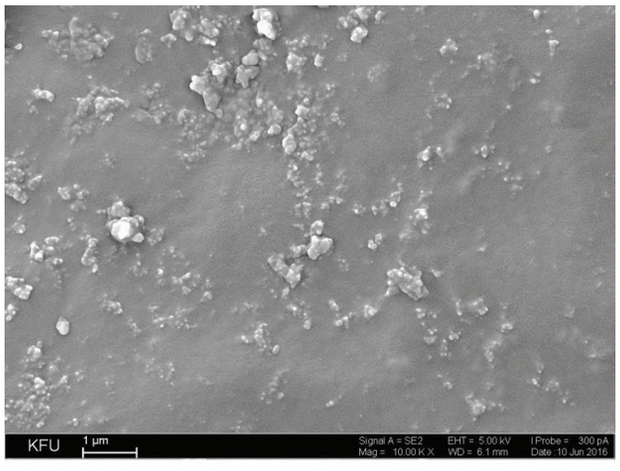
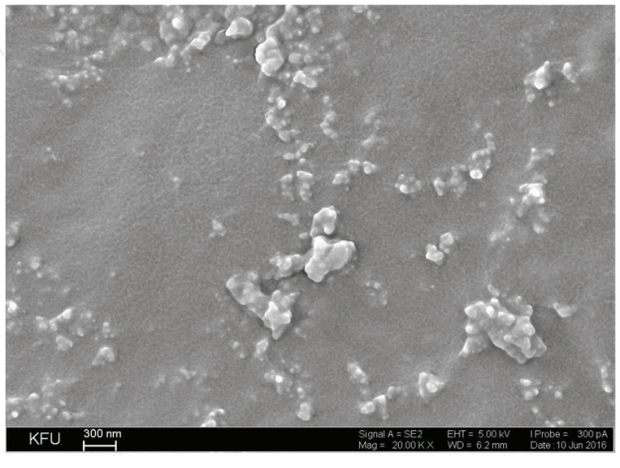


Figure 6. AFM images of the surface structure of composite C 313. Scans XY = 34.8 × 34.8 microns. Left—topography and right—phase contrast.

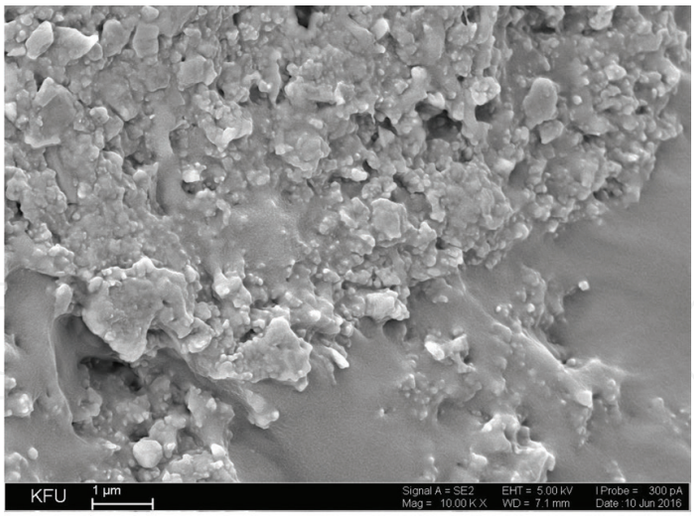


a)

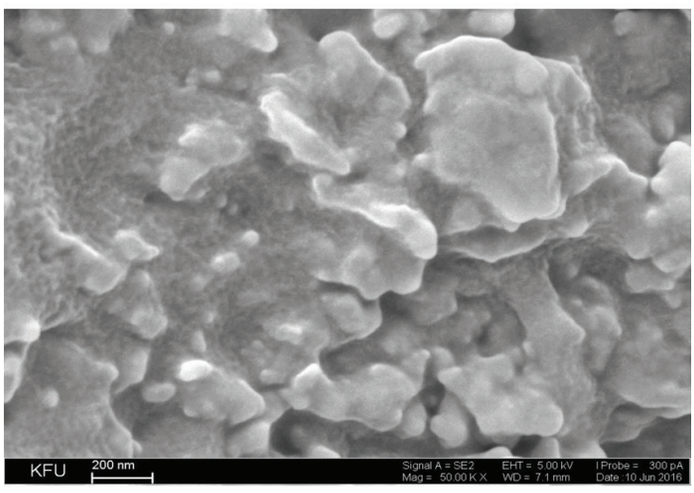


b)

Figure 7. SEM images of the surface structure of sample C 311. Unite scales: (a) 1 micron and (b) 300 nm, respectively.



a)



b)

Figure 8. SEM pictures of the structure of the cross sections of the surface of sample C 311. Unite scales: (a) 1 micron and (b) 200 nm, respectively.

of AFM and SEM, the composite C 308 surface morphology shows that the nanosized schungit fillers are homogeneously dispersed in the polymer matrix and are well adhered to the polymer matrix. This finding is very important for understanding the reasons of reinforcing the physical-mechanical properties of initial CKTH-A rubber with used nano-structured schungit filler.

AFM surface images of C 311 composite CKTN-A rubber with silica SIPERNAT 360 fillers are shown in **Figure 5**, and of composite C313 in **Figure 6**. The internal microstructure and agglomerates sizes of this filler in composites are of the same dimensions as in the case of nanosized schungit filler.

SEM images of the top surface topography of the plate of the same C 311 composite are shown in **Figure 7** and of the plate perpendicular cross section in **Figure 8**.

These SEM images show the same approximate pictures of fillers dispersed distributions in the elastomer matrices and mean values of their aggregate sizes as deduced from AFM measurements; additionally SEM scans of the plate perpendicular cross sections visualized the space arrangement of fillers in these composites.

4. Discussions

The application of SEM and AFM methods to visualize topography of surfaces and cross sections of investigated silicone rubber composites with schungit and silica SIPERNAT 360 fillers allowed direct observation of changes in the structure of composite elastomers on the micro- and nanometer range by increasing their concentrations. It is known that in silicone compositions, along with the interactions between the filler and the polymer matrix, there is also a process of agglomeration and structuring of the filler particles [1, 2]. As established by the data of AFM and SEM (**Figures 3–8**), a rather homogeneous distribution of the filler in the elastomeric matrix takes place in the investigated composites. Correlation of these results with the physical-mechanical properties of these materials, studied in [8], makes it possible to understand the cause of the enhancing ability of nanostructured schungit in organosilicon elastomers, due to the formation of a spatial filler network in the polymer matrix. These data make it possible to understand the reasons for the schungit filler manifestation of the reinforcing properties in the CKTH-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) bounded to silica part of the schungit (silanol groups) interacting with siloxane segments (Si–O–Si) of matrix is also important, because the formed complex prevents the macroscopic agglomeration of initial schungit particles during the introduction of 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 [8], the tests of these composites on a machine UTS-10 showed an increase in the tensile strength from about 0.5 MPa in original CKTH-A rubber to 3.6 MPa in C 308 composite, and tear resistance from 1.3 to 7.0 kN/m, respectively. It was also showed that these rubber composites with nanostructured schungit fillers have values of the specific work deformation for destruction belonging to the same regions of magnitude as silica filled composites with the same matrix. These results, when compared with traditional silicon dioxide filler [1, 2], show good effectiveness of the present nanostructured schungit as reinforcement filler in polydimethylsiloxane.

The obtained images of the topography and material contrast of the surface of the composites with silica SIPERNAT 360 fillers also made it possible to visualize a fairly uniform distribution of silica particles in a matrix of silicone rubber. Tests of vulcanizates of these mixtures on a tensile machine UTS-10 showed an increase in the tensile strength from about 0.5 MPa in C300 to 3.0 MPa in C 311 composites, and tear resistance from 1.3 to 3.4 kN/m, respectively, and in C313 composite to 4.1 MPa and 7.1 kN/m accordingly [8]. Studies on the NanoTest 600 measuring system by the method of nanoindentation are in accord with these results. The obtained data make it possible also to understand the reasons for the manifestation of the

SIPERNAT 360 filler, with the reinforcing properties in the CKTH-A rubber as conditioned not only by the chemical affinity of the silicon dioxide and the matrix, but also by the fairly uniform spatial distribution of the filler in the composite. The role of polar hydroxyl groups (OH) associated with the filler SIPERNAT 360 (silanol groups) interacting with silicone segments (Si–O–Si) of the SKTN-A silicone analogous to nano schungit is important, with the formation of a hydrogen bond. This also makes it possible to prevent macroscopic agglomeration of the silica when introduced into the polymer, ensuring homogeneity of the filler distribution in the composite. The resulting increase in the interaction surface of the filler with the polymer leads to an effective hardening of the initial silicone matrix.

The experimental verifications of numerical semi-empirical quantum-chemical predictions that nano schungit and silica may be active also in the reinforcement of butadiene-styrene rubbers are shown in [9, 10].

5. Conclusions

The application of SEM and AFM methods to visualize topography of surfaces and sections of investigated silicone rubber composites with schungit and silica SIPERNAT 360 fillers allowed direct observation of changes in the internal structure of fillers in composite elastomers in the micro- and nanometer range. The correlation of these results with the physical-mechanical properties of the composites is important for the development of the basic principles of reinforcement material strengths. The preliminary direct numerical calculations within the framework of the cluster quantum-chemical approximation of the schungit nanostructure and its components, predicting the effectiveness of its use as a 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 for computer selection of components for 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.

Conflict of interest

The authors declare that they have no "conflict of interest."

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