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Scanning Probe Microscopy of Elastomers with Mineral Fillers

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Abstract

The results of a comprehensive study of the newly synthesized elastomeric composites filled with micro- and nanoscale modified shungite and also taurit, diatomit, and neosyl fillers are presented. The surface structure study of the prepared composites was conducted using scanning probe microscopy. The use of microscopy allowed visualization of the distribution patterns of filler aggregates and agglomerates in composites. The morphology and micro-nanometer size ranges of these aggregates in the synthesized materials are determined. The proposed method of grinding shungite, taurit, diatomit, and neosyl fillers allows significantly increasing the strength characteristics of these composites. The correlation between the reinforcement of the elastic-strength properties and the distribution of the used fillers in the rubber matrix was established.

Keywords: composites, synthetic rubber, mineral fillers, scanning probe microscopy, physico-mechanical properties

1. Introduction

Considering the high demand for composites made of elastomers with active fillers [1–4], it is necessary to search for renewable and sustainable fillers that are not inferior to those of traditional in reinforcing effect. Of particular interest are mineral fillers, which are fairly common and affordable raw materials, with low cost and environmental friendliness. We investigated the use of minerals: shungite, taurit, diatomit, and a product of rice husk processing—neosyl—of various degrees of dispersion as fillers for elastomeric composites based on industrial synthetic rubber SBR-30 ARK. The use of scanning probe microscopy (SPM) allows us to study the surface structure of these composites and visualize the features of the distribution of macro- and nanofillers in the rubber matrix. Simultaneous testing of the elastic-strength properties of such materials is also important for establishing a correlation with the SPM data and revealing the nature of the reinforcement of composites. To increase the strength characteristics of the materials obtained, additional grinding of the used mineral fillers was required. These complex studies made it possible to establish the possibility of using these minerals as active fillers of the studied composites.

2. Experimental procedure and materials

Shungite is a mineral substance consisting of silicate particles dispersed in amorphous carbon mixed with inorganic substances. The chemical composition of used shungites is presented in **Table 1**.

New model samples of composites based on butadiene-styrene rubber (SBR) were selected in the ratio of the components in weight percentage (wt %): SBR-30ARK, 60 wt. %; shungit filler, 39 wt.%; and vulcanizing group, 1 wt.%. Nanoshungit fillers were produced by milling the initial mineral powder in a medium of isopropyl alcohol on a planetary ball mill RM 100 (Retsch, Germany). The functionalization of nanoshungit by organic modifier organosilanes was made directly during the grinding in the mill. Organosilanes used in parts 1.5 wt. % were:

- "TESPT": bis(3-triethoxysilylpropyl) tetrasulfide (C18H42O6S4Si2) STRUKTOL® SCA98

- "Si-264": 3-thiocyanatopropyltriethoxysilane (C10H21NO3SSi) STRUKTOL® SCA 984

- "Glymo": gamma-glycidoxypropyltrimethoxysilane (C9H20O5Si) STRUKTOL® SCA 960

- "Thiol": 3-mercaptopropyltriethoxysilane (C9H22O3SSi) STRUKTOL® SCA 989

Industrial products of Koksu shungit rocks of Kazakhstan are marketed under the brand name "Taurit." Taurit is a mineral with both organic and silicate parts in its structure (**Table 2**). It contains globular carbon with a metastable supramolecular structure of the siliceous or carbonate type. It has been established that the use of taurit in the composition of rubbers allows not only to reduce their cost but also to obtain improvement in some indicators technological and technical properties of rubbers.

Diatomites are sedimentary rocks of marine or lake genesis; more than 50% consist of siliceous, opal shells of microscopic algae—diatoms. The chemical composition and physical properties of diatomites (Karelia, Russia) depend on the species composition of the rock-forming diatoms and sedimentation conditions, determined by geological, geomorphological, and climatic factors (**Table 3**). Diatomite bulk sorbent is a highly porous material obtained by grinding diatom rock.

Neosyl-120 is a product of rice husk high-temperature processing and low access of oxygen, with grinding to sizes of the order of hundreds of micrometers with a wide distribution of particle size. The chemical composition of Neosyl-120 is shown in **Table 4**.

The grinding of the initial microstructural powders of shungit, taurit, diatomit, and Neosyl-120 to nanoscale was performed using a PM100 planetary ball mill (Retsch, Germany). The dispersion of fillers and blending of all ingredients of elastomers were carried out in a laboratory mixer HAAKE Rheomix

Substance	SiO_2	TiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	S	C	H_2O
%	57.0	0.2	4.0	2.5	1.2	0.3	0.2	1.5	1.2	29.0	4.2

Table 1.
The chemical composition of shungites of the Zazhoginsky deposit type 3 (LTD "Carbon-Shungit" Karelia, Russia).

Element	TS %	Element	TS (%)
C	4–6	Mn	0.1
SiO_2	65–70	Ba	0.06
Al_2O_3	6–8	Zr	0.05
CaO	5–6	Sr	0.04
Fe_2O_3	3–4	V	0.015
Ti	0.5	B	0.01
K_2O	0.5	Zn	60 ppm
Na_2O	0.5	Ni	50 ppm

Table 2.
The average chemical composition of Koksu shale taurit [5].

Substance	SiO_2	Al_2O_3	Fe_2O_3	MgO	$K_2O + Na_2O$	Impurities
%	75	10	6	1	2	6

Table 3.
Chemical composition of diatomite sorbent [6].

Substance	SiO_2	Al_2O_3	FeO	CaO	MgO	K_2O	Na_2O	C	P_2O_5	Cl
%	92	0.5	0.2	1.1	0.5	3.0	0.1	1.5	0.3	0.1

Table 4.
Chemical composition of Neosyl-120.

No	Ingredients	Ш-940	Ш-941	Ш-942	Ш-943	Ш-944	Ш-945	Ш-946	Ш-947	Ш-948
1	SBR-30ARK	100	100	100	100	100	100	100	100	100
2	Sulfur SulfenamideC Altax	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7
3	Zinc oxide	3	3	3	3	3	3	3	3	3
4	Norman 346	7	7	7	7	7	7	7	7	7
5	Stearin technical	2	2	2	2	2	2	2	2	2
6	Taurit	0	65	0	0	0	0	0	0	0
7	Taurit (nano)	0	0	65	0	0	0	0	0	0
8	Sorbent diatomite (initial)	0	0	0	65	0	0	0	0	0
9	Sorbent diatomite (nano)	0	0	0	0	65	0	0	0	0
10	Diatomite (initial)	0	0	0	0	0	65	0	0	0

| No	Ingredients	Ш-940	Ш-941	Ш-942	Ш-943	Ш-944	Ш-945	Ш-946	Ш-947	Ш-948
11	Diatomite (nano)	0	0	0	0	0	0	65	0	0
12	Neosyl 120	0	0	0	0	0	0	0	65	0
13	Neosyl 120 (nano)	0	0	0	0	0	0	0	0	65

Table 5.
The composition of the studied rubber mixtures Ш-940–Ш-948 (weight percentage).

(Germany). Kinetics of vulcanization was investigated by analyzer RPA 2000 (Alpha Technologies, England). The mixture optimum curing was determined from obtained graphs. The composition of the synthesized elastomeric materials Ш-940–Ш-948 with taurit, diatomit, and Neosyl-120 fillers is presented in **Table 5**.

The study of the obtained samples of composites was carried out on an easyScan scanning probe microscope (Nanosurf, Switzerland), which operated in contact or semicontact modes in air at room temperature [7]. The modulation of force or phase contrast was also used to obtain the material contrasts of the composites under study. The processing of the obtained SPM images was carried out using the computer program SPIP (Image Metrology, Denmark). Scanning electron microscopy (SEM) images of the original Neosyl-120 powders were obtained using the electron microscope Jeol JSM-6510LV. Studies of physico-mechanical properties of the composites with these micro- and nanofillers were conducted on a universal tensile testing machine UTS-10 (Zwick Roell, Germany) and tensile testing machine with a pendulum force meter RMI-60 (ZIM, Tochmashpribor, Russia). The five repetitions for each type in tensile tests were done, and the mean values in the figures are presented. Dimensions of the samples of double-sided composite blades (type 1) correspond to the drawing and the table of reference [8].
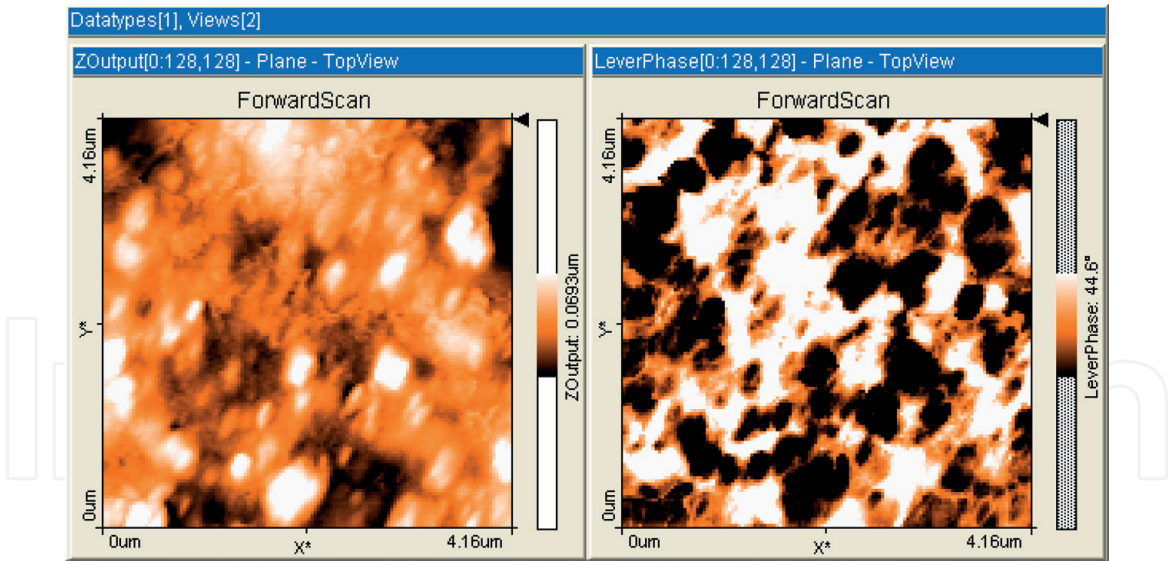
3. Experimental results

SPM images of the surface structure of the synthesized composites with shungit unmodified and modified by organosilanes [9] are shown in **Figures 1**–**4**.
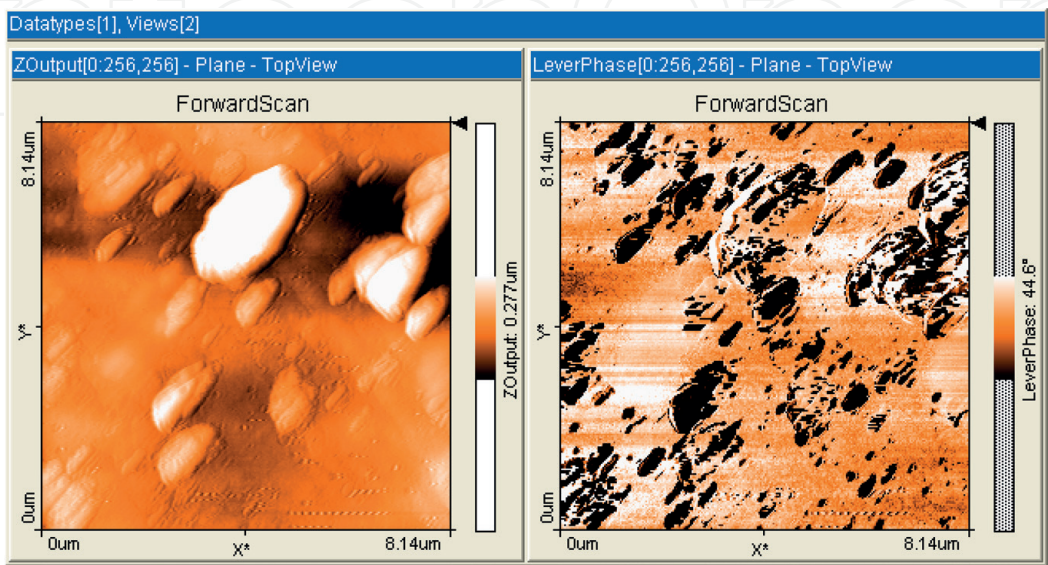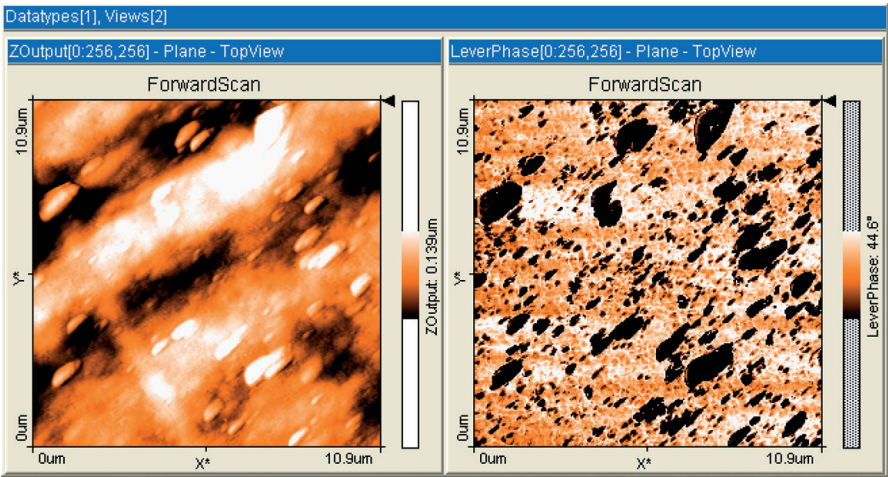

Figure 1.
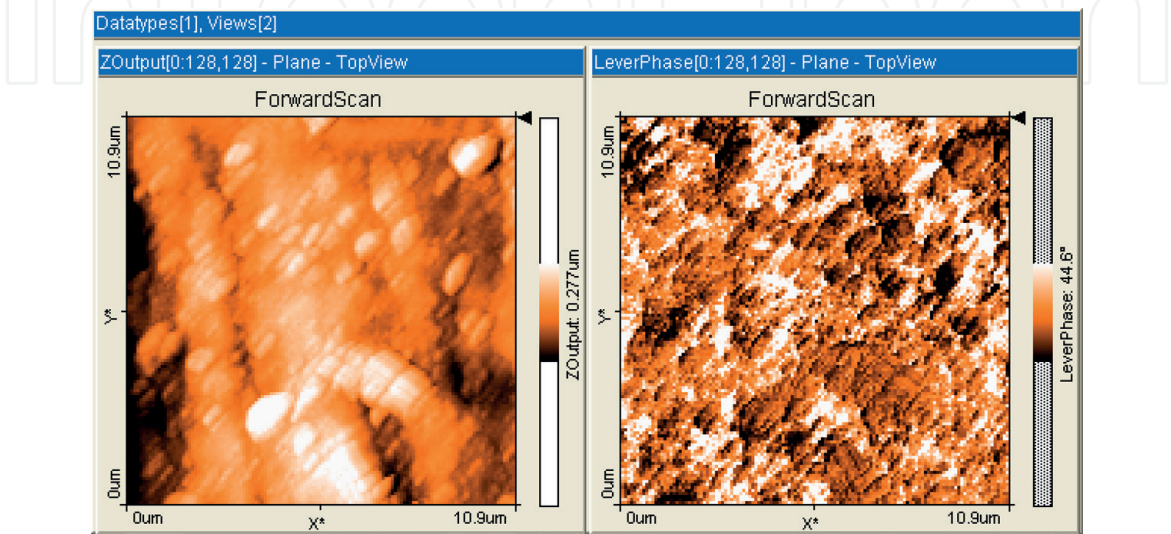*SPM image of distribution in the rubber of original schungit. Scan 8.14 × 8.14 μm². Left—topography; and right—phase contrast.*

Figure 2.
SPM image of distribution in the rubber of milled nanoshungit. Scan 4.16 × 4.16 μm². Left—topography; and right—phase contrast.

Figure 3.
*SPM image of distribution in the rubber of milled nanoshungit, modified by organosilane Glymo. Scan 10.9 × 10.9 μm². Left—topography; and right—phase contrast.*

Figure 4.
SPM image of distribution in the rubber of milled nanoshungit, modified by organosilane thiol. Scan 10.9 × 10.9 μm². Left—topography; and right—phase contrast.
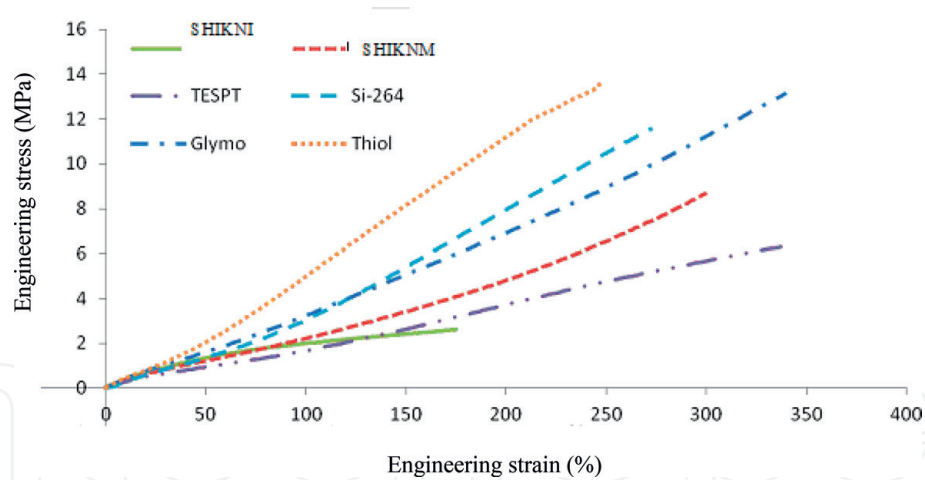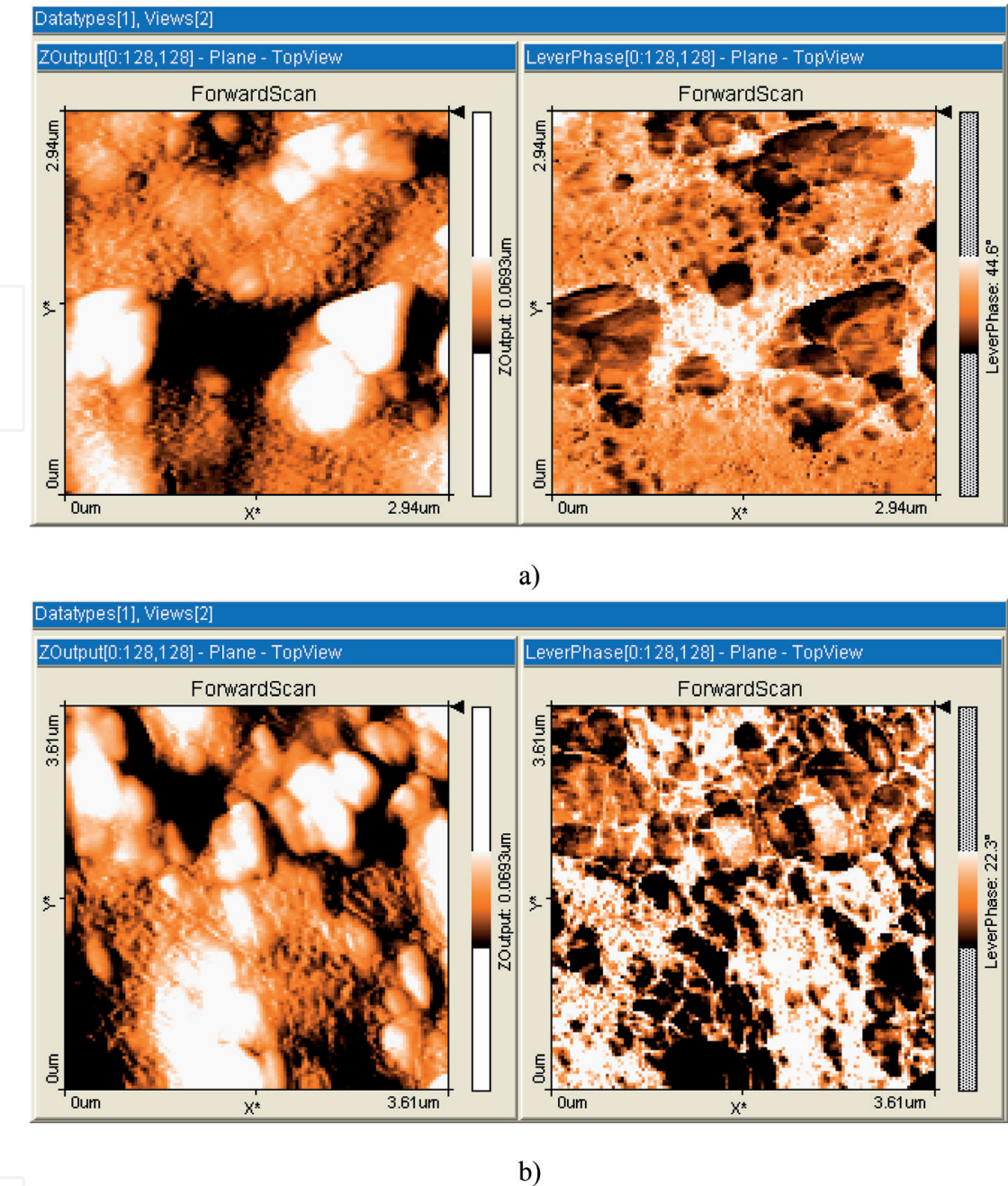
Figure 5.
The graphs of conventional strain-strength properties of studied composites with shungite. Engineering strain (%) are plotted in abscissa and engineering stress (MPa) in ordinates.


a)

b)
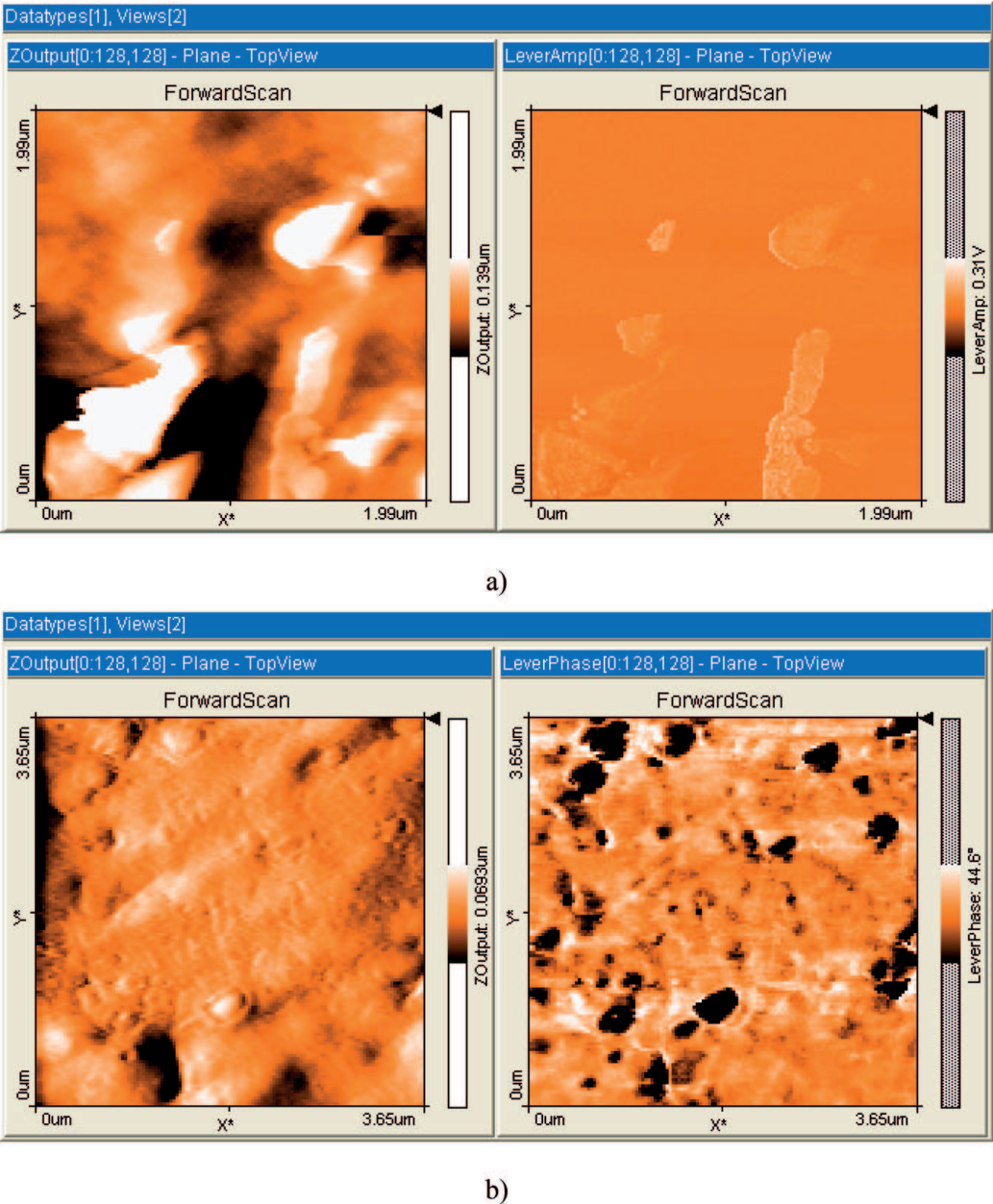
Figure 6.
SPM images of the surface structure of rubber composites with (a) taurit (microstructural), scan 1.99 × 1.99 μm², and (b) taurit (nanostructured), scan 3.65 × 3.65 μm². Topography on the left, and material contrast on the right.

a)

b)
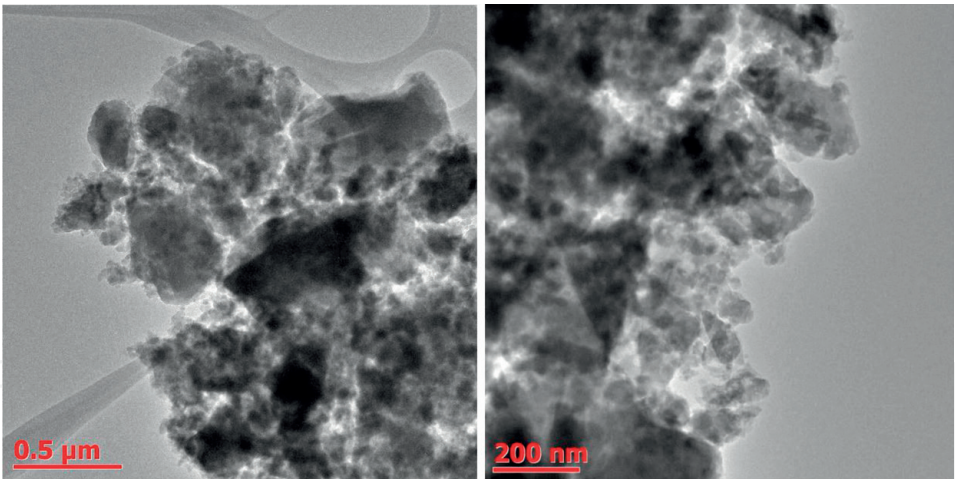
Figure 7.
SPM images of the surface structure of rubber composites with (a) diatomite (microstructural), scan 2.94 × 2.94 μm², and (b) diatomite (nanostructured), scan 3.61 × 3.61 μm². Topography on the left, and material contrast on the right.
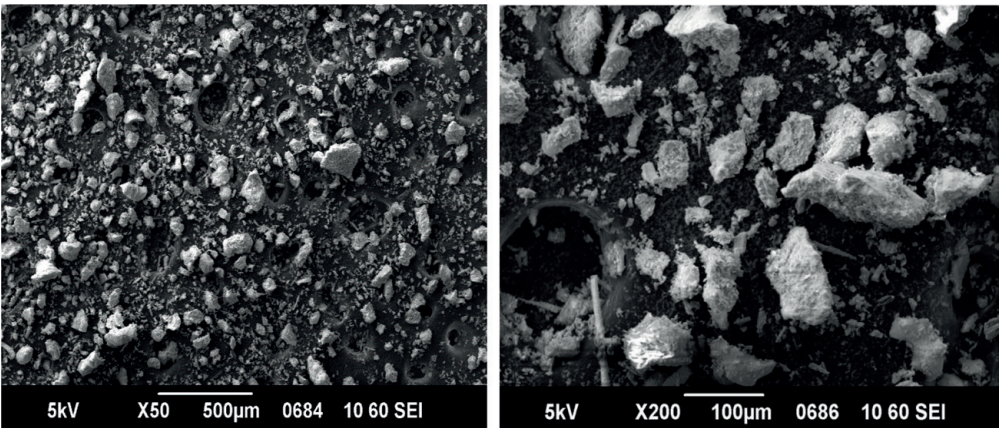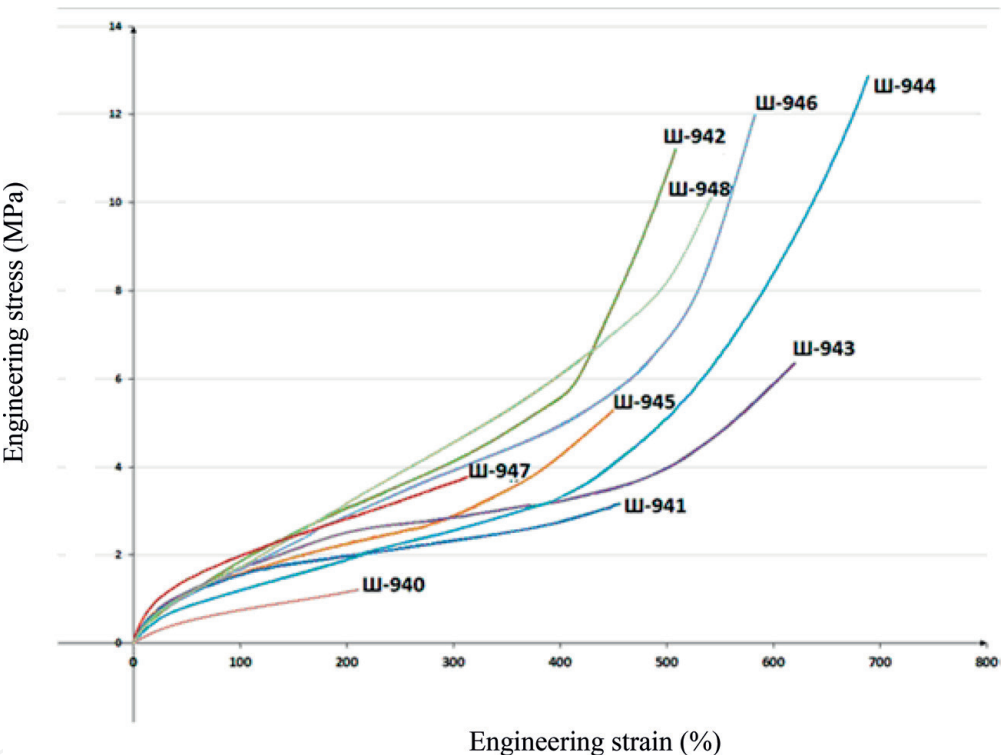

Figure 8.
SEM images of the original "Neosyl-120."

Figure 9.
TEM images of grounded Neosyl-120.

Figure 10.
The graphs of conventional strain-strength properties of studied composites with taurit, diatomite, and Neosyl-120. Engineering strain (%) are plotted in abscissa and engineering stress (MPa) in ordinates.

The graphs of conventional strain-strength properties of these elastomer composites with shungite [9]—are shown in **Figure 5**. These curves are typical ones for each type, corresponding to mean values from five repetitions for tests. Designations SHIKNI and SHIKNM in **Figure 5** mean rubber is filled by original and milled nanoshungit, respectively, and others by nanoshungit, modified by proper organosilanes.

SPM images of the surface structure of the synthesized composites with taurit and diatomit are shown in **Figures 6(a, b)** and 7**(a, b)**.

Scanning electron microscopy images of the original Neosyl-120 powder are presented in **Figure 8**. From the data obtained, it is clear that the particle size varies from submicrosized to large, with a size of the order of several hundred micrometers, with the second prevailing. Particles Neosyl-120 have a rough, sometimes porous, and layered structure, which implies a large value of its specific

surface. However, the large value of the specific surface in this case cannot provide a high interaction area of the filler particles with the elastomeric matrix due to its high structurality.

Transmission electron microscopy has been used to obtain images of grounded Neosyl-120 particles in high resolution (**Figure 9**). Particle size has a wide distribution and amounts to tens and hundreds of nanometers. The particle morphology is close to spherical.

The physico-mechanical characteristics of the SBR-30ARK styrene-butadiene rubber-based vulcanizates, filled with taurit, diatomit, and Neosyl-120 of varying degree of dispersion (Ш-940–Ш-948), are presented in **Figure 10**.

4. Discussion of the results

Surface topography SPM images and the phase contrast of the composite material allowed to directly visualize the distribution of the fillers in the matrix rubber SBR-30ARK (**Figures 1–4**).

Analysis of **Figure 1** revealed the uneven distribution of original micro shungite filler in the rubber matrix. Predominant size of the shungite aggregates remains in the micron region. The distribution of aggregates and agglomerates of milled nanoshungit in the rubber (**Figure 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 of nanoshungit modified by organosilane Thiol (**Figure 4**) are distributed more uniformly at the rubber matrix even in comparison with modification by Glymo.

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 reaching 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 of Si 264 as nanoshungit modifier also showed an increase in elastomer strength about 3 MPa relative to composites 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 30%.

Due to using force modulation or phase-contrast modes, separate aggregates and agglomerates of taurit or diatomit in sizes from 100 nm to 1 μm in the elastomeric matrix are visualized by SPM. The form of these aggregates and agglomerates in **Figures 6** and **7** is characterized by a sharp anisotropy of shape and an isolated heterogeneity of the filler particle structure. The images obtained show that in samples with microdispersed taurit or diatomit, the filler forms large inclusions with a size of several micrometers. When grinding the filler, a much more uniform distribution of nanostructured aggregates in the elastomeric matrix is observed. The results of experiments demonstrate also that the dispersity of the filler has a significant effect on tensile behavior of composites. Materials with microdispersed fillers have much lower tensile strength than samples with nanodispersed fillers. When grinding taurit to the nanodispersed phase, the strength of the vulcanizates increased from 3 to 12 MPa, and diatomit from 5 to 13 MPa, respectively. Grinding of particles of the Neosyl-120 products allows increasing the level of interaction of the filler with the elastomeric matrix, which leads to a noticeable improvement in the elastic-strength

properties: the conventional strength increases from 3 to 10 MPa. Grinding of these fillers did not lead to significant changes in the modulus of elasticity.

Theoretical analysis of obtained results for these different fillers in such elastomer matrix allows to conclude that the reason for strength reinforcement of these composites is due to the redistribution of valence π electrons of butadiene-styrene rubber between acceptor fillers and the donor matrix of the elastomer. The resulting interatomic interactions lead to more uniform distribution of fillers in the rubber matrix and the corresponding effects of enhancing the physico-mechanical characteristics of the composites.

5. Conclusions

The comprehensive study of SPM and physico-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 SPM data with the results of tensile testing machine on the characteristics of these composites has allowed to conduct cross-correlation. The use of SPM made also possible to determine the patterns of distribution of aggregates and agglomerates of taurit, diatomite, and Neosyl-120 in composites with butadiene-styrene rubber. The morphology and micro-nanometer range of the length of these aggregates in the synthesized materials has been established. A correlation between the enhancement of the physico-mechanical properties of the synthesized composite materials and the distribution of the used fillers in the elastomeric matrix was established. The proposed method of grinding the studied minerals in the laboratory allows to significantly increase the strength characteristics of the rubbers filled by them, indicating that they can be used as reinforcing fillers for elastomeric composites. These results are important for both the fundamentals of the theory of the reinforcement of composites and practical applications in industry.

Acknowledgements

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