

Complex microscopy investigation of special purpose elastomers

O O Shcherbakova¹, T I Muravyeva¹, R V Gainutdinov², I V Shkalei¹,
N N Petrova³, E N Timofeeva³ and D L Zagorskiy^{1,2}

¹ Ishlinsky Institute for Problems in Mechanics RAS, 119526, Moscow, Russia

² Shubnikov Institute of Crystallography of Federal Scientific Research Centre
“Crystallography and Photonics” of Russian Academy of Sciences”, 119333, Moscow,
Russia

³ Ammosov North-Eastern Federal University, 677000, Yakutsk, Russia

shcherbakovaoo@mail.ru

Abstract. New types of elastomers (rubbers) for use in extremal conditions of north were proposed and investigated. New type of filler – carbon nanotubes were added to a basic elastomer composition in different proportions. Surface parameters of the samples were studied before and after tribological tests. Electron microscopy was used to study the relief and elemental composition of the surface and section (after the tests). Probe microscopy made it possible to investigate the adhesion and elastic properties of the surface at the nanoscale. Unmodified samples and samples with a small amount of nanotubes are remarkably changing in topography and elemental composition after tribological tests: the amount of carbon increased, while amounts of nitrogen, sulphur, and zinc decreased. Modification of the basic composition by nanotubes significantly changes the properties of rubber. Cross-sections showed that composition of the depth became more stable. Modified samples have a great adhesion strength and Young's modulus.

1. Introduction

Rubbers and other elastomers are widely used in many areas of the national economy, and development of new composites is an important task. In particular, the actual problem is fabrication of the materials operating in the climatic conditions of the north [1-2]. These conditions are often close to extremal. So, the materials must have high frost resistance, strength, and resistance to aggressive media. To achieve these goals, the rubber is modified with various fillers [3-4]. Recently, nanofillers, for example, carbon nanotubes (CNTs), which have a unique structure and properties, are increasingly being used as modifiers [5]. Thus, it is known that the addition of CNTs to a rubber composite often leads to a significant improvement of its properties [6-7]. However, the influence of the CNTs on the structure and the main properties of the resulting composite have not been studied in details to date.

In the present work, a series of samples with different contents of CNTs have been studied at the nanoscale using scanning electron microscopy (SEM) and scanning probe microscopy (SPM). The influence of tribological tests on the surface change was also studied. The aim of the work was to study the effect of the addition of CNTs on the structure and properties of elastomers based on epichlorohydrin rubber.



2. Materials and methods

2.1. Materials

In the present work, samples from epichlorohydrin-based composites (EPCG), which are intended to be used as seals in machine units operating at negative temperatures, were investigated. Samples of rubbers were made using Brabender plasticizer equipment. The components were mixed at 50°C for 15 minutes, then vulcanized on a hydraulic press GT-7014-H10C. The modifiers of rubber were carbon nanotubes (CNTs), added to the base composition in different percentages. For the subsequent study, samples of five different contents were used (Table 1).

Table 1. Composition of the samples under study: the amount of CNTs in the mass parts is given by 10 parts by weight of EPCG.

Sample number	1	2	3	4	5
CNT (m.p.)	0	0.3	1.0	2.0	10.0

2.2. Tribological tests

The operation regime of elastomers was modelled by tribological tests conducted on UMT-2 friction machine under the following conditions: contact pressure varied from 0.1 to 0.3 MPa, the sliding velocity varied from 1 to 100 mm/s, and the bulk temperature of the samples varied from -25 to 22°C. The description of tribological tests is presented in other works [8]. In the present work, the results obtained after tribological tests with the maximum parameters of pressure and velocity are presented.

2.3. Surface investigation

The surface of the obtained samples was studied by various methods of microscopy before and after tribological tests. The topography and elemental composition of the surface were examined on a Quanta 650 SEM using secondary and back-scattered electrons detectors with EDAX analytical equipment. The work was carried out at the low vacuum conditions, which allowed studying dielectric rubber without preliminary metallization of its surface.

NTEGRA Prima SPM (NT-MDT, Russia) was used to study the topography, adhesion, and viscoelastic properties of the sample surface at the nanoscale. HA-NC (NT-MDT) probes were used having stiffness ~ 3.5 N/m, a resonance frequency ~ 140 kHz, and a tip radius ≤ 10 nm. The heat stabilization studies were carried out in a clean climatic zone "TRACKPORE ROOM-05", which ensured the maintenance of temperature and humidity of the air environment with high accuracy.

Measurements of adhesion forces and elasticity (Young's modulus) were carried out by analysing the dependences of force on distance obtained in the regime of power spectroscopy [9]. Another method used, so-called force modulation method, consists in studying the damping of oscillations in a sample: it is known that attenuation is determined by the elastic properties of the surface [10]. The scanner with the sample performs vertical periodic oscillations at the resonant frequency of the scanner (6.2 kHz in the present work). The probe, which is in contact with the sample surface, registers the oscillations of the sample. In this case, the amplitude of oscillations of the probe-sample system is recorded, which depends on the rigidity of the sample surface.

3. Results

3.1. Electron microscopy

The most important characteristic is the changing of the elastomers surface during operation. At the initial stage of work, the surface of the samples before the tests was investigated in the regimes of secondary electrons and back-scattered electrons. The results obtained for the first sample are shown in Figure 1.

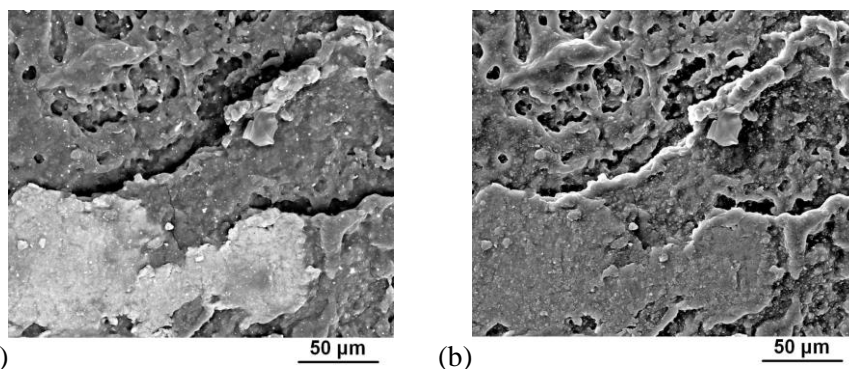


Figure 1. SEM image of the surface of sample 1 regions after tribological tests: (a) in back-scattered electrons regime, (b) in secondary electrons regime.

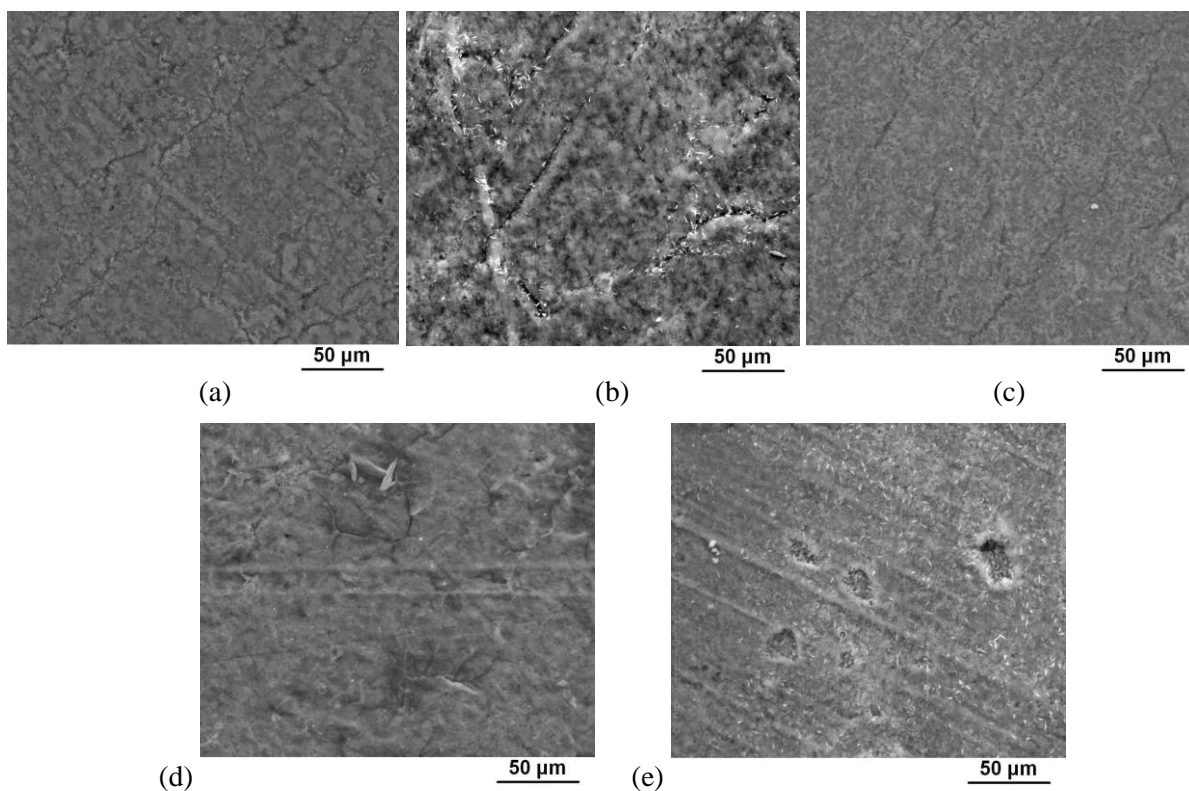


Figure 2. SEM images of the initial sample surface. Sample number: (a) 1; (b) 2; (c) 3; (d) 4; (e) 5.

Table 2. Chemical composition of the initial surfaces of elastomers.

Sample number	Chemical composition (% of mass)										
	C	N	O	Mg	Al	Si	S	Cl	Ca	Co	Zn
1	35,28	8,58	2,79	0,46	0,37	0,10	34,26	1,84	0,25	-	16,07
2	32,22	12,00	5,14	0,58	0,59	0,01	30,30	4,49	0,06	0,11	14,50
3	37,67	11,43	6,04	1,75	1,32	0,27	22,95	4,93	0,20	0,14	13,30
4	35,64	12,49	6,84	1,12	0,89	0,04	25,2	5,13	0,12	0,12	12,33
5	40,76	11,64	7,36	0,94	0,81	0,06	22,57	4,49	0,08	0,13	11,16

It is evident that both methods give practically the same information about the topography. At the same time, the method of backscattered electrons gives a lot of information about the surface because of good visualization of various phases. In other parts of this work, the surface images were also obtained in the two above-mentioned modes and in all cases the mode of the backscattered electrons provided more information. Therefore, the results of the study of other samples, described below, will be presented only in this mode.

Figure 2 shows SEM images of the initial surface of the investigated samples 1-5, and in Table 2 the corresponding elemental composition is given. It can be seen that the initial surface of the samples is smooth and homogeneous; there is no difference in the "colour" of the phases. Samples 2-5 contain fine needle particles. The surface of sample 5 is characterized by the presence of pores of various sizes on the surface. According to the elemental composition, the samples differ insignificantly. The presence of cobalt in the chemical composition of samples 2-4 (with CNTs) can be explained by its presence in the catalytic system, used for production of nanotubes.

SEM images of the surface of elastomer samples after tribological tests (Fig. 3) show that the topography of the surface after the tests has become more developed. The phases, differing in colour and composition, also appeared at the surface. So, on the surface of samples 1 (without CNTs) and 2 (CNTs 0.3 m.p.), the lighter areas are close in composition to the original surface, while the dark ones are different. This can be explained by the nature of the interaction with the counter body: the surface of the sample is uneven and contact during friction does not occur over the whole area. In this case, the light areas correspond to the minimal contact with the counter body, while the darker areas are the contact surfaces. From the obtained results it follows that the parameters of the surface of elastomers without CNTs (or with a small number of them) vary greatly during friction. Elastomers modified with a large number of CNTs (samples 3-5) also have regions on the surface that differ in colour and topography. However, the elemental composition of these regions differs insignificantly (Table 3). Thus, it can be argued that the introduction of CNT into an elastomer stabilizes its composition.

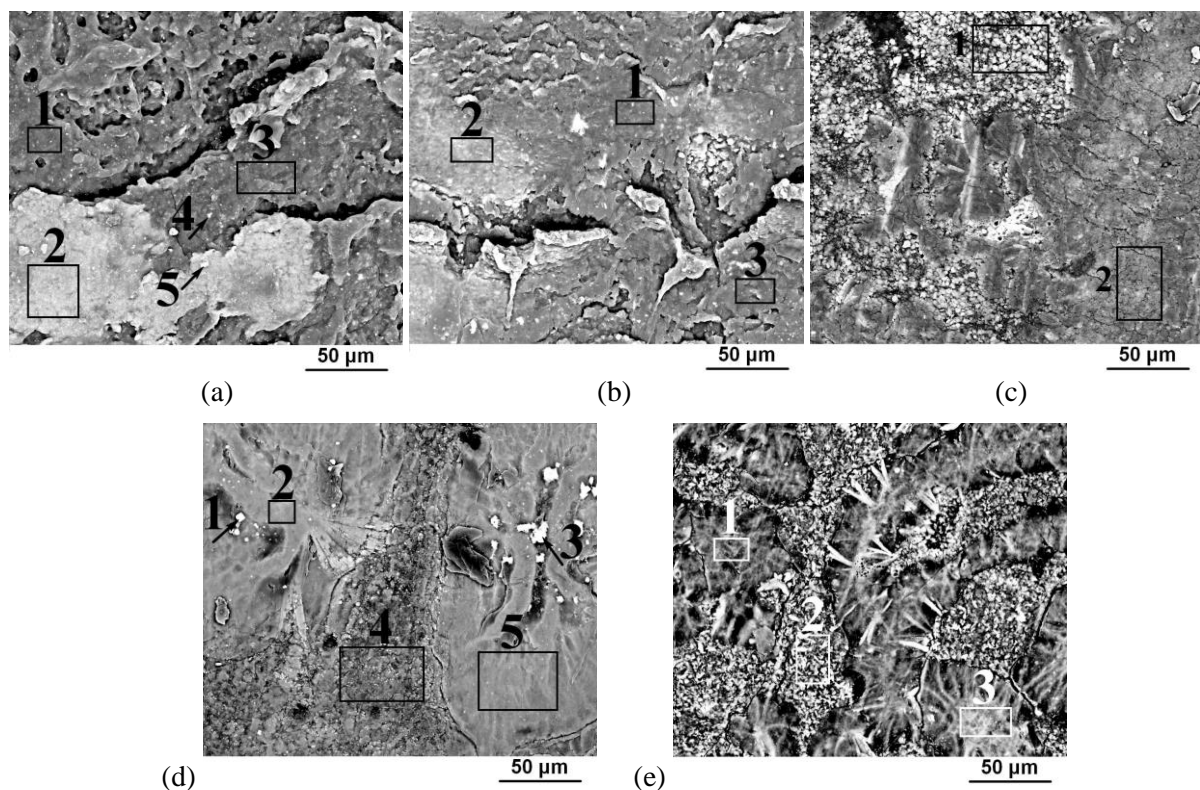


Figure 3. SEM images of the sample surface after the tests. Sample number: (a) 1; (b) 2; (c) 3; (d) 4; (e) 5.

Table 3. Chemical composition of the elastomer surfaces after the tests.

Sample number	Area number	Chemical composition (% of mass)											
		C	N	O	Mg	Al	Si	S	Cl	K	Ca	Co	Zn
1	1	73,47	3,27	9,17	1,93	1,33	0,28	4,71	2,93	-	0,32	-	2,59
	2	48,16	4,44	7,20	0,87	0,56	0,20	24,50	2,42	-	0,21	-	11,44
	3	69,23	3,51	11,67	2,16	1,37	0,27	5,12	3,78	-	0,23	-	2,66
	4	24,11	2,11	16,33	2,06	1,25	0,50	2,83	0,95	-	0,08	-	49,78
	5	21,72	2,81	37,70	1,20	0,49	0,26	7,42	0,80	-	25,51	-	2,09
	All	65,86	3,85	11,18	1,45	1,01	0,23	8,86	2,73	-	0,34	-	4,49
2	1	60,84	4,33	13,89	1,99	1,48	0,33	6,86	5,88	-	0,62	0,05	3,73
	2	48,21	5,95	10,71	1,25	1,06	0,43	17,73	5,14	-	0,28	0,09	9,15
	3	63,74	3,48	13,29	1,39	1,86	0,35	6,05	4,23	-	2,32	0,22	3,07
	All	59,76	4,68	12,78	1,32	1,17	0,29	9,75	4,36	-	0,78	0,14	4,97
3	1	38,93	10,42	7,65	1,57	1,38	0,23	22,01	4,92	-	0,12	0,09	12,68
	2	36,17	9,83	8,24	2,24	1,39	0,38	22,93	5,27	-	0,25	0,19	13,11
	All	39,06	8,87	8,48	1,79	1,31	0,30	21,78	5,08	-	0,19	0,13	13,01
4	1	19,98	3,24	8,75	0,06	0,27	0,31	6,91	27,69	29,15	0,47	0,14	3,03
	2	33,63	5,46	5,04	0,22	0,14	0,07	37,66	0,90	0,06	0,04	0,11	16,67
	3	18,36	1,82	6,64	0,00	0,02	0,07	4,21	33,86	32,09	0,38	0,09	2,46
	4	34,82	9,60	7,38	0,95	0,96	0,31	26,73	3,75	0,09	0,18	0,21	15,02
	5	31,56	5,31	4,71	0,37	0,26	0,14	38,33	1,42	0,10	0,19	0,13	17,48
	All	36,83	6,17	6,58	0,62	0,59	0,20	30,63	2,70	0,29	0,26	0,15	14,98
5	1	35,11	9,41	6,49	0,89	0,85	0,19	28,13	3,46	-	0,06	0,51	14,90
	2	41,30	8,49	8,27	0,78	0,77	0,21	24,50	2,55	-	0,29	0,17	12,67
	3	33,32	7,57	5,26	0,31	0,27	0,09	35,31	1,76	-	0,05	0,16	15,90
	All	39,15	9,39	8,83	1,03	1,00	0,40	23,51	3,39	-	0,67	0,18	12,45

For a more detailed study of the processes occurring during friction on contact surfaces, geological sections of the samples were prepared. Figure 4 shows SEM images of these sections, and in Table 4 – the corresponding elemental composition. It is easy to see a highly altered (in terms of topography and chemical composition) surface layer, but its thickness is small (about 10 μm) – therefore, its features can be estimated only at high magnification.

A study of the topography of sample sections showed that samples 3 and 4 have a more homogeneous and dense structure than samples 1, 2 and 5. Analysis of changes of the elemental composition showed that in samples with a small amount of CNTs, the surface layer significantly differs from bulk. At the same time, for samples 3, 4 and 5 (with a high content of CNTs), the element composition in depth varies to a minimal extent. Thus, it can be concluded that an increase in the number of CNTs stabilizes the composition by volume.

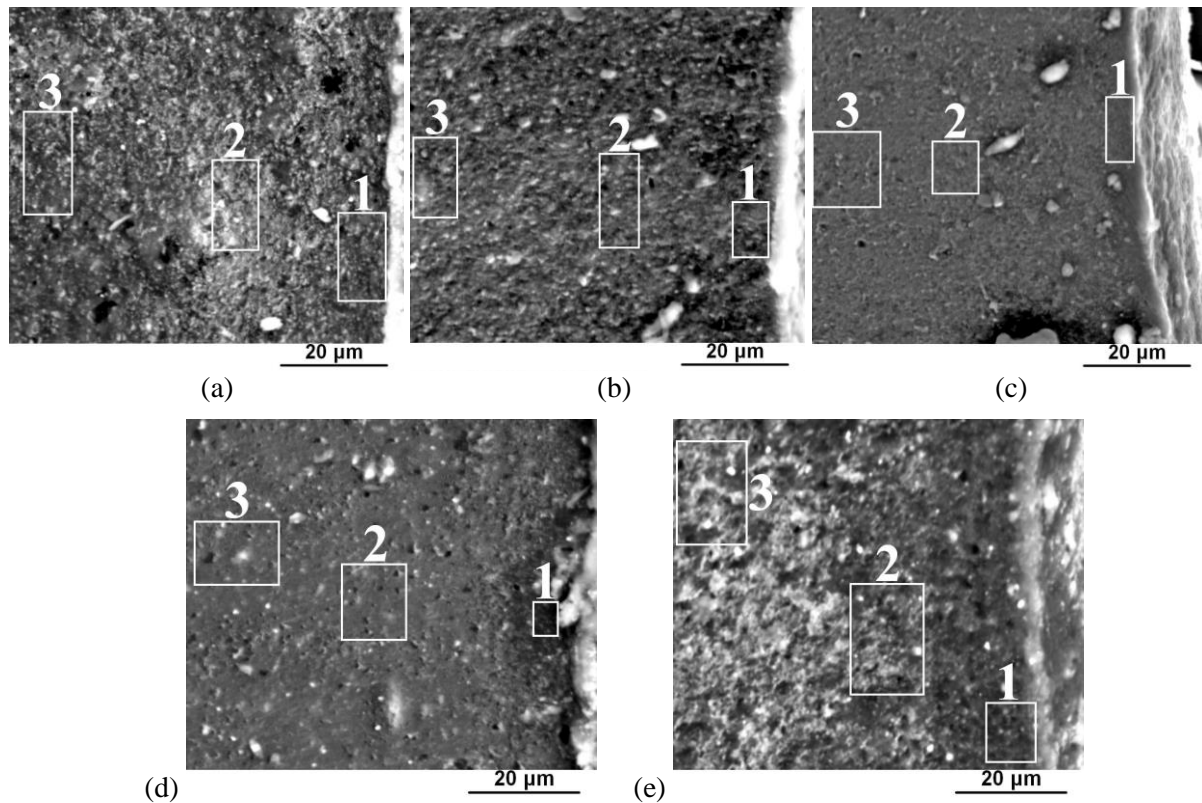


Figure 4. SEM images of the sample sections (magnification x2000). Rectangles marked areas where X-ray spectral analysis was performed. Sample number: (a) 1; (b) 2; (c) 3; (d) 4; (e) 5.

Table 4. Chemical composition of sections of samples of elastomers after testing.

Sample number	Area number	Chemical composition (% of mass)												
		C	N	O	Mg	Al	Si	S	Cl	K	Ca	Ti	Co	Zn
1	1	56,30	0,02	5,71	0,13	0,57	0,03	10,17	13,87	-	2,86	0,69	-	9,45
	3	76,30	0,60	8,75	0,87	0,79	-	3,84	5,49	-	0,13	0,12	-	3,06
2	1	62,13	0,15	7,90	1,05	1,55	0,09	7,41	11,31	0,36	0,92	0,98	0,22	5,93
	3	71,52	1,10	7,77	4,16	0,97	-	3,49	6,57	0,03	0,15	0,21	0,08	3,95
3	1	68,85	0,76	12,04	1,02	0,89	0,14	5,49	5,17	0,09	0,53	0,47	0,13	4,42
	3	72,14	1,33	10,32	1,60	1,20	0,07	4,49	5,13	0,06	0,06	0,10	0,11	3,39
4	1	71,07	0,01	3,87	0,98	0,82	0,00	5,86	9,25	0,02	0,27	0,20	0,27	7,38
	3	71,79	0,95	8,30	1,19	1,35	0,01	4,65	5,18	0,11	0,10	0,14	0,16	6,07
5	1	75,63	0,29	7,97	0,85	0,96	0,00	3,59	5,42	0,03	0,21	0,08	0,27	4,70
	3	76,16	2,10	10,14	1,15	1,03	0,06	2,93	3,78	0,06	0,10	0,07	0,14	2,28

3.2. Scanning probe microscopy

Results of measuring topography, adhesion and visco-elastic properties are given below. Figure 5 shows, as an example, the results obtained for sample 3. Similar results were obtained for other samples. The summary data for all samples are given in Table 5.

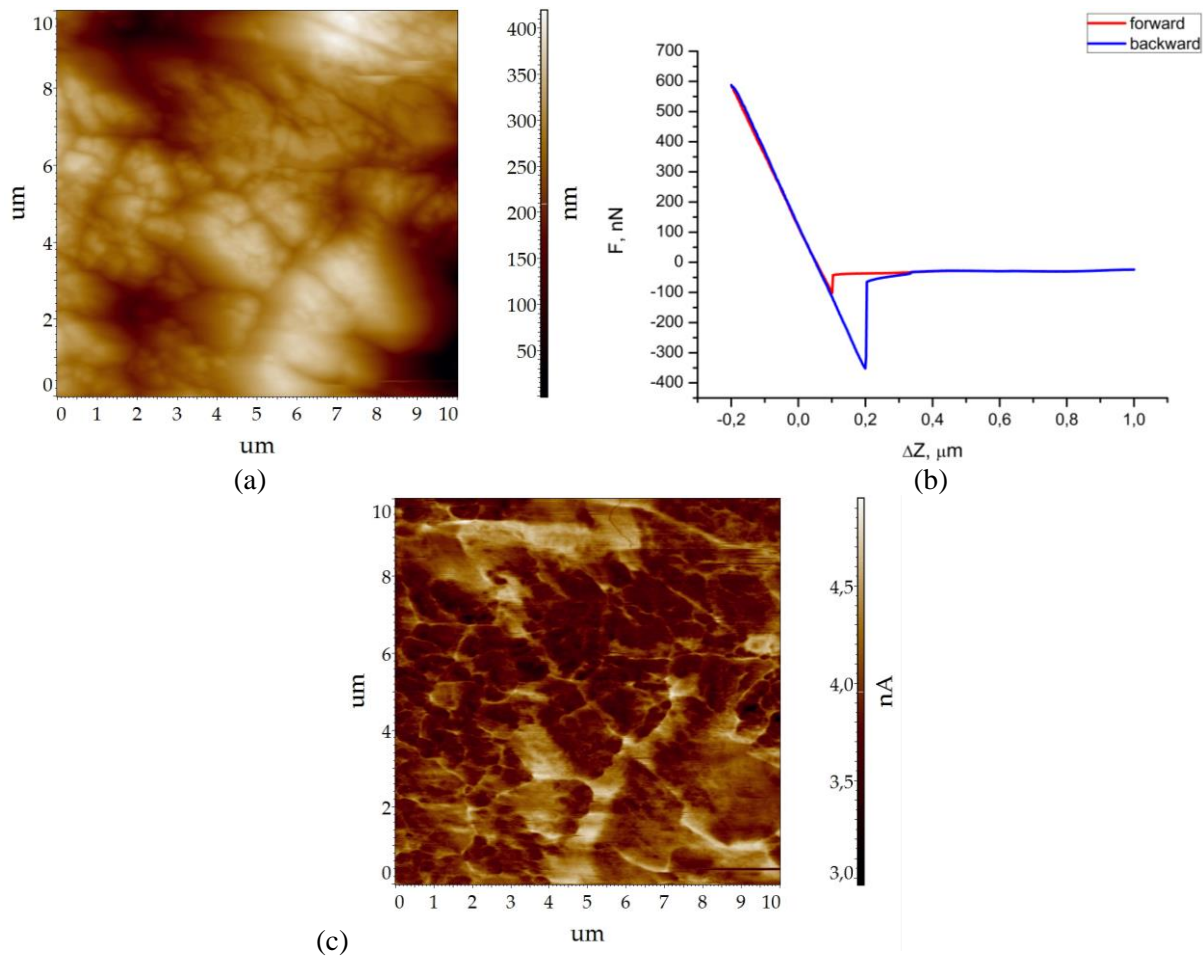


Figure 5. SPM images of the sample №3: (a) the surface topography; (b) the supply-retraction curves; (c) the amplitude of the viscoelastic oscillations.

Table 5. Values of adhesion strength, Young's modulus and visco-elastic characteristics of the test samples before and after tribological tests.

№	ER+ CNTs	F_{ADH} , nN		E , MPa		A , nA	
		before	after	before	After	before	after
1	0 mp	71,8	41	92,8	82,4	2,3	4,2
2	0,3 mp	324,2	203,6	584,4	123,6	2,4	3,8
3	1,0 mp	139	322	309,7	144	3,0	3,9
4	2,0 mp	89,7	136	354,8	197,4	3,2	4,2
5	10 mp	238,3	99,8	251,9	197,1	2,6	3,3

Analysis of the obtained results allows us to make the following conclusions:

Adhesion strength. The addition of CNTs leads to an increase in adhesion: in samples without CNTs, adhesion is small enough, while adding even 0.3 parts of CNTs leads to a sharp increase in adhesion strength. However, a clear dependence of adhesion on the concentration of CNTs could not be identified. The same pattern is observed for samples after tribological tests. We note that it was not possible to reveal a general pattern for the effect of tribological tests on adhesion (after the tests the adhesion strength decreased in samples 1, 2, 5, while it increased in samples 3 and 4).

Elastic characteristics. Young's modulus was measured from the slope of the curve. For samples without CNTs and for samples with a small value of CNTs (up to 0.1 m.p.) Young's modulus is relatively small, but with an increase in the CNTs content (from 0.3 m. p), a sharp increase in the

Young's modulus occurred. For this concentration range (as for the case of adhesion forces), the dependence on the number of CNTs was not revealed. After tribological tests, the Young's modulus decreased for all samples.

Elastic characteristics. The results of the study of elasticity measured by the force modulation method suggest that the elasticity values of different samples differ little. However, it can be seen that, after tribological tests, in all cases a noticeable increase in the rigidity of the sample is observed.

In general, these investigations show that modification of the basic composition of rubber by nanotubes significantly changes the properties of rubber. At the same time, it should be noted that the conclusions obtained do not make it possible to establish an unambiguous correlation between the elastic properties expressed in terms of the Young's modulus and the elastic parameters determined by the force modulation method. Obviously, additional experiments are required here.

4. Conclusion

Unmodified samples and samples with a small amount of CNTs after tribological tests are remarkably changing both in topography and in elemental composition – the amount of carbon increases with decreasing amounts of nitrogen, sulphur, and zinc. Modification of the basic composition with CNTs significantly changes the properties of rubber. The composition of the depth becomes more stable. Samples with CNTs have a great adhesion strength and Young's modulus.

Acknowledgments

This work was supported by the Russian Scientific Foundation, project no. 14-29-00198-P (sample preparation and SEM) and the State Task № State registration AAAA-A17-117021310379-5 (SPM studies). This work was supported by the Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS in part of SPM investigations (measurements of force-distance curves and force modulation).

References

- [1] Diaz R, Gaarder R H and Olafsen K 2013 *Proc. of the Twenty-third International Offshore and Polar Engineering* (Anchorage: ISOPE Conference Paper) 250-6
- [2] Bukhina M F and Kuryland S K 2007 *New concepts in polymer science* (Leiden, Boston: VSP) 187
- [3] Eliseev O A, Chaikun A M, Buznik V M, Sokolova M D and Popov S N 2015 *J. Adv. Mater.* **11** 5-18
- [4] Petrova N N, Popova A F and Fedotova E S 2002 *Kauchuk I Rezina* **3** 6-10
- [5] Shashok J S and Prokopchuk N R 2014 *Application of Carbon Nanomaterials in Polymer Compositions* (Minsk: BSTU)
- [6] Morozov A V, Muravyeva T I, Petrova N N, Portnyagina V V, Ammosova V N and Zagorskiy D L 2015 *Kauchuk I Rezina* **6** 22-7
- [7] Stolyarova O O, Muravyeva T I, Cainutdinov R V, Morozov A V, Zagorskiy D L, Petrova N N and Portnyagina V V 2016 *J. Surf. Invest.* **9** 46-53
- [8] Morozov A V and Petrova N N 2016 *J. Frict. Wear* **37** 124-8
- [9] Lebedev D V, Chuklanov A P, Bucharaev A A and Druzhinina O S 2009 *ZhTF Lett.* **35** 54-61
- [10] Maivald P, Butt H T, Gould S A C, Prater C B, Drake B, Gurley J A, Elings V B and Hansma P K 1991 *Nanotechnology* **2** 103-6