

# Functionalization of 1D Carbon Nanostructures by Components of Curing System and Their Influence on the Properties of the Vulcanizates<sup>1</sup>

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Received March 17, 2016; in final form, June 14, 2016

**Abstract**—The paper investigates sorption of 2-mercaptobenzothiazole (MBT) and zinc ions by 1D carbon nanostructures (CNS) of different morphologies. It was found that the organization of graphene planes in the body of the CNS and pre-activation of the nanomaterial with ultrasound determine the nature of the interaction with functionalizer and the value of adsorption. It is shown that the functionalization products affect complex of physico-mechanical properties of the rubber compositions and vulcanizates. This can be used for obtaining a rubber with high fatigue endurance and with increased frost resistance.

**Keywords:** carbon nanotubes, carbon nanofibers, accelerator, sorption.

**DOI:** 10.1134/S1995078016050116

## INTRODUCTION

The stage of rubber mix vulcanizing is the final one and it influences the properties of rubbers as well as the sphere of their usage. Most of all it is determined by the nature and character of the transverse bonds distribution in the vulcanizate structure. Traditionally a booster compound (or mixed accelerators) and vulcanization activator are used in sulfur vulcanization of rubber. As a vulcanization activator they usually use zinc oxide with higher fatty carbon acids. Zinc oxide contributes to three-dimensional organization of cross-linking action by means of sorption of vulcanizing group components on the surface of its particles in the catalysis of the process of interaction of vulcanizing group components with rubber macromolecules [1], it also helps to lessen the number of side reactions of intramolecular addition of sulfur. Still using zinc oxide in rubber mixtures is limited nowadays because of its toxicity, as well as because it costs much.

In the research literature there is some information on designing the composition of vulcanizing groups with low content of zinc oxide or with replacing it in the formulation. It is shown [2] that zinc nanomethacrylate fully replacing ZnO contributes to forming the network with the increased number of monosulfide bonds. It is stated [3] that zinc chelates on the basis of aromatic 1, 3 dicetones could be used as activators of

sulfur vulcanizing of nitrile butadiene rubbers. Due to zinc ions availability for booster compound activation and forming a sulfiding complex  $Zn^{2+}$ , decrease by 40% is possible in the rubber mix formula. It considerably differs zinc chelates on the basis of aromatic dicetones from zinc oxide particles in which only surface atoms are reactive. Thus the works dealing with getting nanodimensional particles with the shell active in conditions of vulcanization process are of considerable importance.

The research conception is based on the fact that the surface of 1D carbon nanostructures is able to be the centre of adsorbing the vulcanizing group components, that is aromatic booster components, zinc compounds. It is well known that mono- and poly-aromatic compounds are efficient in functionalizing the surface of carbon nanotubes (CNT) by means of  $\pi$ - $\pi$  stacking. The quality in question is at the basis of strategy of making target delivery medicines with CNT functioning as a nanosized container-carrier [4]. In their own turn heavy metal cations are capable of auto-sorption from water solutions on CNT surface by means of electrostatic interaction [5, 6]. Sorption efficiency is changed in the row of metal cations:  $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+}$ . Sorption capacity of single-wall and multi-wall carbon nanotubes as for zinc ions is 3.3 and 2.5 times higher as compared with polyaromatic hydrocarbons [7]. So CNTs are viewed as effective carbonic sorbents for purifying waste water from heavy metals.

<sup>1</sup>The article was translated by the authors.

**Table 1.** Structural characteristics of the CNS samples under research

CNS producer	Series/morphology	Surface area, m <sup>2</sup> /g	Outer diameter, nm	Length of particles, μm
CNT “NanoTechCentre,” Tambov	Multiwall series “Taunit-MD”	180–200	30–80	Over 2 μm
CNF of Borekov Institute of Catalysis, SB RAS Novosibirsk	Coaxial-conic	124	24–57	Over 1 μm
CNT/CNF Carbon nanomaterial centre in Vladimir State University, Vladimir	Mix of multiwall CNT and CNF mostly of type “fish backbone”	102	13–43	Over 2 μm

Thus in theory 1D CNS can serve as a centre of sorption of the vulcanizing group components, can participate in forming an actual vulcanizing agent and its interaction with rubber. The aim of this paper consists in functionalization of 1D with the help of CNS components of the vulcanizing group, as well as assessing their influence on the properties of rubber mixes and vulcatizates. The research object is multi-coat CNTs of the type “Taunit-MD”, carbon nanofibres (CNFs) of coaxial-cone morphology, mixture CNT/CNF (Table 1). Zinc ions and 2-mercaptobenzothiazole (MBT), the widely-known sulfur vulcanization booster compound, were chosen as functionalizers.

## EXPERIMENT

To begin with, the samples of initial CNSs were purified from carbon (high-heat treatment) and metal (acid treatment) impurities. The samples for MBT sorption at first were treated with acid (3M HNO<sub>3</sub>, 24 hours), then with high-heat (400°C, 3 hours) in an incinerator. The samples for zinc ions sorption at first were treated with high-heat, then with acid also under more harsh conditions (concentrated HNO<sub>3</sub>, 100°C, 2 hours of mixing). The treatment was aiming not only at removing the accelerator residue, but also, when possible, at forming oxygen-containing functional groups on the surface of CNS. Mixtures of concentrated mineral acids which are the most effective in forming -COOH and -OH groups [8], as well as long-term ultrasonic CNS suspension exposure, were not used, which was done deliberately. The reason of not using the above mentioned kinds of treatment consists in the fact that these kinds of treatment cause not only forming functional groups, but also forming defects in nanoparticle solids and increasing their number, as well as forming amorphous carbon on the outer and inner surface of nanostructures [9, 10].

MBT sorption was made from its solution in ethanolic concentration 1.54; 3.08 or 4.6 mg/mL. Zinc ions sorption was made from water solutions of ZnCl<sub>2</sub> (Pro Analysis GOST 4529-78) in concentration 0.15 or 0.2 g/L, which is equal to 71.7 and 95.6 mg/l Zn<sup>2+</sup> accordingly. At sorption zinc chloride water solutions had pH = 6, in order to achieve that 0,1M KOH solution was used. The process of sorption took 24 hours

(during this time period it took 6 hours of mixing in a magnetic stir bar) without or with preliminary sonochemical processing (SCP) for 3 minutes. For this purpose a sonicator of an underbody type was used with frequency of 22 KHz and degree of impact of 250 W/cm<sup>2</sup>.

The calculation of the amount of residual MBT or Zn<sup>2+</sup> in filtrates was made using the method of gas chromatography-mass spectrometry (GCMS-QP2010Plus) or photometry [11] accordingly. Extent of sorption *A* was calculated according to the equation:

$$A, \% = [(C_0 - C)/C_0] \times 100,$$

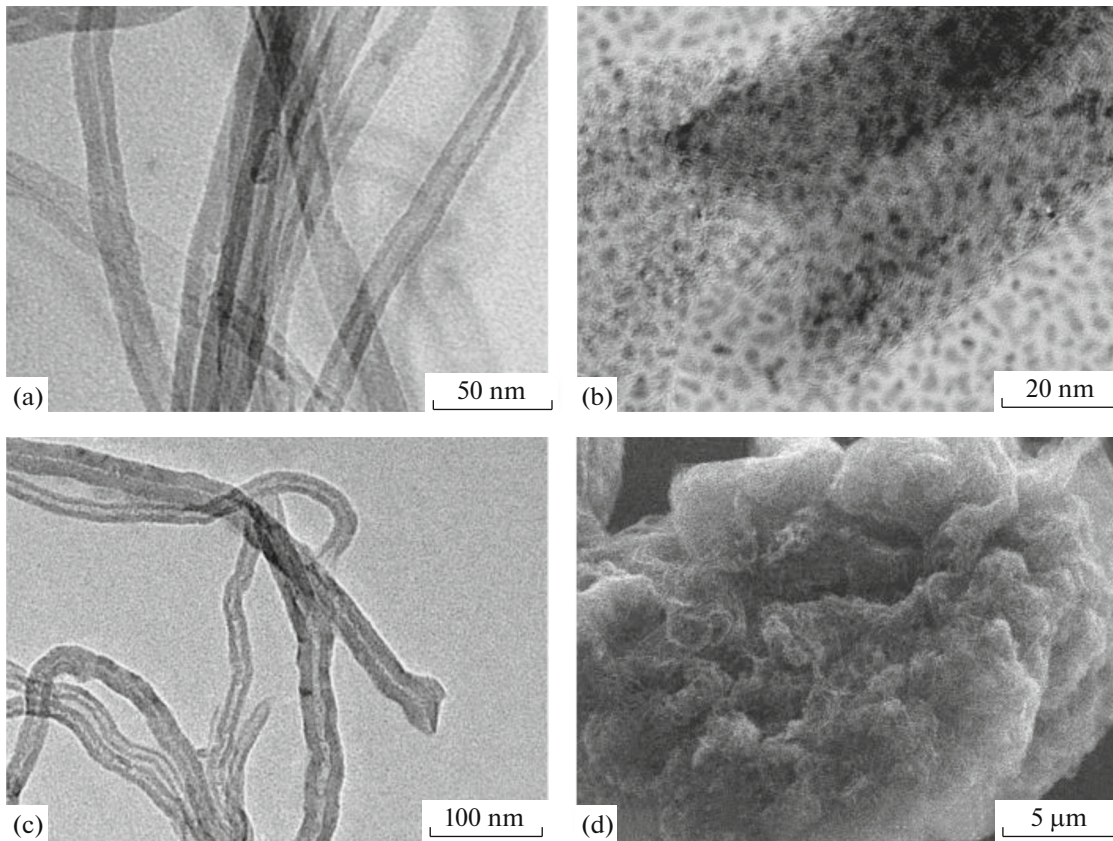
*C*<sub>0</sub> – initial concentration of functionalizer in the solution, mg/mL (mg/L), *C* – functionalizer concentration in the solution after sorption, mg/mL (mg/L).

TEM, SEM images of CNSs were taken using JEM 2100, f. JEOL (accelerating voltage 200 kV) or JEOL GSM 6510 LV (mode SEI). Thermal analysis of functionalized samples of CNSs, rubber mixes and vulcanizates was made using DTG-60, f. Shimadzu (heating up rate 10°C/min, air), DSC analyzer f. Shimadzu (heating up rate 2°C/min). Infra red spectra were measured with spectrometer “Infralume FT-08” using FTIR technique.

Formulation of model rubber mix includes (weight fraction per 100 weight fraction of rubber): NBR-28 – 100.0; sulfur – 2.0; zinc oxide paint – 5.0; 2-MBT – 1.5; stearin – 1.5; heavy hydrocarbon 803P – 45.0; f-CNS – 1.0. Rubber mixes were prepared in the laboratory mill. Rubber mix viscosity (GOST 10722-76) was measured with viscosimeter “Prescott”, cure characteristics (GOST 12535-84) were measured with irrotational vibrorheometer “Prescott”. Mechanical properties of vulcanizates were assessed according to GOST 270–75.

## RESULTS AND DISCUSSION

The CNS samples under research differ from each other considerably in the way of graphene planes lay-up (Fig. 2). For example, a CNT body is a cylinder graphene surface with a relatively low curvature, taking into account its outer diameter (Fig. 2a), and a CNF body is a lay-up of graphene planes, each of them having hydrogenated atoms of carbon at its edges, as well as atoms in the state of sp<sup>3</sup> hybridization



**Fig. 1.** ETM image of objects under research: CNT of the series “Taunit-MD” (a); CNF with coaxial-conic morphology (b); CNT/CNF mixture (c); SEM image of CNT of the series “Taunit-MD” (d).

(Fig. 2b). The basis of the sample CNT/CNF is represented by cylinder one-dimensional bodies, some of them have no hollow inner channel (Fig. 2c). At the same time on micronic level the samples of CNSs are alike, they consist of agglomerates of “interlaced felt” (Fig. 2d).

The character of MBT absorption processes of CNS samples was estimated judging from how the solutions look after the process, from the sorption degree  $A$  (Table 2), as well as from the results of infrared spectroscopy and thermal analysis of functionalized CNS (f-CNS). Taking into account the peculiarities of CNS structure one can suppose that MBT sorption process can take place on the surface of nanostructures, as well as on the surface of agglomerates of nanoparticles in interraggregate populations of nanomaterial. The analysis of Table 2 shows that the character of MBT molecules localization in the material structure is influenced by using short-time UST. In case when UST was not used after sorption the form of CNF samples was that of sediment separated easily with mere filtering. After UST treatment of CNF after sorption the colour of the solutions was deep black and they contained colloid-solved nanofiber. From the solutions CNF particles were separated only by



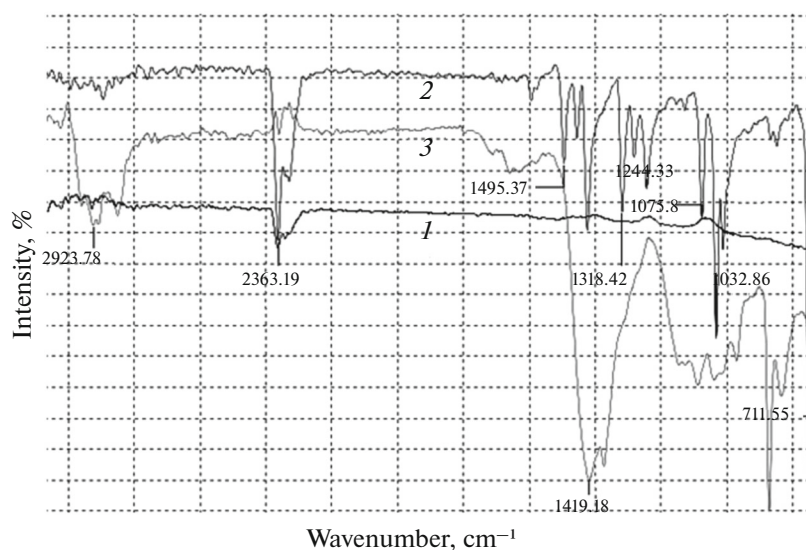
**Fig. 2.** Character of MBT sorption with a CNF sample: (1) CNF agglomerate, (2) monomolecular MBT sorption in micro- and mesopores of the agglomerate; (3) polymeric MBT sorption in macropores of the agglomerate.

**Table 2.** Results of quantitative analysis of MBT in filters after sorption

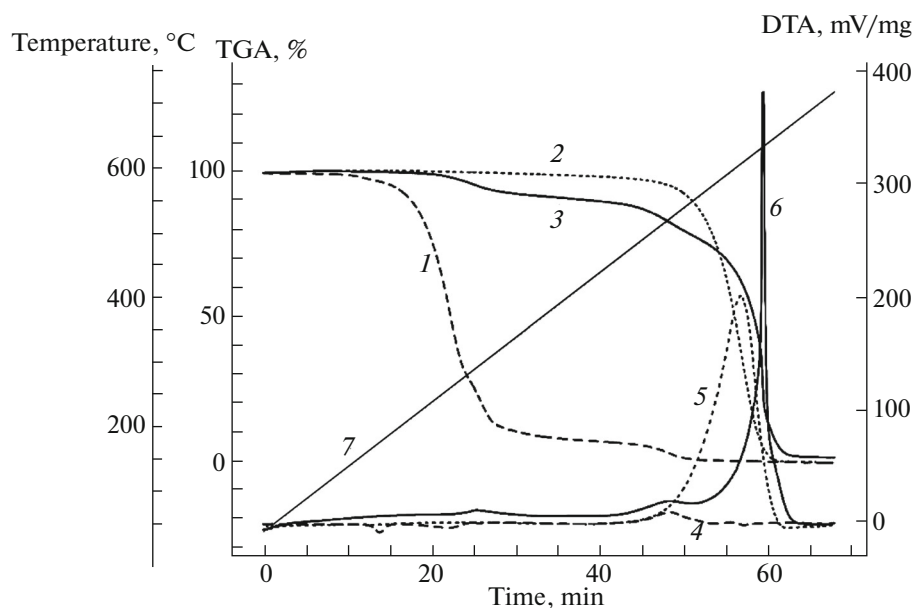
CNS	MBT amount in solution, mg/mL	Appearance, way of CNS extraction after sorption	Sorption amount A, %
CNF	1.54	Sediment; mere filtering	38.9
CNF	1.54	Colloid solution; centrifuging, microfiltering through polymeric membrane "Vladimir"	22.7
CNT/CNF	1.54	Suspension; mere filtering	27.3
	3.08	"	37.0
CNT	1.54	Suspension; mere filtering	34.4
	3.08	"	40.3
	4.62	"	46.8

means of centrifugal separation (the extreme fraction) which was followed by filtering through polymeric membrane with pore diameter 2.0 micrometer (the least fraction). MBT sorption amount is 38.9% without UST and 22.7% with UST. It means that sorption process in the CNF sample without UST takes place in the pores of the material, its character is both mono- and polymolecular (Fig. 3). At the same time extra dispersion of CNF agglomerates as for cavitation mechanism causes monomolecular MBT sorption on the surface of nanoparticles, which, at least, contributes to the colloid solubility of the sample in ethanol. The fact of MBT sorption on the surface of CNF particles is confirmed by the results of infrared spectroscopy of the functionalized product CNF-MBT which was separated by the method of microfiltering (Fig. 4). It is evident that on the infrared specter of the product CNF-MBT there is a sorption band characteristic of the initial MBT.

After sorption the solutions with CNT of the series Taunit-MD turned into spongy suspensions, their volume filled with carbon material, functionalized CNTs were easily separated from the solutions by mere filtering. Table 2 shows that MBT sorption amount on CNTs surface grows with increase of MBT concentration in initial solution and it is higher than when CNF or CNT/CNF mixture is used. Thermal analysis of sorption product CNT-MBT separated from the solution with MBT-concentration of 3.08 mg/mL (Fig. 5) has shown that interaction between nanoparticles surface and MBT is rather strong. Thermal decomposition interval of initial MBT is 223–311°C, on the surface of CNF it is 256–312°C, i.e. the temperature in the beginning of MBT decomposition on the CNT-MBT surface is 30°C higher of that of initial MBT. It is supposed that this is determined by  $\pi$ - $\pi$  stacking interaction between the cylindrical surface of the



**Fig. 3.** Infrared specters of CNF type after purification (1); of initial MBT (2); of sorption product CNF-MBT, separated from the solution by means of microfiltering (3).



**Fig. 4.** Initial MBT thermoanalysis curves (curves (1) TGA and (4) DTA), CNT (curves (2) TGA and (5) DTA) and sorption product CNT-MBT (curves (3) TGA and (6) DTA), (7) temperature.

nanotube and MBT molecules representing aromatic heterocycle.

There are two main types of  $\pi$  stacking [12]: “plane to plane” and “end to plane”. Interactions of the type “plane to plane” provide “slipperiness” and oiliness of graphite. While interactions of the type “end to plane” are viewed as weak carbonic interactions between lightly electron-deficient hydrogen atoms of one benzene ring and electron-enriched  $\pi$ -cloud of the other. Taking into account CNS structure one can suppose that in case of CNT has a cylindrical surface there takes place a more favourable MBT interaction of the type “plane to plane”, and in case of nanofibers have coaxial conic morphology it is probable that the interaction “end to plane” takes place.

Table 3 shows the data on the results of zinc ions sorption from zinc chloride as for CNSs with different morphology after purifying including those additionally treated with acid. Comparative analysis of the data (Table 3) demonstrates that acid treatment of CNS does not lead to increase in zinc ions sorption degree, on the contrary, in case of CNF and CNT the number of absorbed  $Zn^{2+}$  ions is even less that of those not treated with concentrated nitric acid. Functionalizer concentration has little influence on  $Zn^{2+}$  sorption degree, and only in case of CNT structure sorption degree increases with concentration grow by 8%.

Table 4 shows the properties of rubber mixtures and vulcanizates on the basis of nitrile butadiene rubber containing f-CNS. Table 4 demonstrates that input of CNS functionalization products in rubber mixes by means of aromatic accelerator does not cause any considerable change in vulcanizing characteristics of rub-

ber mixes on the basis of NBR-28: the optimum time of vulcanizing, as well as the degree of vulcanizing calculated according to the difference between maximal and minimal twisting moment are the same as in the control sample. Vulcanizates with CNS-MBT show some growth of persistent elongation (from 4 to 29%) and considerable growth of fatigue strength ( $\sim 70\%$ ). As compared with the control, modified vulcanizates are characterized with growth of the interval of macromolecules segmental mobility unfreezing (interval of  $\alpha$ -shift) at low temperature (by 2–3°C), which is not characteristic of raw rubber mixes. The average temperature of this interval, i.e. the glass transition temperature of vulcanizate ( $T_g$ ) is on the level with the control and it is downward biased.

**Table 3.** Results of  $Zn^{2+}$  ions sorption at purified and additionally processed CTS

CNS	Amount of $Zn^{2+}$ in solution, mg/L	Sorption amount A, %
CNF	71.7	31.7
CNF <sub>ox</sub>	71.7	30.3
	95.6	28.9
CNT/CNF	71.7	27.5
CNT/CNF <sub>ox</sub>	71.7	34.5
	95.6	32.5
CNT	71.7	28.9
CNT <sub>ox</sub>	71.7	26.8
	95.6	28.9

**Table 4.** Properties of rubber mixes and vulcanizates containing functionalization products f-CNS

Index	Rubber mixes/vulcanizates						
	control	MBT (functionalization products from solutions with concentration 3.08 mg/mL)			Zn <sup>2+</sup> (functionalization products from solutions with concentration 71.7 mg/L)		
		CNF	CNT/CNF	CNT	CNF	CNT/CNF	CNT
Viscosity, un. Mooney	64	64	61	60	70	70	67
Minimal spinning moment ( $M_{HR}$ ), dNm	1.76	1.83	1.65	1.59	1.87	1.91	1.87
Maximal spinning moment ( $M_L$ ), dNm	15.49	15.22	14.95	14.71	15.01	15.21	14.99
Vulcanization starting time, $T_1$ , min	3.2	2.5	3.1	3.2	3.0	2.6	2.5
Vulcanization optimum $T_{90}$ , min	16.5	16.4	17.3	17.5	18.3	18.2	17.8
Vulcanization speed, min <sup>-1</sup>	7.6	7.5	7.1	7.1	6.6	6.7	6.9
Difference between maximal and minimal spinning moment ( $\Delta M$ ), dNm	13.73	13.39	13.30	13.12	13.14	13.30	13.12
$T_c$ of rubber mix, °C	-36.98	-36.37	-37.03	—	-38.45	-38.60	—
$\alpha$ -Shift interval (rubber mix), °C	From -44.41 to -30.37	From -42.78 to -30.86	From -43.04 to -31.44	—	From -45.07 to -32.25	From -45.29 to -31.57	—
Conventional stress at 100% lengthening, MPa	1.5	1.5	1.5	1.5	1.4	1.5	1.5
Conventional stress at 300% lengthening, MPa	5.1	4.9	4.6	4.7	5.1	5.2	5.0
Nominal strength at tension, MPa	8.0	8.1	8.4	7.9	7.2	7.3	8.3
Extension coefficient, %	540	560	550	510	430	420	580
Persistent elongation, %	19.3	25.0	24.3	20.0	24.3	24.3	26.4
Fatigue strength, number of cycles ( $\epsilon = \text{const}$ , 150%, 250 cycles per minute)	990	1730	1770	1690	2430	2120	1270
$T_c$ of vulcanizate, °C	-30.64	-31.20	-31.47	—	-33.20	-32.51	—
$\alpha$ -Shift interval (vulcanizate), °C	From -34.61 to -26.14	From -37.01 to -25.43	From -37.37 to -26.40	—	From -38.92 to -27.48	From -38.42 to -27.01	—

Input of CNS-Zn<sup>2+</sup> functionalizing products in rubber mixes causes increase of rubber mixes viscosity and decrease in vulcanizing speed (10–13%), at the same time, as rheometric curves show, the extent of cross-linking is on the same level with control. Vulcanizates with CNF-Zn<sup>2+</sup> and CNT/CNF-Zn<sup>2+</sup> demonstrate decrease in aspect ratio at discontinuity in conditions of monoaxial extension (~20%), growth of persistent elongation (~30%) and considerable growth of fatigue strength under dynamic load (more than 2 times). According to DSC glass transition temperature of modified rubber mixes gets lower, which is especially typical of vulcanizates – by 2.6 and 1.9°C accordingly as compared with the control. The lower temperature limit of  $\alpha$ -shift in vulcanizates gets lower by 4.3 and 3.8°C, thus cold endurance of vulcanizates increases.

Change in a number of properties of vulcanizates can be possible due to some reasons, in particular, it could be caused by the impact of f-CNS on the structure of rubber mixes and vulcanizates. For example, by their plasticizing effect in case of CNS-MBT. Keeping in mind that vulcanizates are filled with tread grade carbon black the particles of which consist of the same graphene planes it is possible to suggest that modifying additive components can serve as interstructural plasticizer placed on the surface of per molecular structures, first of all, of filling aggregates. As a result rubber mixes viscosity gets lower and reconfiguration of vulcanizates gets easier in conditions of many-fold cyclic deformations. In this case CNS surface functionalizing with MBT molecules results in lowering the degree of nanoparticles agglomeration. Besides, CNS-MBT can influence the number and nature of

links in the three-dimensional network that is being formed, as, according to DSC data, after vulcanization the liability of macromolecules in the sphere of low temperatures is higher as compared with the control. Finally, CNS-MBT can influence the flaw degree of the forming three-dimensional network. Earlier research of the process of epoxide resin cure with aromatic diamines in presence of CNF [13] has shown that the cure process begins at the CNT surface, at this stage more homogenous three-dimensional networks are formed with less number of structural flaws, such as cycles, “hanging” ends and others.

In case of CNS-Zn<sup>2+</sup> (especially with samples CNF and CNT/CNF) it is possible to suppose that some extra interactions between nanostructures could take place, like salt bridges in pectins. It causes viscosity increase in rubber mixes and decreases the aspect ratio of vulcanizates at discontinuity in conditions of monoaxial extension. At the same time, according to glass-transition temperature and interval of  $\alpha$ -shift, macromolecule mobility increases in vulcanizate structure. It could be connected with the impact of CNS-Zn<sup>2+</sup> on vulcanization process and cross-linking structure, as well as with the sole impact of CNS-Zn<sup>2+</sup> on vulcanizates structure, the interfacial state.

Thus the paper shows the influence of CNS composition and the functionalization conditions on the character and the degree of sorption of the components of the vulcanizing group in the process of sulfur vulcanizing of rubbers. It is shown that the functionalization products influence the complex of physical and mechanical properties of rubber mixes and vulcanizates, which can be used in working out the technology of getting a rubber with a higher fatigue strength and increased low-temperature resistance.

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