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SOME PROPERTIES OF ELASTOMERIC COMPOSITIONS WITH HIGH-DISPERSED CARBON ADDITIVES

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Abstract. The influence of a carbon nanomaterial obtained in a high-voltage discharge plasma on the endurance of elastomer compositions has been investigated. Complex tests of elastomeric compositions with highly dispersed carbon additives allowed us to confirm the model of nonlinear elastic deformation of macromolecules and adhesion between the elastomer and the nanoparticles. The results of these investigations agree with those obtained in determining the Mooney viscosity and relaxation, the parameters of the vulcanization kinetics of rubber mix, conventional tensile strength, and relative breaking elongation of highly filled rubbers based on butadiene-nitrile caoutchoucs. To verify the assumed mechanism underlying the action of a carbon nanomaterial on elastomer compositions, the parameters of their vulcanizing network have been determined using the method of equilibrium swelling.

Keywords: butadiene-nitrile caoutchouc, rubber, carbon nanomaterials, nanotubes, nanofibers, relaxation of rubber mix, elastic-hysteresis property, vulcanization kinetics, crosslink density.

1. Introduction

Performance requirements to rubber products are constantly increasing. This is due to the expansion of their areas of application and the tightening of the conditions of the use. Therefore, the research on various methods dealing with improving the properties of rubber and improving the mix formulations of elastomeric compositions is a promising direction. Adjustment of quantitative and qualitative content of ingredients allows improving the complex of technical properties of products without changing the design of equipment and technological methods of production. This leads to an increasing use of composite materials with a complex structure involving components that have high dispersion ability.

Failure resistance, deformation and strength properties of the materials including nanomaterials are significantly determined by the inhomogeneity of their structure.

Mechanical properties of composite materials are determined by the interaction of the elastomer and fine component at the phase boundary.

2. Experimental

We investigated a filled elastomer composition based on butadiene-nitrile caoutchouc with a content of bound acrylonitrile of 17–23 wt %. The high dispersion additives introduced into rubber mixtures ranged from 0.05 to 0.2 wt parts per hundreds of caoutchouc. For comparison, we used samples free from a nanoadditive. As a highly dispersed additives the fraction of the carbon nanomaterial (CNM) are used.

The starting carbon nanomaterial was obtained in a high-voltage discharge plasma, and then, after complex acid treatment and annealing, it was divided into fractions by ultrasound. The following fractions were used as additives to elastomer compositions: a "film" involving graphite and amorphous carbon particles, relatively large ranges of nanotubes and fibers, and a "suspension" consisting of separate carbon nanotubes with traces of other allotropical modifications.

Development of CNM was initiated in HMTI of the NAS of Belarus. Now they are produced at the FPE "Promising Investigations and Technologies" (the city of Minsk) under the name of "ART-nano" specifications BY 690654933.001-2011. In Fig. 1 TEM-pictures of additives are presented.
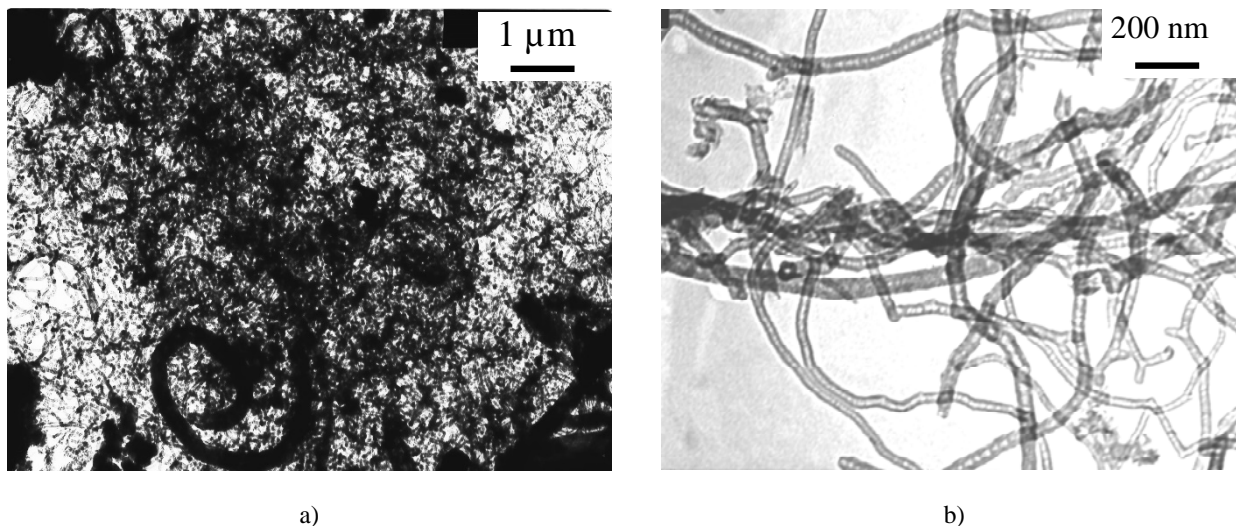
a)   b)

Fig. 1. TEM- pictures of the "film" (a) and "suspension" (b) fractions

The Mooney viscosity was determined with MV2000 viscometer and tests were conducted employing the procedure similar to that recommended by ASTM D1646-07. The parameters of the vulcanization kinetics were determined with the aid of an ODR2000 vibrorheometer in accordance with the state standards. Crosslink density was measured by means of equilibrium swelling method. The test on the rotorless shear rheometer (in accordance with ASTM D6601-02) was used for evaluating cure and dynamic property differences resulting from the use of carbon nanotubes in various dosage. In the work a physical relaxation of tension of vulcanized stocks was also defined. Additionally, the method of dynamic indentation allowed us to estimate the tangent of the mechanical loss. The essence of the method is striking with a stiff indenter on test material in a single pulse mode. After that electrical signal was recorded during impact, further it was converted into a chain of dependencies that allows obtaining physico-mechanical properties of the material upon impact. The method is implemented in the device "IPM-1K", developed at the Institute of Applied Physics of the National Academy of Sciences.

3. Results and Discussion

The rubber composition should provide a product with the specified performance characteristics and it still should be manufacturable at processing. The viscosity of the material determines the dynamics of the processing; it is a measure of material resistance to gradual deformation by shear stress or tensile stress. That parameter is a measure of the force which should be applied to the material for its flow at a given rate at various steps of the process [1, 2]. Introduction of fine component will affect the plastoelastic properties of elastomeric compositions. It is difficult to estimate interaction between matrix and carbon nanomaterial and to determine the mechanism of this process. This is due to the fact that originally the composition contains a large amount of ingredients and it is highly filled. Inactive carbon blacks with a particle size ranging from 9 to 320 microns are used.

The data obtained in the course of the tests (Table 1) indicate that the introduction of carbon nano-materials into elastomeric compositions based on buta-diene-nitrile caoutchouc reduces the Mooney viscosity by 14 %. Minimum values of Mooney viscosity are observed in rubber mixtures containing fraction "suspension" in a dosage of 0.1 phr, containing "film" – 0.2 phr.

The data obtained after tests (Table 1 and Fig. 2) on stress relaxation show that samples of elastomeric composition having the minimum Mooney viscosity are naturally characterized by a higher rate of stress relaxation. This is due to the increased segmental mobility of macromolecules in caoutchouc. Samples of rubber mixtures containing fraction "suspension" in a dosage of 0.1 phr, have values of Slope and Relaxation coefficient totaled -0.417 and 51.7 % (sample comparisons matter slope is -0.386 and K_r = 49.7 %). When adding "film" fraction in a dosage of 0.2 phr the values of the indicators are: slope is -0.406 and K_r = 50.8 %.

The authors [3, 4] indicate that the linkage of macromolecules elastomeric matrix with filler is not absolutely rigid, and under shear loading the matrix (due to the "mobility" of the adsorption bond) is able to move along the surface of the particles. In the context of this hypothesis, the authors have made the structural model which represents the two substrates (surfaces of adjacent particles) united by a spring (macromolecule) associated with the particles of the aid adsorption force (Fig. 3).

Results of the tests of elastomeric compositions on Viscometer MV2000

Fraction of CNM	Dosage, phr	Mooney viscosity, Mooney units	Slope
Without additives	–	57.3	-0.386
"Film"	0.05	55.4	-0.395
	0.10	53.1	-0.400
	0.15	51.2	-0.403
	0.20	50.1	-0.406
"Suspension"	0.05	51.5	-0.410
	0.10	49.5	-0.417
	0.15	49.8	-0.411
	0.20	49.9	-0.405

Kinetics of vulcanization of investigated rubber mixtures

Fraction of CNM	Dosage, phr	$t_c(90)$, min	R_h, min^{-1}
Without additives	–	11.4	11.2
"Film"	0.05	11.0	11.4
	0.10	10.2	11.7
	0.15	10.1	11.5
	0.20	10.3	11.5
"Suspension"	0.05	10.6	11.6
	0.10	10.0	11.8
	0.15	9.9	11.7
	0.20	9.7	12.0

Notes: $t_c(90)$ – time for attaining the optimum vulcanization, min; R_h – vulcanization rate, min^{-1}
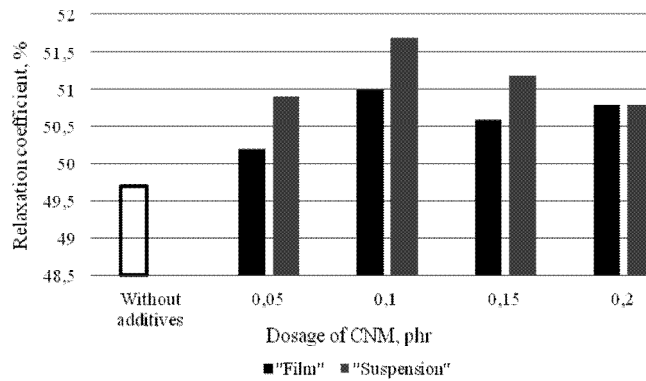

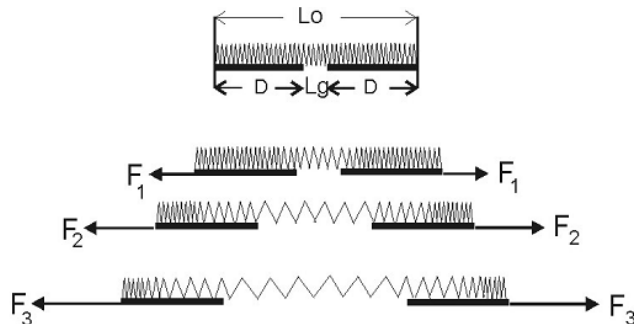**Fig. 2.** Relaxation coefficient of rubber mixtures with carbon nanomaterial particles

Fig. 3. The geometry of the structural unit of the model of the interaction
of macromolecular and carbon nanomaterial particles

The geometry of the structural unit represents the following characteristics: L_o – length of spring, D – length of the substrate and L_g – the gap between the particles.

According to a structural model of the relaxation of the interaction of macromolecules elastomer nanomaterial particles decreases flow resistance of rubber compounds due to the fact that the interaction between the polar groups of acrylonitrile in the structure of macromolecules of caoutchouc is greater than the interaction between macromolecules of caoutchouc and CNM particles. As a result, nanotubes relief of molecular orientation in the direction of flow, which leads to a decrease in the Mooney viscosity of rubber mixtures and acceleration of the relaxation processes in the volume of the elastomeric matrix after removal of the load. The greatest change is observed in the relaxation properties of rubber compounds which contain fraction "suspension", characterized by a more homogeneous structure.

Carbon nanomaterials have a large specific surface area and a functional group which may have impact not only on plasto-elastic properties of rubber compounds, but also participate in the formation of a spatial grid in curing process. In that process particles may interact with components of vulcanizing system and take part in formation of chemical and physical bonds at various steps of the process. Nature and structure of the vulcanization spatial grid defines a wide range of technical properties of elastomeric compositions. Results of the kinetics of vulcanization tests of rubber mixtures are presented in Table 2.

Analysis of the vulcanization kinetics of elastomeric compositions based on the butadiene-nitrile caoutchouc with sulfuric vulcanizing system showed that the introduction of the carbon nanomaterial assists in reducing the time of attaining an optimum degree of vulcanization. In the case of the "suspension" fraction,

there is almost a linear dependence of the time of attaining the optimum on the dosage of carbon nanomaterials (the lowest value is 9.7 min at 0.2 phr), whereas in the case of the "film" fraction, the dependence is of extreme character with the inflection point at the fraction content of 0.15 phr (10.1 min).

Vulcanizing system of the investigated samples of rubber mixtures includes a combination of accelerators: analogue of Accelerator MBTS and *N,N'*-diphenylguanidine (DPG). In the given case, the most probable is the surface interaction of nanoadditives with the polar components of the vulcanizing system (in particular, with DPG). The deactivation of the vulcanizing group polar agent by the particles of nanomaterials can occur, and its tendency to agglomeration or condensation decreases, thus favoring better dispersion of DPG within the mixture. Since in our case it is used as a secondary accelerator for the basic one MBTS, this favors a more intense, joint action of accelerators and of the vulcanizing system as a whole. That may affect the structure of the spatial grid of vulcanizates, which is confirmed by the change in the density of cross-linking (Fig. 4) and the temperature coefficient of linear expansion (TCLE) of vulcanizates (Fig. 5).

According to the obtained data, applying "film" and "suspension" fractions leads to the increase by 30 % in concentration of cross-links and thus reduce the values of the samples TCLE rubber in the temperature range of (313 ± 2)–(393 ± 2) K.

With increasing density of the spatial grid of the vulcanizate to an optimal value, the intermolecular interaction increases, that leads to an increase in modulus of internal friction and hysteresis of rubber [5]. Elastic-hysteresis property of the samples was estimated with a dynamic rheometer rotorless type RPA 2000 and device "IPM-1K" (Table 3).
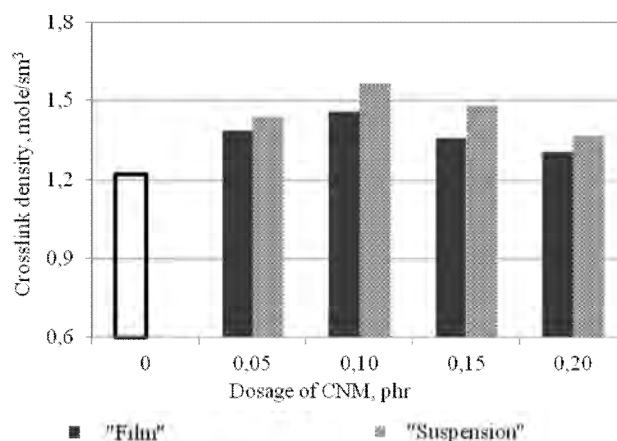

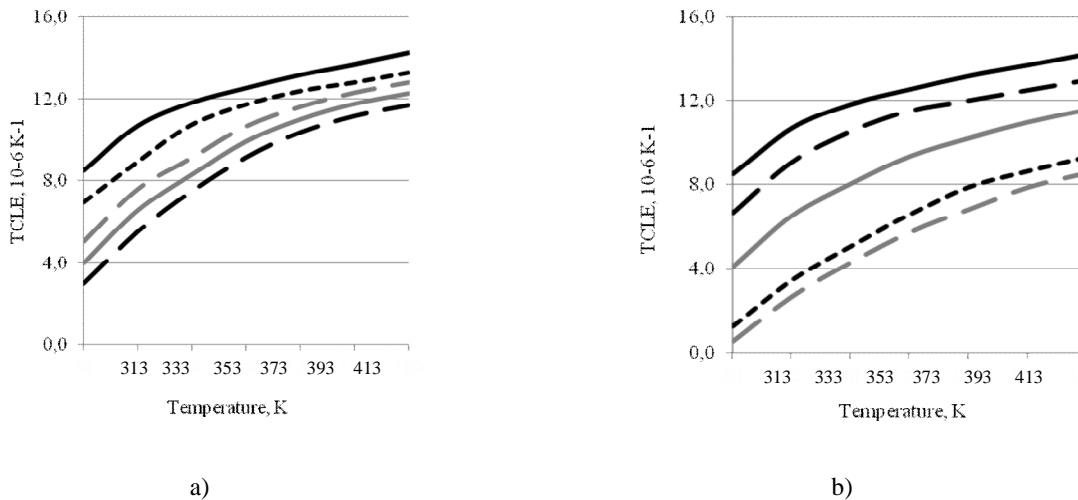**Fig. 4**. Crosslink density of the vulcanizates

a)

b)

Fig. 5. The temperature coefficient of linear expansion of the samples with "film" (a) and "suspension" (b):
dosage of CNM: – without additives; – – – 0.05 phr; ᐧᐧᐧᐧᐧ 0.1 phr; ᐧᐧᐧᐧᐧᐧᐧ 0.15 phr and **- - -** 0.2 phr

Table 3

Elastic-hysteresis property of the samples

Fraction of CNM	Dosage, phr	tgδ	G', kPa	G'', kPa	tg$_d\delta$
Without additives	–	0.157	2502	394.1	0.173
"Film"	0.05	0.154	2450	377.3	0.177
	0.10	0.156	2445	380.9	0.183
	0.15	0.159	2430	386.1	0.197
	0.20	0.162	2435	396.2	0.190
"Suspension"	0.05	0.159	2434	394.2	0.168
	0.10	0.151	2252	339.5	0.161
	0.15	0.140	2221	315.2	0.163
	0.20	0.142	2230	314.1	0.167

Notes: tgδ – tangent of the angle of mechanical losses determined on the RPA 2000; G' – loss modulus, kPa; G'' – storage modulus, kPa; tg$_d\delta$ – tangent of the angle of mechanical losses determined by method of dynamic indentation

The results obtained in testing the samples on an RPA 2000 show that application of the "suspension" fraction of CNM leads to reducing of loss modulus, rather than storage modulus. This behavior of the rubber is probably due to the participation of the nanotubes in the relaxation, load distribution and temperature in the bulk of the sample. It results in reduction of the local overstress and overheating in the volume of the elastomeric matrix. Therefore, the dependence of the tgδ from the dose of the fractions CNM has an extreme behavior. The rubbers containing 0.15 and 0.2 phr have the minimum value of tgδ from 0.140 to 0.142. Addition of "film" fractions allows us to increase slightly (less 3 %) tangent of the angle of mechanical losses value. Similar dependences were obtained in tests on the device IPM-1K (tg$_d\delta$).

4. Conclusions

Thus, complex tests of elastomeric compositions with highly dispersed carbon additives allowed us to confirm the model of nonlinear elastic deformation of macromolecules and adhesion between the elastomer and the nanoparticles. Introduction of the additives leads to lower viscosity and increase the relaxation rate of elastomeric compositions. This can be explained by orientation facilitation of the macromolecules to each other. Furthermore, additives interact with the components of mixtures in the processing and during the vulcanization process. This is probably due to the interaction of the functional groups of the additives and ingredients of vulcanization system. This assumption is confirmed by re-

duced time of attaining an optimum degree of vulcanization by 15 %, increased density of the crosslinking by more than 20 % and the changes in the elastic-hysteresis properties of elastomeric compositions. The studies revealed a complex and multi-stage mechanism of interaction between carbon nanoadditives and components of elastomeric compositions.

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ПРО ДЕЯКІ ВЛАСТИВОСТІ ЕЛАСТОМЕРНИХ КОМПОЗИЦІЙ З ВИСОКОДИСПЕРСНИМИ ВУГЛЕЦЕВИМИ ДОДАТКАМИ

Анотація*. Досліджено вплив вуглецевого наноматеріалу, отриманого в плазмі високовольтного розряду, на довговічність еластомерних композицій. Комплексними дослідженнями еластомерних композицій підтверджено модель нелінійної пружної деформації макромолекул, а також адгезійну взаємодію між еластомером і наночастинками. Результати досліджень узгоджуються з даними, отриманими при визначенні в'язкості за Муні, релаксації та кінетиці вулканізації гумових сумішей, умовної міцності при розтягненні та відносному видовженні при розриві високонаповнених гум на основі бутадієн-нітрильних каучуків. Для підтвердження передбачуваного механізму, який лежить в основі впливу вуглецевого наноматеріалу на еластомерні композиції, параметри вулканізаційної сітки визначені методом рівноважного набухання.*

Ключові слова: *бутадієн-нітрильний каучук, гума, вуглецевий наноматеріал, нанотрубки, нановолокна, релаксація гумових сумішей, пружно-гістерезисні властивості, кінетика вулканізації, густина поперечного зшивання.*