Zhanna S. Shashok*, Konstantin V. Vishnevskii*, Nikolay R. Prokopchuk*

Elastomeric composition with high-disperse carbon additives

The influence of a carbon nanomaterials (CNM) 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, relative breaking elongation of highly filled rubbers based on nitrile rubbers. 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.

Key words: *nitrile rubber, rubber, carbon nanomaterials, nanotubes, nanofibers, relaxation of rubber mix, elastic-hysteresis property, vulcanization kinetics, crosslink density*

Kompozycja elastomerowa z dodatkami wysoko zdyspergowanego węgla

Badano wpływ nanomateriału węglowego uzyskanego w plazmie z wyładowań wysokiego napięcia na trwałość kompozycji elastomerowych . Kompleksowe testy kompozytów elastomerowych zawierających dodatki węgla o dużym stopniu zdyspergowania pozwoliły na potwierdzenie modelu nieliniowego odkształcenia sprężystego makrocząsteczek oraz adhezji między między elastomerem i nanocząstkami. Wyniki tych badań zgadzają się z uzyskanymi wynikami badania lepkości Mooneya oraz relaksacji, parametrami kinetyki wulkanizacji mieszanki kauczukowej, konwencjonalnej, wytrzymałości na rozciąganie, wydłużenia przy zerwaniu wysoko napełnionych wulkanizatów opartych na kauczukach butadienowo-nitrylowych. W celu sprawdzenia założonego mechanizmu leżącego u podstaw działania nanomateriału węglowego w kompozycjach elastomerowych, parametry ich sieci wulkanizacyjnych zostały określone metodą spęcznienia równowagowego.

Słowa kluczowe: *kauczuk butadienowo-nitrylowy, guma, nanomateriały węglowe, nanorurki, nanowłókna, relaksacja mieszanki gumowej, właściwości histerezy elastyczności, kinetyka wulkanizacji, gęstość usieciowania*

1. Introduction

Performance requirements of rubber products is constantly increasing. This is due to the expansion of their area of application, and the tightening of the conditions of the use. Therefore, the research on various methods are dealing with improving the properties of rubber. Improving the mix formulations of elastomeric compositions is a promising direction. In as much an 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.

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Failure resistance, deformation and strength properties of the materials included nanomaterials have 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 part

We investigated a filled elastomer composition based on nitrile rubber 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 rubber. 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 begun 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 Figure 1 TEM – pictures of additives are presented.

The Mooney viscosity was determined with MV2000 viscometer, and tests were conducted employing the procedure similar to that recommended by the GOST 10722–76 standard and ASTM D1646–07. The parameters of the vulcanization kinetics were determined with the aid of an ODR2000 vibrorheometer in accordance with the State Standards GOST 12535–84. Crossslink 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 it was also defined a physical relaxation of tension of vulcanized stocks. 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 to 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.

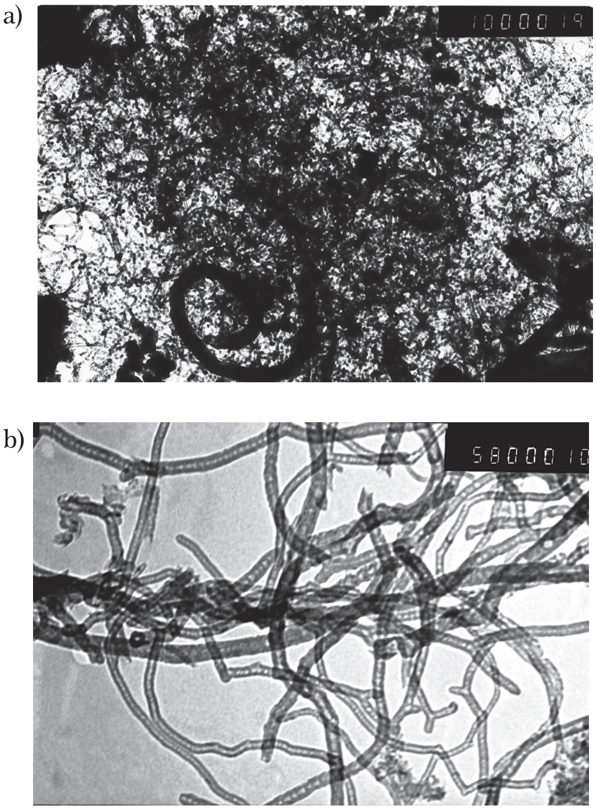


Fig. 1. *TEM – pictures of the “film” (a) and “suspension” (b) fractions*
Rys. 1. *Obrazy TEM frakcji „filmu” (a) i „zawiesiny”(b)*

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 his 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 nanomaterials into elastomeric compositions based on nitrile rubber 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.

Table 1. *Results of the tests of elastomeric compositions on Viscometer MV2000*
Tabela 1. *Wyniki badań kompozycji elastomerowych za pomocą Wiskozymetru MV2000*

Fraction of CNM	Dosage, phr	Mooney viscosity, Mooney units	Slope	Relaxation coefficient K_r, %
Without additives	–	57.3	–0.386	49.7
“Film”	0.05	55.4	–0.395	50.2
	0.10	53.1	–0.400	51.0
	0.15	51.2	–0.403	50.6
	0.20	50.1	–0.406	50.8
“Suspension”	0.05	51.5	–0.410	50.9
	0.10	49.5	–0.417	51.7
	0.15	49.8	–0.411	51.2
	0.20	49.9	–0.405	50.8

We analyzed the data obtained after tests on stress relaxation. The data show that samples of elastomeric composition having a minimum Mooney viscosity naturally characterized by a higher rate of stress relaxation. This is due to the increased segmental mobility of macromolecules in rubber. Samples of rubber mixtures containing fraction “suspension” in a dosage of 0.1 phr have values of Slope and Relaxation coefficient total –0.417 and 51.7 % (sample comparisons matter slope = –0.386 and K_r = 49.7%). When addition fraction “film” in a dosage of 0.2 phr the values of the indicators are slope = –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 with the aid of the adsorption force (Fig. 2).

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.

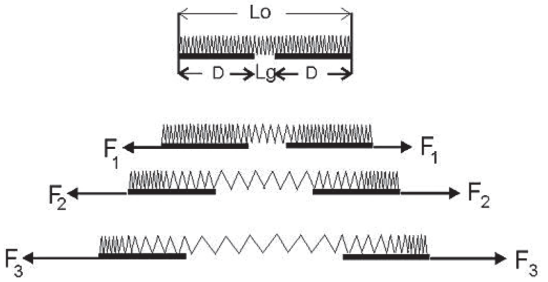


Fig. 2. *The geometry of the structural unit of the model of the interaction of macromolecular and carbon nanomaterial particles*
Rys. 2. *Geometria jednostki struktury w modelu oddziaływania makrocząsteczki i cząstek nanomateriału węglowego*

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 rubber is greater than the interaction between macromolecules of rubber 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 contains fraction “suspension”, characterized by a more homogeneous structure.

Carbon nanomaterials have a large specific surface area and functional groups 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 define a wide range of technical properties of elastomeric compositions. Results of the kinetics of vulcanization tests of rubber mixtures are presented in Table 2.

Table 2. *Kinetics of vulcanization of investigated rubber mixtures*
Tabela 2. *Kinetyka wulkanizacji badanych mieszanek kauczukowych*

Fraction of CNM	Dosage, phr	Time for attaining the optimum vulcanization $t_c(90)$, min	Vulcanization rate 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

Analysis of the vulcanization kinetics of elastomeric compositions based on the nitrile rubber 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 a fraction content of 0.15 phr (10.1 min).

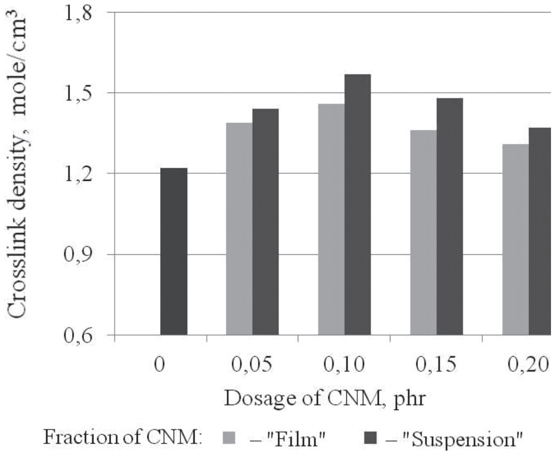
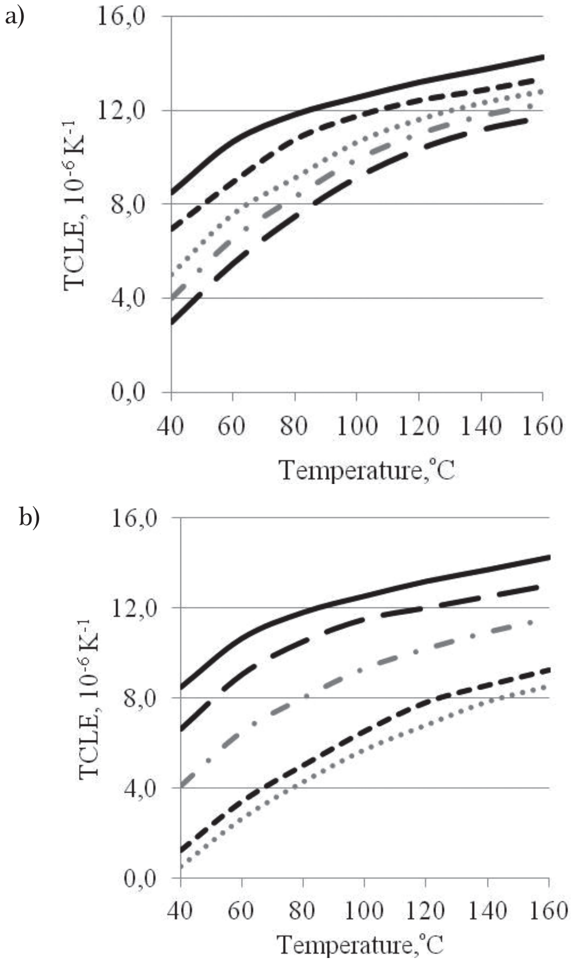


Fig. 3. *Crosslink density of the vulcanizates*
Rys. 3. *Gęstość usieciowania wulkanizatów*



Dosage of CNM: ––– – without additives, – – – – 0,05 phr, -·-·- – 0,1 phr, ······ – 0,15 phr, – – – – 0,2 phr

Fig. 4. *The temperature coefficient of linear expansion of the samples with fraction "film" (a) and "suspension" (b)*
Rys. 4. *Współczynnik temperaturowy rozszerzalności liniowej próbek z frakcjami: „film" (a) i „suspensja"(b)*

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). Deactivation of the polar agent of the vulcanizing group by the particles of nanomaterials can occur, and thus 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 (Figure 3) and the temperature coefficient of linear expansion (TCLE) of vulcanizates (Fig. 4).

According to the obtained data, applying of the fractions "film" and "suspension" lead to an increase of 30% in concentration of crosslinks and thus reduce the values of the samples TCLE rubber in the temperature range of (40 ± 2)÷(120 ± 2) °C.

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).

Table 3. *Elastic-hysteresis property of the samples*
Tabela 3. *Właściwości histerezy sprężystości próbek*

Fraction of CNM	Dosage, phr	tgδ	*G′*, kPa	*G″*, kPa	$\text{tg}_d\delta$
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

Notice: tgδ – tangent of the angle of mechanical losses determined on the RPA 2000; *G′* – loss modulus, kPa; *G″* – storage modulus, kPa; $\text{tg}_d\delta$ – 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 fraction “suspension” of CNM leads to reducing of loss modulus, more than storage modulus one. 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 $\mathrm{tg}\delta$ 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 $\mathrm{tg}\delta$ 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 ($\mathrm{tg}_{d}\delta$).

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 the reducing the time of attaining an optimum degree of vulcanization by 15%, increasing the density of the crosslinking more than 20% and the changing 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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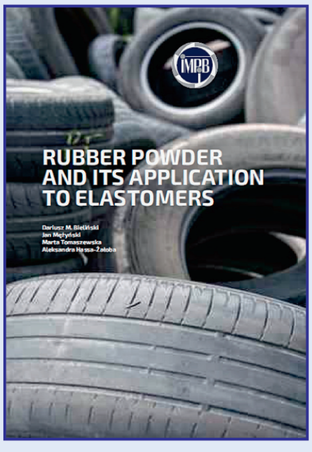

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