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NANOSTRUCTURES

SPECIAL FEATURES OF RELAXATION PROPERTIES OF ELASTOMER COMPOSITIONS WITH HIGHLY DISPERSED CARBON ADDITIVES

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The influence of three different nanostructured carbon materials: nonfunctionalized and functionalized with oxygen- and amino-containing groups on the relaxation properties of elastomer compositions was studied. Rubber compounds based on natural rubber and nitrile butadiene rubber were used as elastomeric matrices. Determination of the relaxation properties of rubber compounds and rubbers based on them was carried out on the basis of calculations of the stress relaxation coefficient and the conditionally equilibrium modulus. It has been established that functionalized carbon nanomaterials exert the most significant effect on the acceleration of relaxation processes in rubber compounds based on polar rubber due to a possible decrease in the intermolecular interaction of its polar groups. In compositions based on natural rubber, the introduction of functionalized nanomaterials increases the rate of relaxation processes only in compositions with semi-reinforcing carbon black, which is due to the lower interactions of elastomer macromolecules with chain structures of the filler. It has been found that in compositions based on nitrile butadiene rubber, the use of carbon nanomaterials, in comparison with rubber without nanoadditives, leads to an increase in the conditionally equilibrium modulus in vulcanizates with both semi-reinforcing and high-reinforcing carbon black at a dosage of 50.0 wt.pts. Rubbers based on nonpolar rubber containing carbon nanomaterials are characterized by increased values of conditionally equilibrium modulus only in the case of compositions with semi-reinforcing carbon black at a dosage of 50.0 wt.pts.

Keywords: *rubber, vulcanized rubber, carbon nanomaterials, relaxation coefficient, conditionally equilibrium modulus.*

Introduction. Inclusion of modifying nanosized additives into elastomeric compositions makes it possible to obtain materials with improved technological and operational properties [1–3]. As a result of the use of even relatively small dosages of nanomaterials, changes occur in the nature of the interphase interaction of the polymer with the filler [4–7] and interaggregation interactions of the filler particles with each other [8, 9], which ultimately makes it possible to obtain a composite with improved performance characteristics. At the same time, during processing of elastomer compositions, in the volume of the elastomer matrix, relaxation processes proceed which determine the mechanisms of viscous flow and the possibility of imparing the desired shape to the polymer. The characteristic features of the relaxation properties of polymer composites are taken into account when choosing a processing method, establishing design and technological parameters of the equipment operation, as well as in forming the performance characteristics of a finished article.

Research Methods. The purpose of this work was to study the effect of three different nanomaterials, nonfunctionalized and functionalized by amino- and oxygen-containing groups, on the relaxation properties of elastomeric compositions based on general- and special-purpose rubbers.

Highly dispersed carbon nanomaterial (CNM) was obtained at the Perspective Research and Technologies enterprise (Minsk) (Specs. BY690654933.001-2011). Three types of nanomaterials were used in the work. The first one (CNM 1) is

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a nonfunctionalized material, which is a mixture of carbon nanotubes and nanofibers with impurities of amorphous carbon, metals, and their oxides. On the basis of CNM 1, the second and third materials were obtained, which underwent special processing (functionalization) for grafting oxygen-containing groups (CNM 2) and amino groups (CNM 3) [10].

Filled elastomeric compositions based on natural rubber (NR) of grade SMR-10, which is a nonpolar general-purpose rubber, and on nitrile–butadiene rubber BNKS-18, which is a special-purpose polar rubber, were used as research objects. Highly reinforcing carbon black of grade N 134 and semi-reinforcing carbon black of grade N 772 were introduced into the compositions in dosages of 25.0 and 50.0 wt.pts. per 100.0 wt.pts. of rubber.

The determination of Mooney stress relaxation in a sample of rubber compound was carried out according to GOST R 54552-2011 [11]. The stress relaxation test was performed on an MV-2000 viscometer automatically after the completion of viscosity measurements by very quickly stopping the rotation of the rotor and recording the drop of the final Mooney viscosity over time according to a power law. Mathematically, this can be represented as an equation [11, 12]

$$M = kt^{-\alpha} . \tag{1}$$

In logarithmic coordinates this expression has the form

$$\log M = -\alpha \log t + \log k . \tag{2}$$

Based on the data obtained, the stress relaxation coefficient is calculated:

$$K_r = \frac{ML(1+4) - k}{ML(1+4)} 100\% . \tag{3}$$

The conditionally equilibrium modulus (E_∞) of vulcanized rubber was determined by stretching test samples by 25% after their preliminary heating for 5 min at a temperature of 70 ± 1°C followed by holding in a deformed state for 60 min at the same temperature. After this time, the equilibrium value of the stress in the sample was determined [13]. The tests were carried out on a T 220 DC tensometer from Alpha Technologies equipped with a thermal camera.

According to the kinetic theory of high elasticity for nonideal meshes, the value of the conditionally equilibrium modulus is determined from the equation [12]

$$E_\infty = \Phi \nu RT . \tag{4}$$

Results and Discussion. The determination of the Mooney viscosity is one of the most common methods of establishing the quality indicators of rubbers and rubber compounds. At the same time, even at the same viscosity values, polymers can differ in branching of macromolecules, supramolecular structure, molecular weight, and molecular weight distribution while rubber compounds can differ in the content of filler and plasticizer. In this regard, tests to determine the relaxation properties of unvulcanized elastomer compositions make it possible to obtain additional information about the elastic and plastic components of material deformation [14].

The results of calculating the stress relaxation coefficient of the studied rubber compounds (Table 1) showed that compositions based on BNKS-18 with semi-reinforcing N 772 and highly reinforcing N 134 grades of carbon black have significantly lower (by 1.46–1.55 times) indicators K_r in comparison with compositions based on natural rubber. This is due to the fact that, unlike natural rubber, the units of butadiene–nitrile rubber contain polar nitrile groups. Through the interaction of these groups of neighboring macromolecules, the movement of units from one equilibrium position to another is difficult, and, consequently, the transition, which determines the relaxation process from extended conformations of macromolecules into folded one (relaxation) slows down.

Deformation of polymer systems in a fluid state leads to a change in their internal structure which is accompanied by the envelopment of an anomaly in viscosity, highly elastic deformations, and normal stresses [15, 16]. At the first moment after stretching of the noncross-linked elastomer, the initial stress is fixed in the sample, which corresponds to the state when the molecular coils unfolded during deformation, and the nodes of the fluctuation network have not yet had time to disintegrate and regroup. Gradually, the nodes of the fluctuation network in the stressed sample disintegrate, and the macromolecular coils are more and more curled. The more network nodes have disintegrated and the macromolecular coils rolled, the lower the stress remains in the sample. After a certain period of time, all the stressed nodes of the fluctuation network are regrouped, which makes it possible for the coils of macromolecules to go into the former folded, thermodynamically most favorable state with disappearance of internal stresses in the elastomer [17]. In compositions

TABLE 1. Stress Relaxation Coefficients of Rubber Compounds Based on BNKS-18 and NR with Carbon Nanomaterials

Additive	Dosage additions, wt.pts.	Stress relaxation coefficient, %							
		BNKS-18				NR			
		N 772		N 134		N 772		N 134	
		25.0	50.0	25.0	50.0	25.0	50.0	25.0	50.0
Without additive	–	48.2	49.6	47.3	43.2	74.7	76.9	68.9	64.1
CNM 1	0.1	49.2	50.4	47.7	43.1	77.5	74.2	68.0	64.3
	0.2	49.6	50.7	46.9	42.9	77.3	73.9	67.8	64.3
CNM 2	0.1	48.9	51.1	51.6	43.3	77.8	74.6	69.7	64.7
	0.2	48.7	49.9	49.9	43.5	77.2	77.5	68.3	64.4
CNM 3	0.1	49.5	50.3	51.8	48.3	81.7	75.2	68.8	63.7
	0.2	49.0	50.3	52.5	47.5	78.6	75.8	68.5	64.6

based on the studied rubbers, semi-reinforcing carbon black N 772 slows down relaxation processes less than the highly reinforcing carbon black N 134. The value of the relaxation coefficient for composition based on BNKS-18 with a filler of grade N 772 is 48.2% at a dosage of 25.0 wt.pts. and 49.6% at 50.0 wt.pts. and for compositions of carbon black of grade N 134, it is 47.3 and 43.2%, respectively. A similar dependence is determined also for compositions based on natural rubber. Particles of highly reinforcing carbon black N 134 interact to a greater extent with rubber macromolecules with formation of bound rubber [6], which leads to retardation of conformation transitions and to an increase in the relaxation time.

It was found that the introduction of CNM 1 nonadditives into elastomer compositions has practically no effect on the relaxation coefficient of the studied rubber compounds (the change is less than 2.0% compared to the mixture without nanoadditives). The use of CNM 2 in the composition of rubber compounds leads to some increase of K_r for a composition based on BNKS-18 filled with carbon black N 134 at a dosage of 25.0 wt.pts. from 47.7% in the case of composition without additives and up to 51.6% at a dosage of 0.1 wt. pts. of a nanomaterial, as well as for a composition based on natural rubber from 25.0 wt.pts. of carbon black N 772 (from 74.7 up to 77.8%). The greatest effect of relaxation acceleration is achieved with the introduction of CNM 3 nanoparticles containing amino groups on their surface. In this case, for a rubber compound based on BNKS-18 with carbon black N 134, the relaxation coefficient, in comparison with the mixture without an additive, increases from 47.3 to 52.5% at a filler dosage of 25.0 wt.pts. and from 43.2 to 48.3% at a dosage of 50.0 wt.pts. and for compositions based on natural rubber with carbon black N 772 at a dosage of 25.0 wt.pts. the value of K_r increases from 74.7 to 81.7%.

Consequently, changes in the relaxation properties of elastomers compositions based on BNKS-18 polar rubber when functionalized nanostructured nanomaterials are used in their composition are due to intermolecular interactions of rubber chains with each other, interactions of the filler with the elastomer, dosage of the filler, as well as to the presence and nature of functional groups on the surface of carbon nanomaterial, which can interact with the polar groups of rubber, as a result of which the interaction between macromolecules can decrease, the flexibility of polymer chains somewhat increases, and the ability to undergo conformational transitions increases. In the case of nonpolar polyisoprene rubber the introduction of functionalized nanostructured carbon materials exerts influence on the course of relaxation processes in mixtures with semi-reinforcing carbon black, which is due to small intermolecular interactions and high kinetic flexibility of elastomer chains.

In the process of vulcanization, as a result of the interaction of the vulcanizing agent with rubber, a three-dimensional network of rubber is formed, in which the elastomer macromolecules are interconnected by chemical bonds. Entanglement of polymer chains and crosslinking can change the rubber structure and, in turn, affect the relaxation rate. Relaxation behavior becomes more complex in filled vulcanized rubber. During relaxation, three processes can occur simultaneously, including: physical relaxation due to the movement of segments of the polymer chains and of the filler network; destruction of macromolecules caused by heat, light or chemicals; destruction or rearrangement of cross-links [18]. In this connection, the course of relaxation processes in the bulk of the vulcanizate differs from the processes occurring in a noncross-linked polymer.

TABLE 2. Conditionally Equilibrium Modulus of Rubbers Based on BNKS-18 and NR with Carbon Nanomaterials

Additive	Dosage additions, wt.pts.	Conditionally equilibrium modulus, kPa							
		BNKS-18				NR			
		N 772		N 134		N 772		N 134	
		25.0	50.0	25.0	50.0	25.0	50.0	25.0	50.0
Without additive	–	813	1178	1154	1468	999	1014	1138	2183
CNM 1	0.1	833	1143	912	1437	1001	1071	1170	1789
	0.2	918	1204	828	1504	852	1154	995	2049
CNM 2	0.1	907	1385	954	1418	797	1200	987	1884
	0.2	766	1226	918	1647	903	1208	950	1848
CNM 3	0.1	855	1219	764	1641	911	1155	997	2013
	0.2	794	960	842	1318	771	1151	1088	1967

If the elastomer is spatially cross-linked, i.e., vulcanized, then, along the fluctuation network, a network of chemical bonds is formed in it, which relaxes much more slowly than the fluctuation network. In a vulcanized sample, the stresses relax until all of them are concentrated at the nodes of the chemical network. The stress in the sample reaches the limit. Chemical bonds prevent the irreversible movement of the coils of molecules, but do not prevent the movement of segments [17].

A very long time is needed to establish equilibrium in rubber. If a rubber sample is deformed at an infinitesimal rate, at which relaxation processes will have time to take place, then at strain values of up to 200%, a close-to-straight dependence of stress on strain is detected. In this regard, the conditionally equilibrium modulus is determined by measuring the stress at a given degree of deformation after the completion of the main relaxation processes [19].

Table 2 contains the results of determining the conditionally equilibrium modulus of rubbers with carbon nanomaterials. In rubbers based on the studied raw rubbers the course of relaxation processes is significantly affected by the dosage of the filler and the type of carbon nanostructured material used. It has been established that in rubbers with 25 wt.pts. of semi-reinforcing carbon black, the conditionally equilibrium modulus, as compared to rubber without nanoadditives, decreases to 22.9% for vulcanizates based on natural rubber, and for vulcanizates based on BNKS-18 it increases to 12.9%. In this case, with an increase in the dosage of functionalized CNM 2 and CNM 3 nanomaterials, the values of the conditionally equilibrium modulus decrease (from 813 kPa in the case of rubber without nanomaterials to 766 and 794 kPa for rubber with CNM 2 and CNM 3, respectably), the value of E_∞ slightly increases (from 833 to 918 kPa). In compositions with 50.0 wt. pts. of carbon black N 772, the use of nanomaterials leads to an increase in the conditionally equilibrium modulus to 17.6 for rubbers based on BNKS-18 (the exception is rubber with 0.2 wt.pts. of CNM 3) and to 19.2% for compositions based on natural rubber (with the exception of rubber with CNM at a dosage of 0.1 wt.pts.). Rubbers containing CNM 2 and CNM 3 in their composition are characterized by the highest values of the conditionally equilibrium modulus.

Vulcanizates with 25.0 wt.pts. of highly reinforcing N 134 grade carbon black and carbon nanomaterials have 16.5–33.8% lower values of conditionally equilibrium modulus compared to rubber without nanoadditives. At the same time, at a filler dosage of 50.0 wt.pts. in compositions based on natural carbon, a decrease in the conditionally equilibrium modulus by 6.4–18.1% was revealed, and in compositions based on polar rubber, the use of certain dosages of nanomaterials contributes to an increase in this indicator by 2.5–12.2%.

The revealed nature of the change in the conditionally equilibrium modulus of rubbers can be due to a number of factors, including primarily differences in the vulcanization structure of vulcanizates, the presence of a carbon–rubber gel formed during interphase interaction of the elastomer with the filler, as well as the secondary network of the filler formed due to interaggregate interactions of filler particles with each other. The decrease in the conditionally equilibrium modulus is associated with the formation of a denser structure of the vulcanizate and, as a consequence, with the difficulty in moving the elastomer segments under the action of a load. An increase in the conditionally equilibrium modulus indicates a lower stress concentration in the elastomer volume, which may be due to the lower density of cross-linking, better ability of parts

of rubber macromolecules to be oriented between the nodes of vulcanization network, and, as a consequence, to the higher reliability and longevity of the rubber article.

Conclusions. Thus, it has been determined that the most significant effect on relaxation acceleration in rubber compounds based on the BNKS-18 polar rubber is exerted by functionalized carbon nanomaterials CNM 2 and CNM 3, which may be due to the decrease in the intermolecular interaction of polar rubber groups and to the increase in the rate of conformational transitions. In compositions based on natural rubber, the introduction of CNM 2 and CNM 3 increases the rate of relaxation process only in compositions with semi-reinforcing carbon black, which is associated with the smaller interactions of the elastomer with the chain structures of the filler.

The obtained results on the determination of the conditionally equilibrium modulus indicate the participation of carbon nanomaterials in the process of formation of the spatial network of the vulzanizate and, thus, their influence of the physical and mechanical properties of rubber. It has been established that in compositions based on BNKS-18 the use of carbon nanomaterials leads, in comparison with rubber without nanoadditives, to an increase in the conditionally equilibrium modulus by 12.9–17.6% in vulzanizates with semi-reinforcing N 772 carbon and by up to 12.2% in vulzanizates which highly reinforcing N 134 carbon black at a dosage at 50.0 wt.pts. Rubber based on natural rubber containing carbon nanomaterials are characterized by the values of conditionally equilibrium modulus increased to 19.2% only in the case of compositions with semi-reinforcing N 772 carbon black at a dosage of 50.0 wt.pts. A decrease in the concentration of stresses in the rubber volume with carbon nanomaterials at a certain dosage will make it possible to obtain industrial rubber goods with an increased resource of performance.

NOTATION

E_∞, conditionally equilibrium modulus, kPa; K_r, stress relaxation coefficient, %; k, value of the torque after 1 s from the beginning of experiment, Mooney arb. units; M, torque, Mooney arb. units; $ML(1 + 4)$, Mooney viscosity, Mooney arb. units; R, universal gas constant, J/(mol·K); T, test temperature, K; t, time, s; α, slope of the tangent to the relaxation graph in 1 s from the beginning of the test (is a measure of the rate of relaxation); ν, crosslink density, mole/cm^3; Φ, network imperfection factor (front factor).

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