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Research Article

MODIFICATION OF RUBBERS WITH CARBON NANOTUBES

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ABSTRACT

The effect of multi-walled carbon nanotubes on the performance characteristics of rubbers based on butadiene-nitrile and silicone rubbers was investigated under various methods of their preliminary treatment and introduction into the composition of rubbers. It is shown that the introduction of 0.5% by weight of carbon nanotubes into elastomers of different chemical structure leads to an increase in their strength and thermal properties.

INTRODUCTION

In the elements of aviation structures of large size and low rigidity rubber thermal protective coatings are used, which do not collapse when the structure is deformed. The use of rubber for supersonic aircraft and spacecraft is limited due to high requirements for heat and frost resistance of materials, as well as to their stability under the conditions of radiation and in a vacuum. Therefore, the development of new rubber with improved characteristics is an urgent problem.

Properties of rubber can be significantly modified by the introduction of fillers of different chemical nature, shape, size and specific surface area. At present, a great scientific and applied interest is given to the possibility of using nanostructured materials in rubber, in particular, carbon, having a special complex of properties. However, the use of such fillers is constrained by their inherent propensity for self-association. Therefore, the main task in the development of elastomeric nanocomposites is the disaggregation of agglomerates of nanostructures and their incorporation into the polymer matrix.

Experimental

The purpose of this work is to investigate the effect of multiwalled carbon nanotubes (CNT) on the performance characteristics of rubbers based on butadiene-nitrile (BNC) and silicone (SCTN) rubbers in various methods of their preliminary treatment and introduction into rubber composition[1].

At present, BNCs are widely used in the manufacture of various oil-and-gas-resistant rubber products due to their high resistance to aggressive agents[2,3].

Polysiloxanes are among the most common eco-friendly polymers and constitute a rather significant class of silicon organic polymers. Recently, increased attention is paid to the regulation of the structure and properties of polysiloxanes by nanofillers of various nature and structure, which in turn determines the nature of the interaction between them and the polymer, as well as the possibility of nanocomposites to acquire high performance[4].

Our previous work has shown that the introduction of multilayer CNTs into the polymer matrix affects the structure of the composite material (the degree of crystallinity of the

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matrix), as well as increases strength characteristics, electro- and thermal conductivity, thermo-oxidation resistance.

CNTs are characterized by extremely high specific strength characteristics (breaking strength at ~ 1.8TPA), electro- and thermal conductivity, etc. In this regard, they have huge prospects for use in modern technologies. The feature that distinguishes CNT from other nanoparticles is the uniquely high aspect ratio *(η)* (ratio of length to diameter) that exceeds 10^3. In this case, the percolation threshold $F\eta$ ($F\eta \approx 1/\eta$), that is, the concentration at which *A* continuous grid of CNTs is formed, provided they are uniformly distributed in the polymer matrix, can be ≈ 0.1 wt.% .

Therefore, the use of CNTs as a modifier of filled rubbers, even with a minimum content of 0.1 wt.% , can provide an increased level of strength of rubber composites as compared to conventional fillers. From this point of view, the modification of the butadiene-nitrile and silicone rubbers of CNTs is an urgent task. Solving this problem can lead to an increase in the elastic, strength properties of rubber while maintaining high processability of rubber compounds during their processing.

Carbon nanotubes were produced by the method of catalytic chemical vapour deposition (CCVD), by pyrolysis of hydrocarbons on complex metal oxide catalysts[5-8]. The synthesis of CNTs was carried out in equipment with a reactor with a volume of $30 dm^3$ and a yield of about 1.5 kg of product per day. According to the Ukrainian standard, the average diameter of CNTs is 10-20 nm, the specific surface that was determined by desorption of argon is 200-400 m^2/g, the bulk density is within 20-4 g/dm^3 (Fig. 1).

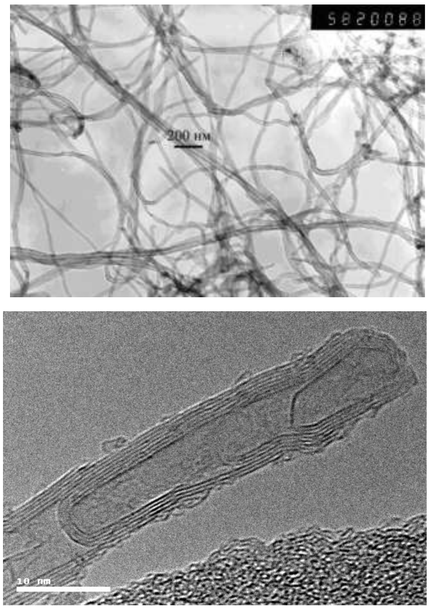

Fig 1 TEM of multi-walled CNTs used to fill elastomers.

The introduction of CNTs into the elastomeric matrix was carried out on a high-speed mixer, followed by homogenization in a wiping trivalent machine.

For the maximum possible degree of dispersion of agglomerates of nanostructures, a method of ultrasonic treatment of carbon nanotubes was used with simultaneous functionalization of the surface of nanoparticles with a surfactant.

Rubber mixtures were prepared on a laboratory mixer, the mixing temperature was 100 °C, the mixing time was 6 min, and the rotor speed was 60 rpm.

The CNTs, in an amount of 0.5 wt.%, were introduced into the oligomeric polysulphide onto a dissolver at a rotor speed of 300 rpm for 5 min into a dissolver mixing chamber. Further, the resulting composition was introduced into a BNK-based rubber mixture on cold rolls for 20 min.

Then, the filler was supplemented with carbon black (30%) and components of the cure system: *p*-quinoneoxim (3% by weight) manganese dioxide (6% by weight), diphenylguanidine (0.2% by weight).

In the composition of silicone rubber was introduced filler - aerosil (25%) and cross-linking components. The total mixing time on the roll is 13min. at a temperature of no more than 40 °C. To evaluate the strength properties on the basis of the resulting compositions, rubber was prepared in a vulcanizing press at 150 °C for 20 min.

RESULTS AND DISCUSSION

Table 1 presents the elastic and strength properties of rubbers based on BNK and polysulphide with a variation in the content of the last 10-30% by weight, with a nanotube content of 0.5% by weight. The results showed that the introduction of nanotubes into the composition leads to an increase in strength at break by 20%. This reduces the relative elongation at break by 30% (Table 1).

Table 1 Mechanical properties of filled CNT rubbers based on BNC with polysulfide

Composition BNP / PSF, wt.%	Mechanical properties with different CNT content (wt. %)					
	ε, %		σ_{100}, MPa		σ, MPa	
100/0	0	0,5	0	0.5	0	05
90/10	330	200	4,1	12	15	18
80/20	300	190	4	11	14,4	18
70/30	340	180	3,6	10	13,3	17

where: ε - Elongation at break; σ_{100} - Module with 100% elongation; σ - Relative strength at break.

The thermal stability of the nanocomposites obtained was investigated by the thermo gravimetric analysis (DTA) method for the Q-1500D Derivatograph in a dynamic mode with a heating rate of 5°C / min and a temperature range of 23-600 °C. The DTA data for the compositions are shown in Table 2.

Table 2 The results of thermal analysis of the composition

Indicators	Composition of BNK / PSF and CNT, wt.%					
	90/10		80/20		70/30	
	0	0,5	0	0,5	0	0,5
$T_{5\%}$, °C	307	327	289	355	260	385

It can be seen from tab.2 that the temperature of the onset of degradation of vulcanizates decreases with an increase in the content of polysulphide in the composition, which is due to the influence of thermally labile S-S and S-H bonds in the polysulphide.

It should be noted that for all the BNK / PSF ratios studied, the introduction of 0.5% CNTs leads to an increase in strength. When CNTs are introduced into the nanocomposite, an increase in the temperature of destruction is observed, that is, its thermal stability is increased. The introduction of CNTs into polysiloxane rubbers led to the following results (Table 3).

Table 3 Mechanical properties of filled CNTs of siloxane rubbers

	Indicators					
	Initial	Content of CNT, wt.%				
		0,1	0,2	0,5	1,5	2
σ, MPa	2,5	3,5	3,0	2,8	2,0	1,2
ε,%	110	200	150	140	100	85
A, rel. un.	45	60	55	40	40	42

where: ε - Elongation at break; σ - Relative strength at break; A - Shore hardness.

The increase in the content of CNT in silicone vulcanized from 0.1 to 2.0% by weight. Leads to a significant increase in the strength of vulcanization, and with a further increase in the degree of filling, the effect of the gain decreases, while the viscosity of the paste increases and the physic mechanical indexes decrease (Table 3).

For both types of elastomers, the introduction of multi-walled CNT affects all the properties studied: the deformation of fracture decreases, the tensile strength and hardness of nanocomposites increase with increasing CNT concentration in the investigated interval. It should be noted that the dependencies are not linear, and one can find the optimal value of the concentration of CNT in terms of consumer characteristics.

The initial composition of many rubbers includes technical carbon (soot), which fulfils the role of filler with the effect of amplification. As it is known, the amplification effect when carbon black or other active fillers is used as a filler occurs due to the formation of a "grid" as a result of the joining of active particles penetrating the entire rubber mass in all directions. That is, the rubber and the filler form two interpenetrating continuous clusters. The functional groups existing on the surface of the carbon black: –OH, –OOH, >C=O, etc., provide for chemical interaction with sulphur and rubber during vulcanization. In the formation of chemical bonds between soot and rubber, the unsaturation of the rubber should decrease. It is believed that in the formation of the grid, only those bonds that are at a distance of 0.3 nm from soot particles with an average diameter of 3 nm can participate. At such distances, not more than 1.5% of the total amount of unsaturated bonds in the rubber is saturated. As a result of such interactions, rubber molecules become less mobile.

Obviously, CNT are more effective filler, which is due, first, to the shape factor. The ratio of the maximum size (length) to the minimum size (diameter) for CNT is 10^3 or more times. The specific surface area of the CNT is > 200 m^2/g, in comparison with technical carbon, for which this value is < 100 m^2/g [9-10].

The relaxation mechanism of CNT dispersion and the model of the molecular-colloidal organization of the rubber structure[11] are based on the heterogeneity of the Newtonian flow of elastomers with forced glass transition of the least mobile high-molecular fractions. Dispersing of CNT begins with the bonding of segments of the elastomer feed through chains that glass in the shear stress zone, forcing the chains to overstress and remove the agglomerates to carbon-rubber particles. Isolation in CNT particles provokes by reducing the segmental mobility of the bonded elastomer, which leads to a decrease and hardening of the particles with each glass transition. The overvoltage chains of the matrix, which are inferior to the particles in strength, are broken at the border with the vitrified segments by macro radicals initiating the cross linking processes, which further strengthen the particles with elastomeric transition layers. Densely cross linked transition layers bind carbon-rubber particles to chain structures that reinforce the matrix, and loose - swell in the segments of the matrix and can collapse under conditions of rolling the rubber mixture.

It follows from the foregoing that the strengthening of elastomers is not an isolated phenomenon at the interphones boundary, but is a complex colloid-chemical process of formation of the interphones region and vulcanization structures in the carbon-rubber rubber mesh nodes. Rubber deformation begins with redeployment of grid nodes by overcoming their physical interactions in chain structures and with a matrix, accompanied by a decrease in their functionality due to the rupture of overvoltage chains. In the final stages of destruction, nodes can also be deformed, which contributes to the dissipation of overvoltage's from the interphones boundary, which additionally increases the strength of the rubber. An important role in increasing the ability to deform the grid nodes is played by occluded rubber, and its polar modifiers reduce.

Polar groups of rubbers interacting with CNT accelerate the vulcanization with sulphur, strengthen the interphone boundary and compact the transitional layers at the nodes of the rubber net, which reduces their ability to deform. With the decrease in the instauration of rubber by hydrogenation, the cross linking processes are redistributed from the interphone boundary to the entire volume of the particles, increasing the thickness of the transition layers and the functionality of the assemblies, and 30% the strength of the rubbers.

It should also be noted that the introduction of CNT as a modifier in the elastomeric matrix must be introduced directly, and then add all the necessary fillers - carbon black, aerosol.

Thus, the combination of prescription and technological ways of controlling the functionality, strength and ability to deform the grid nodes, interphase interactions within them, and the thickness and density of the transition layers is the basis of amplification, which allows the rubber properties to be directed in a directional manner.

CONCLUSIONS

It is established that rubber composites containing carbon nanotubes are characterized by high strength at break and thermal stability. In addition, rubber composites modified with carbon nanotubes are characterized by a higher growth of the elastic modulus and hardness as compared to unmodified ones.

Thus, the introduction of CNTs in an amount of 0.1-5.0% by weight of rubber compositions results in a significant increase in the strength characteristics and thermal stability of the compositions. This indicates that CNT is ideal filler for composites based on polymers of different chemical composition and structure.

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