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Modification of Specialty Rubbers by Carbon Nanomaterials

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Abstract: 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. Multiwall carbon nanotubes are among the most anisotropic materials known and have extremely high values of Young's modulus. Carbon nanotube aspect ratio of length to diameter is more than 10^3; this distinguishes it from other nanoparticles. New composites with carbon nanotubes (CNTs) as additives were studied intensively during the last decade. Composites are characterized by extremely high specific strength properties, electrical and thermal conductivity. The effect of multiwalled carbon nanotubes on the performance characteristics of rubbers based on nitrile-butadiene was studied with various methods of their preliminary treatment and introduction into the composition of rubbers. It was shown that the introduction of 0.5-1.0 wt. % carbon nanotubes into elastomers of different chemical structures leads to an increase in their physic mechanical characteristics, wear resistance and aging resistance, which significantly increases the service life of such products.

Keywords: Polymer Composites, Multiwall Carbon Nanotubes, Modification, Nitrilebutadiene Rubber

1. Introduction

The creation of high-performance polymer composites is an important area of polymer science, which in recent years has changed the direction of nanoscale fillers due to their ability to improve the properties of composites at relatively low concentrations of nanofillers. The obtaining of materials with a complex of improved characteristics can be achieved by the creation of polymeric nanocomposites, which provide a wide range of functional materials for use in the most diverse sectors of the economy. Properties of nanocomposites far exceed traditional polymeric materials and allow creating new systems that can meet the constantly growing needs of society in new materials.

It should be noted that in the open press there is no specific data - neither about the composition of the components of polymer composite materials, no about the technology of their production. Therefore, in order to obtain new polymer composite materials and the technology of their production, it is necessary to carry out their development under the target operational requirements.

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 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.

The purpose of this work is to investigate the effect of multi-walled carbon nanotubes (CNT) on the performance characteristics of rubbers in various methods of their preliminary treatment and introduction into rubber composition.

Multiwall carbon nanotubes are among the most anisotropic materials known and have extremely high values of Young's modulus [1]. Carbon nanotube aspect ratio of length to diameter is more than 10^3; this distinguishes it from other nanoparticles. New composites with carbon nanotubes (CNTs) as additives were studied intensively during the last decade. Composites are characterized by extremely high specific strength properties [2], electrical and thermal conductivity [3].

CNT are characterized by extremely high specific strength characteristics (tensile strength ≈1.8TPA), electrical and thermal conductivity, etc. In this connection, they have great prospects for use in modern technologies. The property 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 (Φη) (Φη ≈ 1/η), 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% by weight.

At present, a great scientific and applied interest is 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 [4-8].

In our time, butadiene-nitrile rubber (BNR) due to its high performance and aggressive agents are widely used in the manufacture of various oil resistant rubber products. However, the processing of butadiene-nitrile rubber is complicated due to the high stiffness that is due to the large intermolecular interaction [9]. The use of carbon nanotubes. as a modifier of rubber, even with minimal content (0.5-1.0 % by weight), can provide a significant improvement in the performance of a rubber composition. Table 1 shows the basic ingredients of the rubber composition.

The modification of rubber and rubber compounds allows the creation of composite materials that have high stability to heat, light, good elastic-hysteresis properties and a sufficient level of cohesive strength. The lag of their properties from the quality characteristics, primarily, cohesive strength, is due to imperfection of their structure and the presence of non-rubber components.

Table 1. *Ingredients of rubber composition.*

Raw	Mass fraction
BNRS-40	100,0
Zinc whitewash	5,0
Soot 803	50,0
Stearin	2,0
Paraffin	2,0
Dibutylphthalate	10,0
Neozone D	1,0
Sulphur	0,1
Tiuram	2,0
Diafen FP	1,0

The carried out work showed that the introduction of multilayered CNTs into the polymer matrix influences the structure of the elastomeric material (the degree of crystallinity of the matrix), and also increases the strength characteristics, electrical thermal conductivity, thermal oxidation resistance. The introduction of CNTs into the elastomeric matrix was carried out according to the developed technology, which makes it possible to obtain the maximum possible degree of dispersion of agglomerates of nanostructures.

From this point of view, the modification of BNR is an urgent task. Solution of this problem can lead to increase of elastic, strong properties of rubber with the preservation of high technological properties of rubber mixtures during processing.

2. Main Body

The purpose of this work is to investigate the effect of multi-walled carbon nanotubes (CNT) on the performance characteristics of rubbers based on butadiene-nitrile (BNR) rubbers in various methods of their preliminary treatment and introduction into rubber composition [10-13].

In this work, the filled rubber compound was used on the basis of butadiene-nitrile rubber. As filler was technical carbon, and as a modifier were carbon nanotubes.

CNTs were obtained by the method of catalytic chemical vapor deposition (CCVD) by pyrolysis of hydrocarbons on complex metal oxide catalysts. Synthesis of CNT was carried out in equipment with a reactor volume of 30 dm^3 and an output of about 1.5 kg of product per day. According to the Ukrainian standard (TU U 24.103291669-009: 2009 (ISC NAS of Ukraine), the average diameter of the CNT was 10-20 nm, the specific surface determined by desorption of argon was 200-400 m^2 / g, the bulk density - within 20-40 g / dm^3 [14-15].

The introduction of CNT into a polymer matrix was carried out on a high-speed mixer with subsequent homogenization on a rotary three-wheeler machine.

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

Rubber mixtures were prepared on a laboratory mixer, mixing temperature - 100°C, mixing time – 6 minutes, speed of rotation of rotors - 60 rpm. CNT in the amount of 0.5 wt.% was injected into a technical carbon on a dissolver with a rotational speed of 300 rpm for 5 minutes in a mixer chamber of a dissolver.

The resulting composition based on technical carbon was then introduced into a rubber mixture based on BNRS-40 on cold rollers for 20 min [12-13].

Then rollers introduced the components of the vulcanizing system: para-hinondioxime (3% by weight). Manganese dioxide (6% by weight), Thioure D (0.6% by weight), diphenylguanidine (0.2% by weight). The total mixing time on rollers is 13 minutes. At a temperature which is not more than 40°C.

To assess the strength of the properties on the basis of the resulting compositions, rubber was produced in a vulcanization press at 150°C for 20 min.

3. Details

Table 2 shows the physic - mechanical characteristics of rubbers based on BNKS-40, with different contents of nanotubes. The results showed that the introduction of nanotubes into the composition leads to an increase in tensile strength by 14%. In this case, there is also an increase in elongation at break by 38%. In addition, significantly increases (165%) the wear resistance of the modified rubber compositions.

Table 2. *Physic-mechanical characteristics of vulcanizes.*

Specifications	Modified rubber by CNT			
	1	2	3	Δ,%
Concentration CNT, wt.%	0	0,5	1,0	
Conditional tensile strength, MPa	9,02	104	102	14
Elongation at break,%	142	185	208	38
Wear ability, cm^3/Wh	255	105	96	58
Erase, J/ mm^3	144	391	361	165
Aging at 100 °C, 24 h, %	15	4,1	8,1	27

The thermal stability of the obtained nanocompositions was studied by the method of thermogravimetric analysis (DTA) on a Q-1500D derivatograph in dynamic mode with a heating rate of 5°C / min and in the temperature range 23-600°C. DTA data for the compositions are presented in Table 3.

Table 3. *The results of thermal analysis of the composition.*

Indication	The composition of BNR with different CNT content, wt.%	
	0	0,5
$T_{5\%}$, °C	307	355

When CNTs are introduced into the nanocomposite, an increase in the temperature of destruction is observed, i.e., its heat resistance increases.

The polar groups of butadiene-nitrile rubbers by interaction with nanocarbon accelerate sulfur vulcanization, strengthen the interphase boundary and condense transition layers at the nodes of the rubber grid, which reduces their deformation ability.

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, aerosil. 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.

Thus, a set of prescription-technological methods for controlling the functionality, strength, and ability to deform grid nodes, interfacial interactions inside them, and the thickness and density of transition layers is the basis for reinforcement, allowing directionally changing the properties of rubber. The simultaneous use of known methods for increasing the ability to deformation and the strength of the mesh nodes allowed raising the maximum rubber strength to 45 MPa.

4. Conclusion

Thus, the method of modification of the rubber composition UTN provides a rubber with significantly higher physical and mechanical characteristics. In addition, this method of modification provides a rubber with higher resistance to wear, which significantly increases the efficiency of rubber products on the basis of the proposed composition. It is important that a significant improvement in the strength of the UTN modified rubber is not accompanied by a change in other performance characteristics.

It should be noted that modification of the rubber composition of the proposed CNT composition leads to a synergistic effect of increasing the technical characteristics of the rubber mixture, which helps to increase the life of the rubber products.

The proposed technology of modification of rubber by carbon nanotubes is much more reliable and effective known, and the spectrum of its use is extremely wide. The solution of this issue will improve the performance of rubber, which is very important for its use in aircraft engineering and others.

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