Effect of Conductive Carbon Black Concentration on Tyre Regenerate Properties

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Abstract. Electrically conductive rubber on the basis of tyre regenerate and conductive carbon black (OMCARB CH85) is developed. It is shown that an increase in conductive carbon black concentration leads to an increase in tensile strength and Shore A hardness of the tyre regenerate. However, due to insufficient dispersion of carbon black, a decrease in relative elongation and resistance to abrasive wear is observed. A study of volume resistivity showed that the obtained rubbers are semiconductor materials. Dependence of specific resistance on temperature in a range from 10 to 80°C is constructed. It is shown that the effect of positive thermal coefficient is observed in all obtained samples.

1. Introduction

The problem of energy efficiency and energy saving has recently been one of the key tasks of the global economy. The use of modern self-regulating heating devices based on polymer or ceramic materials allows for significant energy savings. However, the use of expensive materials in the design of these devices, strongly affects the final cost of the heating system. Polymer materials with positive temperature coefficient of resistance (PTC) - a sharp increase in the resistance of the material in a narrow temperature range, are used in small volumes in electrical engineering to create thermo resistive sensors, strain gauges, flexible conductor materials, elastic antistatic materials, coatings for printing shafts, self-regulating heating devices, etc. [1-2]. The use of materials with PTC, for example, for anti-icing systems of road pavements and building structures is not possible because of the high cost of the heating device. Therefore, creation of inexpensive materials with PTC for self-regulating heating systems is relevant.

There are many recipes and technologies for producing conductive rubber, but the main principle of their production is to fill rubber of different grades with conductive fillers such as coke [3], carbon black [4-7], carbon fibers [8], carbon nanotubes [9], ceramics [10-11], etc. The main reason why it is impossible to use these current-conducting rubber formulations in the manufacture of massive structural materials is the high cost of raw materials, due to the use of expensive rubbers as the basic matrix.

In the present work results of research of possibility of development of electrically conductive rubber with PTC from inexpensive raw materials, namely from tire regenerate [12-14] which is a product of devulcanization of the rubber crumb received from the spent tires are presented. Devulcanization is a process in which wastes of vulcanized rubber are transformed by mechanical, thermal and chemical energy to a condition in which they can be mixed, processed and vulcanized
again [15-17]. The use of inexpensive raw materials will make it possible to establish large-tonnage production of elastomers with PTC as well as to expand the directions of introduction of self-regulating heating devices based on elastomers with PTC, for example, for anti-icing systems of road surfaces and building structures. Also, the use of tire regenerator as the main raw material for self-regulating heating devices, in addition to reducing the cost of developed products, will increase the recycling of used tires, which is expedient from an environmental point of view [18].

2. Experimental details
For reception of a rubber mix the following materials were used: the tyre regenerate received by devulcanization of a rubber crumb made NPO "SIBPROMMASH"; high structure electrically conducting carbon black (CB) OMCARB CH85 made by Open Company "Omsktehuglerod"; altax (CAS 120-78-5); biphenylguanidine (CAS 102-06-7); sulphur (CAS 7704-34-9). Filling of conductive CB and vulcanizing group (altax, biphenylguanidine and sulfur) was carried out on laboratory rollers Sm350 150/150. The composition of conductive rubber is given in Table 1.

Table 1. Recipes of the electrically conductive rubber compounds (indicated in phr: parts per hundred of rubber).

| Ingredients               | Sample 1 | 2 | 3 | 4 | 5 |
|---------------------------|----------|---|---|---|---|
| Tyre regenerate           | 100,0    | 100,0 | 100,0 | 100,0 | 100,0 |
| Carbon black OMCARB CH85  | 0        | 5,0 | 10,0 | 15,0 | 20,0 |
| Altax (MBTS)              | 1,0      | 1,0 | 1,0 | 1,0 | 1,0 |
| Diphenylguanidine         | 0,5      | 0,5 | 0,5 | 0,5 | 0,5 |
| Sulfur                    | 1,0      | 1,0 | 1,0 | 1,0 | 1,0 |

Samples for research were Vulcanized in a hydraulic press 100-400 2E (Russia) at 155°C during 15 min. Determination of physical and mechanical parameters was carried out on the testing machine UTS (Germany) according to GOST 270-75. Shore A hardness is determined according to GOST 263-75. Resistance of rubbers to abrasive wear was estimated by the method of abrasion resistance determination in accordance with GOST 23509-79 on friction machine AR-40 (Russia). Research of volume loss of conductive rubbers was carried out according to GOST 20214-74. Resistance of the samples in the temperature range from 10 to 80°C has been measured for the effect of PTC.

3. Results and discussion
The study of physical and mechanical properties of vulcanisates has shown that the sample without CB has indicators inherent in the regenerate obtained by the thermomechanical method [19]. In table 2 it is visible, that increase in the content of CB leads to increase in tensile strength and decrease in relative elongation. The greatest increase in tensile strength is observed in the sample with 15 phr of CB (7.3 MPa), which is more than the unfilled regenerate by 0.7 MPa. Decrease in relative elongation at increase in the content of CB on each 5 phr, leads to consecutive decrease in relative elongation on 20-25%. Introduction of 20 phr of CB leads to reduction of elongation on 58%. The decrease in elongation is associated with a poor distribution of CB in the rubber. Inside the regenerate obtained from crumb rubber, there are sections with different densities of macromolecular packages. In less dense areas, CB accumulates. An increase in the concentration of CB leads to an increase in the accumulation of agglomerates, along which the destruction of the material occurs during tension.

The study of abrasion resistance has led to unexpected results. It is established that despite the fact that with the introduction of TU, the hardness and tensile strength increase, the wear resistance decreases. The explanation of the inconsistency of the most common theory of increasing wear resistance with increasing strength may be different conditions for testing wear resistance and strength.
It is known that the study of wear resistance occurs when the surface layer of rubber is in a difficult state in the contact zone, and the study of deformation is carried out at a high speed (tens of thousands of percent per second), i.e. 3-5 orders of magnitude greater than the strain rate when determining strength according to GOST 270-75 [24]. Perhaps, due to the insufficient bond strength of the filler-matrix, the observed slight increase in strength (Table 2) does not manifest itself in any way at high strain rates that occur when determining abrasion resistance. Therefore, an increase in volumetric wear is also associated with the formation of TU agglomerates.

Table 2. Effect of CB content on properties of tire regenerate.

| Properties                  | Sample |
|-----------------------------|--------|
|                             | 1      | 2      | 3      | 4      | 5      |
| Relative elongation, %      | 180    | 148    | 122    | 100    | 76     |
| Tensile Strength, MPa       | 6,6    | 7,1    | 7,1    | 7,3    | 7,0    |
| Shore A Hardness            | 69     | 73     | 76     | 80     | 84     |
| Density ρ, g/cm³            | 1,149  | 1,171  | 1,189  | 1,205  | 1,222  |
| Volume loss, cm³            | 0,51   | 0,54   | 0,66   | 0,80   | 0,98   |
| Electrical resistivity, Ωm  | -      | 1134,038 | 38,296 | 8,454  | 3,039  |

The study of the electrical conductivity of the samples showed that all samples belong to semiconductor materials, because resistivity values of all samples are in the range of $10^{-6}$–$10^9$ Ωm. An increase of electrically conductive CB concentration leads to a decrease in volume resistivity. Moreover, a significant increase in conductivity is observed from 10 phr CB. The volume resistivity of a sample with 10 phr is 2 orders of magnitude lower compared to a sample with 5 phr CB.

The results of measuring the resistivity of the samples in the temperature range from 10 to 80 °C for the manifestation of the PTC effect are shown in Fig. 1. The dependence of resistivity on temperature was measured for samples with 10 phr, 15 phr and 20 phr CB. A sample containing 5 phr of conductive CB has a too high value of resistivity (1134.038 Ωm) and is not suitable for creating a heating device with PTC.

Figure 1. Effect of temperature on resistance for different concentrations of carbon black.
It is known [4] that the electrical conductivity of rubbers arises due to the tunneling current, when gaps filled with rubber exist between the particles of the electrically conductive filler. This gap acts as a potential barrier, and electrons pass through this gap due to thermal fluctuations, which causes electrical conductivity. Tunnel current is distance sensitive. It changes inversely and exponentially with respect to the change in distance. When the temperature increases, due to the thermal expansion of the rubber, the gap between the particles of electrically conductive carbon black increases, which leads to a sharp decrease in electrical conductivity. It is seen that the PTC effect is observed in all samples. An increase in the concentration of electrically conductive CB leads to a decrease in resistivity and an increase in the temperature of the resistance jump. PTC values in the temperature range of 10 - 80 °C for samples with 10 phr, 15 phr and 20 phr CB is 0.054, 0.223 and 0.285 deg-1, respectively.

4. Conclusions
Possibility of development of electrically conducting rubber with effect of positive thermal coefficient of resistance on the basis of tire regenerate and OMCARB CH85 carbon black is shown. The research of properties of electrically conductive rubber has shown that the most optimal content of carbon black is 15 phr.

Researches of technical properties of vulcanizates have shown that increase in the concentration of carbon black leads to increase in tensile strength and Shore A hardness and decrease in relative elongation and wear resistance.

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