Estimating the Stability of Electrical Conductivity ofFilled Polymers under the Influence of Negative Temperatures

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Abstract. One of the key problems in modern materials technology is synthesis of materials for electrotechnical devices capable of operating under severe conditions. Electrical and power engineering, in particular, demands for electrically conductive composite materials operating at high and low temperatures, various mechanical loads, electric fields, etc. Chaotic arrangement of electrically conductive component in the matrix and its structural and geometrical inhomogeneity can increase the local electric and thermal energy flux densities up to critical values even when their average values remain moderate. Elastomers filled with technical carbon being a promising component for electrotechnical devices was chosen as an object of study.

Keywords: stability, electrical resistance, elastomers, structure, technical carbon, amorphous rubber

INTRODUCTION

Electrically conductive polymeric materials are used as heaters, antistatic devices, etc. Among their advantages are low mass of final products, available production technology, suitability for profiling into products of almost any form, etc. [1]. This makes them attractive for application under specific service conditions, for example, to heat special sections of roads (especially viaducts or platforms), in shipbuilding to protect against icing, etc. The filled polymers in such devices can be exposed to influence of extremely low temperatures. With regard to this, the studies are traditionally focused on changes in electrical conductivity of filled elastomers at increased temperatures [2–5]. To reveal special features in their resistive properties under the influence of low temperatures, additional studies are required.

Therefore, the present work solves this task, namely, the following:
– to reveal the nature of changes in volume electrical resistance of materials upon cooling,
– to determine the value of temperature resistance coefficient at negative temperatures for elastomers with different chemical compositions,
– to reveal special features of changes in volume electrical resistance of materials upon cyclic cooling,
– to compare values of temperature resistance coefficients of filled elastomers at positive and negative temperatures,
– to suggest a structural parameter for estimation of temperature resistance coefficient at negative temperatures depending on the material structure.

MATERIALS AND METHODS

Test specimens were vulcanized in specially developed compression moulds in the form of cylinders 0.05 m in diameter with a height of 0.05 m. It is well known that the frost resistance of elastomers is influenced by crystallinity and glass transition temperature [2, 5, 6].
FIGURE 1. Dependence of TRC value (1/°C) on the number of cooling cycles. Curve 1 stands for BK-2055 elastomer and curve 2 for SKMS-30ARK elastomer.

Therefore, we used Butyl Rubber IIR according to the Designation System of the American Society for Testing and Materials (ASTM) or BK-2055 according to the Russian Designation System) and amorphous Styrene Butadiene Rubber (SBR-1500 according to ASTM or SKMS-30ARK according to the Russian Designation System).

We experimentally determined the following parameters:
- temperature resistance coefficient (TRC),
- change in specific volume electrical resistance of materials under the cyclic mode.

A chamber from which the air was pumped out (to vacuum of 6.6×10⁻⁴ Pa) was used to test the samples at negative temperatures. The chamber was filled with nitrogen vapors through a valve located at the bottom of the chamber and connected with a hosepipe to Duar’s vessel. The materials were tested upon cyclic cooling and heating. Each cooling cycle included tests at temperatures from +20 to –60°C with subsequent restoration to +20°C. The temperature resistance coefficient was determined according to requirements of GOST 2134215-78. Upon heating, the temperature changed from +20 to +200°C. The volume electrical resistance of a specimen before and after the test cycle was measured. Figures 1–4 show data measured for elastomers of the above-indicated chemical compositions. Carbon black P-366E with concentration of 65 weight parts per 100 weight parts of rubber served as electrically conductive filler.

RESULTS AND DISCUSSION

It was established that upon cooling, the volume electrical resistance of the material decreased. Figure 1 shows the TRC (1/°C) at temperatures in the range of +20...–60°C for 3 cycles of cooling and temperature restoration to +20°C. The material with amorphous rubber matrix has lower TRC values. The behavior remains unchanged upon cyclic cooling.

Figure 2 shows TRC upon heating (at temperatures from +20 to +200°C) and cooling (at temperatures from +20 to –60°C). Irrespective of the matrix type, the TRC value at positive temperatures was higher than that at negative temperatures for all examined specimens.

FIGURE 2. Dependence of TRC value on the number of cycles. Curve 1 stands for heating and curve 2 for cooling of SKMS-30ARK elastomer.
The results obtained can be explained as follows. The resistance to the influence of temperature in a particular way depends on properties, physical state, and composition of elastomer [2, 5, 7]. The behavior of filled elastomers at negative temperatures is determined by joint influence of two processes—vitrification and crystallization [8, 9]. For the materials containing noncrystallizing (styrene butadiene) rubber, it can be caused by slow relaxation processes and decrease in mobility of macromolecules [5, 9].

The volume electrical resistance is determined by physical and chemical interactions in the material, depending on the structures of both technical carbon and elastomer. The character and the area of contact also influence this parameter. This makes it difficult to predict the material properties.

To reveal special features in the behavior of such materials under extreme conditions, a tool capable of analyzing the results of physical and chemical interactions is required. A relationship between obtained experimental results and processes proceeding in electrically conductive filler of the mesh became known by analyzing the structural parameter that considers the special features of electrically conductive mesh in electronic microscopic images. The formation of mesh depends on character and magnitude of interphase interactions. The parameter was determined using the formulas of fractal geometry from photomicrographs of material texture [10, 11].

In [12] it was shown that for the constant step $\varepsilon$ of the squared mesh covering photomicrographs of the structure of different materials, the plots of dependence $p_i$ on $\ln \varepsilon$ are well described by a linear dependence (here $p_i$ is the probability to find a fractal point in the $i$th mesh). The slope angle of the straight line yields information of dimension $D_1$. The vertical displacement of the straight line illustrating this dependence is designated by $D_{1b}$. This parameter represents the entropy averaged over the entire image of the fractal set.

**FIGURE 3.** Dependence of TRC on structural parameter $D_{1b}$. Curve 1 shows TRC values upon heating, and curve 2 shows TRC values upon cooling.

**FIGURE 4.** Dependence of the volume electrical resistance change during the cycle on structural parameter $D_{1b}$. Curve 1 stands for cooling, and curve 2 for heating.
Figures 3 and 4 show the dependences of TRC on structural parameter $D_{1b}$ upon heating and cooling. Studies were performed with the use of photomicrographs of materials based on BK-2055 with P-366É as fillers. The filler concentration was 80 weight parts per 100 weight parts of rubber. The volume electrical resistance was changed by treating the technical carbon surface [5].

Analysis of the correlation between structural geometrical parameter $D_{1b}$ and TRC at negative temperatures demonstrated the presence of such correlation; the correlation coefficient made 0.92.

**CONCLUSIONS**

Based on our investigations, we can recommend the application of amorphous rubber for operation at negative temperatures and high requirements to the stability of volume electric resistance. It was experimentally confirmed that the suggested structural parameter was sensitive to TRC value and the change in electrical conductivity at low temperatures. This parameter can be used for comparative estimation of photomicrographs of materials being synthesized and material with stated properties.

**REFERENCES**