

THERMAL CONDUCTIVITY OF SILICON-ORGANIC  
ELASTOMERS WITH MINERAL POWDER FILLER

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A study was made concerning the thermal conductivity of silicon-organic elastomer systems with mineral filler, depending on the chemical composition, on the amount, and on the dispersion of the latter.

In the manufacture of hermetic sealants, resins, and other materials based on silicon-organic elastomers, as well as of organic rubbers, one often uses fine-disperse mineral fillers, mainly metal oxides, for reinforcement. The addition of such fillers not only upgrades the mechanical properties of unfilled vulcanites but also modifies their chemical, physical, and particularly thermophysical properties [1]. In the latter case the modification is determined not only by the thermophysical properties of the pure components alone but also by the characteristics of interaction between elastomer and filler, which in turn depends on their chemical nature, their dispersion, and the shape as well as the surface characteristics of filler particles. In the presence of active centers on the surface of particles and of reactive groups in the elastomer molecule, the interaction between filler and elastomer can be chemical [2].

A study and an analysis of the thermophysical properties of filled elastic silicon-organic materials over their entire working temperature range, the upper limit of which reaches 300°C, may prove useful for explaining the structure of their ingredients and for estimating the characteristics of interaction between filler and elastomer. Only very few data are found in the technical literature pertaining to the temperature characteristics of silicon-organic elastomers, i. e., of their thermal conductivity. The values for

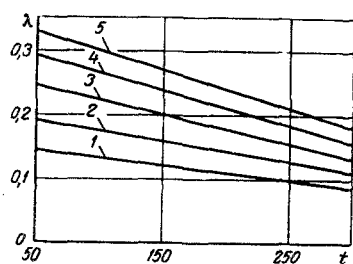


Fig. 1

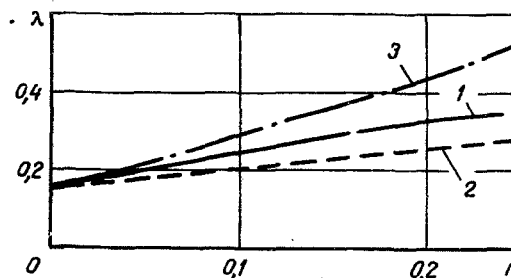


Fig. 2

Fig. 1. Thermal conductivity ( $\text{W/m} \cdot ^\circ\text{C}$ ) of composites with  $\text{TiO}_2$  filler, as a function of the temperature ( $^\circ\text{C}$ ): pure SKTN (1), 6 volume fractions of  $\text{TiO}_2$  (2), 12 volume fractions of  $\text{TiO}_2$  (3), 18 volume fractions of  $\text{TiO}_2$  (4), 24 volume fractions of  $\text{TiO}_2$  (5).

Fig. 2. Comparison between measured and calculated values of the thermal conductivity ( $\text{W/m} \cdot ^\circ\text{C}$ ) of composites with  $\text{TiO}_2$  filler: test data (1), calculations according to formula (2) (2), calculations according to formula (3) (3).

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TABLE 1. Characteristics of Mineral Fillers

Filler	Density $\rho$ , kg/m <sup>3</sup>	Specific surface S, m <sup>2</sup> /g
Grade BS-50 Silica gel (SiO <sub>2</sub> )	2200	47,0
Grade PK quartz powder (SiO <sub>2</sub> )	2200	5,0
Zinc oxide (ZnO)	5600	15-17
Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> )	5700	—
Titanium dioxide (TiO <sub>2</sub> )	4300	45-50

TABLE 2. Values of Parameters A and B in Equation (1)

Material	Coefficient	
	A · 10 <sup>4</sup>	B
SKTN	-2,2	0,159
SKTN + 6 volume fractions TiO <sub>2</sub>	-3,3	0,21
SKTN + 12 volume fractions TiO <sub>2</sub>	-4,7	0,272
SKTN + 18 volume fractions TiO <sub>2</sub>	-5,5	0,321
SKTN + 24 volume fractions TiO <sub>2</sub>	-6,0	0,362
SKTN + 6 volume fractions ZnO	-3,9	0,255
SKTN + 12 volume fractions ZnO	-5,7	0,349
SKTN + 18 volume fractions ZnO	-6,9	0,418
SKTN + 6 volume fractions Fe <sub>2</sub> O <sub>3</sub>	-3,4	0,209
SKTN + 12 volume fractions Fe <sub>2</sub> O <sub>3</sub>	-4,7	0,271
SKTN + 18 volume fractions Fe <sub>2</sub> O <sub>3</sub>	-5,6	0,316
SKTN + 6 volume fractions BS-50	-2,9	0,187
SKTN + 12 volume fractions BS-50	-3,5	0,213
SKTN + 18 volume fractions BS-50	-3,9	0,232
SKTN + 6 volume fractions PK	-2,7	0,177
SKTN + 12 volume fractions PK	-3,3	0,202
SKTN + 18 volume fractions PK	-3,6	0,221
SKTN + 24 volume fractions PK	-3,9	0,239

content is shown in Fig. 1. The variation of this thermal conductivity within the test range of temperatures can be accurately enough approximated by the linear relation

$$\lambda = At + B. \quad (1)$$

The thermal conductivity is a linear function of the temperature also when other substances are used as filler. The values of parameters A and B have been determined by the method of least squares and are given in Table 2. An analogous temperature-dependence of thermal conductivity was noted in the case of silicon resins [3].

The trend of the relation between thermal conductivity and temperature can be explained on the basis of the hypothetical model in [5, 6]. It has been established that, as the temperature rises, the thermal conductivity of vitrified polymers increases somewhat; after transition to the superelasticity state it decreases, because the thermal fluctuations of macromolecules and the consequently greater distance between molecular chains (greater free volume) result in a higher internal thermal resistance. The validity of this concept has been confirmed by experimental studies in [5, 7, 8] concerning the temperature-dependence of thermal conductivity in the case of linear weakly cross-linked three-dimensional polymers. The composites in our study here were linear weakly cross-linked polymers with a glass transition temperature within the below-zero range.

In analyzing the processes of heat transfer through the simplest multicomponent systems, for the purpose of determining the thermal conductivity, one usually assumes to some extent the macroscopic viewpoint, i. e., one ignores the fact that substances consist of atoms and molecules and one treats them, instead, as continua [9-14]. On this premise, it is possible to establish the dependence of the effective thermal conductivity on the substance structure, on the heat transfer coefficients of the substance components, and on the concentrations of the components, and it is possible to comprehensively enough study the effect of one or another of these factors on the thermal conductivity of the substance. With such an approach

a few silicon-organic resins are given in [3], where it is also shown that the thermal conductivity of the resin is almost unaffected by the form of the raw rubber but depends entirely on the type of filler.

In this article the authors present the results of a study concerning the effect of mineral fillers, their chemical composition and their content level, on the thermal conductivity of vulcanized composites with a low-molecular grade SKTN-A dimethylpolysiloxan rubber base within the 20-300°C temperature range. The choice of fillers was determined essentially by their applicability to resins or hermetic sealants and compounds with this rubber as the base (zinc oxide, titanium dioxide, silicon dioxide, ferric oxide) and also by their different dispersion characteristics in the case of practically the same chemical composition (quartz powder and silica gel).

The density and the specific surface of these filler materials are given in Table 1.

Considering the widely different densities of the tested fillers, their effect on the thermal conductivity of the composites was measured at equal volume fractions.

The thermal conductivity was measured under a monotonically rising specimen temperature. The instrumentation consisted of a flat bicameral calorimeter with two identical test specimens lying symmetrically between the center device and a flat heater on each side [4]. The relative error of the thermal conductivity measurement was 6-8%, with some degree of specimen inhomogeneity taken into account.

The thermal conductivity of unfilled SKNT vulcanite and of its composites with various levels of titanium dioxide

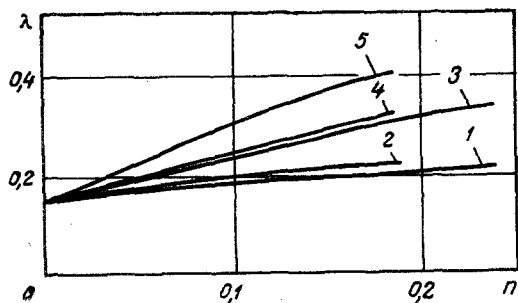


Fig. 3. Thermal conductivity (W/m · °C) of composites as a function of the filler content (volume): SiO<sub>2</sub> (quartz powder) (1), SiO<sub>2</sub> (silica gel) (2), TiO<sub>2</sub> (3), Fe<sub>2</sub>O<sub>3</sub> (4), ZnO (5).

Considering that the principle of generalized conductivity is based on ideal model structures, A. Misnar has proposed an empirical formula for calculating the thermal conductivity of two-phase systems [12]:

$$\lambda = a\lambda_{\text{mix}} + b\lambda'_{\text{mix}} \quad (3)$$

Here  $\lambda'_{\text{mix}}$  and  $\lambda_{\text{mix}}$  are the values calculated according to (2), if first the substance with the higher thermal conductivity and then the substance with the lower thermal conductivity is treated as the filler. The values of parameters  $a$  and  $b$  for silicone resins are taken equal to 0.2 and 0.8 respectively [12].

The measured thermal conductivity of composites is shown in Fig. 2 as a function of the TiO<sub>2</sub> content, along the values calculated according to formulas (2) and (3). The test values agree better with formula (3) for volume concentrations  $n < 0.1$  and with formula (2) for volume concentrations  $n > 0.1$ . At higher values of  $n$ , the difference between calculated and measured values of thermal conductivity increases, reaching 30% if formula (2) is used for  $n \sim 0.25$ . This discrepancy reflects the imperfection of the model selected to represent the actual elastomer filler system structure. For instance, a comparison between test results and values based on formula (2) indicates that some chemical interaction occurs between the dimethylpolysiloxan molecules and the filler, just as in the case of organic rubbers [15], and also that contact between filler particles themselves is possible with a resulting decrease in the thermal conductivity of the composite, if  $\lambda_2 > \lambda_1$ .

It is to be noted that the values of thermal conductivity obtained by the empirical formula (3) can be brought closer to the test values by correcting the numerical values of parameters  $a$  and  $b$ . Thus, with  $a = 0.15$  and  $b = 0.7$ , the calculated values will differ from the measured ones by less than 5% over the entire range of concentrations.

The thermal conductivity of a system as a function of the filler content is shown in Fig. 3 for various mineral fillers. The relation is nearly linear for  $n < 0.15$ , while for  $n > 0.15$  the thermal conductivity increases somewhat slower — possibly because of local contact resistances between elastomer and filler particles. Systems containing zinc oxide have the highest thermal conductivity, because this substance has the highest thermal conductivity of all the different mineral fillers considered here [15].

The dispersion characteristics of the filler (for example, quartz powder or silica gel) also affect the thermal conductivity of the composite. The increase in thermal conductivity with a decrease in the size of particles (at the same volume content of the given filler), which has been established experimentally, can evidently be explained by stronger surface effects at the interphase boundary [17]. The activity centers at the surface of silica gel particles enter into a chemical bond with the elastomer molecules, moreover, and thus strengthen the cross-linkage between molecules; if a sufficient number of such centers exists, then the filler particles may become incorporated into the three-dimensional structure of the vulcanite material and will act as conduction bridges between two or more elastomer molecules.

#### NOTATION

$\lambda$  is the thermal conductivity;  
 $\lambda_1, \lambda_2$  are the thermal conductivity of binder and of inclusions respectively;

to the analysis of heat transfer processes, one makes several assumptions: that there is no thermal resistance across the interface between substance components, that the thermal conductivities of pure components are independent of one another, etc. At the same time, the addition of filler may change the supermolecular structure of a polymer during mixing [2], which in turn will affect the thermal conductivity of the composite.

A study of the analytical relations in the case of structures with isolated closed inclusions has shown the formula proposed by V. I. Odelevskii

$$\frac{\lambda}{\lambda_1} = 1 - n \left( \frac{1}{1-v} - \frac{1-n}{3} \right)^{-1} \quad (2)$$

to rank among the most general ones.

t is the temperature;  
n is the volume concentration of filler substance;  
 $\nu = \lambda_2/\lambda_1$ .

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