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INTERRELATIONSHIP OF THERMOPHYSICAL AND ELECTROPHYSICAL PROPERTIES OF PVC SYSTEMS

V. S. Kolupaev, N. A. Bordyuk,
V. A. Sidletskii, and V. A. Mashchenko

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It is shown that physical properties of PVC systems that are different in nature exhibit general laws of interaction between structural elements of the compositions that are responsible for the characteristic properties of the material. The presence of a correlation between thermophysical and electrophysical properties of PVC compositions is established.

Production of materials for modern technology requires a knowledge of their thermo- and electrophysical properties. Here, the issue of the interrelationship between thermophysical characteristics of polymer composite materials (PCMs) and their electrophysical, elastic, and other properties remains open [1]. The aim of this work is to establish such an interrelationship in the form of a correlation, using which we can subsequently obtain relations of theoretical and practical importance.

Experimental. We investigated systems based on PVC that was produced by suspension polymerization and purified by from solution redeposition with MW = $1.4 \cdot 10^5$ and a Fickentcher constant of 65. "KhCh"-grade (chemically pure) cyclohexanone ($T_b = 425.5$ K and $n_D^{290\ K} = 0.9466$) was selected as the solvent. Highly disperse tungsten (W) and copper (Cu) were taken as fillers. The filler-particle dispersity was 7–10 μm. Initially, the highly disperse fillers, degreased with tetrachloride carbon and vacuum-dried at $T = 393$ K, were introduced in the polymer under study by mixing them mechanically. Specimens with a uniform distribution of the filler in the polymer matrix were produced by the method of hot molding. The PVC compositions became monolithic with formation of homogeneous blocks at a temperature of 393–403 K and a pressure of 10^7 Pa. The quality of the specimens was monitored with a metallographic microscope and an ultrasound flaw detector.

The thermal conductivity (λ) of the PVC compositions was determined according to the procedure of [2, 3], and their bulk resistivity (ρ_v) was determined according to [4].

Results and Their Discussion. As follows from the data presented, the variation in ρ_v for PVC systems begins as soon as the first fractions of the filler (0.9–1.0 vol.% Cu; 1.4–1.8 vol.% W) are introduced. It is characteristic that as the content of the metallic ingredients increases to more than 5–6 vol.%, after a singularity we observe a tendency toward a decrease in the resistivity of the PCM whose rate depends on the type and content of the filler (Fig. 1).

Under the assumption of sphericity of the particles and uniform dispersion of them in the polymer volume, a calculation of the distance between the filler particles shows that, in the region of their maximum content in the PVC systems investigated, it is, respectively, 120 (W) and 300 (Cu) Å [5]. Thus, in the system, no conducting bridges of filler particles are formed and the distance between the particles is large for a tunnel conduction mechanism.

To elucidate the conduction mechanism for PVC systems that contain metallic fillers, we used pressure as an additional parameter. Measurements showed that the baric coefficient of electrical conductivity ($K = (\partial(\log \rho_v)/\partial p)_T$) is negative [6]. This points to ionic conduction of PCMs in the glassy state, i.e., a dominant role is played by the polymer matrix when the properties of PVC systems are formed. Analysis of the dependence $\log \rho_v = f(T)|_\varphi$ shows that it is linear in the glassy state and, it is curvilinear in the high-elasticity state. Near the glass transition temperature (T_{gl}) the curves of $\log \rho_v = f(T)|_\varphi$ (Fig. 2) experience a break. This form of the dependence

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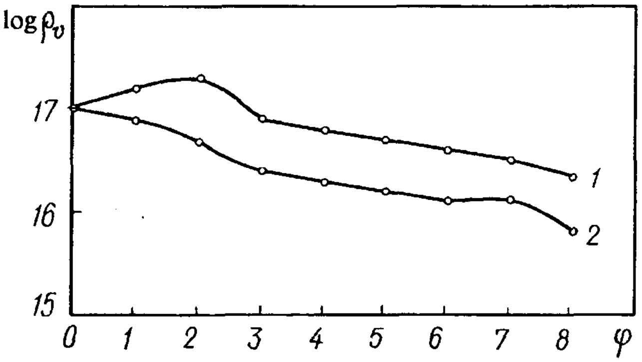


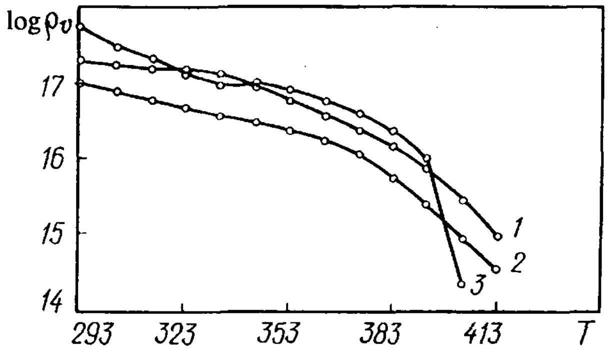
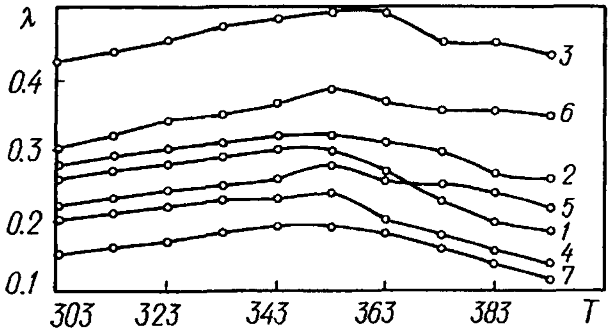


Fig. 1. Concentration dependence of log ρ_v for systems at T = 293 K: 1) PVC+W, 2) PVC+Cu. φ, vol.%.

Fig. 2. Temperature dependence of log ρ_v for PVC systems: 1) PVC+7 vol.% W, 2) PVC+3.8 vol.% Cu, 3) PVC+0.8 vol.% Cu. T, K.



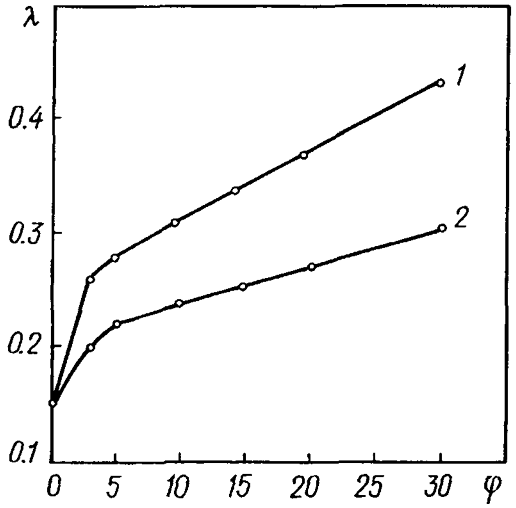


Fig. 3. Temperature dependence of λ for PVC systems: 1) PVC+3 vol.% Cu, 2) PVC+5 vol.% Cu, 3) PVC+30 vol.% Cu, 4) PVC+3 vol.% W, 5) PVC+5 vol.% W, 6) PVC+30 vol.% W, 7) PVC. λ, W/(m·K).

Fig. 4. Concentration dependence of λ for PVC systems at T = 303 K: 1) PVC+Cu, 2) PVC+W.

is further proof of the dominant ionic character of conduction for these PVC systems. The results obtained can be interpreted successfully using the mechanism of the change in the macromolecular and ionic mobility under the action of temperature and electric fields [7].

Results of experimental investigations of the thermal conductivity of PVC systems in a wide temperature region show that, for all the compositions, an increase in λ with temperature is observed. After the maximum in the region of T_{gl} is attained, the thermal conductivity decreases (Fig. 3). Here, the values of λ and the temperature coefficient $(\partial\lambda/dT)|_{\varphi}$ depend on the type and amount of highly disperse metal in the system. It should be noted that the most intense variation in λ is observed for a content of the filler in the system of 0.6–4.0 vol.% (Fig. 4). The character of the variation in λ for PCMs can be explained by the presence of highly disperse metal in the system and the structural changes in PVC under the action of the filler [8].

In the general case, one attempts to calculate the kinetic coefficients (λ, ρ_v) using methods of physical kinetics. However it is known that experimental dependences of the thermal and electrical conductivities of PCMs that contain highly disperse metallic fillers do not obey theoretical relations obtained using the Boltzmann equation and the equation of the generalized conductivity of two-component systems [9]. In the case of differential heat and current fluxes in PCMs, for $\varphi \to \varphi_{cr}$ there is no exact solution of the Poisson equations so far. Therefore an efficient

TABLE 1. Parameters of the Equation of Linear Regression between log (λ/λ_p) and log (γ/γ_p) for PVC Systems

Type of composition	a	b	A	B	Confidence interval according to Fisher's ratio test
PVC+W	0.166	2.100	0.951	8.922	0.812–0.987
PVC+Cu	0.192	2.471	0.947	8.252	0.782–0.956

approach to the study of the set of properties of PCMs and the interrelationship between them is direct comparison of the parameters of the systems and analysis of the corresponding dependences between them by the methods of mathematical statistics [10].

Taking into account that the complexity of the investigation of solids led to extention of the notion "thermophysical properties" (emission, optical, electrophysical, and thermodynamic properties are classified among them now), let us analyze the interrelationship between the thermal and electrical conductivities of PVC systems. To evaluate their correlation, we represent the relationship between the logarithms of the relative values of these parameters as a direct linear regression:

$$\log\left(\frac{\lambda}{\lambda_p}\right) = a + b \log\left(\frac{\gamma}{\gamma_p}\right). \quad (1)$$

The dimensionless parameters a and b were determined by the least-squares method. The confidence interval of the correlation coefficient A and the critical region were found using Fisher's ratio test (see Table 1). Comparison of the calculated values of the sampling function

$$B = \frac{A}{\sqrt{1 - A^2}} \sqrt{n - 2}, \quad (2)$$

where n is the volume of the sample ($n = 10$), with the theoretical goodness-of-fit test $t_{0.05;8} = 2.31$ demonstrates that, for the investigated systems, there is a linear correlational relationship between log (λ/λ_p) and log (γ/γ_p). Large coefficients of the correlation between λ and ρ_v for PVC systems indicate the generality of the physical nature of the irreversible energy and charge transfer processes that occur in inhomogeneous systems due to a change in the mobility of their structural elements.

Thus, by the methods of mathematical statistics, we established a correlational interrelationship of a set of PCM properties that can be recommended for practical application.

NOTATION

T_b, boiling point; $n_D^{290\ K}$, refractive index at 290 K; λ, thermal conductivity; ρ_v, bulk resistivity; γ, electrical conductivity; φ, filler concentration; T, temperature; K, baric coefficient of thermal conductivity; p, pressure; φ_{cr}, critical concentration of the filler; MW, molecular weight.

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