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INFLUENCE OF THERMAL EXPANSION ON THE CONDUCTIVITY OF POLYMER CONDUCTING COMPOSITES

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The temperature dependence of conductivity in systems that undergo a metal-dielectric phase transition is investigated. A quantitative theory is developed that makes it possible to calculate electrical conductivity as a function of temperature for these systems with allowance made for thermal expansion of a polymer and a filler.

The observed effect of a sharp change in the conductivity in composite polymer conducting materials makes it possible to use the latter as temperature-sensitive resistors [1] and heating elements [2] in electronics. However, a description of the basic characteristic of these materiala, i.e., the electrical conductivity σ as a function of the temperature T with allowance made for the thermal expansion of the material, is still at the approximation level.

The aim of the present work is to develop a quantitative theory that makes it possible to calculate σ of conducting composites as a function of T.

Composite polymer materials based on R-100 carbonyl iron and F-42 fluorine-containing polymer (tetrafluoroethylene-vinylidene fluoride copolymer) produced by mechanical mixing in an agate ball mill served as the objects of investigation [3]. Figure 1 gives the temperature dependences of the composites.

Most authors hold to the idea that the main reason for the character of the dependence $\sigma(T)$ of composites is thermal expansion of the matrix, which increases the distance between the filler particles [2], which form an infinite cluster (IC). As the temperature increases the IC becomes less dense up to some critical temperature T_k at which the IC disintegrates.

As is known, it is flow theory [4] that currently gives the character of change in the structure of binary composite polymer materials as a function of the volume fraction of the filler. According to this theory the dependence $\sigma(V_1)$ of composite polymer materials with drastically different σ is described by the equations

$$\sigma(V_1) = \sigma_1 \left(\frac{V_1 - V_c}{1 - V} \right)^t \quad V_1 > V_c = 0.15\,, \tag{1}$$

$$\sigma(V_1) = \sigma_2 \left(\frac{V_c - V_1}{V_c} \right)^{-q} \quad V_1 < V_c\,, \tag{2}$$

where q and t are the critical indices of flow theory, equal to 0.98 and 1.6 respectively; V_c is the critical volume fraction at which an IC forms from the filler particles.

However, the issue of using these relations in systems that undergo a metal-dielectric phase transition as the temperature changes remains open since we still must find the volume fraction of the filler V_1 and relate it to the temperature: $V_1 = V_1(T)$. Assuming that thermal expansion of the composition leads to a decreased volume

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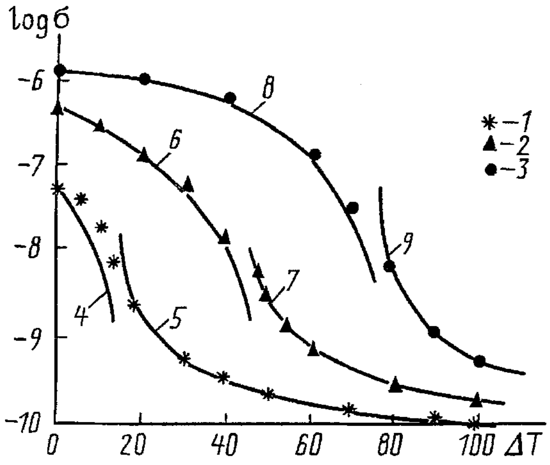

Fig. 1. Experimental dependence of the electrical conductivity σ of the compositions on the temperature ΔT for the composites with the volume content of the filler $V_1 = 0.236$ (1), 0.238 (2), and 0.240 (3) at $T_0 = 293$ K. The calculated dependence $\sigma(\Delta T)$ by Eqs. (4) (4, 6, 8), and (5) (5, 7, 9). log σ, $\Omega^{-1}\cdot\text{m}^{-1}$; ΔT, K.

fraction of the filler, which is associated with the difference in the coefficients of thermal expansion of the polymer β_2 and the filler β_1, we obtain the sought dependence $V_1(T)$.

It is well known that the change in the volumes of the filler ϑ_1 and the polymer ϑ_2 as a function of the temperature is described by the equations

$$\vartheta_1 = \vartheta_{01}(1 + \beta_1 \Delta T) \quad \text{and} \quad \vartheta_2 = \vartheta_{02}(1 + \beta_2 \Delta T), \tag{3}$$

where ϑ_{01} and ϑ_{02} are the filler and polymer volumes at $\Delta T = 0$, i.e., at room temperature $T_0 = 293$ K; ΔT is the temperature change.

We calculate the volume fraction of the filler using the well-known equation $V_1 = \vartheta_1/(\vartheta_1 + \vartheta_2)$; by substituting (3) into it we obtain

$$V_1 = \frac{1}{1 + \dfrac{\vartheta_{02}(1 + \beta_2 \Delta T)}{\vartheta_{01}(1 + \beta_1 \Delta T)}}.$$

Taking into account that $V_{01} = \vartheta_{01}/(\vartheta_{01} + \vartheta_{02})$, $V_{01} + V_{02} = 1$, we can write

$$\frac{\vartheta_{02}}{\vartheta_{01}} = \frac{1 - V_{01}}{V_{01}},$$

and then the volume fraction of the filler as a function of temperature will have the form

$$V_1(\Delta T) = \frac{1}{1 + \dfrac{(1 - V_{01})(1 + \beta_2 \Delta T)}{V_{01}(1 + \beta_1 \Delta T)}}. \tag{4}$$

It follows from (4) that for $\beta_1 = \beta_2$ the dependence $\sigma(T)$ determines σ of the IC, i.e., $V_1(\Delta T) = \text{const}$. To elucidate the dependence $\sigma_1(T)$, we performed an experiment in a chamber, which made it possible to retain the geometric dimensions of the specimen as the temperature varied. The experiment showed that the dependence $\sigma(T)$ in the fixed-volume chamber differs from this dependence taken under ordinary conditions: with increasing temperature the value of σ increases continuously, while in heating with thermal expansion of the specimens σ decreases. This fact can easily be explained if we assume that there are two competing processes in heating of polymer conducting composites: a decrease in σ of the filler due to an increased distance between particles, which is taken into account by relation (4), and an increase in σ on account of increase in activation of electron thermal emission in the IC, i.e., obeying the dependence [5]

$$\sigma_1 (T) = A \exp \left(- \frac{\Delta E}{kT} \right) .$$

Thus, on the basis of the foregoing and Eqs. (1) and (2) we obtain the calculated dependence $\sigma(T)$ of the polymer conducting composites:

$$\sigma (\Delta T) = A \exp \left(\frac{- \Delta E}{k (T_0 + \Delta T)} \right) \left[\frac{V_1 (\Delta T) - V_1}{1 - V_c} \right]^t \Delta T < T_k , \tag{5}$$

$$\sigma (\Delta T) = \sigma_2 \left(\frac{V_c - V_1 (\Delta T)}{V_c} \right)^{-q} , \quad \Delta T > T_k . \tag{6}$$

It should be mentioned that T_k is determined from the equality $V_1 (T) = V_c$. For the specimens under study the values of A and ΔE are equal to 0.6 and $9.72 \cdot 10^{-21}$ J respectively. The values of V_c, t, and q are taken from [3]. As Fig. 1 shows, satisfactory agreement of the calculation with experiment makes it possible to use the proposed method of calculating $\sigma(T)$ in structural phase transitions in conducting composites. Thus, Eqs. (5) and (6) can be used for composite polymer temperature-sensitive resistors and heating elements.

NOTATION

σ, electrical conductivity; T, temperature; ϑ_1, filler volume, V_1, volume fraction of the filler; T_k, critical temperature; σ_1, electrical conductivity of the infinite cluster; σ_2, electrical conductivity of the polymer; V_c, critical volume fraction of the filler; t and q, critical indices; β_1 and β_2, coefficients of thermal expansion of the filler and the polymer; ΔT, temperature change; T_0, room temperature; A, preexponential factor; ΔE, activation energy; k, Boltzmann constant.

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