# Percolation transition and inversion of conductivity hysteresis upon cooling of electroconductive polymer composites

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The possibility of obtaining a thermogenic percolation transition upon cooling of polymer composites with initial concentration of the electroconductive filler far below the percolation threshold is demonstrated. The obtained data are in qualitative agreement with the Muenchhausen ramrod model, which predicts the existence and peculiarities of this low-temperature transition. A change in the character of the conductivity hysteresis is observed when the composite is cooled below the percolation transition temperature.

A mechanism (the so-called "Muenchhausen ramrod" mechanism), described in Ref. 1, explains the reason for the appearance of the percolation transition upon cooling of a two-phase system of the type polymer matrix–dispersive conductor, whose components have substantially different values of the thermal expansion coefficients (TEC's). It was shown that when the temperature is lowered by an amount $\Delta T_c$, depending on the initial concentration $Q_0$ of the conducting phase, the percolation threshold is reached. In such a case a thermogenic (temperature-induced) percolation transition takes place even when the system in its initial state is so far from the geometric percolation threshold $Q_c$ that it is not possible to explain it solely on the basis of a change in concentration $Q$ (due to the difference in TEC's of its components).

A different explanation is offered in the Muenchhausen ramrod model,[1] which considers how the interaction of the particles in an isolated cluster changes as the temperature is varied and which allows for the fact that a lowering of the temperature of the system is equivalent to an increase in the diameter of the filler particles (thermal expansion). In otherwords, the filler volume fraction grows as the temperature falls. A characteristic property of the behavior of particles grouped together in an isolated cluster, in contrast to a solitary particle, is that for no one of them can the thermal expansion be canceled by the ejection of the intercalation layer between the particles (i.e., the intercalation layer is either small or absent). This leads to a displacement of neighboring particles relative to the matrix. In a chain of particles the displacement is multiplied as a result of the thermal expansion of each particle, and the magnitude of the displacement of the last particle is determined by the number of particles in the chain in the direction of the displacement. Such a scenario of temperature-induced increase of the filler concentration differs fundamentally from ordinary percolation systems, in which the percolation threshold is reached as a result of random redistribution in the system of the additional quantity of conducting phase during preparation. This additional quantity of conducting phase appears immediately after cooling

  

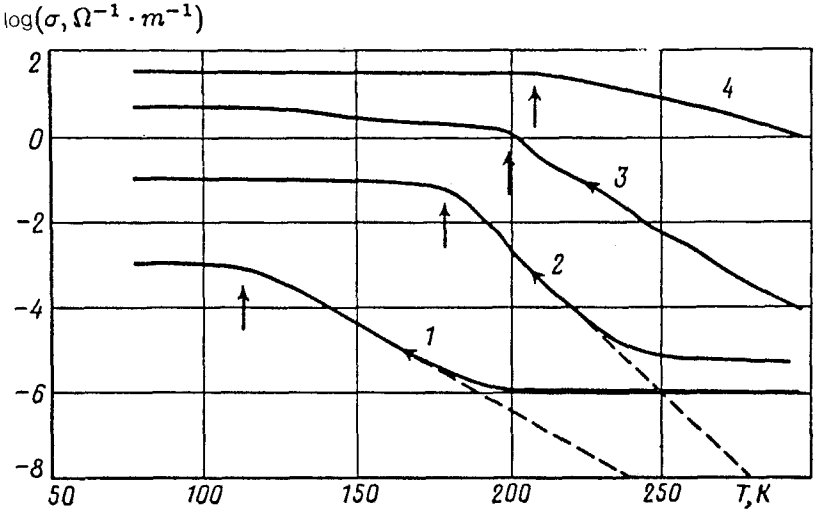


FIG. 1. Characteristic dependences of log $\sigma(T)$, obtained upon cooling of composites with $Q_0=7.5\%$ (curve *1*), 10% (curve *2*), 16% (curve *3*), and 18% (curve *4*). The sensitivity limit of the measuring circuit was $10^{-9}$ $\Omega^{-1}$ for the solid curves and $10^{-11}$ $\Omega^{-1}$ for the dashed curves.

in complete star contact with the particles of the conducting phase which are already present, which is equivalent to the appearance of a strong attraction potential between these particles.

One of the consequences of the Muenchhausen ramrod model[1] is the prediction of the presence of hysteresis in the temperature dependence of the electrical conductivity temperature $\sigma(T)$, which arises as a result of the buckling of the surfaces of the contacting particles during cooling of the composite by an amount $\Delta T > \Delta T_c$. Another important consequence[1] is the possibility of achieving the percolation transition during a corresponding cooling by an amount $\Delta T_c$ of compositions with $Q_0=5$–6 vol.%, in which in the absence of cooling the geometric percolation threshold $Q_c$ is 18–20 vol.%.

For an experimental check of the Muenchhausen ramrod mode, compositions of the type polymer matrix–dispersive filler were obtained by curing SKTN liquid polydimethylsiloxane rubber in the presence of 6–18 vol.% ($Q_0$ in the different samples) carbonyl nickel of brand PNK. Strips of dimensions $2\times5\times20$ mm were cut out of the synthesized material. Measurements of $\rho(T)$ were made by the two-contact method at constant voltage 0.5 V in the temperature range 77–300 K. The measurement scheme made it possible to record changes in conductivity of the samples down to a level of $\sim10^{-9}$ $\Omega^{-1}$. Spring contacts ensured a contact resistance no greater than 0.1 $\Omega$.

Figure 1 shows curves of log $\sigma(T)$ obtained by cooling samples with composition $Q_0=7.5$, 10, 16, and 18% in liquid-nitrogen vapors. The solid curves correspond to measurements at the above-noted sensitivity limit of the setup. Increasing the sensitivity to a level allowing recording of conductivity changes down to $10^{-11}$ $\Omega^{-1}$ (which in fact corresponds to the conductivity of the polymer matrix itself) showed that even

for compositions with small $Q_0$ (curves *1* and *2*) the conductivity begins to increase even upon moderate cooling (dashed lines, Fig. 1). Thus, the length of the plateau in the high-temperature segments of these curves turned out to depend only on the limitations of the apparatus. In this connection, the temperatures $T$ indicated by an arrow in the graph (the temperatures at which $\log \sigma$ stops increasing, which we have taken tentatively as the percolation transition temperature $T_c$) remained constant for a given sample and, clearly, are connected with $Q_0$ according to Ref. 1. Consequently, the improved dependences $\log \sigma(T)$ (the dashed lines) correspond to the Muenchhausen ramrod model, according to which the conductivity of a two-phase system grows exponentially upon cooling in the range $0 < T < T_c$.

In model representations it is usually assumed that the effective conductivity of an extremely inhomogeneous two-phase system undergoes a jump from a value on the order of the conductivity of the matrix to a substantially greater value at some threshold value of the concentration.[2,3] In actual experiments this jump is connected, first of all, with the sensitivity threshold of the apparatus, below which the dependence $\sigma(T)$ degenerates into a straight line, and, second, with the complication of obtaining by ordinary methods (e.g., by mechanical mixing of the components) a series of samples with sufficiently small variations of $Q_0$ near $Q_c$ since moderate errors in the concentration result in large changes in the properties of the system near the percolation transition.[4] In any case, in the thermogenic percolation transition, which provides a smooth change in the concentration, indicators of a pump are absent. In this case the use of the traditional concept of a percolation threshold as a critical concentration is impeded and, since now any change in $Q$ depends on the variation of the temperature, it makes sense to introduce the concept of a critical temperature $T_c$, as was done in Ref. 1. Beyond this temperature, we chose a special point on the graph of $\log \sigma(T)$ as a constant value for a given $Q_0$.

To check the assumption made in Ref. 1 of the appearance of hysteresis in the dependence $\log \sigma(T)$, when the samples are cooled by an amount $\Delta T > \Delta T_c$, we thermally cycled a series of samples with $Q_0 = 12\%$, each of which was cooled from 300 K to some temperature $T_{\min}$ and then warmed, whereby the minimum cooling temperature was successively decreased (Fig. 2). It is clear that for $\Delta T_{\min} < \Delta T_c$ (curves *1* and *2*) we have a positive hysteresis, in which the curve of $\log \sigma(T)$ in the warming phase lies higher than in the cooling phase. When the temperature $T_c$ is reached (curve *3*), hysteresis disappears: the shape of the curve is nearly independent of the sign of the change in the temperature. At $\Delta T_{\min} > \Delta T_c$, (curve *4*) a negative hysteresis appears and continues to grow. Note that Fig. 2 displays data for cooling to but not below the glass transition temperature $T_{gl}$ of the polymer. Cooling of the composite to lower temperatures amplifies the negative hysteresis; however, here specific effects associated with the virtrification of the matrix begin to manifest themselves. This topic requires a separate discussion. The observed change in sign of the hysteresis upon passing through the point $T_c$ during cooling is present in all the samples with $Q_0 = 6$–$18\%$.

In terms of the Muenchhausen ramrod model, the observed inversion of the hysteresis can be explained by assuming that the parameter $v$ of this model (which is a measure of the attractive potential between the conducting particles) depends on the

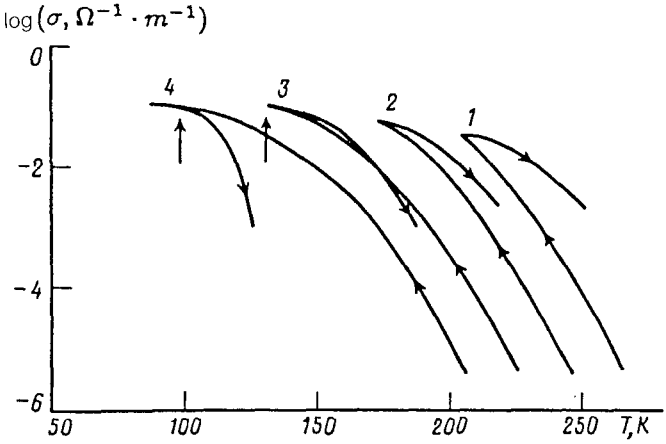


FIG. 2. Characteristic dependences of log $\sigma(T)$, obtained upon thermal cycling of the composition $Q_0 = 12\%$ with cooling by $\Delta T = 90$ K (curve *1*), 110 K (curve *2*), 130 K (curve *3*), 150 K (curve *4*). For ease of visualization, all of the curves starting with curve *2* are shifted by 20 K to the left.

history of the polymer. In this case the positive hysteresis is probably attributable to the increase of the parameter $v$ as a result of cooling. In other words, relatively moderate internal stresses, which arise in the composite at small values of $\Delta T$ of cooling, cause agglutination of the conducting particles into chains which are relatively stable to moderate changes in temperature (in particular, due to a lowering of the free surface energy). This, correspondingly, leads to retention of the enhanced conductivity upon warming the composite.

A further lowering of the temperature, causes the compression forces to increase in the composite, "raking" isolated clusters together into one conducting clump. This process terminates at $\Delta T = \Delta T_c$ by the formation of such a conducting ensemble that the addition of new particles produces hardly any change in its conductivity [the log $\sigma(T)$ reaches a plateau]. At $\Delta T > \Delta T_c$ the compression forces then continue to grow. However, the chains which have formed place bounds on the possibilities of mutual displacement of the particles and their surfaces begin to buckle at the point of contact. Obviously, as the composite expands (upon heating), contacts between neighboring deformed particles break faster than they are formed during cooling. The conductivity decreases more abruptly upon warming from $T_{\min} < T_c$.

Thus, the temperature $T_c$ at which the $\log\sigma(T)$ curve reaches, a plateau acquires, in addition to a singular point on the plot, another meaning as the temperature below which inversion of the hysteresis occurs.

In conclusion, we note that the method which we have described for bringing the system to the percolation threshold is suitable for use in careful studies of the properties of inhomogeneous two-phase systems since it allows $Q_c$ to be approached from both above and below in a controllable manner and with the required speed. At any

point of the percolation transition, a process can be put in place for measurement of the characteristics of the composite.

The phenomenon of the thermogenic percolation transition in electrically conducting composites and the hysteretic effects associated with it also can be used to create heat-sensitive, current-conducting devices for use at low temperatures. Thus, on the basis of the composite described here, we have developed and tested a current-limiting element for protection from overheating due to the flow of current during the transition from the superconducting state to the normal state of high-current switching devices based on high-temperature superconductors.

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