Thermogenetic percolation transition of conducting polymer compositions and "Munchausen ramrod"

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A study was made of the effect of temperature on a percolation transition in polymer compositions in which the concentration of conducting filler is below the percolation threshold. A simple model of this phenomena is presented and the calculated temperature dependence of the thermogenetic percolation transition on the original concentration of the conducting phase was obtained.

Disordered two-phase systems based on an electrically insulating matrix and conducting dispersed filler, in particular a mixture of polymers and metal powders, are materials whose properties strongly and nonlinearly depend on the filler concentration, especially near the percolation threshold. The percolation threshold is attained when isolated clusters, consisting of a finite number of conducting particles, coalesce into an infinite cluster. In this case many properties of the material (electrical conduction, permittivity, internal capacitance, etc.) change so strongly that the attainment of the leakage threshold can be interpreted as a phase transition of a percolation type. To obtain such systems, polymer compositions are mainly employed, which have significantly different values for the coefficients of temperature expansion (CTE) of the matrix and filler, usually powders of carbon or a metal; here the filler content by volume may vary within wide limits from 6 to 30%. In this case the percolation threshold in systems based on isotropic fillers is approximately 14% and may be larger or smaller according to the sign of the potential of the filler particles and quality of the components in the mixture.

Analysis of the anomalous properties of such percolation systems arouses great interest, although creating a system as close as possible to the percolation threshold by conventional techniques[1] is a complex experimental problem, because small mistakes in the concentration significantly change the system properties.[2] Thus, achieving the percolation threshold in the polymer composition is usually connected with a technological increase in the concentration Q of the conducting phase up to a critical value Q_c, and it is assumed that the temperature is of no importance. Indeed, the simplest estimates show that the change ΔQ in the concentration due to the difference between the CTE of the matrix and filler when the temperature changes substantially ($\Delta T \sim 100$–150 K) amounts to fractions of a percent and should not significantly affect the characteristics of the system with $Q < Q_c$.

For high temperatures such systems have a resistance characteristic of a pure matrix, since clusters consisting of a finite number of conducting particles are separated from each other by thin layers of insulating matrix. However, when such systems cool an abrupt typically percolation transition of the system into a conducting state can be observed, where the electric conductance increases by a several orders of magnitude in the interval 10–30 K.[1,3] Regarding this abrupt change in electric conductivity σ as a manifestation of a temperature-induced (thermogenetic) percolation transition, we note that this behavior of $\sigma(T)$ cannot be explained only by the form of $\Delta Q(T)$ in a real temperature interval. Obviously, there exists a stronger dependence $Q_c(T)$ whose character is not clear at present.

The aim of the present work is to discuss a possible mechanism for a thermogenetic percolation transition in the interval ΔT for compositions with $Q < Q_c$ (for a given initial temperature T_0) and to estimate the value ΔT necessary for reaching Q_c in a system with the initial concentration $Q(T_0)$.

To construct a physical picture of this process we make the following assumptions:

(1) the filler particles are approximated by spheres of unit volume;

(2) the CTE of the filler and matrix do not depend on temperature;

(3) the strength and elastic properties of the filler significantly exceed the corresponding properties of the matrix.

These assumptions to a lesser extent correspond to polymer mixtures with dispersed carbon due to the low mechanical characteristics of the latter.

To simplify the picture we go over to coordinates which are invariant with respect to thermal variation of the matrix volume. Here an increase (reduction) in the system temperature is equivalent to a decrease (increase) of the diameter of the filler particles (thermal expansion), i.e. the volume fraction of the filler increases when the temperature decreases. However, a system with such a temperature increment in the filler concentration differs in principle from the usual systems in which the percolation threshold is attained by a random arrangement of an additional amount of the conducting phase during preparation. Here the additional amount of the phase "arises" in connection with rapid cooling in full contact with the available particles of the conducting phase, which is equivalent to the appearance of a strong attraction potential between these particles.

Consider a system in which there is no conductivity at high temperatures. In it there are conducting insulated clusters of different dimensions separated by layers of insulating matrix with thickness sufficient to eliminate contact.

A characteristic property of these clusters, in contrast with a single particle, is that thermal expansion of each particle in them cannot be balanced by pushing out a layer between the particles (the layer either is too thin or is absent altogether), which leads to a displacement of neighboring

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particles with respect to the matrix. In the chain of particles a displacement is multiplied due to thermal expansion of each particle and the displacement value of the last particle is connected with the number of particles in the chain in the direction of displacement, just as the number of roasted birds on the ramrod fired from Baron Munchausen's gun was related to the number of birds that collided with the ramrod.

We replace the volume distribution of the clusters by one characteristic volume, called a "blob," just as is done in the physics of disordered systems,[4] and the whole mixture we represent as a system of tightly packed blobs separated by insulating layers of the matrix. Naturally, inside a blob there are smaller clusters and also matrix material. Increasing the size of an arbitrarily chosen blob by decreasing the temperature leads, with a certain probability, to its making mechanical contact with the surrounding blobs and to their merging. In this case the maximum possible increase of the blob is threefold in size (the central blob plus two neighbors) and 27-fold in volume. As a result, a system is formed consisting of tightly packed blobs of a larger size, which becomes characteristic at this stage. Repeating the procedure many times, we can obtain a blob of an infinite size (percolation transition).

This argument can be represented in differential form as

$$dV=dV_1+dV_2, \tag{1}$$

where dV is the increment in the blob volume associated with a variation in temperature by dT, dV_1 is the increment in the blob volume due to thermal expansion, and dV_2 is the increment in the blob volume due to merging with the neighboring blobs.

In this case the first term is determined from the law of thermal expansion of the bodies:

$$dV_1=-aVdT, \tag{2}$$

where a is the difference between the volume expansion coefficients of the matrix and filler, and V is the current volume of the blob.

The second term is proportional to the volume of the interpenetration of the given blob and its surroundings due to thermal expansion, equal to $2dV_1$, the total volume of the blobs undergoing merging, which is equal to $26V$ (if the blobs merge completely, the volume increases by 27 times minus its own volume), and the probability p for blobs to merge unit intersection volume:

$$dV_2=-52aVpdT. \tag{3}$$

Taking into account (2) and (3), Eq. (1) is reduced to the form

$$dV=-aV(1+52pV)dT$$

and after integration

$$V=\frac{v}{\exp(a\Delta T)-52pv[1-\exp(a\Delta T)]}, \tag{4}$$

where v is the initial volume of the blob and V is the finite volume upon cooling the system by ΔT.

Taking into account the facts that the processes of connecting each blob to its surroundings are equivalent and simultaneous and the probability of each of them is x, we have

$$p=2x-x^2.$$

The probability x, in its turn, is proportional to the filler concentration Q and the fraction f of the filler's particles which belongs to the growing blob of a characteristic size:

$$x=Qf.$$

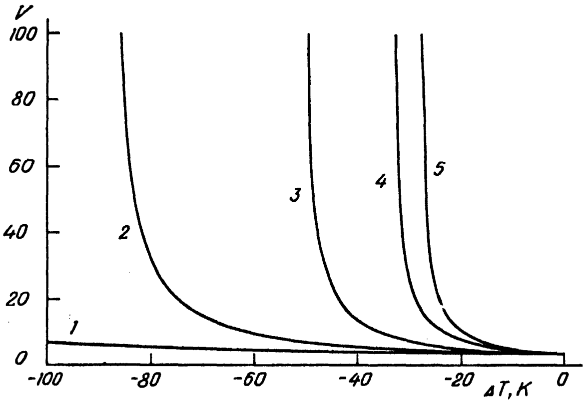

FIG. 1. Relations between the average volume of a blob and the temperature differential with $v=3$, $a=0.001\ \text{K}^{-1}$, for different values of the filler volume fraction: $Q=0.1$ (1), 0.15 (2), 0.2 (3), 0.25 (4), 0.275 (5).

We estimate f as the ratio of the filler volume fraction Q to the maximum possible fraction for a random tight packing of spheres, equal to 0.64 (for $Q=0.64, f=1$), i.e. $f=Q/0.64$. When a certain temperature differential is reached, the blob volume increases rapidly (Fig. 1). Naturally, the coefficients of the functions $V=V(\Delta T)$ [see (4)] are of an illustrative character and do not pretend to a high accuracy.

Obviously, for

$$\Delta T_{\text{cr}}=\frac{1}{a}\ln\left[1-\frac{1}{1+52pv}\right] \tag{5}$$

the denominator of the right-hand side of Eq. (4) vanishes, which corresponds to a blob of infinite volume (percolation transition). The relation between the temperature gradient of the percolation transition ΔT_{cr} and the initial volumetric content of the filler is given in Fig. 2.

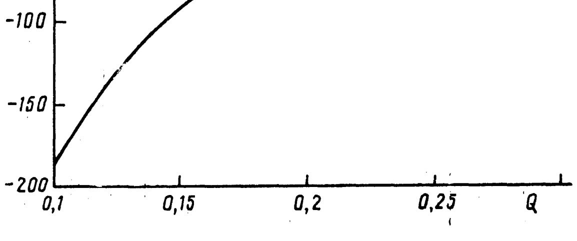

FIG. 2. Relation between the temperature differential ΔT_{cr} at the moment of percolation transition and the filler volume fraction for $v=3$, $a=0.001\ \text{K}^{-1}$.

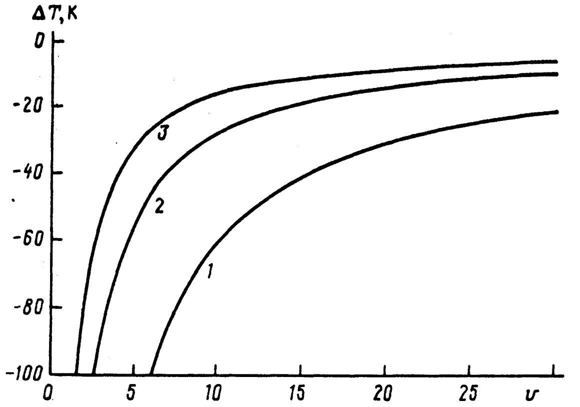

FIG. 3. Relation between the temperature differential ΔT_{cr} at the moment of percolation transition and the blob's initial size v for $a = 0.001\ K^{-1}$, $Q = 0.1$ (1), 0.15 (2), 0.2 (3).

In the proposed model the parameter v for fixed temperature and volumetric content of the filler is a measure for the attractive potential between the particles. An increase in the attractive potential leads to an increase in the value of v and accordingly reduces, for the given Q, the value of the temperature gradient of the percolation transition (Fig. 3).

Thus, from simple physical considerations we have obtained a visual picture of a thermogenetic percolation transition. Now we indicate briefly some results of this model, which can be observed in experiments.

1. Cooling of a two-phase system with a rigid filler, having a relatively low CTE as compared to the matrix, results in the appearance of regions containing a rigid frame composed of the compressed particles of the filler, which merge into one conducting ensemble. Upon further cooling the forces that compress the frame increase and a situation may develop in which the stability of the elements of the frame against compression will be lost, which will cause a "collapse" of supporting structure of the conducting ensemble and a loss of conductance. A system, which has lost conductance as a result of "collapse," may, upon further cooling, regain it again according to the mechanism described in the present paper, and, apparently, this can be repeated many times.

2. Since real composite systems do not follow the assumption 3 introduced here, the presence of forces compressing the frame and increasing with cooling will lead, for some $\Delta T > \Delta T_{cr}$, to crushing of the surface of contacting particles and to the appearance of hysteresis on the relation $\sigma(T)$ after the samples complete a thermal cycle.

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