Anomalously high tensosensitivity of the electrical conductivity of inhomogeneous media

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The experimentally demonstrated anomalously high sensitivity of electrical conductivity γ of conductor–insulator mixtures to changes in pressure P is explained within the framework of percolation theory. The increase ΔP in pressure that produces the sharp change in γ is related to the compressibility β of the conductor and insulator and the difference between the existing and threshold densities of the conductor. The shape of the function $\gamma(P)$ in the region of the critical pressure P_c is discussed.

The anomalously high tensosensitivity (ATS) of the electrical conductivity γ of inhomogeneous media (conductor–dielectric mixtures), whereby the value of γ of the system increases by orders of magnitude for a small change in the pressure, was discussed in Ref. 1. According to percolation theory,[2] an increase in the volume fraction Φ of the conductor in this kind of mixture to the critical value Φ_c (percolation threshold) is accompanied by the insulator-conductor transition. The sharp increase in the electrical conductivity of the mixture as $\Phi \rightarrow F_c$ has suggested the possibility of an anomalously high pressure sensitivity of the electrical conductivity of mixtures close to the critical state.[1]

The anomalous tensosensitivity effect has been observed in powdered mixtures of soot and solid polymers with roughly equal particle dimensions (Fig. 1). Uniaxial compression of this type of mixture in a cylindircal cell was found to be accompanied by threshold phenomena, namely, a sharp increase in the electrical conductivity at a particular (critical) pressure P_c (Ref. 3). As the fraction Φ of the conducting component is reduced as compared with Φ_c, there is an increase in the pressure necessary to produce the sharp rise in conductivity.

We shall now try to estimate in the first approximation the effect of pressure P on the attainment of the percolation state in the mixture for different initial (with $P_a \simeq 10^5$ Pa) "deficit" of the conducting phase as compared with the critical volume Φ_c. The volume fraction of the insulator $(1 - \Phi)$ consists of the volume fraction of the solid polymer and air.

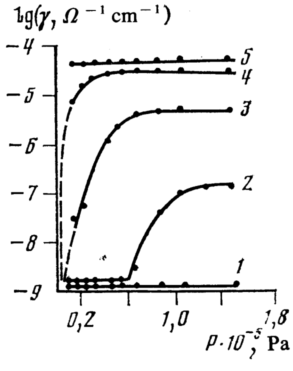

FIG. 1. Conductivity of a powdered conductor-insulator (polymer–soot) mixture as a function of pressure for different initial volume fractions Φ_0 of the conductor; 1—$\Phi_0 = 0.23$, 2—$\Phi_0 = 0.265$, 3—$\Phi_0 = 0.28$, 4—$\Phi_0 = 0.31$, 5—$\Phi_0 = 0.39$. The threshold concentration under atmospheric pressure is $\Phi_c \simeq 0.32$. The conductivity was measured at 20 kHz.

In the elementary description of the effect, we start with the model in which: (1) the mixture is deforemd in a "congruent" manner under pressure, so that the conducting particles, which take the form of spherical inclusions, approach one another without change of shape or volume, i.e., only the surrounding insulating medium is compressed and (2) the electrical conductivity of the mixture can be calculated within the framework of the random-site problem.

The critical volume fraction Φ_c of the conductor can be determined experimentally for a given type of mixture (see Fig. 1), or can be calcualted from the known structure of the mixture. For a given system at $P = P_a$, we have $\Phi_c \simeq 0.30$, which is close to the estimated critical volume fraction in the random-site model ($\Phi_c \simeq 0.29$). In that case, for $\Phi_0 < \Phi_c$, which is the necessary condition for attaining the critical threshold, the increase ΔP_c in pressure can be obtained from the formula

$$\Phi_0/(1-\beta\Delta P_c)=\Phi_c\approx 0{,}3, \tag{1}$$

where β is the compressibility of the insulating matrix, or

$$\Phi_c-\Phi_0=\Delta\Phi_c=\beta\Delta P_c\Phi_c. \tag{2}$$

It is clear that, when $\beta = \text{const}$, the dependence of ΔP on $\Delta\Phi$ must be linear. On the other hand, if we know Φ_c, $\Delta\Phi$, ΔP_c, we can calculate the compressibility β. From the data of Fig. 1, i.e., $\Phi_c \approx 0.30$, $\Phi_0 \approx 0.27$, and $\Delta P_c = 0.6\cdot 10^5$ Pa, we find that $\beta \sim 0.1$. This is a very large value for β, but we must recall that, firstly, powders have high "initial" compressibility at low values of P and, secondly, the model is crude, since the compression of the matrix is in fact accompanied by considerable deformation of the conducting inclusions in the system of pores. Moreover, for plastic conducting inclusions in a rigid porous medium, one would expect that percolation due to the change in the shape of the inclusions is more probable than compression of the matrix. Let us examine this particular case.

We shall suppose that the concentration of inclusions remains constant, but the size R of the effective sphere of influence of the particles changes (increases) by an amount proportional to the degree of compression:

$$\Delta R=k\beta'\Delta P, \tag{3}$$

where k is the proportionality factor and β' is the compress-

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ibility of the inclusions. To reach the percolation threshold in a system with initial concentration N_0 for $P = P_a$ and initial radius R_0 of the sphere of influence (which can be the initial size of the conducting inclusions), we must increase the pressure by $\Delta P_c = P_c - P_a$ where P_c is the pressure that has to be reached to satisfy the percolation condition[2] $4\pi N R_c^3/3 = 2.7$. The condition for the appearance of the sharp rise in electrical conductivity due to compression is

$$(R_0+k\beta'\Delta P_c)^3=R_c^3, \quad \Delta R_c/R_c=k'\beta'\Delta P_c, \tag{4}$$

where k' is a constant given by $k' = k/R_0$, and $\Delta R_c = R_c - R_0 = k\beta'\Delta P_c$.

The critical (effective) volume fraction Φ_c for percolation with $\Delta R_c \ll R_0$ is then given by

$$[\Phi_0(1+3\Delta R_c/R_0)]/(1-\beta\Delta P_c)=\Phi'/(1-\beta\Delta P_c)=\Phi_c, \tag{5}$$

where the denominator $1 - \beta\Delta P_c$ represents the compression of the matrix, as in (1). The difference $\Delta\Phi'_c = \Phi_c - \Phi'$ is, naturally, less than the $\Phi - \Phi_0$ in (2), so that ΔP_c can be reached for lower values of the matrix compressibility β. In particular, when $\beta \sim 0.001$, the fraction $\Delta R/R_0$ must be of the order of 0.03 for $\Delta P_c = 0.6 \times 10^5$ Pa for the soot-polymer mixture analyzed here (Fig. 1). Since soot is readily deformed, the large values of $\Delta R/R_0$ seem reasonable.

It is probalbe that the second model for calculating the tensoresistance is closer to reality although, unfortunately, it includes the relative increase in the effective radius of the sphere of influence, $\Delta R/R_0$, due to the deformation of the inclusions, which is difficult to determine.

Apart from the concentrational dependence of the pressure shift of the conductivity threshold, it is also interesting to analyze the dependence of γ on P when the pressure is increased near the critical point P_c. In the first model (deformation of the insulating matrix alone), the dependence of γ on P is determined only by the increase in the concentration of the conducting particles due to the compression of the matrix. In this case, we may wrrite for $P > P_c$

$$\gamma(P)=\gamma_\infty\left(\frac{\Phi_0}{1-\beta\Delta P}-\frac{\Phi_0}{1-\beta\Delta P_c}\right)^t=\frac{\gamma_\infty\beta^t\Phi_0^t}{(1-\beta\Delta P_c)^t}\frac{(P-P_c)^t}{(1-\beta\Delta P)^t} \tag{6}$$

or, when $\beta\Delta P < 1$,

$$\gamma(P)\approx\gamma_\infty\beta^t\Phi_0^t(P-P_c)^t, \tag{7}$$

where γ_∞ is the asymptotic conductivity corresponding to $P \gg P_c$ and t is the critical conductivity exponent:[2] $t = 1.5$ for $3D$, where D is the dimensionality. A power-law relationship is thus seen to appear with the exponent t.

In the second model (highly deformable conducting inclusions), the calculation is more complicated. As already noted, in this case, the effective size R of the sphere of influence increases under the influence of P. This does not, of course, imply isotropic "inflation" under the influence P, but the "flow" of the readily deformable conductor into the system of pores and cracks, the consequence of which is that the roughly spherical soot grains are transformed into an amoeba-like body with z protrusions, where z is the coordination number of the network of cracks and pores. Since the flow effect is not random but is confined to the pore space, we may conclude that there is a certain correlation between the directions of penetration, and the inclusions must grow toward one another.

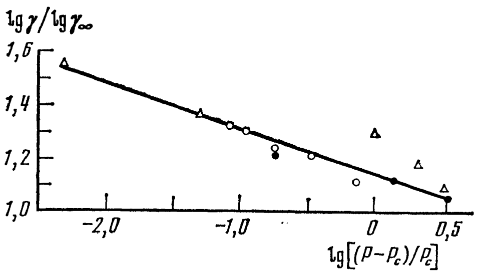

FIG. 2. Dependence of log γ on log($P - P_c$ for $P > P_c$: the points correspond to the curves of Fig. 1: 2—○, 3—△, 4—●.

It would seem that the exponent may be different in the second model.

To estimate the exponent in the function $\Delta(P)$, we have plotted the experimental data on the $\lg\gamma/\lg\gamma_\infty$, $\lg[(P - P_c)/P]$ plane. The experimental value P_c was known only for $\Phi_0 \simeq 0.27$ (Fig. 1). For this value of Φ_0, the data can be described by the linear relationship

$$\lg\gamma/\lg\gamma_\infty=a+b\lg[(P-P_c)/P_c]. \tag{8}$$

For the other curves, P_c was chosen so as to ensure that the experimental data lay on the straight line obtained for $\Phi_0 \simeq 0.27$ (Fig. 2). The coefficient b obtained after this (scaling) operation turns out to be approximately 0.2. This is much less than the value $t = 1.5$ expected on the basis of the first model. As already noted, this may be due to the deformation of the conducting inclusions. The exponent 0.2 is close in its order of magnitude to the exponent $1/\delta$ for three-dimensional systems. More detailed data on the behavior of γ near P_c will be necessary before more reliable conclusions may be drawn.

The anomalously high tensosensitivity can be characterized by the tensosensitivity coefficient $k_t = (d\gamma/\gamma)/(dL/L)$ where dL/L is the relative deformation. The dependence of k_t on Φ takes the form of a λ-shaped curve with a narrow maximum corresponding to $\Phi \rightarrow \Phi_c$, for which k_t lies in the range 10^5–10^6. Tensosensitive components can, in principle, be made from such mixtures.

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