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Transport properties of the composite material carbon-poly(vinyl chloride)

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We have found that at low temperatures the transport properties of carbon-poly(vinyl chloride) composites are governed by tunneling of carriers across a barrier that is modulated by temperature-activated fluctuations. The current-voltage characteristics can be divided into three regimes. At low dc fields the materials are Ohmic; at a critical dc field, the materials enter a thermally activated breakdown regime; above the breakdown field the I-V characteristic may be studied with voltage pulses and the material is non-Ohmic. The dependence of the resistivity ρ on temperature is discussed.

I. INTRODUCTION

Carbon-impregnated plastics are widely used as moldable conductors at room temperature. Their use in the audio-video products industry[1] has stimulated interest in the transport mechanisms in carbon-poly(vinyl chloride) composites. We have found that at low temperatures the transport properties of carbon-poly(vinyl chloride) (C-PVC) composites are governed by tunneling of carriers across a barrier which is modulated by temperature-activated fluctuations.[2] The carbon grains are typically 100–400 Å in diameter and are dispersed in the insulating PVC matrix, which forms a barrier between carbon grains. There is an extensive literature dealing with the low-temperature transport properties of *metal* grains embedded in insulating matrices.[3] The C-PVC composites have many features similar to the granular metals but they differ in their tunneling properties. In this paper we discuss the I-V characteristics of the C-PVC materials and the temperature-dependent resistivity ρ.

II. EXPERIMENTAL

Three types of carbon pigments were used in this work. Ketjenblack EC, a product of Akzo Chemie, the Netherlands, is a carbon black of hollow spheres, ~360 Å in diameter with 10-Å-thick walls. When dispersed in PVC, the Ketjenblack grains tend to aggregate forming chains, often 1 μm in size.[4] Columbia carbon SA40-220, an experimental product of Cities Service Company, is a hollow carbon sphere ~140 Å in diameter with 10-Å-thick walls and it aggregates[4] in a way similar to Ketjenblack when dispersed in PVC. Mogul L, a product of Cabot Corp., is a carbon black of solid spheres ~200 Å in diameter[4] with less tendency to aggregate than the other two pigments. Thus all specimens are composed of aggregates of carbon grains separated by narrow gaps of PVC.[4]

The samples were prepared by milling the carbon and the PVC together and injection molding. Samples in the shape of disks 2 mm thick and 4-mm diam were cut from the molded piece and gold electrodes were evaporated onto the surfaces. By comparing two-lead and four-lead resistivity measurements, we found that contact resistance was not a problem with our electrodes and samples.

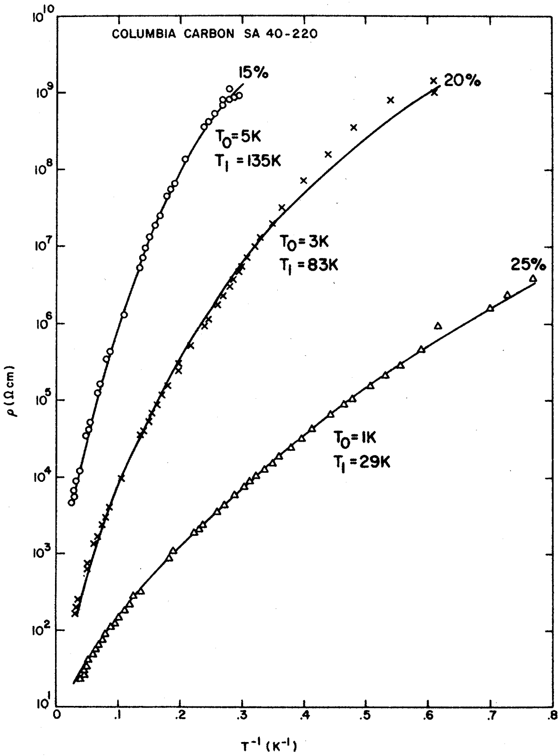

FIG. 1. Temperature-dependent dc resistivity of Columbia carbon SA40-220 in PVC for three different carbon loadings: 15%, 20%, and 25% by weight. Solid curve is the theoretical fit to Eq. (1) with the best values of T_1 and T_0 noted.

The samples were immersed in a liquid helium bath for experiments at 4.2 K and below. This assured excellent thermal contact with the helium bath heat sink. Above 4.2 K the sample was in an atmosphere of helium exchange gas and glued to a single-crystal sapphire substrate with General Electric 7031 varnish.

Measurements were done with dc below the critical breakdown voltage. Above that voltage, voltage pulses were required to reduce sample heating. The *I-V* characteristics were obtained with a sampling oscilloscope.

III. THEORY

We find the transport properties of all the samples to be well described by a tunneling model with a fluctuation modulated barrier.[2] Electrical conductivity of C-PVC composites results from percolation of electrons in the carbon networks. When the concentration of carbon is low enough that there are no continuous carbon pathways across the sample, conduction is dominated by electron tunneling across small barriers separating large conducting regions. Tunneling can be essentially regarded as between two bulk conductors.

Sheng *et al.*[2] have shown that for small applied electric fields

$$1/\sigma(T) \equiv \rho = \rho_0 \exp[T_1/(T+T_0)]\,, \qquad (1)$$

where T_1 may be regarded as the energy required for an electron to cross the PVC gap between carbon aggregates and T_0 determines the low-temperature temperature-independent resistivity.

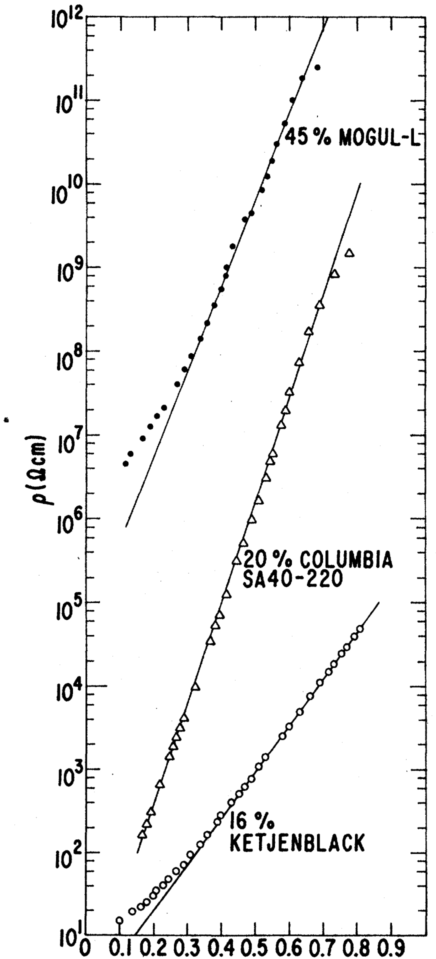

FIG. 2. Logρ vs $T^{-1/2}$ for three types of carbon blacks in PVC. Only the Columbia carbons SA40-220 fit an equation of the form log$\rho \propto T^{-1/2}$. The percents quoted are by weight.

IV. RESULTS

In Fig. 1 we show the temperature dependent resistivity of Columbia carbon SA40-220 for three different carbon loadings with a best value of T_1 and T_0 for each set of data. As the carbon loading increases, the samples become more conducting and the conductivity is less sensitive to temperature and T_1 decreases, as expected. Other carbon blacks dispersed in PVC are also well represented

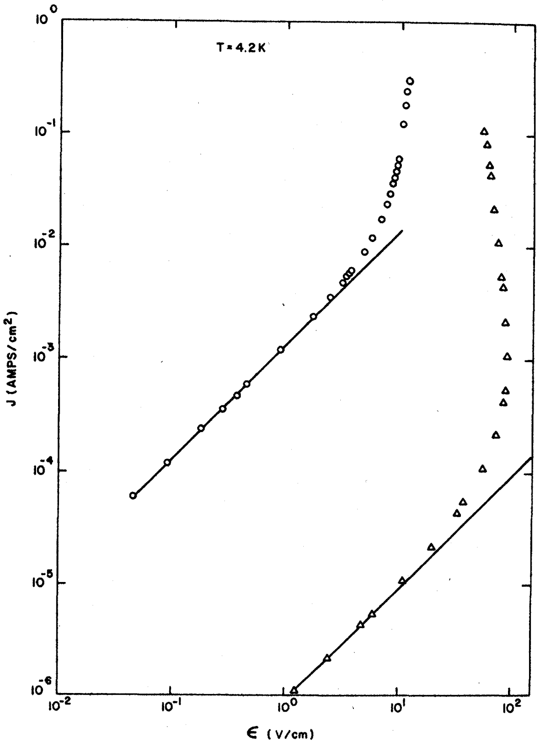

FIG. 3. Current density as a function of applied dc electric field for 16-wt.% Ketjenblack in PVC (open circles) and 20 wt.% Columbia carbon SA40-220 in PVC (triangles). The solid line indicates Ohmic behavior. Data were taken at 4.2 K.

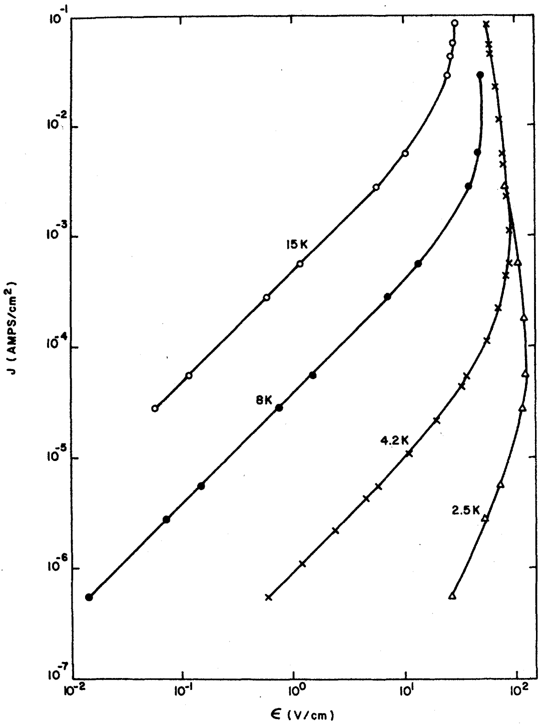

FIG. 4. Current density as a function of applied dc electric field for 20-wt.% Columbia carbon SA40-220 in PVC at several temperatures.

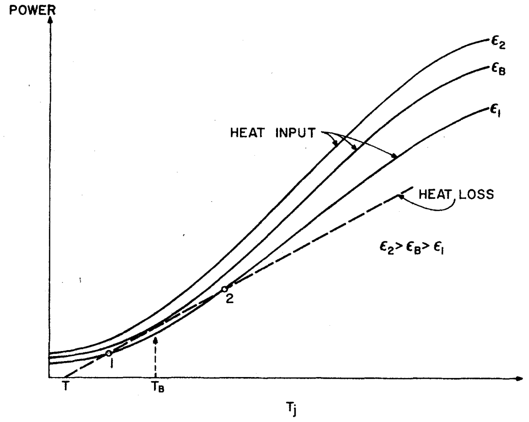

FIG. 5. Heat input [$\sigma(T_j)\epsilon^2$, σ from Eq. (3)] and heat loss [proportional to $(T_j - T)$] curves to describe the breakdown behavior of C-PVC composites.

by Eq. (1) as shown previously.[2]

We should mention that the granular metals[3] usually have a temperature dependent resistivity of the form $\rho \propto \exp(b/T^{1/2})$. The charging energy plays a critical role in the small metal grains which is not present in the large (~1 μm) carbon aggregates. We found that no law of the form $\exp(b/T^{\alpha})$ for a single value of α described the resistivity of all our carbon samples. However, the Columbia carbon SA40-220 can be fitted to a $\rho \propto \exp(b/T^{1/2})$ form as shown in Fig. 2. In view of the excellent fit of all our data to Eq. (1) (see Ref. 2), we regard the dependence described by Eq. (1) as fundamental to all the carbon composites here.

At the low fields applied for the $\rho(T)$ measurements shown in Fig. 1, the C-PVC composites are Ohmic. If the applied voltage is raised, a critical voltage is reached, and then the sample undergoes a reversible breakdown and the voltage is limited. Some results are shown in Fig. 3 and Fig. 4 for a Ketjenblack and a SA40-220 Columbia carbon. The interesting feature of the breakdown voltage is that it occurs at average fields of less than 100 V/cm which is unusually low for a dielectric breakdown. However, the electric field is very large in the PVC gaps between carbon aggregates where the breakdown actually occurs. The field strength at the junctions is expected to be larger than the value measured at the electrodes by a factor M equal to the ratio of the average size of the conducting aggregate to the average junction width. This ratio M is the order of a few hundreds.

The I-V behavior of Figs. 3 and 4 is characteristic of thermal breakdown phenomenon observed in semiconductors[5,6] and insulators.[7,8] It arises when the heat generated at the junction, $\sigma(T_j)\epsilon^2$, cannot be balanced by heat loss from the junction, $\alpha(T_j - T)$. Here T_j is the junction temperature, α is a constant proportional to the heat conductance per unit area of the junction, and $\sigma(T)$ is given by Eq. (1). In Fig. 5 we plot the heat loss and the heat input as a function of the junction temperature. At ϵ_1 heat balance is obtained at points labeled as 1 and 2. The system is stable at point 1 but is unstable at point 2 since a small perturbation at 2 can lead to increasing imbalance between the heat input and the heat loss. However, point 2 can be made stable if there is a resistance in series with the junction to limit the current flow. In such cases stable operation of the system for a given voltage can be achieved at two current levels such as observed in Fig. 3. As the electric field is increased, Fig. 4 also shows that the two current levels tend to come together at a well-defined voltage. This reflects the merging of points 1 and 2 in Fig. 5 at the breakdown field ϵ_B, where the heat loss curve becomes tangent to the heat input curve. Mathematically, the breakdown condition is given[9] by

$$\epsilon_B^2 \left.\frac{d\sigma(T_j)}{dT_j}\right|_{T_B} = \alpha , \qquad (2)$$

$$\sigma(T_B) \Big/ \left.\frac{d\sigma(T_j)}{dT_j}\right|_{T_B} = T_B - T , \qquad (3)$$

where T_B is the junction temperature at breakdown

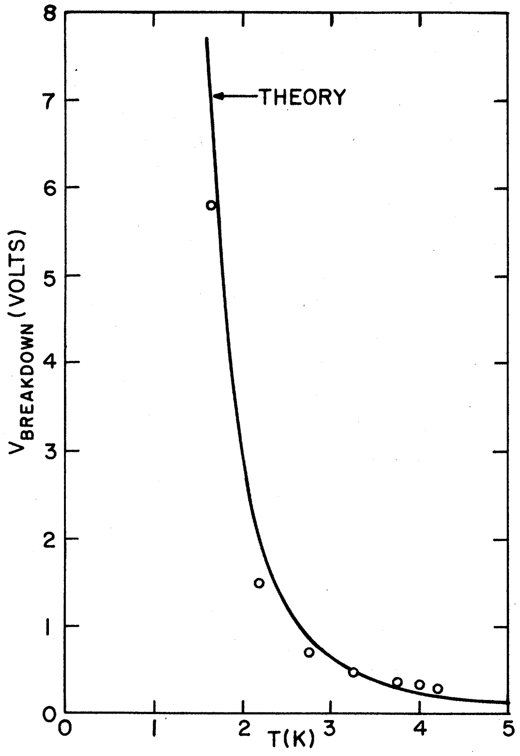

FIG. 6. Breakdown voltage as a function of temperature for 20 wt.% Columbia carbon SA40-220 in PVC. The geometrical factor was nominally 2 mm $=l$ where $\epsilon_B = V_{\mathrm{breakdown}}/l$. The solid curve is the theoretical fit to the data.

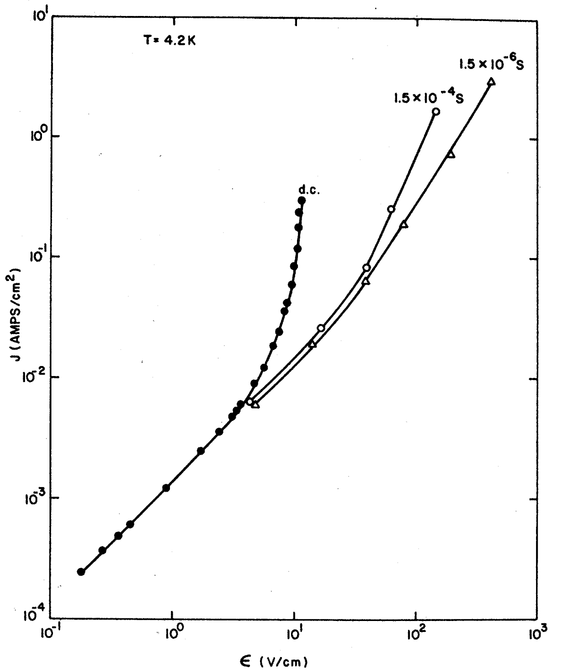

FIG. 7. Current density as a function of electric field for 16-wt.% Ketjenblack in PVC. Closed circles are dc data, open circles 1.5×10^{-4}-sec pulses, triangles 1.5×10^{-6}-sec pulses. Data taken at 4.2 K.

and $\sigma(T)$ is given by Eq. (1). Equation (2) gives the tangent condition, and Eq. (3) is simply obtained by substituting Eq. (2) in the heat balance equation, $\epsilon_B^2\sigma(T_B)=\alpha(T_B-T)$. Solution of Eqs. (2) and (3) yields ϵ_B as a function of the ambient temperature T. Since the variation in T corresponds to a parallel horizontal shift in the heat loss curve in Fig. 5, a little examination of the graph will show that ϵ_B should be a decreasing function of T. This is indeed verified in Fig. 6, where the theoretical curve obtained from numerical solution of Eqs. (2) and (3) is seen to be in excellent agreement with the experimental data. Equation (3) was first solved numerically for the best value of T_B for each temperature and that value was substituted into Eq. (2). By choosing a best value of α and M, ϵ_B and thus the breakdown voltage could be fitted to the data.

When $T\sim4$ K, T_B-T is about 0.6 K. When $T\sim20$ K, $T_B-T\sim6.8$ K. T_B-T is a measure of the local heating at the gaps between carbon aggregates.

A similar breakdown effect has been seen at room temperature in C-PVC composites by Reboul and Moussalli.[10] van Beek and van Pul[11] observed a non-Ohmic I-V characteristic in carbon-rubber composites at room temperature and concluded that an internal field emission effect was occurring due to the "magnification" of the applied electric

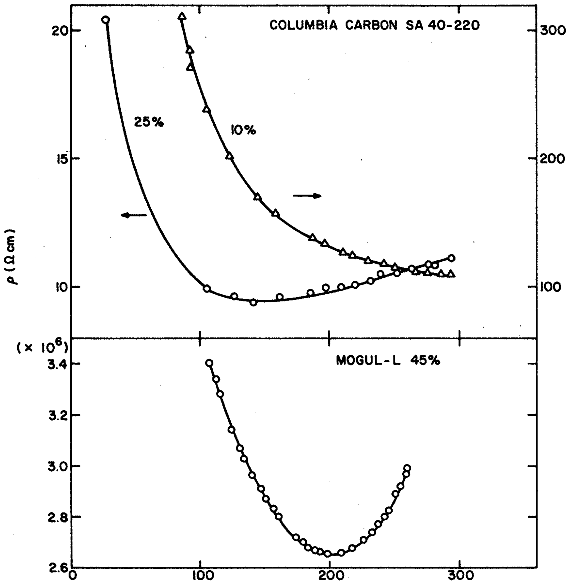

FIG. 8. Resistivity as a function of temperature above 100 K for 25- and 10-wt.% Columbia carbon SA40-220 in PVC and 45-wt.% Mogul-L in PVC.

field across the gaps between carbon aggregates.

To obtain the I-V characteristic above the breakdown voltage, we used fast pulses and low duty cycles. At voltages above the breakdown voltage, the I-V characteristic is superlinear and does not exhibit the catastropic breakdown. As the pulse width increases, the high-field behavior approaches the dc result because of heating, as shown in Fig. 7. For voltage pulses less than 150 ns in duration the I-V curves become independent of pulse width, presumably because heating has become negligible.

We turn now to the temperature dependence of the resistivity above 100 K. At temperatures near 100 K, the differential thermal expansion of the carbon and the PVC plays a role in the $\rho(T)$ behavior. At high T the tunneling current increases because the thermal fluctuations decrease the potential barrier between carbon aggregates. In competition with this effect, the PVC expands more rapidly than the carbon,[12] widening the gap between carbon grains, and increasing the resistivity as the temperature rises. At some temperature a crossover occurs and the material C-PVC has a resistance minimum. This is shown in Fig. 8 for Mogul L and two different loadings of Columbia carbon SA40-220.

V. CONCLUSIONS

We have presented evidence that in C-PVC composites consisting of aggregates of carbon spheres (100–400 Å) dispersed in the insulating matrix, the electrical conductivity can be ascribed to tunneling with potential barrier modulation by thermal fluctuations. We have found that the low-temperature Ohmic regime can be fitted to the theory. The dependence of the breakdown voltage on temperature as well as the high-field non-Ohmic behavior is also in excellent agreement with the theory. The parameters T_0 and T_1 are the same for both the low-field data and the high-field data demonstrating the internal consistency of the theory.[2] The higher-temperature data (100–300 K) can be understood in terms of the different thermal expansion coefficients of the PVC matrix and the carbon.

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