Temperature dependence of the resistivity in polymer–conducting-carbon-black composites

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The electrical dc resistivity of variously prepared polymer–conducting-carbon-black composites has been studied over a wide temperature range (4.2–300 K). For the different composites, the resistivity follows a $\ln\rho \sim T^{-\alpha}$ law over the whole temperature range, with the α parameter, varying between $\frac{1}{2} \leq \alpha \leq \frac{3}{4}$, determined by the carbon-black concentration and the dispersion in the carbon grain sizes. The experimental facts can be understood on the basis of a critical-path-method analysis for hopping conduction developed for granular disordered metallic systems.

INTRODUCTION

A well-known technique to make intrinsically insulating polymers conducting is to incorporate in their matrix a dispersion of macroscopic conducting particles such as carbon black or fine metallic particles.[1] These composites show a drastic increase in conductivity of many orders of magnitude at a critical concentration of the conducting particles, indicating a percolative threshold. In order to elucidate the mechanism of electrical conductivity in the different concentration regimes, the temperature dependence of the resistivity has been studied extensively, and, accordingly, various models have been suggested to interpret the widely varying temperature dependence. At low concentrations, with which this present work is concerned, a hopping mechanism is usually assumed to be the main cause of electronic conduction in these composite polymeric systems. However, it has not been found possible to describe the resistivity data of various different polymeric composites on a general and consistent basis. It is the purpose of this work to discuss this aspect and to show that it is possible to explain the experimentally found temperature dependence of several different carbon-black composite polymers with models usually used to describe transport phenomena in granular metals.

THEORETICAL FRAMEWORK

In order to elucidate the detailed mechanism responsible for the electric conduction in conducting-particle–polymer composites, just as in the case of homogeneous systems, an analysis of the temperature dependence of the conductivity is of considerable interest. To explain current transport in these composite polymers, which are disordered on a macroscopic scale, two rather different approaches have been used with emphasis on different aspects of the physics of the motion of the electrons in the composite structure; these methods, accordingly, lead to different results.

(1) In the "local" approach, the main focus of which is on the hopping mechanism of conduction between neighboring sites in the composite material, it is assumed that the global conductivity is essentially determined by the single-junction characteristics. In particular, in granular metal assumed to be a composite of insulating junctions and conducting metallic particles, the experimentally found dependence of the resistivity ρ on temperature of the type $\ln\rho \sim bT^{-1/2}$ has been interpreted as being due to hopping between neighboring grains in the presence of an electrostatic barrier due to the charging energy E_c of the grains.[2] However, in order to explain the data satisfactorily, a scaling law for the separation S between the different grains had to be assumed; this law was of the type $SE_c = \text{const}$. This is somewhat justified by the very peculiar structure of the film under study but is not generally applicable in rather heterogeneous composite systems.

For conducting-carbon-loaded polymer composites, another local approach has been proposed.[3] Here, the hopping of the electron from one conducting particle to another adjacent one is considered to be critically influenced by the temperature fluctuation of the tunnel barrier height. The temperature dependence of the tunnel mechanism is then due to the intrinsic thermal fluctuation of the voltage between the junctions, given by $(kT/C)^{1/2}$, where C is the capacitance of the junction. This fluctuation in turn induces a fluctuation of the barrier height and consequently of the electric field across the junction. This model gives, for the tunneling conductance of the junction, σ, a dependence $\ln\sigma \sim T_1/(T + T_0)$, where T_1 and T_0 are parameters of the model. It is restricted to homogeneous systems with relatively small barrier heights.

(2) A more "global" approach for the analysis of conduction near the percolation threshold in conducting composites can be based on the critical-path method (CPM) by Ambegaokar, Halperin, and Langer,[4] although it has never been applied to polymer-based composites. For the case of transport phenomena in granular metals, a CPM was developed by Sheng and Klafter[5] and dis-

cussed recently by Mostefa and Olivier.[6,7] The method consists of a statistical approach to the transport mechanism by an equivalent-network analysis, as originally done in the pioneering work of Ambegaokar, Halperin, and Langer[3] for the study of percolation in semiconductor-impurity systems.

In the CPM, an important parameter is the local conductance G_{ij} between two conducting particles i and j. The percolation threshold is attained when this quantity is equal to or larger than a critical value G_c at which the connected clusters form an infinite "connected" network through the polymer matrix. For relatively low concentrations, the "connection" between the particles is due to a hopping of electrons between neighboring sites. At the threshold, there is a critical average number of bonds per site b_c which is given by the geometry and the dimensionality d of the system, and one gets[8,9] $b_c = d/(d-1)$.

In order to calculate G_c explicitly for a whole system, the conduction mechanism has to be considered in detail. If a tunneling process is assumed to give rise to a conductance between two grains i and j, one gets

$$G_{ij} = G_0 \exp(-2\chi S_{ij} - E_{ij}/kT) ,$$

where χ is the tunneling parameter. S_{ij} the spatial separation between sites i and j, and $E_{ij} = \frac{1}{2}(|E_i - E_j| + |E_i| + |E_j|)$ with E_i and E_j being the electron energy at sites i and j, respectively. From percolation theory, the condition $G_{ij} \geq G_c$ leads to the relation

$$\frac{S_{ij}}{S_m} + \frac{1}{2}\frac{|E_{ij}| + |E_j| - |E_i - E_j|}{E_m} \leq 1 ,$$

where $S_m = \frac{1}{2}\chi \ln(G_0/G_c)$ and $E_m = kT \ln(G_0/G_c)$. S_m and E_m represent the maximum hopping distance and the maximum energy difference between the initial and the final states the electrons could have satisfying $G_{ij} \geq G_c$.

In their treatment of finite-size systems by the CPM method in the presence of a tunneling mechanism, Sheng and Klafter[5] have shown that the average number of bonds b_c at the percolation threshold is related to the average particle dimension D_0 and the density of states $N(E_i)$ of electrons in grain i by

$$b_c = n\frac{\int_{-E_m}^{+E_m} dE_i N(E_i) \int_{-E_m}^{+E_m} dE_j(E_j)\frac{4\pi}{3}(S_a^3 + 3S_a^2 D_0 + 3S_a D_0^2)}{\int_{-E_m}^{+E_m} dE_i N(E_i)} ,$$

where n is the number of grains per unit volume and S_a the maximum value of the particle separation. The energy difference between E_i and E_j is given by the charging energy $E_c \sim e^2/D$ of the conducting particles.

When a particle- or grain-size distribution is introduced, the density of states has to be averaged over the different sizes as

$$N_G(E) = \frac{1}{\Delta} \int_0^E P(E_c) dE_c ,$$

with Δ the average value of the electronic level separation inside the metallic grains and $P(E_c)$ the distribution function for the charging energy of the grains. The size distribution can be characterized by a parameter $\mu = D_{max}/D_{min}$ and introduces an average state density which is not constant but energy dependent, and which can be written as

$$N_G(E) = N_0 + aE^\beta,$$

where a and β are determined by the size distribution. It has been shown by Sheng and Klafter[5] that this energy-dependent average density of states leads to a well-defined value for the temperature parameter α in the $\ln\rho(T)$ relation

$$\ln\rho(T) \sim T^{-\alpha} \quad \text{with} \quad \alpha = \frac{\beta+1}{\beta+2} .$$

This model seems to be particularly justified for conducting polymer composites, as there the randomly dispersed particles in the matrix are often found to have a rather large size distribution. For instance, in the case of conducting carbon-black mixtures in polymers, the grains can vary in diameter from a few nanometers to tens of micrometers

EXPERIMENTAL PROCEDURES AND RESULTS

Several different samples have been prepared, using various polymeric matrices: polystyrene, polyethylene, ethylene-propylene copolymer and styrene-butadiene copolymer. The conducting carbon black used in all these samples was Ketjenblack EC from AKZO Company.

The samples were prepared in two different ways. In the first method, the polymer is heated in an internal mixer (Brabender) and the carbon black is added progressively. The temperature of the polymer matrix is adjusted between 150 and 180 °C in order to attain a sufficiently low viscosity. Then the solid paste is pressed at high temperatures to a sheet of a thickness of 1 mm from which samples $(10 \times 10 \text{ mm}^2)$ are cut. The second type of samples are obtained by dissolving the polymer in a solvent (xylene, toluene), to which a given amount of carbon black is then added. After deposition on a glass plate and evaporation of the solvent, strips $(4 \times 40 \text{ mm}^2)$ are cut from the films (200 μm thick), which are then detached from the glass substrate.

The measured distribution of the isolated conducting carbon particles confirms the findings of various authors.[10] After introduction into the matrix, a wider distribution of grain sizes is found, corresponding to an increase of the parameter μ which characterizes the size
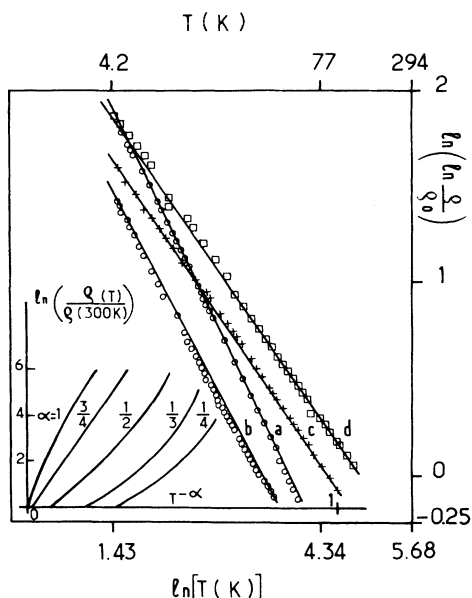
T (K)

FIG. 1. Temperature dependence of the resistivity in polymer–conducting-carbon-black composites of the samples of Table I, plotted in the form of $\ln \ln[\rho(T)/\rho_0]$ vs $\ln T$, showing the straight lines with the slope values of α (Table I). For illustrative purposes, the inset again shows the experimental results of sample a, plotted for different values of α, to illustrate the typical $\ln\rho \sim T^{-\alpha}$ behavior in order to compare different theoretical models.

distribution.

dc conductivity measurements are made by the four-contact technique on all the samples in a helium-flow cryostat (Oxford Instruments). The cryostat is carefully calibrated for the temperature measurements with a germanium resistance thermometer (Cryocal-Florida).

It is well-known to be difficult to fit experimental results, measured over a limited temperature range, to a $\ln\rho \sim T^{-\alpha}$ law. Our procedure is illustrated in Fig. 1; all the data over the whole accessible temperature range (4.2–300 K) have been plotted, using a relation of the form $\rho = \rho_0 e^{-T_0/T^\alpha}$, where ρ_0 together with T_0 are parameters. Plotting $\ln[\ln(\rho/\rho_0)]$ versus $\ln T$, one should get straight lines which allow a determination of α. In order to illustrate this point and to improve the discussion, in the inset at the lower left part of the figure various curves for the experimental results on sample a are drawn. ρ_0 was determined experimentally by plotting $\ln[\rho(T)/\rho(300 \text{ K})]$ as a function of $T^{-\alpha}$ for different

values of α. For this plot, the abscissa scale is a function of α; the α value which would be the best fit for the $\ln\rho \sim T^{-\alpha}$ law corresponds to a straight line. In this way, a visual comparison and analysis of the results is rather easy and direct. For the particular sample represented in the inset of Fig. 1, a clear $\ln\rho \sim T^{-3/4}$ behavior is found over a rather extended temperature range. This can be expected for a system with a wide distribution of grain sizes, leading to variation of the density of states formally characterized by $N_G = N_0 + aE^2$, resulting in[5] $\alpha = (2 + 1)/(2 + 2) = \frac{3}{4}$.

Using the same type of analysis for other polymeric mixtures, we have found the same good agreement with $\ln\rho(T) \sim T^{-\alpha}$ over the whole temperature region between 4.2 and 300 K. For the different preparation procedures, different characteristic α values have been determined. The relevant facts for the different conducting-Ketjenblack-carbon-loaded polymers are summarized in Table I.

Qualitatively, the difference in α for the different samples can be understood on the basis of the theoretical predictions of Sheng and Klafter[5] and Mostefa and Olivier,[6,7] who predict a decrease of α when the average conducting-grain diameter decreases. Samples c and d have a small amount of carbon black (room-temperature resistivity of 10^8–10^{10} Ω m). As a result of the very low particle concentration, the average grain diameter is small,[11] leading to a value close to $\alpha \simeq \frac{1}{2}$.[5,6,7] System b has, due to its preparation, a more reduced size distribution μ in the matrix than system a, where a more brutal high-temperature roller-mixing technique was used; this should lead to a smaller value for α for system b than for system a, which is, indeed, observed experimentally.

CONCLUSION

The temperature dependence of the conductivity of polymer-based conducting-particle composites, with particle sizes ranging from some nanometers to tens of micrometers, does not follow the famous $\ln\rho \sim T^{-1/4}$ law, valid for localized impurities of atomic scale. As discussed by Sichel, Knowles, Rubner, and Georger,[12] a change towards a $\ln\rho \sim T^{-1/2}$ behavior has been observed.

In general, the temperature dependence of the conductivity of conducting-particle—polymer composites can be explained in the low-concentration regime by a hopping mechanism between particles with various size distributions within the framework of the critical-path-method theory, as developed by Sheng and Klafter,[5] for granular metals.

TABLE I. Relevant parameters for the temperature dependence of the resistance $\ln[\rho(T)/\rho(300 \text{ K})] \sim T^{-\alpha}$ for different carbon-black composite polymers at the percolation threshold.

System	Polymer	Preparation method	ρ(300 K) (Ω m)	α
a	polystyrene	high-temperature mixing	10^6	0.75
b	polystyrene	solvent evaporation	10^6	0.70
c	polystyrene	high-temperature mixing	10^8	0.5
d	ethylene-propylene copolymer	high-temperature mixing	10^{10}	0.55

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