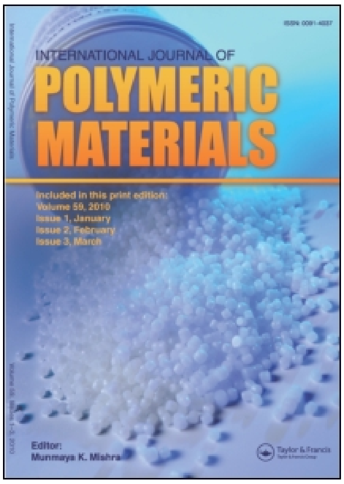

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Tunnelling and Thermally Stimulated Phenomena in Highly Filled PMMA Composites

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Films of polymethylmethacrylate composites, filled with high volume fractions ($P \geqslant 26\%$) *of* Fe fine powder, were prepared by casting method. The electrical resistivity was measured in the temperature range of 305–406 K. Composites of $P = 26$–34% exhibited a temperature (T) independent resistivity in the range of $T = 305$–400 K indicating the predominance of a tunnelling conduction. Relatively sharp resistivity peaks were observed at $T > 400$ K, due to the thermally stimulated discharging current (TSDC). Composites of $P > 34\%$ were characterised by broad TSDC peaks without tunnelling region. The results were interpreted on the basis of a previously suggested theoretical model which considers the discharge process in a dielectric with two bipolar deeply trapped charge layers. It is implied that the present system exhibits a high effective surface charge density and a low value of the average electric field inside the layers. These results ruled out the application of simple percolation models and confirmed the internal conduction mechanisms in such multiphase networks.

KEY WORDS: Electrical resistivity, PMMA composites, Fe powder

1. INTRODUCTION

Electrical properties of polymers filled with transition metals have been studied primarily in the last decade.[1] The electrical conduction, in metal-polymer composites is best treated as an interfacial phenomenon.[2] As the filler content increases the interparticle separation plays an important role in the conduction process due to the influence of the electrostatic field between the neighbouring filler particles. Thus the various nonlinear conduction mechanisms are expected to take place at various filler contents. It is also important to identify the probable type of conduction mechanism predominating at a certain temperature range. The present study is concerned with these problems.

2. EXPERIMENTAL

The investigated composites were prepared by casting method.[3] Benzene was used as a solvent for the PMMA polymer and Fe as a filler (of particle size

$\simeq 40\,\mu m$). The dc electrical resistivity (ρ) was measured by standard techniques[4] using a digital multimeter type (PM 2521 Philips) of accuracy $\pm 0.2\%$. The samples were in the form of films of dimensions $1.6 \times 1.6 \times (0.02\text{–}0.06)\ cm^3$. Contacts were of highly conductive carbon dag with an area of $1\ cm^2$. The sample was short circuited for about two days, at a constnat temperature 300 K, before the dc voltage was applied. The measurements were done in the steady state to avoid errors due to relaxation effects.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the temperature dependence of ρ for PMMA composites of $P = 26$ and 34 vol.% respectively. It is clear that ρ exhibits a temperature independent character in the ranges of 305 to 390 K and 305 to 400 K for $P = 26$ and 34, respectively. This indicates that a tunnelling conduction mechanism proceeds in the mentioned temperature regions. Moreover, relatively sharp resistivity peaks appear in Figures 1 and 2 at temperatures 412 and 436 K for $P = 26$ and 34, respectively. These peaks may be associated with thermally stimulated discharging (TSD) current which can be interpreted on the basis of a theoretical model previously suggested by Sodolski.[5] Sodolski considered the discharge process in a dielectric with two bipolar deeply trapped charge layers. This model may be represented by polymers of ionic-conduction in which some part of the ions during polarization are deeply trapped in a narrow electrode region. The term "deep trap" means that the detrapping energy is higher than the activation energy of intrinsic conductivity in bulk. As a consequence, the discharge of this system will take place mainly by drift of the thermally generated charges which are responsible for intrinsic conductivity. Drifting in the electric field generated by the layers, the charges will cause a gradual compensation of the layers. Thus the gradual disappearance of the electric field in the bulk of the sample will occur.

Our experimental results correspond to the nonisothermal discharge case of Sodolski's method. In this case, the TSD current $J(T)$ can be expressed as

$$J(T) = \frac{\rho_0 b \kappa\, e^{-W/kT}}{\left[\kappa \xi(T) + \frac{1}{(\Delta x)_0}\right]^2} \tag{1}$$

$$\kappa = \gamma_0 / 2L\varepsilon_0 \varepsilon\, b, \tag{2}$$

$$\xi(T) = \int_{T_0}^{T} e^{-W/kT}\, dT, \tag{3}$$

where b is the rate of heating, L is the sample thickness, Δx is the width of the layers, near the electrodes, within which ions are deeply trapped and uniformly distributed with volume charge density ρ_0. Generally, $\Delta x \ll L$. The initial value of Δx is $(\Delta x)_0$, ε_0 and ε are the dielectric permittivity of vacuum and PMMA respectively. γ_0 is the pre-exponential factor in the intrinsic conductivity expression $\gamma(T) = \gamma_0 \exp(-W/kT)$, and W is the activation energy.

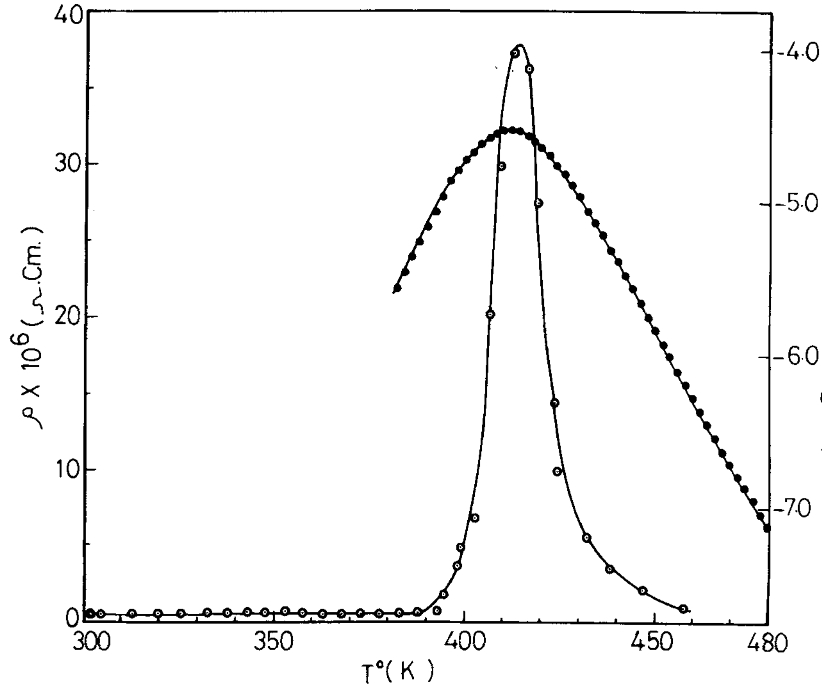

FIGURE 1 Temperature dependence of ρ (obtained experimentally) and $\log J(T)$ (calculated according to Sodolski's model[5] for PMMA composite loaded with Fe 26 vol.%.

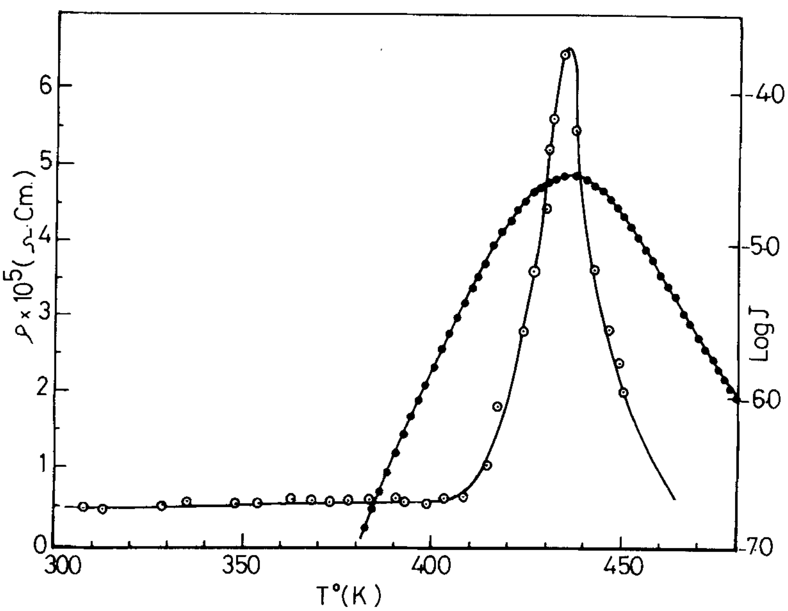

FIGURE 2 As in Figure 1 but for Fe 34 vol.%.

Sodolski examined the influences of some parameters such as ρ_0, b, L and W on the TSD current and he found that the most sensitive parameter is the value of W. This value particularly strongly influences the position of the maximum.

The effective surface charge density σ can be expressed as[6]

$$\sigma = \frac{1}{L}\int_0^L x\rho(x)\,dx \tag{4}$$

The strength of the electric field $E(T)$, decreasing with time (t) and acting between the layers in the region $\Delta x < x < L - \Delta x$, can be obtained from the relation:

$$E(t) = \frac{-\rho_0}{\varepsilon\varepsilon_0 L}(\Delta x)^2. \tag{5}$$

We have used Eqs. (1)–(3) in a computer program to calculate $J(T)$ for PMMA composites with $P = 26$ and 34 and the results are plotted in Figures 1 and 2. The values of the corresponding parameters are as follows:

$B = 0.5\ \mathrm{K\,min^{-1}}$, $L = 0.02\ \mathrm{cm}$, $(\Delta x_0) \doteq 2 \times 10^{-4}\ \mathrm{cm}$
$\rho_0 = 10^{-4}\ \mathrm{C\,cm^{-3}}$, $\kappa = 4.1 \times 10^{23}\ \mathrm{cm^{-1}\,K^{-1}}$, $\varepsilon = 3$ and
$\gamma_0 = 3.4 \times 10^7\ \Omega^{-1}\,\mathrm{cm^{-1}}$.

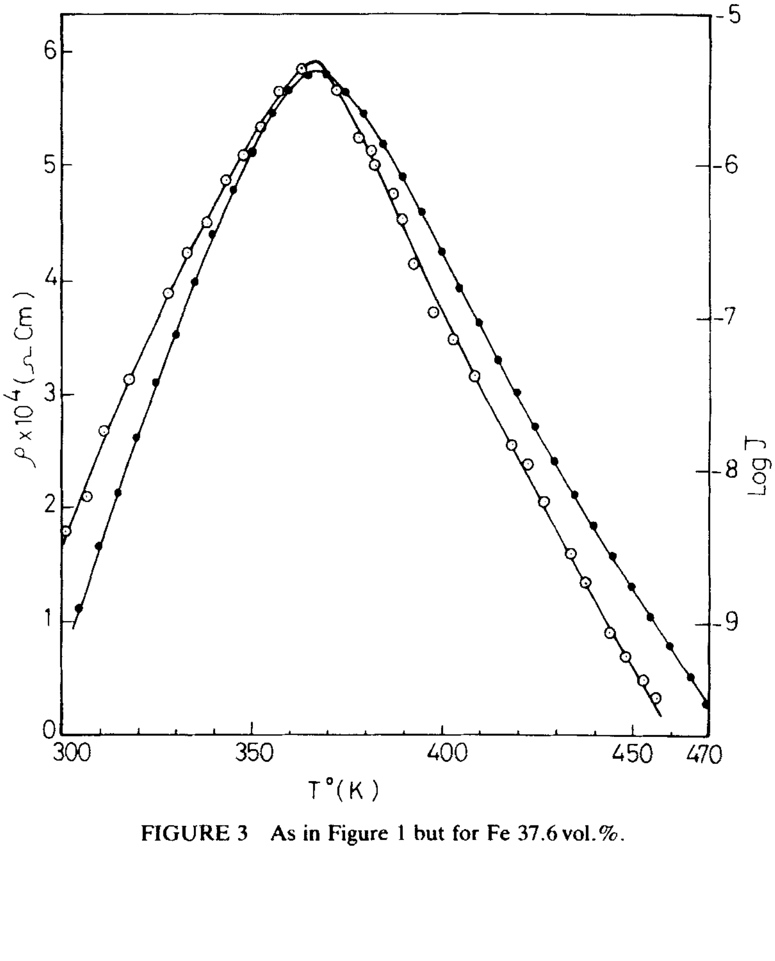

FIGURE 3 As in Figure 1 but for Fe 37.6 vol.%.

The fitting procedure was carried out for the temperature value corresponding to the maximum of the sample resistivity. The fitted W values were 1.7 and 1.8 ev for $P = 26$ and 34, respectively. It is clear from Figures 1 and 2 that the peaks of the calculated TSD currents are wider than the corresponding resistivity peaks. This discrepancy might be explained if one would notice that Sodolski's model does not account for the predominance of the tunnelling mechanism in temperature extents around (and relatively close to) T_m in the present cases.

Figures 3–5 present the temperature dependences of ρ (obtained experimentally) and $\log J(T)$ calculated according to Eqs. (1)–(3), for highly loaded samples with $P = 37.6$, 46, 58, respectively. These figures are characterized by:

a) Both of the resistivity and current plots exhibit similar shapes, and
b) The TSD current predominates in the studied temperature range ($\simeq$300–470 K) with no indication of the tunnelling mechanism.

The above two features can be reasonably explained as follows. For $P \geqslant 37.6$ the

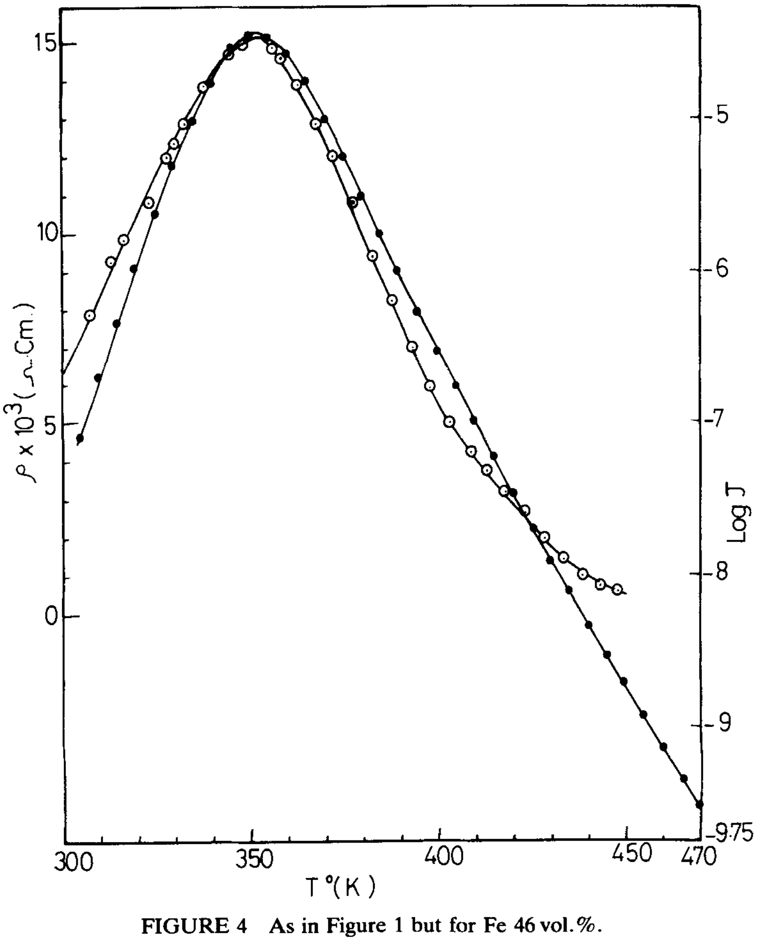

FIGURE 4 As in Figure 1 but for Fe 46 vol.%.

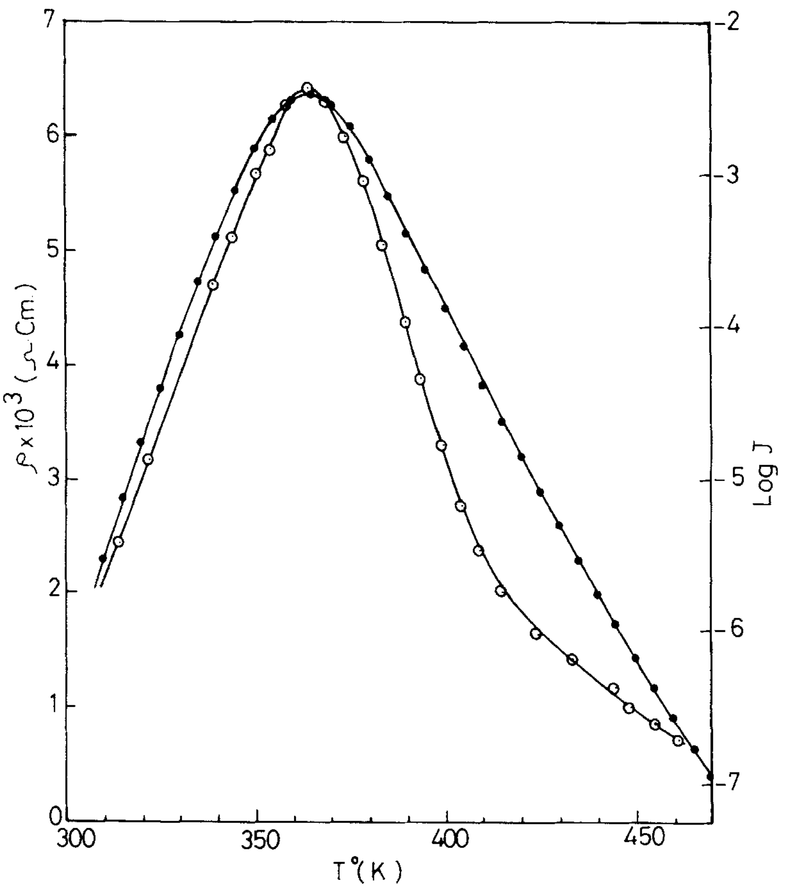

FIGURE 5 As in Figure 1 but for Fe 58 vol.%.

deeply trapped charge layers become very close to each other allowing of the TSD mechanism to predominate.

Using Eqs. (4) and (5) one may calculate the typical values of σ $(t=0)$ and E $(t=0)$ to be $2\times10^{-6}\,\mathrm{C/cm^2}$ and $-7.54\,\mathrm{V/cm}$ respectively. The literature data, obtained for other dielectrics[7] were

$$\sigma(t=0)=\pm8.1\times10^{-11}\,\mathrm{C/cm^2} \quad \text{and} \quad E(t=0)=3.5\times10^{2}\,\mathrm{V/cm}.$$

This implies that the present system is characterized by a high effective surface charge density and a low value of the average electric field inside the layers.

It should be noted that the obtained results of $\rho(T)$ for the highly loaded PMMA $(P\geqslant37.6)$ implies that the temperature dependence of ρ does not obey the corresponding dependence for the predominant phase, which is the metallic one in this case. This implication contradicts that obtained from the computer simulations, adopted by Ahmed *et al.*[8] assuming a simple percolation phenomenon (SPP). Thus it is remarkable that SPP alone cannot account for the total resistivity of the multiphase networks, particularly if there are more than one conduction mechanism.

On the other hand the obtained results agree with the suggestions of Ahmed and Tawansi[9] about the induced charged thin layers (shells) around the metallic granules in the polymeric matrix. They considered these charged shells as a third phase in the composite. Moreover, the appearance of the tunnelling model for $26 < P < 37.6$ and the predominance of the space charge (and thermally stimulated) phenomena for $P \geqslant 37.6$ agrees with findings of the modified internal conduction model postulated by Tawansi and Zidan.[10]

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