

Mott-hopping processes in polymethylmethacrylate matrices filled with polypyrrole particles

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The electrical properties of polypyrrole/polymethylmethacrylate composites containing 2 - 8 wt% polypyrrole particles were characterized. For temperatures below the glass transition of the composite, the frequency dependence of the ac conductivity, in the range $10^2 - 2 \times 10^5$ Hz, showed a sub-linear dispersive behaviour, i.e., it was found to be proportional to ω^s , where ω is the angular frequency. The frequency exponent s was interpreted using the correlated barrier-hopping model. The temperature dependence of the dc conductivity gave evidence of a transport mechanism based on the three dimensional Mott's variable-range hopping. Using this model we were able to calculate meaningful values for the density of states, hopping distance and hopping energy.

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1. Introduction

Research on conducting polymer composites and blends has become very popular in the field of material science owing to their promising and novel electrical properties, as well as for interest in their fundamental science. Investigation of the electrical properties of these materials shows that these composites represent an important class of materials with potential applications like shielding of equipment from electromagnetic interference [1,2], organic light emitting diodes [3-5], anticorrosive materials [6,7], electrostatic dissipation of charges [8], etc. In the last several decades, much investment has been made in developing high performance polymer composites, which combine the electrical and mechanical advantages of the matrix with the charge conducting fillers introduced in that matrix [9,10].

The conductivity of conjugated polymers covers a very wide range, from 10^{-12} to about 10^5 S cm⁻¹, depending on the doping [11]. A wide variety of processes are involved in charge transport in these materials. The chain relaxation or deformation that results from adding electrons (or holes) to the polymer chain produces a variety of localized electronic defects such as solitons, polarons, and bipolarons, each one with its own characteristic transport properties. The transport mechanism, that is charge conduction, in semiconducting polymers has been of great interest since the synthesis of polyacetylene by Ito et al. in 1974 [12]. Since that time, numerous renewed efforts have been made to enhance and understand the charge transport characteristics of these quasi-one-dimensional electronic disordered materials [13], providing new concepts and a mechanism for conductivity. Both direct current (dc) and alternating current (ac) conductivities measurements are directly

related to the electronic structure and hence they have been used to investigate the mechanism of transport in conjugated systems and to compare the obtained results with predictions of various theoretical models [14-16].

This work presents a study on the electrical conductivity of the composites made up of polypyrrole (PPy) particles in an insulating matrix of polymethylmethacrylate (PMMA). The objective of this work was to analyse these composites by using impedance spectroscopy in the frequency range 100 Hz to 2×10^5 Hz and in the temperature range from 23 to 110 °C. The temperature-dependent direct current conductivity of the composites was examined using the Mott's variable-range hopping model in three dimensions and the frequency-dependent alternating current conductivity was analysed using the Jonscher model at different temperatures.

2. Materials and methods

The PPy powder used in this study was obtained by doping intrinsic PPy with tosylate anions (TS⁻). The doping degree was characterized by the X-ray photoelectron spectroscopy technique (XPS) and was found to be of the order of one sulphur (S) for four nitrogens (N), i. e., one tosylate anion (TS⁻) for four pyrrole monomers [17]. The PPy particles had a diameter of 20-40 μm , dc conductivity $54 (\Omega\cdot\text{m})^{-1}$, and density $1.2 \text{ g}\cdot\text{cm}^{-3}$. The insulating polymethylmethacrylate (PMMA) matrix had a conductivity of the order of $3 \cdot 10^{-15} (\Omega\cdot\text{m})^{-1}$, glass transition temperature about 113 °C [18] and density $1.14\text{-}1.20 \text{ g}\cdot\text{cm}^{-3}$. The PPy, PMMA and tosylate used in the present paper were obtained from Sigma-Aldrich Chemical, France.

The samples investigated in this study were obtained by mixing the PPy and PMMA powders, in four

concentrations of PPy, 2, 4, 6, and 8%. This mixture was heated at 150 °C and then pressed at 5 ton.cm⁻² to prepare solid, disc shaped composite samples. The conductivity percolation threshold, Φ_c , for this series of samples was approximately 3.85 % [18].

The complex permittivity function, $\varepsilon^* = \varepsilon' - i\varepsilon''$, was measured by using a Hewlett Packard Network Analyzer (Model 4192A, USA). The dielectric constant ε' , and the loss factor ε'' , of the samples were calculated from the admittance $Y^* = G + iB = iC_0 2\pi F \varepsilon^*$ of the equivalent circuit leading to $\varepsilon' = 2hB/\varepsilon_0 d^2 \pi^2 F$, $\varepsilon'' = 2hG/\varepsilon_0 d^2 \pi^2 F$ and $\sigma_{ac} = 2\pi\varepsilon_0 F \varepsilon''$, where B is the susceptance, G the conductance, F the frequency, ε_0 the vacuum dielectric constant, and h and d are the thickness and the diameter of the sample, respectively. The measurements were performed in the frequency range 100 Hz to 0.2 MHz under isothermal conditions for temperatures ranging between 23 and 110 °C. The dc conductivity was obtained from the ac conductivities by extrapolation ($F \rightarrow 0$).

3. Results and discussion

3.1 Temperature dependence of dc conductivity

In conducting polymers the conduction mechanisms are usually analysed using the direct current conductivity versus temperature, $\sigma_{dc}(T)$, measurements. Fig. 1 shows the temperature-dependence of the dc conductivity of the polypyrrole/poly(methylmethacrylate) composites; it is clear that the dc conductivity increased with increasing temperature, suggesting that the electrical conduction occurred by charge hopping between polymeric chains. Mott and Davis [19] developed a model to describe the conduction mechanisms in amorphous silicon; when applied to conducting polymers, assuming that electron transport originates from localized or fixed states in the polymer chain, the charge transfer between chains takes place by hopping, referred to as phonon assisted hopping between two localized states [20]. Mott's Variable-Range-Hopping (VRH) model is extensively used to analyse the temperature-dependence of dc conductivity.

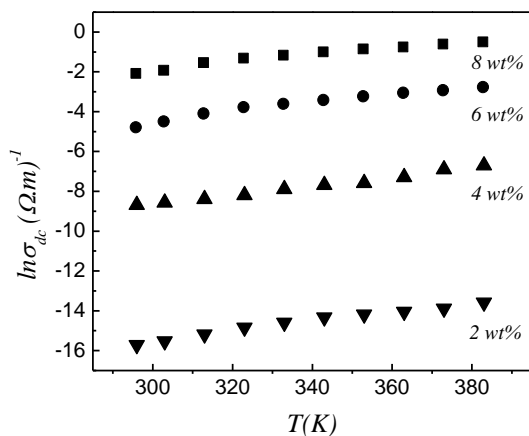


Fig. 1. dc conductivity of PPy-PMMA composites versus temperature.

For the usual three dimensional case, the VRH model predicts a temperature conductivity dependence given by the analytic equation [21]:

$$\sigma_{dc}(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/4} \right] \quad (1)$$

where σ_0 is the pre-exponential constant and T_0 is the Mott's characteristic temperature following the relation:

$$T_0 = \frac{\lambda}{k\xi^3 N(E_F)} \quad (2)$$

where $N(E_F)$ is the density of states, assumed constant, over the range kT at the Fermi energy E_F , k is the Boltzmann constant (8.616×10^{-5} eV.K⁻¹), and λ is a dimensionless constant (≈ 18.1). Bredas et al. [22], have reported that, for PPy, the hopping state is delocalized over four pyrrole rings, so it is assumed that the localization length (ξ) will be of the order of 10 Å for the monomer dimension of ~ 3 Å. The characteristic temperature, T_0 , can be associated with the effective energy barrier between localized molecular chains [23]. A high value of T_0 implies strong localization of carriers inside the molecular chains, resulting in a decrease of the conductivity [24].

Two other important parameters introduced by Mott, the average hopping distance, R_{hop} , between two localized states and the average hopping energy, W_{hop} , were also evaluated, using the expressions given below:

$$R_{hop} = \left[\frac{9\xi}{8\pi k T N(E_F)} \right]^{1/4} \quad (3)$$

$$W_{hop} = \frac{3}{4\pi R_{hop}^3 N(E_F)} \quad (4)$$

Fig. 2 shows the variation of $\ln(\sigma_{dc})$ as a function of $T^{-1/4}$ for different fractions of added PPy particles. The hopping parameters were calculated from the experimental data, in the temperature range from 23 to 110 °C, using Eqs (2-4), and are summarized in Table 1.

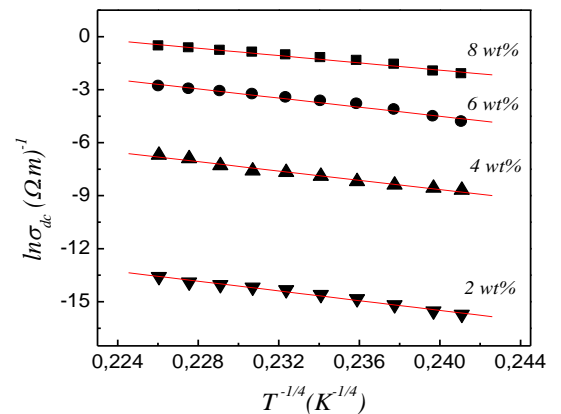


Fig. 2. Natural log of dc conductivity vs ($T^{-1/4}$) for PPy-PMMA composites. The full lines represent the best theoretical fits to the data with the correlation coefficient between 0.987 and 0.993.

Table 1. Mott parameters for PPy-PMMA composites at room temperature.

wt (%)	T_0 (10^8 K)	$N(E_F)$ (10^{19} eV $^{-1}$ cm $^{-3}$)	R_{hop} (nm) (300K)	$\alpha.R_{hop}$ (300 K)	W_{hop} (eV) (300K)
2	3.61	2.16	3.72	12.4	0.214
4	2.99	2.61	3.55	11.8	0.204
6	2.76	2.82	3.48	11.6	0.200
8	1.14	6.83	2.79	9.3	0.160

In this table the observed values of T_0 point to an effective energy separation between the localized states, decreasing as PPy content increased and to a good linearity of $\ln(\sigma_{dc})$ versus $T^{-0.25}$ (Fig. 2), which we suggest indicates that the conductivity is associated with polaron transport in the extended (non-localized) states at the mobility edge [25]. Inspection of Table 1 reveals that $\alpha.R_{hop} \geq 9.32$, $W_{hop} \geq 0.16$ eV (the parameter α describes the spatial extent of the localized wave function) and the density of localized states $N(E_F)$ was in the range 2×10^{19} to 7×10^{19} eV $^{-1}$ cm $^{-3}$. Hence, these results were found to be consistent with the Mott and Davis requirement for variable range hopping conduction which are $\alpha.R_{hop} \gg 1$, $W_{hop} \gg kT$ and the density of states $10^{19} - 10^{20}$ eV $^{-1}$.cm $^{-3}$, respectively [24]. At room temperature, the average hopping distance, R_{hop} , decreased from 3.72 to 2.79 nm with the increase in the concentration of PPy from 2 to 8%, probably due to the improvement of the chains disorderliness and interfacial quality of composites with high inter-chain coupling or closer particles. The expected requirement of the Mott parameters has been widely observed and had a better agreement with those expected from many types of disordered systems [26, 27], indicating the suitability of Mott's model to these samples.

As shown in Figs 3 and 4 the hopping distance, R_{hop} , decreased and the hopping energy, W_{hop} , increased with temperature, for each of the different volume fractions of PPy loaded in the amorphous PMMA matrix. This type of behavior may be due to an increase of the disorder of the system with temperature which indicates that the conduction took place by hopping of carriers to states located close to the initial state and between chains, resulting in decreased R_{hop} value. Similarly, W_{hop} increased because, with the increase of disorder, more energy is required by the carriers to make a transition between two states in the hopping process.

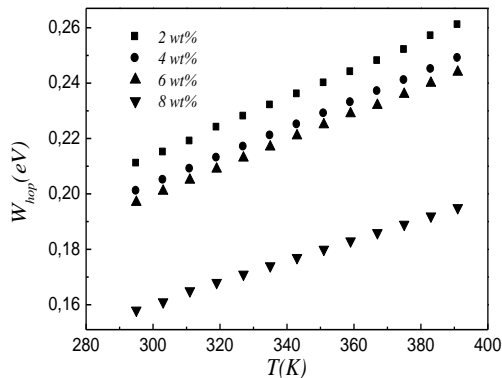


Fig. 3. Hopping distance vs. temperature for different concentrations of PPy loaded in PMMA matrix.

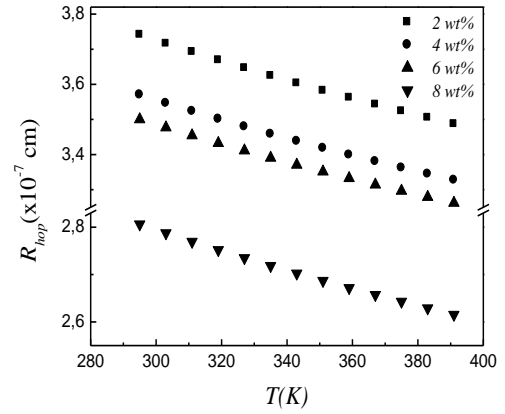


Fig. 4. Hopping energy vs. temperature for different concentrations of PPy loaded in PMMA matrix.

3.2 Frequency dependence of ac conductivity

Fig. 5 shows the log-log representations of the ac conductivity as a function of frequency at different temperatures, for two concentrations of PPy well above the percolation threshold (3.85%). From this figure we can distinguish two domains: at low frequencies and high temperatures the conductivity was approximately constant, and at high frequencies it depended on the frequency.

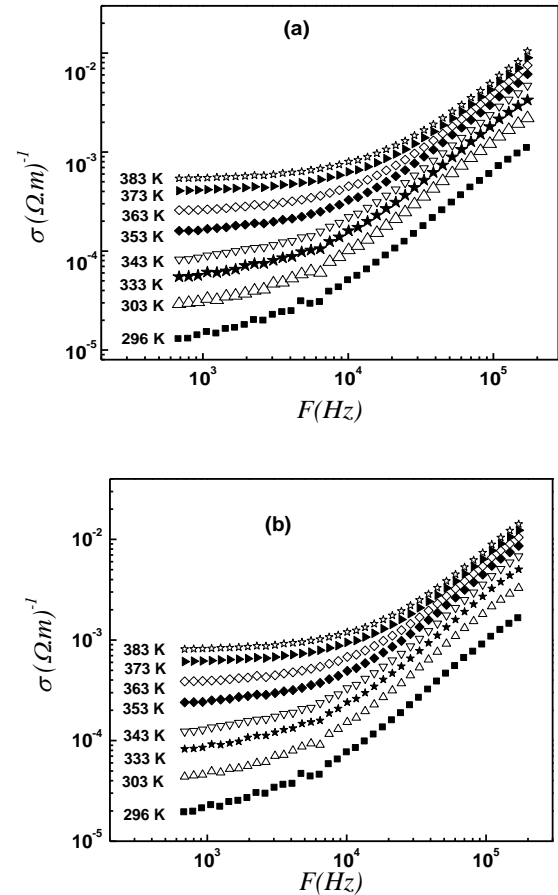


Fig. 5. Variation of the ac conductivity of: (a) PPy(6wt%)-PMMA and (b) PPy(8wt%)-PMMA samples, with frequency and temperature in the range of 296 – 383 K.

The electrical conductivity of many solids, including polymers, glasses and crystals, has been discussed by Jonscher [28] and Ngai [29]. They both suggested that the total conductivity, $\sigma_t(\omega)$, for different temperatures, can be expressed as:

$$\sigma_t(\omega, T) = \sigma_{dc}(T) + \sigma_{ac}(\omega, T) \quad (5)$$

where σ_{dc} and σ_{ac} are the *dc* and *ac* conductivities, respectively. At low frequencies, the conductivity would be dominated by a percolative behavior (the *dc* conductivity, as described in subsection 3.1) and at high frequency, a new contribution to the conductivity appears which is related to the σ_{ac} contribution of the conducting polymer resulting from the hopping process contribution to the conductivity [30-32]. This term varies according to the Jonscher's power law $\sigma_{ac} = A\omega^{s(T)}$ [33], where A is a characteristic constant and $s(T)$ a parameter that depends on the temperature and can present values between 0 and 1.

Various models, such as overlapping-large polaron tunnelling (QLPT) [34], quantum mechanical tunneling (QMT) [35] or correlated barrier-hopping (CBH) [36], have been proposed to describe the charge transfer mechanism. The frequency exponent $s(T)$ was used to characterize the electrical conduction mechanism in different materials. This value can be accessed by $s(T) = d \ln \sigma_{ac}(\omega, T) / d \ln \omega$. As shown in Fig. 6, the values of $s(T)$ were temperature-dependent with a linear relationship, indicating that there was a good agreement with the correlated barrier-hopping CBH mechanism [36]. In addition, the obtained values of $s(T)$ showed a decreasing tendency with temperature. For the range of temperatures studied, the highest value was obtained for the composite having 8 wt% fraction of PPy, whereas the lowest one originated from the composite having 6 wt%. It is clear from Figs. 4 and 6 that the hopping energy increased and the parameter s decreased, respectively, with increasing temperature; this correlation between the two parameters lets us know that the interactions between the dipoles decreased for PPy loadings above the percolation threshold ($\Phi > \Phi_c$). These analyses were confirmed by electric modulus and *ac* conductivity studies in conducting PPy/ethylene-vinyl alcohol copolymer composite films at low temperatures [37]. According to our results, it was found that the analysis of *ac* conductivity using the Jonscher's power law can be explained in terms of the hopping between localized states at the Fermi level [38].

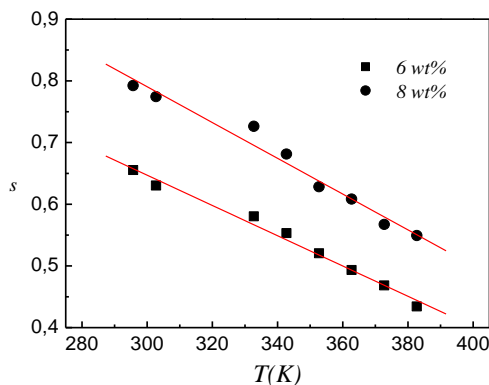


Fig. 6. Variation of the exponent s as a function of temperature for: PPy(6 wt%)-PMMA and PPy(8 wt%)-PMMA samples.

4. Conclusions

This study showed clearly that the *ac* conductivity behavior of the PPy/PMMA composites was frequency dependent and its variations follow the Jonscher's power law at high frequency. An analysis of the experimental data, using the *dc* conductivity, showed that hopping of charge carriers between localized states was the dominant conduction mechanism, and the physical Mott model, based on the classical hopping of charge over a barrier, predicts the decrease of the exponent $s(T)$ with increasing temperature that was observed.

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