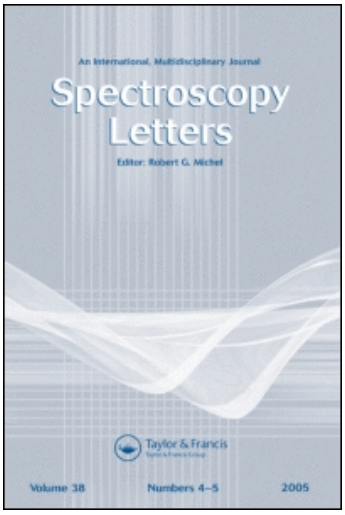

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Electrical Conductivity of Polypyrrole–Polymethylmethacrylate Composites Determined by Impedance Spectroscopy

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ABSTRACT Thermal properties of polypyrrole–polymethylmethacrylate (PPy–PMMA) composites are analyzed by differential scanning calorimetry (DSC). A decrease in the glass transition temperature Tg with the PPy concentration content reveals the increase of segmental motion. The ac conductivity of these composites is studied in frequency range of 600 Hz to 1 MHz and temperature interval 23°C to 110°C. The study depending on the frequency has highlighted three domains: at low frequencies the conductivity is independent of frequency; at intermediate frequencies, the ac conductivity follows a power law in frequency; and at high frequency the ac conductivity can be explained in terms of hopping process.

KEYWORDS composites, conducting polymer, polymethyl methacrylate polymer, polypyrrole, Dielectric properties, glass transition temperature, hopping process

INTRODUCTION

The conducting polymers constitute a family of organic conductors whose electric and mechanical properties are studied since the end of 1970. These materials are, still today, the subject of many researches on the fundamental level as well as on the level of their potential applications. In this family, one finds composite materials obtained from the dispersion of a conducting polymer in an insulating matrix. These composites are increasingly required in industry for their great potentialities of applications in various fields. The incorporation of conductive particles (carbon black, metal, etc.) into a polymer matrix modifies considerably the electrical conductivity of the composite,[1–3], but the presence of this type of load deteriorates considerably the mechanical characteristics of the composites compared with those of noncharged materials. The use of conducting polymers made it possible to obtain composites having at the same time a raised electric conductivity associated with good mechanical properties.[4] These materials have the effect of combining electric properties, of conducting polymers with the mechanical properties of the plastics.[5] The description of the

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mechanisms of electronic transport of these mixtures calls upon the concept of percolation.[6]

This work presents a study on thermal and electrical properties of the composites made up of polypyrrole (PPy) particles in an insulating matrix of polymethylmethacrylate (PMMA). Differential scanning calorimetry (DSC) has been used to estimate the glass transition temperature in these composite materials. The electrical properties were investigated by impedance spectroscopy in the frequency range 600 Hz to 1 MHz and in temperature range 23°C to 110°C. The ac conductivity of the composites will be analyzed using Jonscher's power law.

MATERIALS AND METHODS

Materials

PPy powder was obtained by doping intrinsic PPy with tosylate anion TS^-. The doping rate was controlled by the XPS technique and was found of order one sulfur (S) for four nitrogen (N), that is, one tosylate ion TS^- for four pyrrole monomers.[7] The average grain size of PPy is in the range 10–15 μm. The two powders, PMMA and PPy, are mixed in several proportions and pressed at 5,000 Kg/cm^2 and 150°C. After pressing, the samples are allowed to cool freely to room temperature to give solid disk-shaped samples ready for measurements. All disks had a diameter of 13 mm and 3–4 mm thickess. A set of samples was made with PPy weight concentrations (wt). The dc conductivities of the PPy and the PMMA matrix are 54 and 3×10^{-5} $(\Omega\,\mathrm{m})^{-1}$, and the densities are 1.20 and 1.14–1.20 g cm^{-3}, respectively. The glass transition temperature of PMMA polymer is $T_g \approx 115$ °C.

Differential Scanning Calorimetry Measurements

The differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC-50 (Kyoto, Japan) programmed between 20°C and 150°C at heating rate of 10°C/min and under nitrogen flow of 30 mL/min. The sample is placed in a platinum cell with a lid, and the reference cell is empty.

Electrical Measurements

The complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon^{**}$ was measured by using a Hewlett Packard Network Analyzer (model 4192 A, CA, USA). The relative permittivity ε' and the loss factor ε'' of the sample are determined from the admittance $Y^* = G + iB = iC_o\omega.\varepsilon^*$ 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 (Ω^{-1}), G is the conductance (Ω^{-1}), F is the frequency, ε_0 is the vacuum permittivity, and h and d are respectively the thickness and the diameter of the sample. The measurements were performed, in the frequency range 600 Hz to 1 MHz, under isothermal conditions for temperature ranging between 23°C and 110°C.

RESULTS AND DISCUSSION

DSC Results

DSC makes it possible to characterize the physical changes of states in the sample, in particular the glass transition. All measurements were carried out on samples of mass between 2.5 and 8 mg. The determination of the glass transition temperature was carried out according to the method of the tangents.[8] This transition is characterized by a variation of the degree of freedom of the macromolecules in the PMMA matrix in the amorphous zones under the effect of an increase in the temperature.[9] Figure 1 shows the DSC thermogram of the four contents in PPy in the temperature range from 23°C to 140°C. It is noted that the glass transition temperature T_g decreases by 115°C (wt = 0%) and 85°C (wt = 8%). This behavior was also observed on composites PCV-PMMA.[10] The authors attributed T_g to miscibility between the two polymers. It is known that the

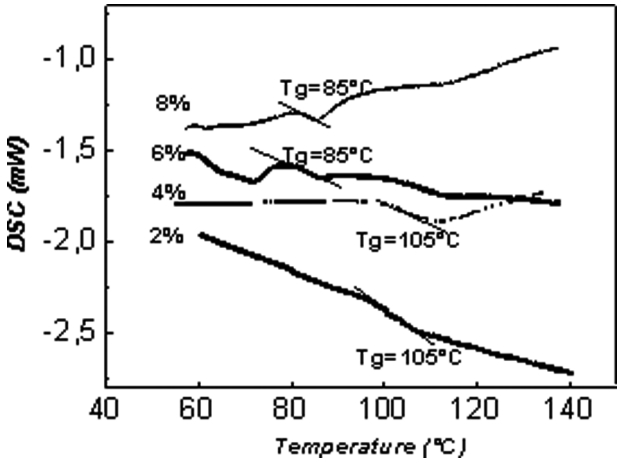

FIGURE 1 DSC measured T_g of PMMA-PPy composites for various concentrations.

presence of plasticizer in the PMMA matrix results in a reduction of viscosity of the molten state and a fall in the glass temperature T_g.[11]

Room Temperature Electric and Dielectric Properties

The dielectric permittivity ε^* of PPy–PMMA composites is plotted in Fig. 2 as a function of frequency for various PPY weight concentrationsat ambient temperature. The dielectric response of the two concentrations 6 and 8 wt%, which are higher than the conduction threshold 4%, is an abnormal low frequencies dispersion characterized by two linear regimes in the low and the high frequency regions.[12] These two modes are separated by an intermediate regime covering a frequency range of a few decades.

The total conductivity $\sigma_{tot}(\omega, T)$ at a given temperature over a wide range of frequency can be written as [13]:

$$\sigma_{tot}(\omega, T) = \sigma_{dc}(T) + \sigma_{ac}(\omega, T) \quad (1)$$

where $\sigma_{dc}(T)$ is the dc conductivity and is $\sigma_{ac}(\omega, T)$ the ac conductivity. The total conductivity $\sigma_{tot}(\omega, T)$ of the PPy–PMMA composites is plotted in Fig. 3 as a function of frequency for two concentrations of PPy at 6% and 8%. At low frequencies (domain 1), the conductivity does not almost depend on the frequency and is dominated by a percolative behavior.[14] The dc conductivity obtained from the extrapolation to $\omega = 0$ can be expressed theoretically as $\sigma_{dc} \propto (\phi - \phi_c)^t$ where ϕ is the volume faction of the conductor, ϕ_c is the percolation threshold, and t is the critical exponent. Because the densities of the polymer PMMA and PPy are similar, the mass fraction, wt, and the volume fraction, ϕ, of the PPy in the polymer PMMA are almost the same. For PMMA–PPy, the value of the exponent t is 1.95,[7], which is in good agreement with the literature.[15,16]

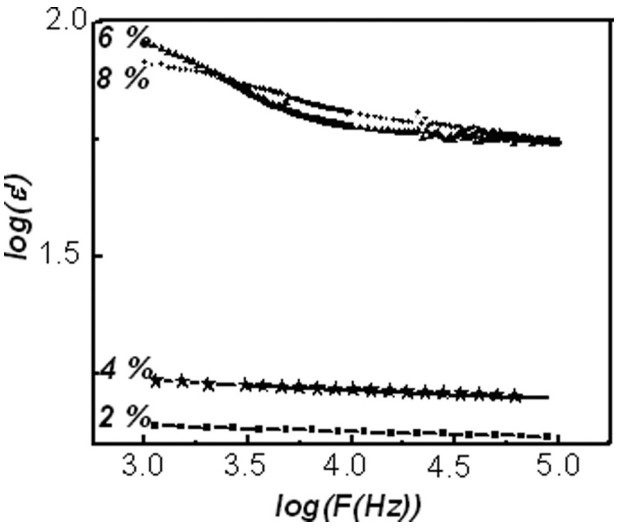

FIGURE 2 Permittivity versus frequency of composites with given weight concentration of PPy at room temperature (23°C) in a log–log plotting.

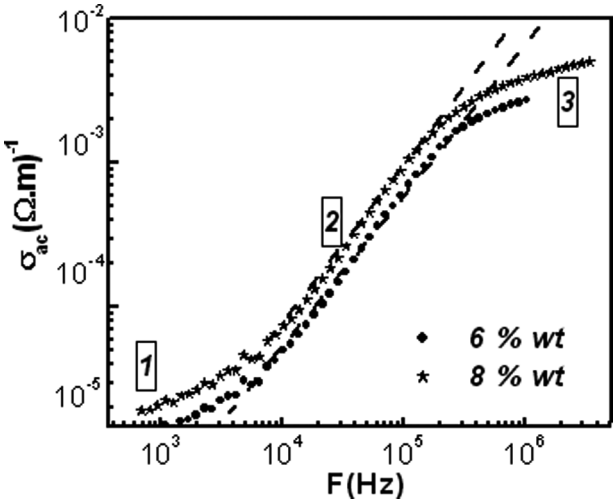

FIGURE 3 The ac conductivity versus frequency of composites with given weight concentration of PPy at room temperature (23°C).

At intermediate frequencies (domain 2), the ac conductivity increases following power law behavior such that [13]

$$\sigma_{ac}(\omega, T)) \propto \omega^{S(T)}, \quad (2)$$

where *s(T)* is the power exponent depending on the temperature $(0 \leq s \leq 1)$. The obtained values of exponent s at room temperature, for all PPy concentrations, are $0.70 \leq s \leq 1$. These materials obey the universal law of Jonscher. The value of the exponent s close to 1 traduces a completely correlated system.[13]

At high frequency (domain 3), a new contribution appears, which is related to the σ_{ac} contribution of intrinsic hopping conductivity in the composite material.[17] Belhadj-Mohamed et al.[7] have studied the dielectric response of PPy samples and PPY–PMMA composites in the radio frequency and microwave range with PPy concentration $p = 6$–12% by weight. It is found that the conductivity has a rather complicated behavior. This study has enabled

identification of the three domains: at low frequencies the conductivity is independent of frequency; at intermediate frequencies a relaxation phenomenon occurs; at high frequencies the conductivity depends on frequency where an ac conductivity contribution is observed.

Temperature Dependence of Conductivity

The variation of ac conductivity as a function of the frequency at different temperatures for the PPy weight concentrations 6% and 8% is reported in Figs. 4 and 5, respectively. At low frequencies, the conductivity of these composites remains constant but is strongly dependent on temperature; this is due to the dc conductivity contribution: $\sigma_{\text{tot}}(\omega, T) \approx \sigma_{\text{dc}}(T)$. When the frequency is increased, the ac conductivity is found to obey a power relation $\sigma_{\text{tot}}(\omega, T) \approx \sigma_{\text{ac}}(\omega, T) \propto \omega^{S(T)}$. The values of s derived by least squares fitting of the data in the approximately linear region have been evaluated. Table 1 represents the dependence of the frequency exponent s on temperature. It should be noted that the values of s are found to be less than unity and decrease with rise of temperature. This behavior can be explained in terms of the correlated barrier hopping model proposed by Elliott[18] in which the charge transport between localized states is mainly due to hopping over the potential barrier separating the states. At high frequencies ($F > 2 \times 10^5$ to 4×10^5 Hz), the shape of the curves $\sigma_{\text{tot}}(\omega, T)$ change due to the intrinsic hopping conductivity.[15]

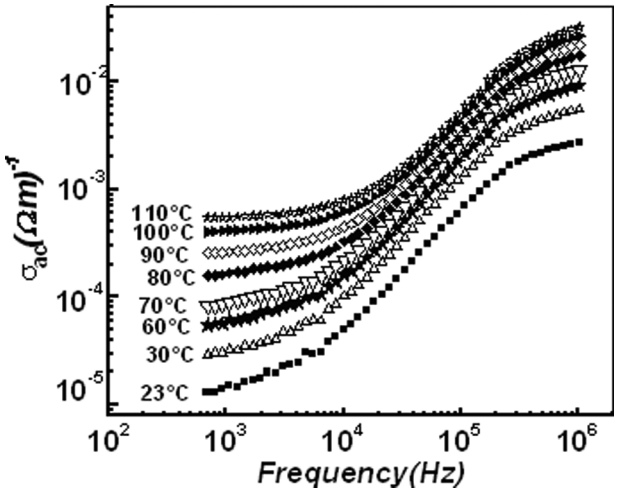

FIGURE 4 Frequcency dependence of ac conductivity for the PPy–PMMA composite containing 6 wt% PPy at various temperatures.

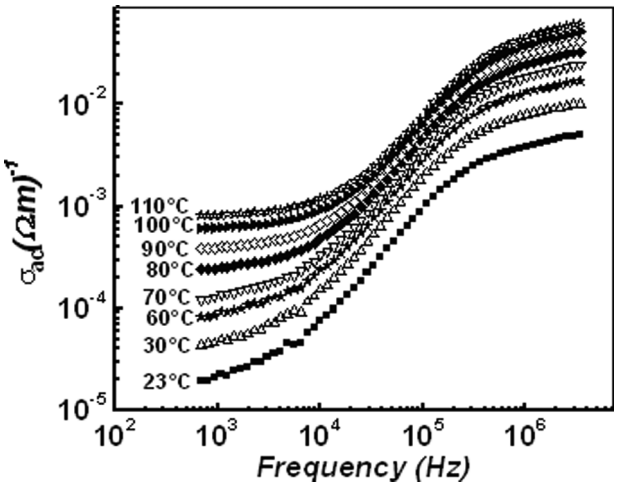

FIGURE 5 Frequcency dependence of ac conductivity for the PPy–PMMA composite containing 8 wt% PPy at various temperatures.

The extrapolation of the frequency-dependent electrical conductivity to $\omega = 0$ was used to determine the values of dc conductivity at different temperatures. Figure 6 is a plot of the weight concentration wt dependence of the dc conductivity for the PPy–PMMA composites at a constant temperature $T = 110$°C. The conductivity of the composite increases only after a particular value of weight concentration of PPy, known as the electrical percolation threshold. The percolation threshold is visible, at a critical weight concentration wt_C ($4\% \leq \text{wt}_C \leq 5\%$) where the conductivity begins to increase abruptly.[9] It is well-known that the value depends strongly on the shape of the conducting inclusions,[12,13] on the conductor particle structure and its morphology,[14] as well as on the other materials processing.

In general, for polymer composite materials, dc conductivity increases exponentially with temperature indicating that the conductivity is a thermally activated process. Mathematically, it can be expressed by the well-known Arrhenius relation as

$$\sigma_{\text{dc}} \propto \exp\left[-\frac{E_a}{K_b T}\right] \tag{3}$$

TABLE 1 Values of the Exponent s of Two Samples

T (°C)	60	80	100	110
S (wt = 6%)	0.58	0.58	0.49	0.43
S (wt = 8%)	0.72	0.63	0.56	0.55

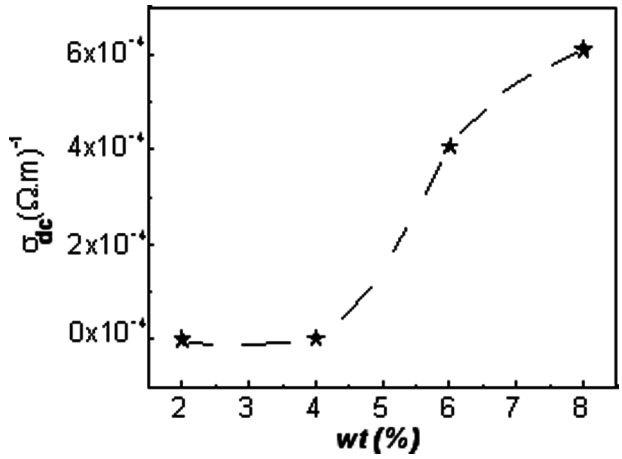

FIGURE 6 The variation of dc conductivity as function of the weight concentration of PPy at 110°C.

where E_a is the activation energy, T is the absolute temperature, and k is Boltzmann's constant. These parameters are of significance to differentiate the nature of various conduction mechanisms. Figure 7 is a plot of $\log(F_{max})$ versus $1/T$ for different weight concentrations. By least squares fit of our data, we obtain the slope of Arrhenius plot with a linear correlation coefficient r_{co} higher than 0.99. The values of the activation energy for various PPy concentrations are reported in Table 2. The values of E_a, as the glass transition temperature T_g, decrease slightly when PPy is present inside the PMMA polymer matrix, which means that the PPy particles do not interact or only weakly with the chain segments of the macromolecules in the PMMA polymer. Further, it gives us an understanding that there is a poor bonding between the polymer matrix and the PPy particles. The study on 17 polymers made by Wang et al.[19] concluded the correlation between E_a and T_g by using the Simha–Boyer expression.[20] They have also discussed the influence of the factors such as composition, molecular weight, branching, and microstructure on the activation energy and the glass transition temperature of polymer materials.

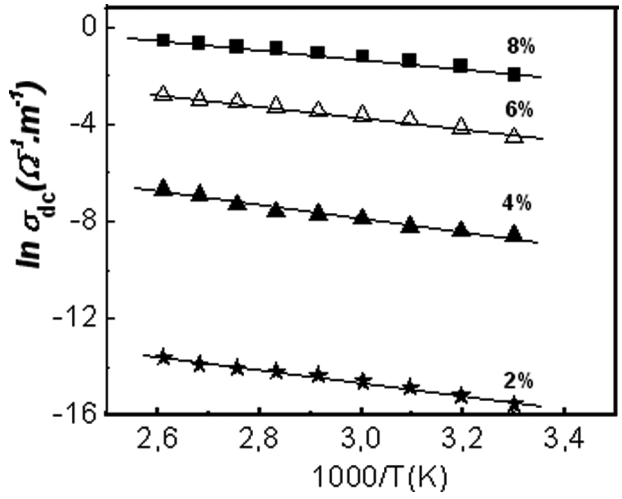

FIGURE 7 Arrhenius plot of log dc conductivity versus the inverse of temperature for the PPy–PMMA composites. The linear best fittings are also shown.

TABLE 2 PPy Weight Concentration Dependence on the Activation Energy

PPy (wt%)	2	4	6	8
E_a (eV)	0,23	0,22	0,22	0,18

CONCLUSION

In this work, we report thermal and dielectric properties of the composites consisting of polypyrrole (PPY) particles in a polymethacrylate (PMMA) matrix. The thermal (DSC) study carried out on this series of samples shows that the glass transition temperature T_g decreases slightly with the concentration on PPY in PMMA. This result indicates that the PPy particles do not interact with the chain segments of the macromolecules in the PMMA polymer, or only weakly. The study of ac conductivity depending on the frequency allowed us to identify different mechanisms of the conduction in the PPy–PMMA composites. At low frequencies, the conductivity is dominated by a percolative behavior, and at intermediate frequencies it obeys the Jonscher power law. At high frequency, a new contribution appears, which is related to the intrinsic hopping conductivity in the composite.

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