

*Full Length Research Paper*

## Thermal and dielectric properties of polypyrrole-poly(methyl methacrylate) nanocomposites

M. E. Achour<sup>1\*</sup>, A. Droussi<sup>1</sup>, D. Medine<sup>2</sup>, A. Oueriagli<sup>3</sup>, A. Outzourhit<sup>3</sup>, A. Belhadj Mohamed<sup>4</sup> and H. Zangar<sup>4</sup>

<sup>1</sup>Département de Physique, Faculté des Sciences, Equipe: Systèmes, Propagation et Caractérisation des Matériaux (LASTID), B.P:133, 14 000 Kénitra, Morocco.

<sup>2</sup>Institut National de la Recherche Scientifique INRS, 1650, Bd Lionel Boulet C.P 1020, Varennes (Québec) J3X 1S2, Canada.

<sup>3</sup>Laboratoire de Physique des Solides et des Couches Minces, Semlalia, Marrakech, Morocco.

<sup>4</sup>Département de Physique, Faculté des Sciences, Campus Universitaire 2092 El Manar, Tunis, Tunisia.

Accepted 16 December, 2010

**Thermal properties of the polypyrrole-poly(methyl methacrylate) (PPy)-(PMMA) composites were analyzed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). A decrease in the glass transition temperatures  $T_g$  with the PPy concentration content reveals the increase of segmental motion. Dielectric properties of these composites were studied in the frequency range between 100 Hz and 100 KHz at room temperature for various weight percentage of PPy. The results of the spectra of complex permittivity obey power laws of Jonscher. The values of the exponents  $n$  and  $p$  are close to 1, which corresponds to a fully correlated system.**

**Key words:** Composites, dielectric properties, percolation threshold, conducting polymer.

### INTRODUCTION

Conducting polymers constitute a family of organic conductors whose electric and mechanical properties have been studied since the end of 1970. These materials are still the object of many investigations on the fundamental level as well as on the level of their potential applications (Freund and Deore, 2007; Rubinson and Mark, 2002; Skotheim et al., 1998). This class of materials also includes composite materials obtained by dispersing a conducting polymer in an insulating matrix. These composites are increasingly used in industry for their great potential applications in various fields.

Traditionally, a conducting load, such as carbon black, metal powder, etc. ensures conductivity in the composites,

but the presence of this type of load deteriorates considerably the mechanical characteristics of the composites compared to those of the non-charged matrix. The use of conducting polymers made it possible to obtain composites having at the same time, a high electronic conductivity associated with good mechanical and often optical properties of the polymer host (Das et al., 2007; Wang and Feng, 2002; Ekramul et al., 2005). These materials have the effect of combining the electrical properties conducting polymers and the mechanical properties of the plastics. The description of the mechanisms of electronic transport in these mixtures calls upon the concept of percolation.

This work presents a study on the dielectric and thermal, that is thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) properties of the composites made up of polypyrrole (PPY) particles in an insulating matrix of polymethacrylate (PMMA). The first objective of this work is to analyze these composites by using impedance spectroscopy in the frequency range of 5 to 13 MHz. The observed dielectric response of the

\*Corresponding author. E-mail: sachoum@yahoo.fr.

**Abbreviations:** TGA, Thermal gravimetric analysis; DSC, differential scanning calorimetry; PPy, polypyrrole; PMMA, poly(methyl methacrylate).

composites will be examined using the model of Jonscher (1983). The second objective is to study the influence of load factor (PPY) on some thermal properties.

## MATERIALS AND METHODS

### Materials

The samples investigated in this study are particles polypyrrole with a diameter of 20-40  $\mu\text{m}$ , dispersed in insulating poly(methyl methacrylate) (PMMA) having conductivity of order  $\sigma_{DC} \approx 0.03 \cdot 10^{-15} (\Omega \cdot \text{cm})^{-1}$  with the glass transition temperature  $T_g \approx 115^\circ\text{C}$  (Sun, 2004).

### DSC and TGA measurements

The DSC was carried out using a Shimadzu DSC-50 differential scanning calorimeter programmed between 20 and 500°C at heating rate of 10°C/min and under nitrogen flow of 30 ml/min. The sample was placed in an aluminum cell or plate with a lid and the reference cell was empty. TGA was carried out using a Shimadzu TGA-50 Thermo gravimetric analyser. The measurements were taken under an atmosphere of nitrogen with a flow rate of 30 ml/min, at temperatures between 20 and 800°C and a heating rate of 5°C/min. The sample was placed in a platinum cell.

### Dielectric measurements

The complex permittivity function  $\epsilon^* = \epsilon' - i\epsilon''$ , was measured using a Hewlett Packard network analyzer (Model 4192A). The relative permittivity  $\epsilon'$  and the loss factor  $\epsilon''$  of the sample were determined from the admittance  $Y^* = G + iB = iC_0 \omega \epsilon^*$  of the equivalent circuit leading to  $\epsilon' = 2h \cdot B / \epsilon_0 \cdot d^2 \pi^2 F$  and  $\epsilon'' = 2h \cdot G / \epsilon_0 \cdot d^2 \pi^2 F$ , where B is the susceptance ( $\Omega^{-1}$ ), G is the conductance ( $\Omega^{-1}$ ), F is the frequency,  $\epsilon_0$  is the vacuum permittivity, h and d are the thickness and the diameter of the sample, respectively. The measurements were performed in the frequency range from 5 Hz to 13 MHz, under isothermal conditions for temperatures ranging between 23 and 110°C.

## RESULTS AND DISCUSSION

### Thermal study

Differential scanning calorimetry (DSC) makes it possible to characterize the physical changes of states taking place 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 (Abu-Surrah et al., 1997). 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 (Baskaran et al., 2005). Figure 1 shows

the DSC thermogram of the four contents in PPy, in the temperature range from 23 to 140°C. It is noted that the glass transition temperature  $T_g$  decreases by 115°C (= 0%) à 85°C (= 8%). This behaviour was observed on composites PCV-PMMA (Bensemra et al., 2002). The authors regarded  $T_g$  as a sign of miscibility between the two polymers. It is known that the presence of plasticizer in the PMMA matrix results in a reduction of viscosity of the molten state and a fall in the glass temperature  $T_g$  (Verrier, 1995). Thermo-gravimetric analysis (TGA) measurements were carried out using PMMA/PPY samples. We reported in Figure 2, the evolution of the relative weight loss of various concentrations  $\phi$ , obtained by TGA, as a function of the temperature. It is noted that the thermal degradation for all the concentrations starts near 300°C and the speed of degradation depend slightly on the PPy contents in the matrix. In addition, introduction of PPy into matrix PMMA to concentrations lower than 8% does improve the thermal resistance.

### Dielectric behaviour

Figures 3a and b present the variations of the real and imaginary parts of the complex permittivity as a function of frequency for four concentrations of polypyrrole. The dielectric response of the two concentrations 6 and 8 with respect to percentage, which are higher than the conduction threshold (Das et al., 2007)  $\phi_c$  ( $\phi_c \approx 3.85\%$ ), is an abnormal low frequencies dispersion characterized by the absence of any loss peaks and by two linear regimes in the low and the high frequency regions. These two modes are separated by an intermediate regime covering a frequency range of a few decades.

The dielectric response obtained for the concentrations 2 and 4 with respect to percentage, which are lower than  $\phi_c$ , is characterized by  $\epsilon'(F)$  spectra presenting almost horizontal plateaus. The loss spectra  $\epsilon''(F)$ , on the other hand, do not exhibit a clear dipolar relaxation peaks observed in insulating media. This is attributed to the fluctuations observed in the  $\epsilon''(F)$  spectrum for these two concentrations. Figures 4a and b represent the variations of  $\epsilon'$  and  $\epsilon''$  as a function of frequency for the composites PPy/PMMA for two concentrations in PPy 6 and 8 with respect to percentage. They show an abnormal low frequency dispersion characterized by two linear regimes. These two abnormal dispersion regimes can be described by the fractional power laws of Jonscher (1983).

$$\epsilon'(F) \propto \epsilon''(F) \propto F^{-p} \quad \text{for } F \ll F_c \quad (1)$$

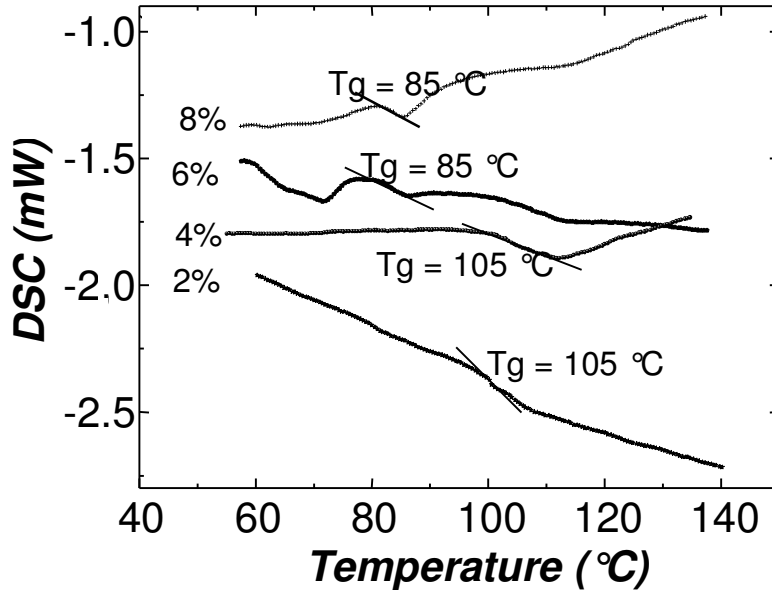


Figure 1. DSC measured  $T_g$  of PMMA/ PPy composites for various concentrations.

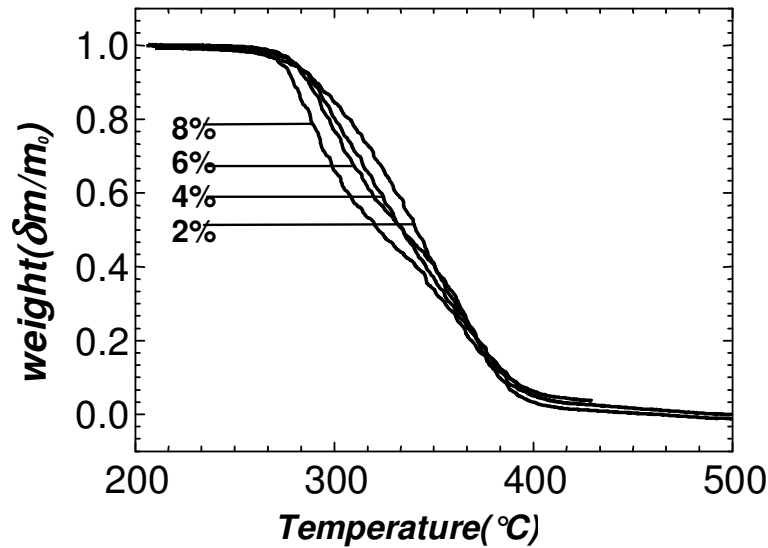


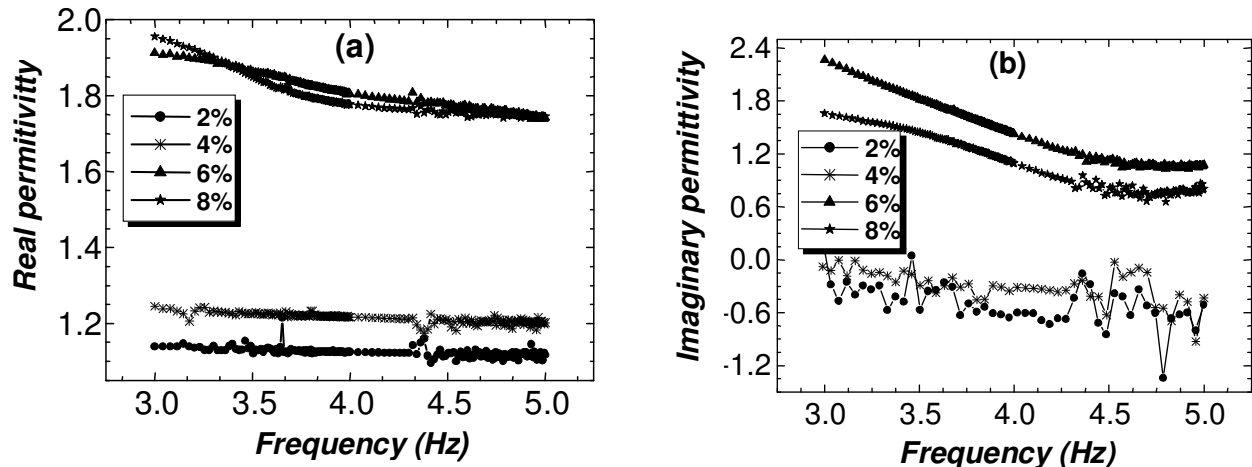
Figure 2. TGA curves of of PMMA/PPy composites for various concentrations.

$$\epsilon'(F) \cdot \epsilon_\infty \propto \epsilon''(F) \propto F^{n-1} \quad \text{for } F \gg F_c \quad (2)$$

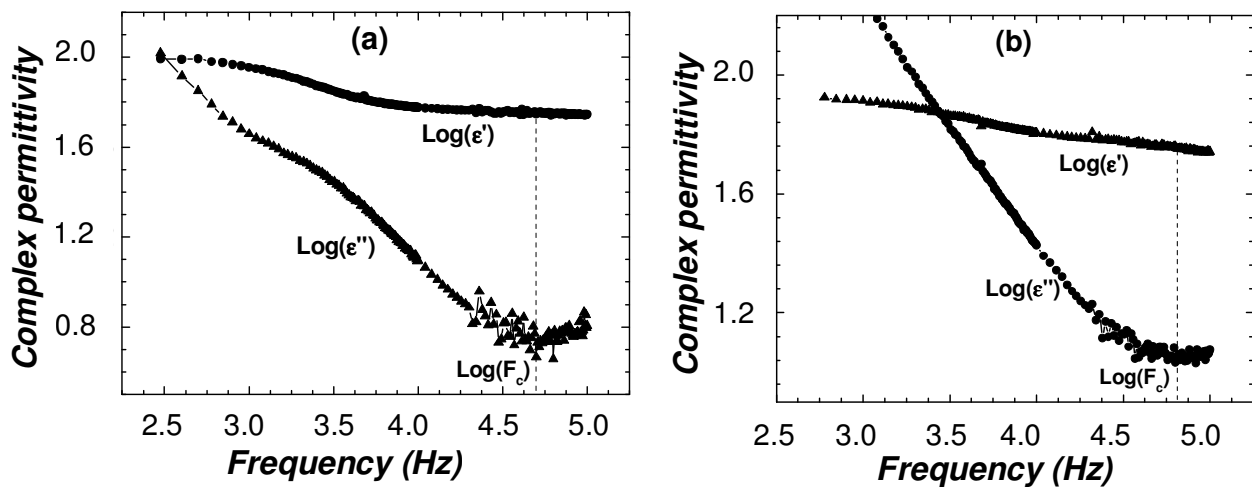
where  $F_c$  is the cross-over frequency between the two power laws and  $n$  and  $p$  are the fractional exponents. This theory describes the so-called anomalous low frequency dispersion, first identified by Jonscher. The

limit  $p = 0$ , that is, also  $n=0$ , corresponds to complete screening, as in free system, while  $p = 1$  and  $n = 1$  corresponds to the absence of screening, as it would be the case with immobile charges which are unable to follow local potential changes,  $\phi_c$ .

The variable exponents  $n$  and  $p$  are given by the slopes of best fit straight lines representing  $\log \epsilon''$  as a function of  $\log F$ , respectively for  $F \ll F_c$  and  $F \gg F_c$ . This



**Figure 3.** Variation of  $\epsilon'$  (a) and  $\epsilon''$  (b) with frequency  $F$  for the composites PMMA-PPY for various concentrations and at ambient temperature.



**Figure 4.** Variation of  $\epsilon'$  and  $\epsilon''$  as a function of frequency  $F$  for the PMMA-PPY composites and for the concentrations 6% (a) and 8% (b) greater than the conduction threshold.

universal behaviour allows us to determine the energy ratio and the parameter  $z$  which are given by:

$$\text{Energy loss/Energy stored} = \frac{\epsilon''}{\epsilon'} = \frac{1-z}{z} \cotan(n\pi/2) \quad (3)$$

In the frequency region above, the loss peaks is observed for our samples (Figure 3) which is referred to as the 'universal' law developed by Jonscher. The originality is the independence of frequency, whereas from Debye ideal theory, the same equation (Equation 5) is frequency dependent and is equal to  $2\pi F\tau$ . In contrast to the classical Debye response, which comes about due to a system of non-interacting permanent

dipoles (Rubinson and Mark, 2002; Skotheim et al., 1998), the dielectric response arises due to a highly dispersive and lossy system yielding a frequency independent ratio. This result has nothing whatsoever to do with any particular physical mechanism or interpretation. It is the consequence of the principle of causality, on which Kramers-Kronig theory is based and its applicability testifies to the self-consistency of the result obtained experimentally (Belhaneche-Bensemra and Bedda, 2001). The results obtained for  $n$ ,  $p$ ,  $z$  and  $\cotan(n\pi/2)$  for samples PPY (6%)/PMMA and PPY (8%)/PMMA are given in Table 1.

These materials obey the universal law of Jonscher. The value of exponent  $n$  is close to 1, which corresponds

**Table 1.** Values of the parameters for the PPY/PMMA samples for two concentrations in polypyrrole 6% and 8% (in weight percent).

$\phi$ (%)	p	n	cotan( $n\pi/2$ )	z
Sample	6	0.85	0.79	0.62
Sample	8	0.80	0.73	0.68

to a completely correlated system (El Malhi et al., 1999). The exponent p is between 0.53 and 0.98 and is in agreement with the experimental values already obtained (Jonscher, 1983).

### Conclusion

In this work, some dielectric and thermal properties of the composites consisting of polypyrrole (PPY) particles in a polymethacrylate (PMMA) matrix is reported. The study under thermal stress (TGA, DSC) carried out on this series of samples shows that the thermal parameters such as the glass transition temperature and the degradation rate depends on the mass concentration on PPY in PMMA. In addition, the dielectric study shows that the response of these materials is abnormal low frequency dispersion, for concentrations higher than the threshold of conduction, due to the localized or almost free charge carriers.

### ACKNOWLEDGMENTS

This work was supported by the program PCSI (AUF, Ref.: 6301PS445) and the Integrated Action Programme Morocco-Tunisia (04/TM/38). Thanks are due to Pr. L. H. DAO (INRS, Varennes, Canada) for TGA and DSC experiments.

### REFERENCES

- Abu-Surrah AS, Wursche R, Rieger B (1997). Polyketone Materials: Control of Glass Transition Temperature and Surface Polarity by Co- and Terpolymerization of Carbon Monoxide with Higher 1-Olefins. *Macromol. Chem. Phys.*, 198(4): 1197–1208.
- Baskaran R, Selvasekarapandian S, Kuwata N, Kawamura J, Hattori T (2006). Conductivity and thermal studies of blend polymer electrolytes based on PVAc-PMMA. *Solid State Ionics*, 177 (26-32): 2679-2682.
- Belhaneche-Bensemra N, Bedda A (2001). Analysis of structure-properties relationship of PVC-PMMA blends. *Ann. Chim.*, 26 (3): 79-90.
- Das RN, Lin HM, Papathomas KI, Lauffer, JM, Card N, Markovich VR (2007) Electronic Components and Technology Conference (ECTC), apos; 07. Proceedings, 57th: 316-322.
- El Malhi M, Achour ME, Lahjomri F, Bensalah Y (1999). Dielectric response in carbon black-epoxy resin composites. *J. Mater. Sci. Lett.*, 18: 613-616.
- Freund MS, Deore BA (2007). Self-Doped Conducting Polymers, Edition: John Wiley & Sons.
- Jonscher AK (1983). *Dielectric Relaxation in Solids*, Edition: Chelsea Dielectric, London.
- Rubinson JF, Mark H (2002). *Conducting Polymers and Polymer Electrolytes: From Biology to Photovoltaics*, Edition: American Chemical Society.
- Skotheim TE, Eisenbaumer RL, Reynolds JR (1998). Edition: Handbook of Conducting Polymers, ed., M. Dekker.
- Skotheim, TA, Eisenbaumer, RL, Reynolds JR (1998) Handbook of Conducting Polymers, 2nd Edition, Marcel Dekker, New York.
- Verrier P (1995). Plastifiants. *Techniques de l'Ingénieur*, A 3231: 1-12
- Wang XS, Feng XQ (2002). Effects of thickness on mechanical properties of conducting polythiophene films *J. Mater. Sci. Lett.*, 21(9): 1573-4811.