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Interfacial and space charge dielectric effects in polypyrrole/ZnO composites

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Interfacial and space charge dielectric effects in Polypyrrole/ZnO composites

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Polypyrrole/zinc oxide composites were studied by Broadband Dielectric Spectroscopy in the frequency range 10 mHz to 1 MHz for temperatures ranging from 15 K to room temperature. Lowering temperature, the dc conductivity was suppressed revealing underlying dielectric relaxation mechanisms. For 20, 30 and 40 wt % ZnO composites, a relaxation was detected in the vicinity of range $10^4 - 10^5$ Hz. Its typical mean relaxation time and its concentration dependence are compatible with Sillar's

model for interfacial polarization in heterogeneous matter. At high ZnO concentration, a low-frequency relaxation also appeared around 0.01 - 10 Hz, stemming from space charge polarization. The shift of the relaxation upon temperature provides an insight to the dynamics of relaxing charge entities. Composites consisting of 10 wt % ZnO are most suitable optoelectronic material, as they combine good electrical conduction, low capacitance effects and ohmic sample-electrode contacts.

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1 Introduction The search for novel functional optoelectronic material has emerged significant progress in exploring the properties of electron conducting polymers [1-3] and as well as metallic or semi-conducting polymers, blends and composites [4, 5]. Among many different experimental schemes used for this purpose, Broadband Dielectric Spectroscopy (BDS) has a unique feature studying electrical conductivity and capacitance over a broad frequency range. [6-11]. Carriers created in polypyrrole (PPy) by photoexcitation recombine much faster than those produced in inorganic semiconductors. Polymer/inorganic semiconductor composites can achieve tuneable electrooptic properties upon composition: photo-generated excitons are dissociated at the polymer/inorganic semiconductor interface with electrons and holes being transferred to the inorganic and to the polymer phases, respectively. ZnO is a transparent metal oxide, with a direct energy gap of 3.4 eV (which is comparable to a 2.4 eV energy gap for PPy). in the UV range because of electron excitations from the top of the valence band to the bottom of the conduction band and exhibits a high exciton coherence (60 eV), is biocompatible and low-cost manufacturing, yielding applica-

tions such as solar cells [12], fuel cells [13], chromatic sensors [14], microwave absorption layers [4], etc.

The present work addresses the problem of distinguishing between the intense dc-conductivity, capacitance and dielectric loss. Cooling affects dc hopping conductivity more drastically than dielectric relaxation processes. We exploit these different dependencies by performing BDS at temperature ranging from room temperature (RT) to 15 K, in order to discriminate and study different contributions of the broad-frequency band spectra.

2 Experimental details The protocol for the preparation of PPy/ZnO x% w/w composites has been published earlier [15, 16]. SEM imaging evidences about the incorporation of ZnO into PPy [15, 16]. Disc-shaped pellets with diameter 13 mm and thickness 1.5 mm had their parallel surfaces covered with silver paste to ensure good electrical contact with the electrodes of the sample holder for BDS. The liquid helium cryostat (ROK, Leybold-Hereaus) could establish isothermal conditions for temperatures between 5 K and RT with an accuracy of 0.01K. BDS measurements were performed in the frequency range

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between 1 mHz and 1 MHz with a Solartron SI 1260 Gain-Phase Frequency Response Analyzer, and a Broadband Dielectric Converter (BDC, Novocontrol). Data were collected by employing the the WinDeta (Novocontrol) software [17, 18].

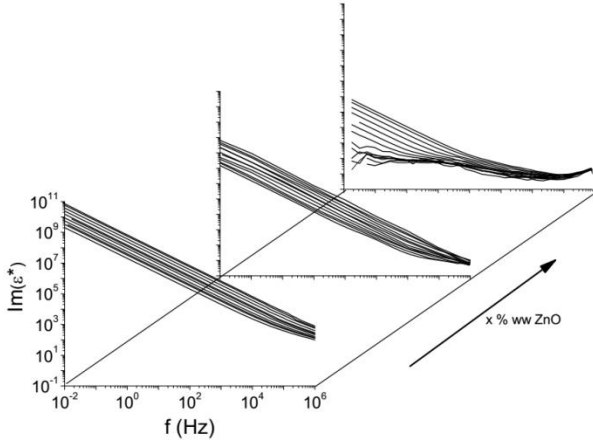


Figure 1 Imaginary part of the complex permittivity vs frequency for 20, 30 and 40 wt % ZnO composites (front to back diagrams, respectively). In each diagram, isotherms range from room temperature to 15 K (from upper to lower curves, respectively).

3. Results and discussion

3.1 Cooling as a simple tool for revealing relaxation mechanisms in conducting polymers Isotherms of the imaginary part of the dielectric permittivity vs are depicted in Fig. 1. On increasing the ZnO loading, the dc conductivity σ_0 is suppressed and and, above 10 wt % ZnO, a dielectric relaxation mechanism close to 10^5 Hz (HF relaxation) appears. A left hand side tail of another relaxation peak with maximum beyond the frequency range of our instrumentation is detected and cannot be explored in the present study. For 30 and 40 wt % ZnO composites an additional strong relaxation is positioned around 0.1 - 10 Hz (LF relaxation). Its time scale ranges from about 0.1 to 10 s, which is typical for space charge relaxation. Isotherms were fitted by:

$$\text{Im}(\epsilon^*) = \frac{\sigma_0}{\epsilon_0 2\pi f^n} + \frac{\Delta\epsilon_{\text{LF}}}{\left(1 + (f/f_{0,\text{LF}})^a\right)^{b_{\text{LF}}}} + \frac{\Delta\epsilon_{\text{HF}}}{\left(1 + (f/f_{0,\text{HF}})^a\right)^{b_{\text{HF}}}} \quad (1)$$

where LF and HF refer to the above mentioned relaxation mechanisms, respectively, $\Delta\epsilon$ is the intensity of the relaxation mechanism, a and b are fractional exponents and f_0 is a parameter that coincides with the peak maximum frequency when $b=1$. Each relaxation peak is assumed to obey the Havriliak - Negami (H-N) model [19], where a and b are symmetric and asymmetric broadening parameters, respectively. For a Debye peak, the parameters amount to unity ($a=b=1$) [20, 21].

The contribution of the first term of the sum appearing in eq. (1) becomes weaker on cooling and, subsequently, dielectric relaxation mechanisms, appearing as ‘knees’ in log-log plots of $\text{Im}(\epsilon^*)$ vs frequency (Fig. 1) are revealed. At least one dielectric loss peak is detected (one is beyond the available upper frequency limit). In the present work, we shall only refer to relaxations within the working frequency range of the available instrumentation. In Fig. 2, typical fits of eq. (1) to the data points collected at a given temperature for 20, 30 and 40 wt % ZnO composites are presented. The frequency f_{max} , where a relaxation peak has its maximum, is plotted as a function of reciprocal temperature (Fig. 3). Relaxation HF is activated around 105 Hz and appears in 20, 30, 40 wt % ZnO composites, while relaxation LF if detected in 30 and 40 wt % ZnO composites is appears around 10 Hz. $\log f_{\text{max}}$ vs reciprocal temperature of relaxations HF and II, respectively, are depicted in Fig. 3.

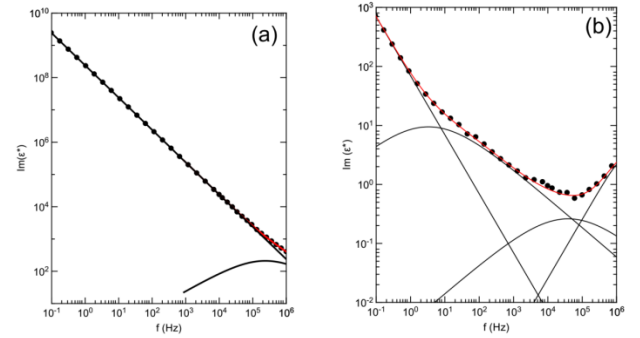


Figure 2 Spectra recorded at 205 K for 20 and 40 wt % ZnO composites (diagrams (a) and (b), respectively). Straight line is the dc conductivity component. The components of the fitting curves (straight lines and H-N relaxation peaks are also depicted. HF relaxation appears in both spectra, while LF relaxation is present for 30 and 40 wt % ZnO. The fitting parameters are: (a): $\log\sigma_0=-3.874$ (σ_0 in S/cm), $n=1.000$, $\log f_0=5.63$ (f_0 in Hz), $\Delta\epsilon=422$, $a=1$, $b=1$; (b): $\log\sigma_0=-9.696$ (σ_0 in S/cm), $n=0.998$, $\log f_0=1.34$ (f_0 in Hz), $\Delta\epsilon=422$, $a=0.5$, $b=1$ (left peak, $\log f_0=4.76$ (f_0 in Hz), $\Delta\epsilon=1.3$, $a=0.5$, $b=1$ (middle peak); the left peak positioned beyond the upper measuring frequency limit has been added to match the high frequency tail.

3.2 Interpretation via the Sillars theory for heterogeneous matter. The variation of composition has little effect on the position of relaxation HF. PPy/ZnO composite can be described approximately as a heterogeneous system consisting of the matrix (phase D) and randomly dispersed spheres (phase S). The inter-sphere spacing is assumed to be larger than the sphere’s radius. Labeling σ_j and ϵ_j , the dc conductivity and the relative dielectric constant, respectively, of phase j ($j=M, S$), the relaxation time for interfacial polarization due to electric inhomogeneity of the composite, has been estimated by Sillars [22]:

$$\tau = \frac{\varepsilon_0 [2\varepsilon_M + \varepsilon_S - v_S (\varepsilon_S - \varepsilon_M)]}{[2\sigma_M + \sigma_S - v_S (\sigma_S - \sigma_M)]} \quad (2)$$

where v_S denotes the volume fraction of the dispersed phase. Conducting PPy is the matrix (phase M) and ZnO is the dispersed phase (phase S). Dc- conductivity values of un-doped ZnO distribute around a mean value $\sigma_S \approx 0.4 - 6 \times 10^{-3} \text{ S/m}$ and a typical dielectric constant value is $\varepsilon_S \approx 10^1$ [23]. For conducting PPy, $\sigma_M \approx 10^{-1} \text{ S/m}$ and $\varepsilon_M \approx 10^4$, Using these values, which imply that $\sigma_M \gg \sigma_S$ and $\varepsilon_M \gg \varepsilon_S$, eq. (2) provides the corresponding relaxation has its maximum approximately around $f_{\max} \equiv \tau^{-1}$ and is practically independent on ZnO fraction. Both predictions about the location of the relaxation and its weak sensitivity on composition are consistent with the experimental results. Furthermore, by replacing the above mentioned typical values into eq. (2), we get $f_{\max} \approx 7 \times 10^5 \text{ Hz}$, which practically coincides with the maximum frequency of relaxation HF.

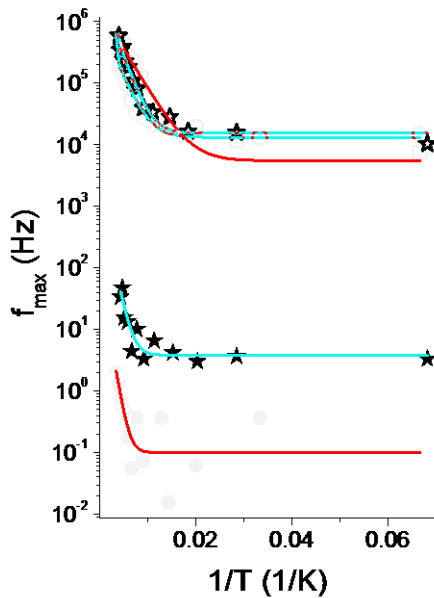


Figure 3 Arrhenius plots of the peak maxima f_{\max} of LF (solid symbols) and HF relaxation, respectively. Circles, squares and stars correspond to 20, 30 and 40 wt % ZnO composites, respectively.

3.3 Single and multi-phonon assisted hopping relaxation analysis The temperature dependence of f_{\max} is depicted in Figure 3. The temperature variation of the maximum frequency for relaxation via phonon assisted tunneling of electrons of mass m through a potential barrier of height u separating two neighboring equilibrium positions at distance δ , consists of a linear low-temperature single phonon term and, at higher temperatures, a multi-phonon hopping term:

$$f_{\max}(T) = AT + C \exp\left(-\frac{E}{kT}\right) \quad (3)$$

Where:

$$A = 2\nu \exp\left\{\left(\frac{\hbar^2}{8\delta^2 m u}\right)^{1/2}\right\} \left\{\left(\frac{2\delta^2 m}{\hbar^2 u}\right)^{1/2}\right\} kT$$

and ν denotes the vibrational frequency and C are practically temperature independent [24, 25]. Best fits of eq. (3) to the data points depicted in fig. 3 are shown as solid lines. The fitting parameters are enlisted in Table 1. The values of all fitting parameters for relaxation HF increase systematically on ZnO content. More specifically, the increase of the activation energy indicates that locally relaxing charges sense a less conducting environment as the composite becomes richer in ZnO. This visualization is in agreement with the decrease of the dc conductivity on ZnO and the gradual transition from a semi-conducting state to an insulating one, respectively.. Relaxation LF is sensitive to the electrode material, which typically characterizes pace charge phenomena, resulting from the non-ohmic sample-electrode contact.

Table 1 The parameters of eq. (3), which best fits the data points depicted in Fig. 3.

| wt % ZnO | Relaxation | Parameters of eq. (3) | | |
|----------|------------|--------------------------------------|----------------------|--------|
| | | A (s ⁻¹ K ⁻¹) | C (s ⁻¹) | E (eV) |
| 20 | HF | 53 | 1.5x10 ⁶ | 0.03 |
| 30 | LF | 0.04 | 2.1x10 ³ | 0.09 |
| | HF | 406 | 1.0x10 ⁷ | 0.07 |
| 40 | LF | 92 | 0.9x10 ² | 0.105 |
| | HF | 557 | 4.7x10 ¹⁰ | 0.29 |

4 Conclusions PPy/ZnO composites exhibit variable electrical conductivity vs capacitance effects, depending on their composition. More specifically, below 20 wt % ZnO, they behave as loss free semiconductors in the frequency range 10 mHz to 1 MHz and temperatures ranging from 15 K to room temperature. For 20, 30 and 40 wt % ZnO composites, a common high frequency relaxation activates within 10⁴ - 10⁵ Hz.. Its characteristic mean relaxation time and its concentration dependence are compatible with the predictions of interfacial polarization Sillars theory for dis-

persions. For 30 and 40 wt % Zn, an additional space charge relaxation appears around 10^{-2} - 10 Hz. The dependence of the relaxation mechanisms upon temperature complies with low temperature single phonon and high temperature multi-phonon assisted hopping relaxation. Composites consisting of 10 wt % ZnO are most suitable for optoelectronic applications, as they combine good electrical conduction, low capacitance effects and practically good ohmic sample-electrode interfaces.

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