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Electrical conductivity and TSDC study of the thermal aging in conductive polypyrrole/polyaniline blends

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The thermal aging of conducting polypyrrole/polyaniline (PPy/PA) blends heated at 70°C for up to about 600 hours was studied by d.c. conductivity measurements and by thermally stimulated depolarization current (TSDC) spectroscopy in the temperature range from 80 to 300 K. The composition of the samples varied from pure polypyrrole to pure polyaniline with the PA content increasing in steps of 10%. Although the $\sigma = \sigma(T)$ curves seem smooth, the corresponding $\Delta\sigma/\Delta T = f(T)$ curves exhibit systematically a scattering of points in the temperature ranges from 100 to 140 K and from 225 to 320 K approximately for all the samples before and after the heat treatment. TSDC measurements with the MISIM (metal-insulator-sample-insulator-metal) configuration, show a low temperature peak at 100–120 K and a high temperature peak at 280–300 K. The first disappears when the polypyrrole content exceeds 70% and for all the samples after heat treatment, although the high-temperature peak persists. The explanation given to this correspondence between d.c. conductivity and TSDC signals is based on the destruction of conformons and the mobility change of the polymer chains with rising temperature.

1. Introduction

The irreversible conductivity degradation under thermal treatment in environmental conditions is a serious disadvantage of conductive polymers for their use in technological applications. Polyaniline and polypyrrole exhibit high stability and the understanding of their aging processes can lead to a further reduction of this undesirable phenomenon [1–3]. In this article, the thermal aging process in polypyrrole/polyaniline blends is studied by d.c. conductivity and thermally stimulated depolarization current (TSDC) measurements. The conductivity behavior can give information about the structure of the blends and the conduction mechanisms involving long-range movement of the charge carriers. On the other hand, the TSDC spectra can reveal the activation of certain relaxation processes concerning the charge carriers' mobility, which depend on the changes of the polymer induced by the thermal aging and by conformational defects produced by the thermal treatment [4–6].

2. Experimental

The conductive samples of polypyrrole/polyaniline blends were made from freshly distilled monomers (Merck) under vacuum and then mixed in the proper ratio and polymerized in the presence of $FeCl_3$ (Merck) as oxidant in HCl acid-water solutions at pH = 2.00 in an ice bath (monomers/oxidant = 1 : 1 mol/mol) under nitrogen atmosphere. The blends were obtained as black powders, purified by Soxhlet extraction for 36 h [7]. The fact that the chemical analysis of the solution above the precipitates revealed a negligible concentration of the initial monomers confirms that the blends have the same polypyrrole/polyaniline ratio as the initial monomers. Finally, disc shaped specimens 13 mm in diameter and about 1.5 mm thick were produced by pressing the powder in an IR sample press.

An oven thermostated at 70°C was used for the thermal aging of the samples at room atmosphere. Differential scanning calorimetry and thermogravimetry revealed that chemical degradation of the blends occurs well above 150°C. The time of the thermal treatment ranged from 0 to about 600 h. The d.c. conductivity versus temperature from 300 to 80 K was measured with a four-probe method in a cryostat filled with inert He gas.

The TSDC measurements were performed on specimens placed in a sample holder consisting of two platinum electrodes located inside an appropriate cryostat operating from 80 to 420 K. The specimens were polarized at room temperature (298 K). The depolarization current was measured by a Keithley 617 electrometer. The temperature was monitored via an Air Products temperature controller, which could maintain a constant heating rate of 2 K/min. The electrometer and the temperature controller were connected to a computer.

3. Results and discussion

The decrease of σ with aging time for all the blends follows the law:

$$\sigma = \sigma_0 \exp[-(t/\tau)^{1/2}] \tag{1}$$

where σ_0 is the conductivity of the nonaged sample, t is the time of the heat treatment and τ is the time which characterizes the aging rate. Such an aging law reveals that the blends have an heterogeneous structure of the granular metal type [8, 9].

The conductivity σ vs T at a given aging time t for all the samples, except polypyrrole, followed the law:

$$\sigma = \sigma_0 \exp\left[-(T_0/T)^{\alpha}\right] \tag{2}$$

with the exponent α ranging from (0.26 ± 0.02) to (0.46 ± 0.02). This relation is also consistent with the granular metal structure of the material, where the conduction is due to charge carrier tunneling between the conductive grains and the exponent α can take values between $1/4$ to 1 for different distributions of the grain size [10, 11].

The exponent α in Equation 2 was determined by calculating from the experimental $\sigma = \sigma(T)$ the reduced activation energy

$$W(T) = T\frac{\mathrm{d}\ \ln(\sigma(T))}{\mathrm{d}T} \tag{3}$$

and then from Equation 2 we get

$$\ln W = A - \alpha\ \ln T \tag{4}$$

from which α is given by the negative slope of the straight line $\ln W = f(\ln T)$ obtained. By this way polypyrrole samples gave α between 0.05 and 0.08 indicating that other conductivity models must be taken into account. The fluctuation-induced tunneling model consistent with the heterogeneous structure implied by Equation 1, where conducting grains are larger and the intervening insulating barriers narrower than in polymers following Equation 2 was considered [8, 12]. This model predicts

$$\sigma = \sigma_0 \exp[-T_1/(T_0 + T)] \tag{5}$$

The following three mechanisms contribute to the bulk electrical conductivity σ of a polymer with granular metal structure: carrier movement along the chains; their hopping between neighboring chains; and their tunneling through the insulating polymer between the conductive grains. The dependence of σ upon T, as expressed in Equations 2 and 5, is determined from the tunneling process, although improvement of the first two contributions increases the bulk conductivity.

Fig. 1 shows the conductivity of nonaged samples at 300 K and the time τ, which characterizes their aging rate, calculated from the slope of Equation 1, as a function of polypyrrole/polyaniline ratio. A "complementary" behavior is revealed: the samples with high conductivity σ are characterized by low τ, i.e., they age quicker than the samples with lower σ and vice versa.

In Fig. 2 the conductivity σ and the corresponding $\Delta\sigma/\Delta T$ as functions of the temperature T, calculated from point to point, are shown for a polypyrrole sample. Although σ seems to increase smoothly with T, the $\Delta\sigma/\Delta T$ exhibits two regions of point scattering, one at low temperatures approximately from 100 to 140 K and the other at higher temperatures from 225 to 320 K. The same behavior was exhibited systematically by all the blends of the system, with the low temperature scattering being of smaller amplitude than the high temperature one and both amplitudes decreasing with

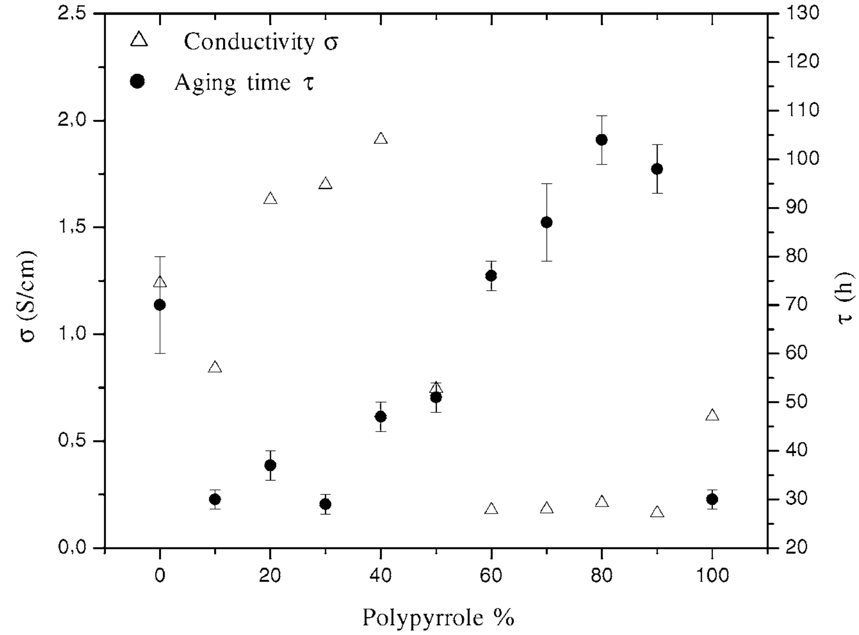

Figure 1 The conductivity of nonaged samples at 300 K and the time τ, which characterizes their aging rate, as functions of the polypyrrole/polyaniline ratio. Samples with high σ are characterized by low τ and vice versa.

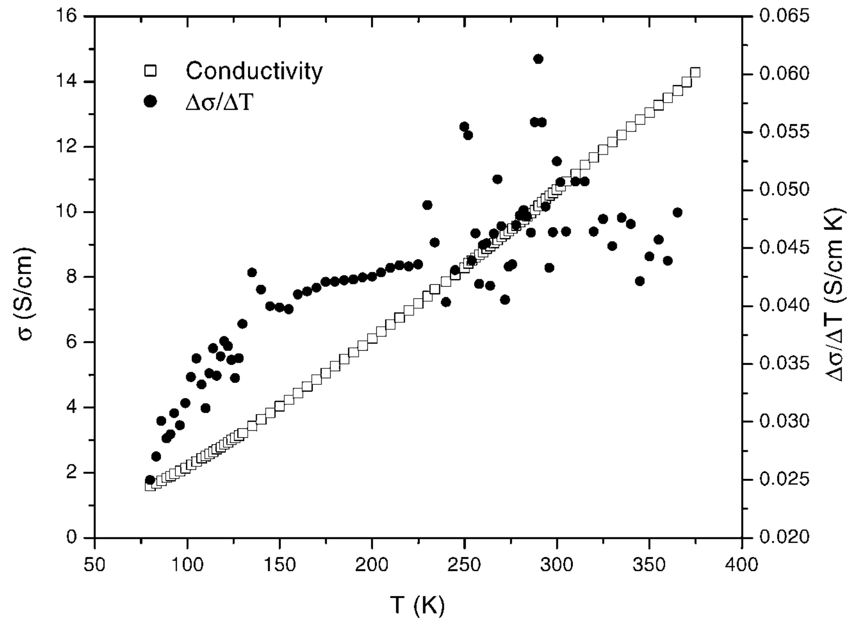

Figure 2 The dc conductivity σ and the corresponding $\Delta\sigma/\Delta T$ as functions of the temperature T for a polypyrrole sample. Although the first curve seems smooth, the second exhibits two regions of point scattering, at low temperatures between 100 and 140 K and at higher temperatures from 225 to 320 K approximately.

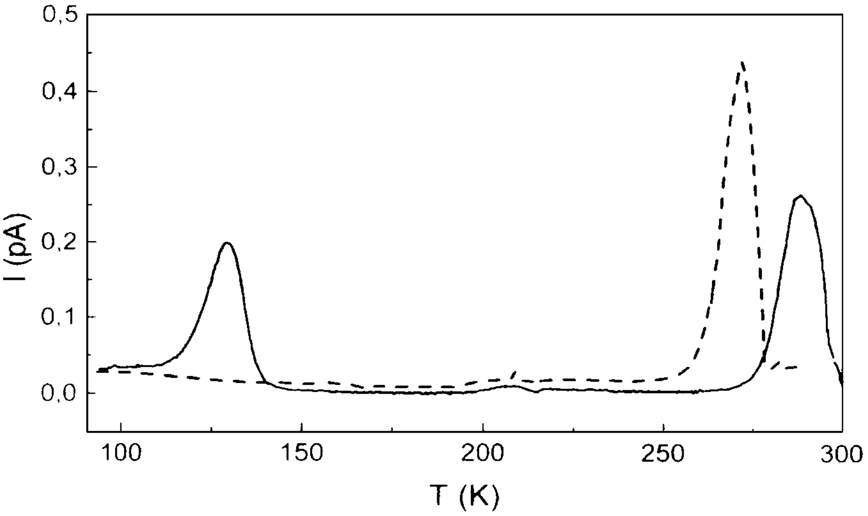

Figure 3 TSDC thermograms obtained from an nonaged (solid line) and a heated at 70°C for 570 h (dashed line) 40% PPy/60%PA sample, by employing the MISIM arrangement of the electrodes. The polarization was achieved by polarizing at $T_p = 290$ K for a time interval $t_p = 1$ min.

aging time. As the same method of $\Delta\sigma/\Delta T$ evaluation was used for all the samples, the systematic scattering of points in two distinct regions of T interrupted by an intermediate smooth interval, is a strong indication that the scattering is due to an intrinsic cause.

A typical thermogram of the 40% PPy/60% PA sample before the heating treatment is depicted by the solid line in Fig. 3. The experiments were performed by employing insulating electrodes in a MISIM configuration [13]. Two peaks appear; the first one (LT band) ranges over 100–120 K and the second one (HT band) over 280–300 K. The apparent correspondence between the two TSDC peaks and the point scattering in $\Delta\sigma/\Delta T$ vs. T curves prompted us to consider the possibility of their common origin and to examine the blends with both techniques. However, the correspondence in the low temperature range breaks down for nonaged samples containing more than 80% polypyrrole and for all the samples after heat treatment, as the low temperature TSDC peak disappears although the $\Delta\sigma/\Delta T$ scattering persists. Fig. 3 accommodates also the thermogram obtained after heating the sample at 70°C for 570 h (dashed line), in which the LT peak has disappeared.

On the other hand, the high temperature TSDC peak, which appears in all the nonaged samples, survives the heat treatment and shifts towards lower temperature, while its amplitude does not change significantly. The corresponding $\Delta\sigma/\Delta T$ disturbance appears in all the samples of the system, its amplitude decreasing with increasing time of thermal aging.

To the best of our knowledge, the present work is the first employing TSDC experiments with the MISIM configuration to study thermal degradation in conductive polymers. There is merely one work reporting TSDC studies in conductive polymers, in which two peaks corresponding to the LT and HT bands, are reported [14]. However, any speculation about the origin of the mechanisms is lacking in the literature.

3.1. Low temperature peak

The position of the LT peak is practically insensitive to the modification of the electrode configuration. By constituting the MISM (metal-insulator-sample-metal) configuration, the shift of the maximum of the LT peak is less than about 1 K. This is a strong indication that the LT peak is due to short-range (localized) charge motion [15].

It has been found that disordered conducting polymers, exhibit dielectric loss peaks around 130 K associated with the hopping of charge carriers between neighboring localized sites [4]. The activation energy values E, for the LT band range from 0.08 eV to 0.15 eV, but there is no clear dependence of E on the composition of the specimen. These values are comparable to those mentioned in [4]. The d.c. conductivity originates from the motion of the charge carriers across the volume of the sample, while the dielectric relaxation is due to the localized hopping of charge carriers confined in deep potential wells (traps) along the polymer chains.

Moreover, the chlorium anions Cl^-, which are introduced between the polymer chains during oxidation and protonation with hydrochloric acid, act as trapping centers for the positive polarons, impeding their motion and contributing to the low temperature TSDC peak. Another factor that can contribute to the LT dispersion is that in a TSDC experiment, the sample is cooled rapidly from room temperature to 80 K, favoring the formation of short and long-range conformons, which obstruct the carrier transport.

The disappearance of the LT peak after heat treatment can be explained, as during thermal aging Cl^- dopants combine with H^+ and leave the sample as gaseous HCl, a process which decreases the number of the trapping centers. Moreover, the destruction of the short-range conformons during heating has the same result. Loss of HCl is one of the main degradation processes, as revealed by elemental analyses, FTIR, XPS, XPD and conductivity measurements [3]. The characteristic time τ of the aging process appearing in Equation 1 is $\tau = (0.67 \pm 0.03)$ h for protonated polyaniline, though in polyaniline with sulphonic groups aging is much slower, characterized by $\tau = (3000 \pm 500)$ h. This is due to the fact that sulphonic groups are attached to the polymer chain more strongly than protons [2].

It is remarkable that the LT peak appears only in pure polyaniline and in polyaniline rich blends. It seems that the LT peak is related to conformational defects developing in the polyaniline phase. Polyaniline chains may be distorted easier than in polypyrrole, because of the intervention of nitrogen atoms along them. It is worth noting that the LT peak does not disappear gradually with increasing polypyrrole content, but abruptly at about 70% PPy/30% PA.

The scattering of the points in $\Delta\sigma/\Delta T$ vs T curves resembles a disorder to order transition probably connected with the destruction of the short-range conformons occurring discontinuously with increasing temperature. The subsequent influence in the carrier movement along the polymer chains results in the observed scattering of the experimental points.

3.2. High temperature peak

The nature of the HT relaxation mechanism is entirely different from that of the LT band. The position of the HT peak is sensitive to the modification of the electrode configuration, evidencing that the relaxation is related to the motion of free charges along macroscopic distances toward the electrodes (space charge polarization) [15]. The thermal treatment probably makes the polymeric chains more flexible. Subsequently, the disordered phase relaxes faster during the heating stage of the TSDC experiment and the relaxation time of the HT peak is shorter in the aged than that of the nonaged samples. A short relaxation time implies that the HT peak should appear at lower temperatures after aging and this does actually occur.

The HT peak lies within the temperature range where the above mentioned conformational transition occurs. Recalling that the standard characterization through the electrode modification proved that the HT peak is a space charge mechanism, the relation between the conformational transition and the HT peak can be as follows: The conformational defects (conformons) act like obstacles (traps) to the motion of charges. As conformons annihilate on raising the temperature during the TSDC scan, the polymeric chains get gradually mobile in a large scale and do actually assist cooperatively the transfer of charge along long distances. The enhanced charge mobility is reflected through the appearance of the HT peak. The phenomenon resembles the well-known glass transition of polymers, which produces TSDC peaks, but, as mentioned above, the process is quite different. The value of the activation energy obtained from the analysis of the HT signal is about 1 eV, compatible with the values reported for similar transitions [14, 15]. However, the activation energies obtained from conductivity data are one order of magnitude smaller, indicating that the HT peak is not directly connected to the carrier movement governed by tunneling between conductive grains.

Differential scanning calorimetry on slow heating of a previously rapidly cooled (5 K/min) BF_4^- doped polypyrrole sample has revealed annihilation of conformons in the polymer chains accompanied by an increase of the electrical conductivity in the temperature range between 250 and 310 K [17]. A correlation between dielectric relaxation and d.c. conduction in polypyrrole based copolymers has been found [18]. Moreover, deviations from linearity in the thermopower of polypyrrole at temperatures in the range between 230 to 300 K and of polyaniline at temperatures of about 160 and 310 K have been observed [16, 19] supporting the suggestion of the conformational changes mentioned above. In our samples, even after rapid cooling, such increases did not appear in the temperature dependence of the electrical conductivity σ, but scattering of the points in the corresponding $\Delta\sigma/\Delta T$ vs T curves, as shown in Fig. 2. This is an indication that the long-range conformon annihilation proceeds discontinuously with increasing temperature.

From the above it can be concluded that there is a strong correlation between the high temperature TSDC peaks and the scattering of points in the $\Delta\sigma/\Delta T$ vs T curves. However, at low temperatures the TSDC peaks disappear in nonaged samples with polypyrrole content more than 70% and for all the samples after heat treatment, although the scattering in conductivity continues. This can be explained as the low temperature TSDC peaks are due to the activation of strongly localized charge carriers, though for the dc conductivity contributes the long-range charge migration.

The heterogeneous granular metal type structure of the samples, the complicated thermal aging processes, which apart from the dedoping by the removal of HCl involves oxidation/hydrolysis/scission and crosslinking of the chains [3], the uncontrolled formation of conformons during rapid cooling and the specific features of each sample determined by their construction method, make impossible any detailed correlation between TSDC and dc conductivity. However, the correspondence between the TSDC peaks and the dispersion of points of the $\Delta\sigma/\Delta T$ vs. T curves give general information about processes governing the migration of charge carriers by hopping between localized sites (LT peak) and along the polymer chains (HT peak).

4. Conclusions

The conductivity decrease of polypyrrole/polyaniline blends with thermal treatment and the $\sigma = \sigma(T)$ dependence at any given aging time reveal an heterogeneous structure of the granular metal type for all the blends. Conductivity vs T curves seem smooth, though the corresponding $\Delta\sigma/\Delta T$ curves exhibit two regions of point scattering, one at low temperatures, between approximately from 100 to 140 K and from 225 to 320 K. On the other hand, TSDC spectroscopy with MISIM configuration, cutting off the carrier conduction, detects two relaxation mechanisms, which are sensitive to thermal treatment and they are connected to Cl^- departure induced by aging and to conformational changes due to thermal treatment of the samples. The TSDC spectroscopy, which, as far as we know, is used for the first time to study such relaxation processes in conductive polymers, has high enough sensitivity to detect conformational changes, whose consequence is expected to be an increase of the hopping rate between localized sites along polymer chains at low temperatures between 100–120 K and the transfer along long distances at high temperatures between 280–300 K. Such conformational changes do not increase the d.c. conductivity, but they produce a scattering of the experimental points in the $\Delta\sigma/\Delta T$ vs T curves indicating a discontinuous process.

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