

Hopping charge transport mechanisms in conducting polypyrrole: Studying the thermal degradation of the dielectric relaxation

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(Received 13 December 2004; accepted 23 August 2005; published online 6 October 2005)

Isotherms of the imaginary part of the permittivity from 10^{-2} to 2×10^6 Hz from liquid nitrogen to room temperature for fresh and thermally aged specimens of conducting polypyrrole reveal a dielectric loss peak, which is affected by the reduction of conducting grains with aging. Charge trapping at the interfaces separating the conductive islands seems invalid. Thermal aging indicates that macroscopic conductivity and short range one have different aging evolution. The first (dc conductivity) is dominated by the tunneling of the carriers between neighboring grains through the intermediate insulating barriers, though the second (ac conductivity) is due to a backward-forward movement of the carriers and is controlled by the intrachain transport of them and their hopping between the chains. © 2005 American Institute of Physics. [DOI: 10.1063/1.2103388]

The requirement of modern technology to produce novel conducting polymers and blends led to the development of materials chemistry and engineering.¹ Despite the burst in materials preparation, the fundamental concept of different types of electric charge transport remains still an open question. Significant theoretical and experimental work is going on in order to understand transport phenomena.²⁻⁴ The dc conductivity measurements at various temperatures and the thermal degradation of the electrical conductivity can judge the validity of theoretical models about the macroscopic charge flow. The dominant model of polypyrrole is that of an inhomogeneous structure of the granular metal type, in which conducting grains are embedded in an insulating matrix.⁵ Conductive grains consist of polymer chains rich in polarons.⁶ To a crude approximation, metallic conduction occurs within the grain and hopping from one grain to another proceeds by phonon assisted tunneling through the insulating separation. The dc conductivity measurements trace the transfer of charge species throughout the specimen (macroscopic conductivity) controlled by the site and height disorder of potential barriers. The activation energy value for dc transport is a measure of the height of the potential barriers. On the other hand, ac conductivity involves the backward and forward motion of charges. When the frequency of the external ac field becomes larger than a percolation value, better use of the sites separated by lower potential barriers is made, the conductivity becomes dispersive on frequency and a dielectric loss mechanism takes place.⁷ Thus, the study of the relaxation mechanism of conduction modes may be different than that investigated by the dc measurements. Low frequency complex impedance measurements was carried out on conducting polypyrrole and other conducting polymers.⁸⁻¹⁰ In the present letter, we report the degradation

of the dielectric response of conducting polypyrrole, when subjected to thermal treatment. We shall try to find out the features of the dielectric loss by subjecting the sample to different duration thermal aging. The evolution of the dielectric relaxation with aging is used as a tool to distinguish different types of electric charge flow. To the best of our knowledge, the thermal degradation of the dielectric relaxation linked to dedoping, oxidation/hydrolysis/scission of the polymer chains, and crosslinking in conducting polymers has not been discussed in the literature, yet.

Details about the sample preparation have been given earlier.¹¹ The measurements were performed in a vacuum cryostat within the frequency range 10^{-2} – 2×10^6 Hz by employing a Solartron SI 1260 frequency response analyzer. The thermal aging of the specimens took place in a furnace working at atmospheric conditions at 70 °C. The aging duration was 144 and 312 h.

The frequency dependence of imaginary part of the permittivity ϵ'' for various temperatures for fresh specimen and after 312 h anneal is presented in log-log representation in Fig. 1. A relaxation mechanism is activated as a “knee” in the $\log \epsilon''(\log f)$ plots. Thermal aging lowers the dc contribution, as a result of deprotonation of polypyrrole. A *modified* empirical law of the form of Williams, Lander, and Ferry¹² was used to describe the temperature variation of f_{\max} (after subtracting the dc contribution) (Fig. 2) for fresh and aged samples

$$f_{\max} = f_0 \exp\left(-\frac{T_1}{T + T_0}\right), \quad (1)$$

where T_1 and T_0 are fitting parameters. $E \approx kT_1$ is labeled as activation energy for relaxation. E is actually the height of the effective potential energy barrier separating sites involved in the relaxation process. T_0 is negative for cooperative dipole rotation. The parameters obtained by fitting Eq. (1) to the experimental data points appearing in Fig. 2, are

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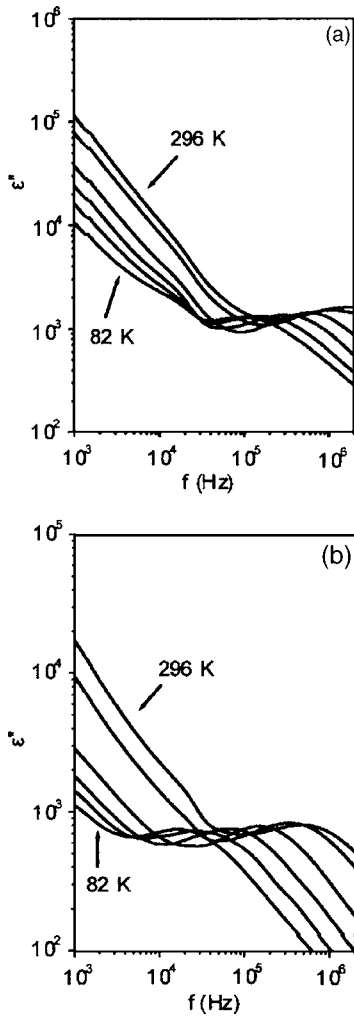


FIG. 1. Isotherms of the imaginary part of the permittivity vs frequency for fresh polypyrrole [diagram (a)] and thermally aged for 312 h [diagram (b)]. Starting from the upper curve, the plots correspond to the temperatures where the experiments were performed: 296, 247, 173, 135, 107, and 82 K.

enlisted in Table I. The phenomenological “apparent” activation energy $E_{app} \equiv d \ln \tau(T)/d(1/kT) = -d \ln f_{max}(T)/d(1/kT)$ increases at high temperatures (Fig. 2), opposing the behavior of dipolar relaxation.¹⁰

Figures 1 and 2 indicate a shift of f_{max} to lower frequencies [or an increase of the relaxation time $\tau(T) = 1/2\pi f_{max}(T)$] after anneal, in agreement with the increase of the activation energy values upon aging duration (Table I). The reduction of the size of conductive grains in the polymer phase yields an increase in the effective potential barrier separating sites involved in the relaxation process. Thermal aging results in a decrease of the strength $\Delta\epsilon$ of the relaxation peaks (inset of Fig. 2). This might be related with the corrosion of the conductive grains and the subsequent reduction of the interfacial area separating the conductive phase from the insulating matrix, and the subsequent charge density trapped in the interface. In other words, such behavior might be attributed to interfacial [Maxwell-Wagner-Sillars (MWS)] polarization,¹³ but this aspect will further be criticized in the next paragraphs. $\Delta\epsilon$ seems to decrease with temperature as $\Delta\epsilon \propto T^{-1}$, in accordance with the random free-energy barrier model.⁷

The thermal degradation of the dc conductivity σ_{dc} of conductive polymers on aging duration is qualitative by the following law:^{11,14,15}

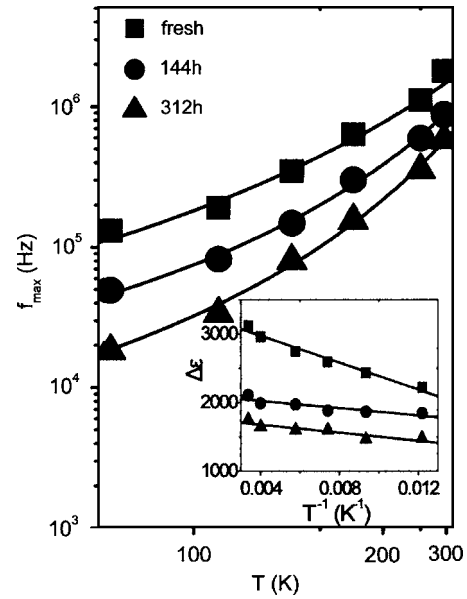


FIG. 2. Temperature dependence of the position of the dielectric loss peaks. Lines are the best fits of Eq. (1) to the experimental data points. In the inset, the dielectric strength is plotted upon reciprocal temperature. Straight lines best match the experimental data points.

$$\sigma_{dc}(t) = \sigma_{dc}(t=0) \cdot \exp\left(-\sqrt{\frac{t}{\tau_{aging}^{aging}}}\right), \quad (2)$$

where t denotes the aging time, $\sigma_{dc}(t=0)$ is the dc conductivity of the fresh specimen and τ_{aging}^{aging} is a time constant. The $\ln \sigma \propto \sqrt{t}$ dependence is consistent with the granular metal structure, with conducting grains embedded into an insulating matrix, contracting with aging in a corrosion-like manner. The equivalent conductivity σ^* calculated from the dielectric data is

$$\sigma^* = 2\pi f_{max} \epsilon_0 \Delta\epsilon, \quad (3)$$

where ϵ_0 is the permittivity of free space. In Fig. 3, we see the evolution of the equivalent conductivity σ^* vs $t^{1/2}$. By using Eq. (2) to match the experimental data points $\sigma^*(t^{1/2})$, we get values of τ_{aging}^{aging} (Fig. 4). The aging time constants obtained from the study of the thermal degradation of the dc conductivity are an order of magnitude smaller than those obtained from the ac results and τ_{aging}^{aging} increases linearly with temperature (Fig. 4). The linear increase of the aging time constant with temperature means that the shrinking of the conductive grains has as a result a faster decrease of the conductivity in lower than in higher temperatures. It seems that at lower temperatures the increasing (with aging) of the

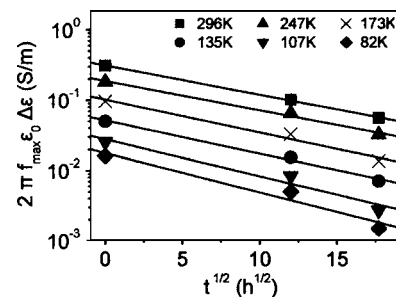


FIG. 3. The quantity $2\pi f_{max} \epsilon_0 \Delta\epsilon$ vs aging time. Straight lines are the best fits of Eq. (2) to the experimental data points.

TABLE I. The parameters of Eq. (1) used to fit the temperature dependence of f_{\max} . The activation energy for dc conductivity E_{dc} is depicted in the last column.

Aging time (h)	f_0 (Hz)	T_1 (K)	T_0 (K)	E (eV)	E_{dc} (eV)
0	$(8.03 \pm 0.09) \times 10^6$	617 ± 5	63.3 ± 0.9	0.0532 ± 0.0004	0.1478 ± 0.0004
144	$(1.12 \pm 0.02) \times 10^7$	1031 ± 9	106 ± 1	0.0888 ± 0.0008	0.168 ± 0.002
312	$(1.26 \pm 0.03) \times 10^7$	1270 ± 10	113 ± 1	0.1094 ± 0.0009	0.192 ± 0.001

potential barriers with aging can be overcome with greater difficulty, than in higher temperatures. This is expected, as the conductivity is thermally activated. The aging time constant is an order of magnitude greater for the ac conductivity than the dc conductivity as a result of a much slower decrease of the ac conductivity takes place at any given temperature with aging, than in the dc conductivity. This is reasonable as the ac conductivity is due to the forward-backward movement of the carriers, which is connected to their intrachain movement. On the contrary, the dc conductivity is very much affected from the tunneling between the grains and their shrinking affects greatly the carrier movement. Both the dc and ac conductivity studies probe the augmentation of intergrain separation with aging duration, but the different time constants indicate that the dc and ac transport operate along different modes through the same insulating effective intergrain barrier.

Conductive inclusions embedded in an insulating matrix might produce interfacial polarization (MWS) phenomena. The interface in the present case separates conductive regions from the insulating host. The relaxation time, for the simple case of ellipsoid inclusions, is¹⁶

$$\tau_{\text{MWS}} = \epsilon_0 \frac{\epsilon_1(\lambda - 1) + \epsilon_2}{\sigma_2}, \quad (4)$$

where ϵ_1 is the static permittivity of the matrix, λ is a geometrical factor depending on the shape of the inclusions, and ϵ_2 and σ_2 are the static permittivity and conductivity of the inclusions, respectively. If interfacial process is responsible for the dielectric loss peak, the relaxation time (and f_{\max}) should be—regarding Eq. (4)—insensitive to the thermal aging: in polypyrrole, the size of the conductive islands is reduced and the distance between them increases. However, our results do indicate that the dielectric response is affected by thermal anneal (Fig. 2), indeed. Thus, the scenario of charge trapping at the interfaces separating the conductive island from the insulating matrix fails to explain the thermal degradation of the loss peak. The latter concept is in accor-

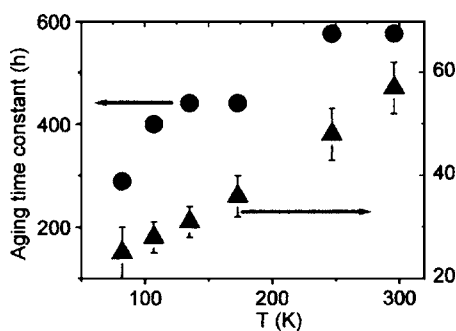


FIG. 4. The aging time constant vs the temperature where the isotherms of permittivity (circles) and the dc conductivity (triangles) were obtained.

dance with our observation mentioned above that the curvature of f_{\max} versus temperature (Fig. 2) is the inverse of that exhibited by dipolar species, like extended MWS “dipoles.”

The dc conductivity measurements on the present fresh and aged polypyrrole that have been reported earlier¹⁴ led to activation energy values which are higher than those corresponding to relaxation (Table I). The first is mainly connected to the tunneling between grains, although the latter refer mostly to intrachain movement of the carriers. The thermal aging experiments reinforce the aspect that the dc and ac conductivity are in-correlated.

The activation energy values (Table I) indicate that the short-range backward-forward hopping involves different process than that of the macroscopic conductivity. We speculate that both types of charge motion (macroscopic dc and short-range ac) involve phonon assisted hopping through the insulating barrier separating the conductive islands the first and the potential barrier between polymeric chains the second. Both are affected by aging, but in different ways, as indicated by different aging-time constants. In the dc conductivity, hopping is dominated by charge transfer along polymeric chains (interchain) linking conductive grains, which provide a conductive network throughout the volume of the specimen.⁶ The dielectric loss mechanism is related to the degradation of the chains reducing the intra- and inter-chain hopping. So, the different evolution of these two mechanisms with thermal aging makes possible the distinction between them. The different manner the two transport mechanisms evolve with thermal aging that makes possible to distinguish them.

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