

Low frequency a.c. conductivity of fresh and thermally aged polypyrrole–polyaniline conductive blends

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Received 31 March 2003; received in revised form 16 June 2003; accepted 25 July 2003

Abstract

The low frequency (10^{-2} to 10^6 Hz) a.c. conductivity of fresh and thermally aged polypyrrole–polyaniline blends of various compositions was studied at room temperature. The cross-over frequency that separates the d.c. regime from the dispersive region is a function of the composition and is influenced by the thermal aging for the polyaniline-rich blends. The frequency-dispersive conductivity is determined by a sublinear law. The fractional exponent is close to unity for the fresh samples. The thermal aging results in values of the fractional exponent, which depend on the composition. This picture reflects what has been observed previously in d.c. vs. temperature studies: thermal aging reduces the size of conducting grains in polyaniline, while in polypyrrole, results in a modification of the backbone matrix. It seems that a.c. measurements at room temperature may well serve as a parallel way to the time consuming d.c. conductivity vs. temperature technique, to detect thermal degradation of the transport properties in conducting polymers.

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Keywords: Conducting polymers; Polyaniline; Polypyrrole; Electrical conductivity; Thermal aging

1. Introduction

A serious problem in using conducting polymers in technological applications is the thermal degradation of their electrical conductivity. Polyaniline and polypyrrole are exceptionally stable under environmental conditions. The mechanisms of thermal degradation of the electrical conductivity have been studied experimentally recently and the results were viewed in terms of different models [1,2]. Additionally, thermally stimulated currents [3,4] and high-pressure experiments [5] in fresh and aged polypyrrole–polyaniline blends were published recently. The mechanisms of degradation in polyaniline is different from that of polypyrrole. Both polymers have an inhomogeneous structure of the granular metal type and the thermal degradation of the conductivity is attributed to the reduction of size of the conducting islands [1,2]. On the other hand, what distinguishes the two conductive polymers, is that different laws govern the change of their conductivity vs. temperature, suggesting that the distance between conductive grains in

polypyrrole is less than in polyaniline. In the present work, we intent to investigate these different modes in non-aged (fresh) and thermally aged polypyrrole–polyaniline blends by measuring the a.c. conductivity at room temperature in the frequency range from 10^{-2} to 10^6 Hz.

2. Results and discussion

The d.c. and a.c. transport are both due to the same mechanism. A proper understanding of the a.c. conductivity is significant to have a complete picture of the d.c. transport [6]. The low frequency a.c. conductivity of conducting polymers consists of a frequency-independent behavior in the limit of low frequencies and a sublinear response at higher frequencies. The real part of the electrical conductivity $\sigma'(\omega)$ can be expressed as:

$$\sigma'(\omega) = \sigma_0 + A\omega^n \quad (1)$$

where σ_0 denotes the d.c. conductivity, A the constant, ω the angular frequency of the applied field and $n \leq 1$ is a fractional exponent. By hopping backward and forward at places with high jump probability a charge carrier may

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significantly contribute to the a.c. conductivity, while the d.c. conductivity is determined by the overcoming of unfavorable places in the solid for the formation of a continuous ‘percolation’ path between the electrodes. The higher the frequency of the applied field, the larger the a.c. conductivity because better use is made by the places with very large jump probability [6]. The fractional dependence of the a.c. conductivity upon frequency has been observed in a wide variety of disordered materials, such as amorphous semiconductors, polymers and ionically conducting glasses [7]. It has been suggested that the exponential law of Eq. (1) originates from many-body interactions between the hopping charges [7]. Eq. (1) is widely used to describe a.c. conductivity in conducting polymers [8–10]. In disordered systems, where hopping transport occurs, the a.c. conductivity increases as the frequency of the applied electric field increases, because the contribution of charge carriers moving along smaller and smaller distances, i.e., confined inside clusters of progressively decreasing sizes, increases [6,11]. In this sense, the fractional exponent expresses the relative reduction of clusters upon frequency. Exponents close to unity are associated with ‘lattice’ response, while values smaller than unity are related with the presence of impurities or injected carriers [12]. Therefore, the fractional dispersion of the a.c. conductivity may provide a useful diagnostic tool for characterizing charge transport [12].

The boundary in the frequency domain that separates the d.c. region from the frequency-dependent behavior is the cross-over frequency ω_c , which is determined from the d.c. conductivity and the static permittivity ϵ_s [10]:

$$\omega_c = \frac{\sigma_0}{\epsilon_0 \epsilon_s} \quad (2)$$

where ϵ_0 is the permittivity of free space. As can be seen from Eq. (1), the a.c. conductivity vs. frequency experiments may provide more fruitful information than the d.c. measurements; both the d.c. component σ_0 , the cross-over frequency ω_c and the fractional exponent n can be determined from a.c. measurements at different frequencies.

Conductive samples of polypyrrole–polyaniline blends were prepared from freshly distilled monomers (Merck) under vacuum in the proper ratio 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 [13]. The composition of the samples varied from pure polypyrrole to pure polyaniline with increasing gradually by 10% of the one constituent against the percentage of the other. Disc-shaped specimens 13 mm in diameter and about 1.5 mm thickness were formed by pressing the powder in an IR press. Aging was performed by placing the samples in an oven operating at 70 °C at ambient atmosphere for about 600 h. The measurements were performed by a Solartron SI 1260 impedance analyzer.

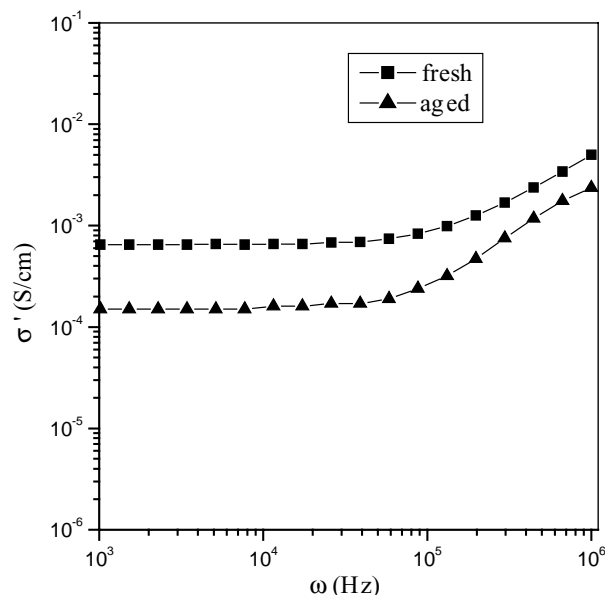


Fig. 1. Log–log plot of the room temperature electrical conductivity in fresh and thermally aged blend 90 wt.% polypyrrole.

The real part of the electrical conductivity of fresh and thermally annealed polyaniline with 90 wt.% polypyrrole is plotted as a function of the angular frequency in Fig. 1. The behavior is typical of a disordered solid. A d.c. plateau is followed by a frequency-dependent region as frequency increases. The values of the low frequency conductivity (where d.c. conductivity dominates) are suppressed after the thermal treatment. In Fig. 2, where $\log \omega_c$ is plotted as a function of the polypyrrole weight content, we see that ω_c is higher in polyaniline-rich ($x < 60$ wt.% polypyrrole) fresh specimens. After the thermal aging, ω_c falls to a practically constant value. The reduction of $\log \omega_c$ with the thermal anneal indicates a direct connection between the size reduction of the clusters where backward and forward hopping occurs [6] and the decrease of the size of the protonated grains in polyaniline phase. The different way the conductivity process is affected by thermal anneal in polypyrrole and polyaniline has been observed in d.c. measurements [3].

The fractional exponent n has been derived from the frequency-dispersive region. Regardless the specimens' composition, n is close to unity for fresh specimens. Such value indicates evidences for a weak interaction between polarons and the polymer backbone. Charge carriers transfer along an effective conductive media consisting of conductive islands embedded in a less conductive background. Thermal aging is actually a very complicated process including de-doping by the removal of the HCl, oxidation/hydrolysis/scission and cross-linking of the chains [14]. In polyaniline, thermal degradation occurs as a reduction of the size of conductive islands in the insulating matrix. In polypyrrole, thermal degradation takes place mainly on the insulator polymer between the conductive grains [1]. We feel that the different way electrical transport is affected by

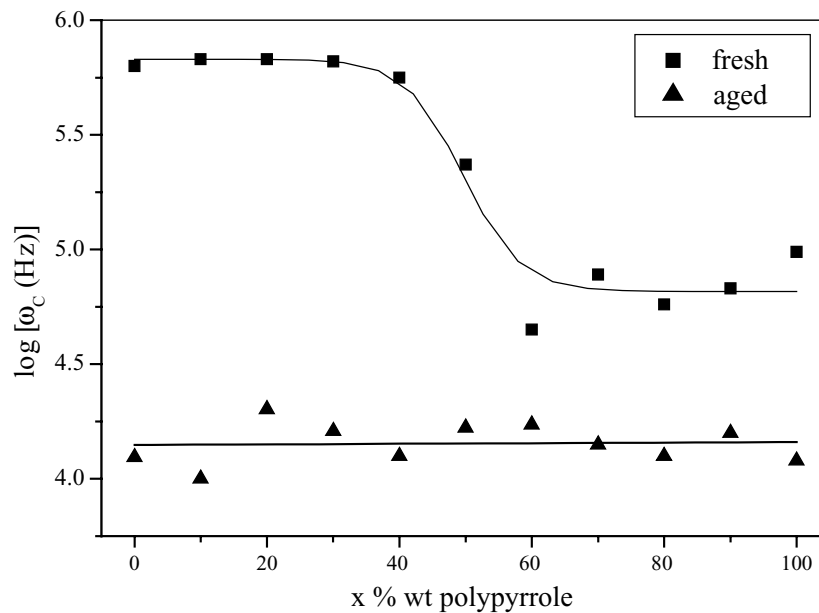


Fig. 2. The logarithm of the cross-over frequency ω_c as a function of the composition (x denotes the wt.% polypyrrole content) for fresh and aged specimens.

the thermal treatment is probably reflected in the $n(x)$ plot (Fig. 3) where the fractional exponent of the conductivity varies from about 0.8 for pure polyaniline and reaches a minimum of about 0.6 at $x = 50\%$. For $x > 70$ wt.% polypyrrole, n holds values close to unity. The thermal degradation does not modify the nature of the conductivity in polypyrrole-rich blends. This speculation is in accordance with d.c. conductivity studies that showed that the degradation of the polymer takes place in the insulating background, rather than affects the inter-grain transport [1].

Although thermal aging reduces the polaron concentration, it does not alter the mode of conduction in the background of polypyrrole: in polypyrrole-rich blends, the fractional exponent holds values close to unity. On the contrary, in polyaniline-rich blends, thermal aging affects the grain size and the inter-grain separation and this fact is reflected in the modification of the fractional exponent. In the latter case, n is a function of the blend composition to polypyrrole concentration less than 70 wt.%, where the system rather abruptly treats like a 'metal'. The above-mentioned

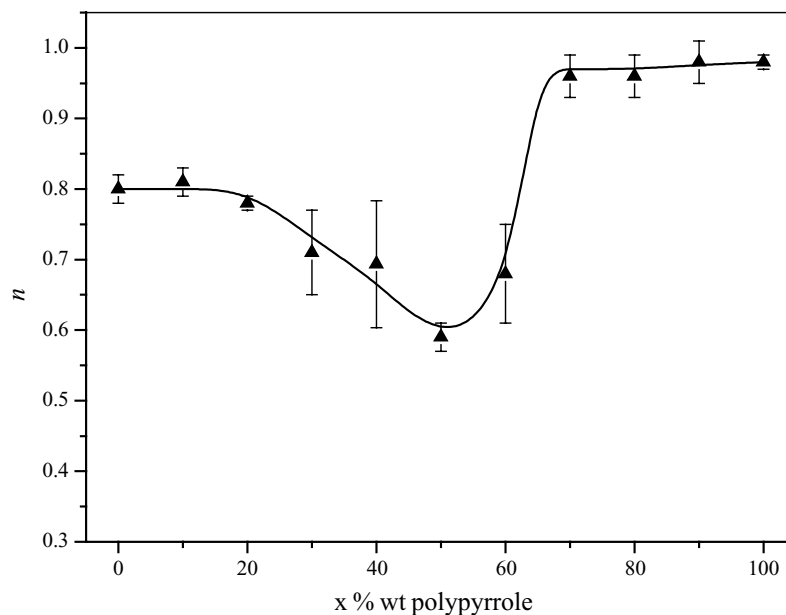


Fig. 3. The exponent n of the fractional law (Eq. (1)) that governs the a.c. response in aged samples. For the fresh samples, n falls to unity regardless the composition (see details in the text).

probable interconnection between the fractional exponent n and different ways of thermal degradation of the conductivity is a preliminary speculation; to the best of our knowledge such explanation has not appeared in the literature. Further investigation is required on a large collection of experimental data from different materials are needed to seek if a general rule holds.

3. Conclusion

The room temperature a.c. conductivity of fresh and thermally aged polypyrrole–polyaniline blends of various compositions is determined by a d.c. plateau followed by a fractional dispersive region on increasing working frequency. The cross-over frequency of the aforementioned frequency regions is a function of the composition and is reduced by the thermal aging in polyaniline-rich blends. The reduction of the size of the conductive grains seems to interrelated with the reduction of the size of clusters where localized hopping occurs. The fractional exponent that determines the frequency-dispersive region of the conductivity is close to unity for all the fresh samples. Thermal aging results in values of the fractional exponent which depend on the composition in polyaniline-rich specimens. This is in accordance with previous d.c. vs. temperature studies: thermal aging reduces the size of conducting islands in polyaniline,

while, in polypyrrole, results in a modification of the backbone matrix. The a.c. measurements at room temperature can profile easily the thermal degradation of the electric charge transport properties in conducting polymer blends.

References

- [1] S. Sakkopoulos, E. Vitoratos, E. Dalas, *Synth. Met.* 92 (1998) 63.
- [2] E. Dalas, S. Sakkopoulos, E. Vitoratos, *Synth. Met.* 114 (2000) 365.
- [3] S. Sakkopoulos, E. Vitoratos, J. Grammatikakis, A.N. Papathanassiou, E. Dalas, *J. Mater. Sci.* 37 (2002) 2865.
- [4] A.N. Papathanassiou, I. Sakellis, J. Grammatikakis, S. Sakkopoulos, E. Vitoratos, E. Dalas, *J. Phys. D* 35 (2002) L85.
- [5] A.N. Papathanassiou, J. Grammatikakis, S. Sakkopoulos, E. Vitoratos, E. Dalas, *J. Phys. Chem. Solids* 63 (2002) 1771.
- [6] J. Dyre, *J. Appl. Phys.* 64 (1988) 2456.
- [7] A.K. Jonscher, *Dielectric Relaxation in Solids*, Chelsea Dielectrics Press, London, 1983.
- [8] E. Singh, A.K. Narula, R.P. Tandon, A. Mansingh, S. Chandra, *J. Appl. Phys.* 80 (1996) 985.
- [9] P. Dutta, S. Boswas, K.D. De, *J. Phys.* 13 (2001) 9187.
- [10] K.-M. Jager, D.H. McQueen, Tchmutin, M. Kluppel, *J. Phys. D* 34 (2001) 2699.
- [11] S. Capaccioli, M. Lucchesi, P.A. Rolla, C. Ruggeri, *J. Phys.* 10 (1998) 5595.
- [12] A.K. Jonscher, *Nature* 267 (1977) 673.
- [13] C. Menardo, M. Nechtschein, A. Rousseau, J.P. Travers, *Synth. Met.* 25 (1988) 311.
- [14] P. Rannou, M. Nechtschein, J.P. Travers, D. Berner, A. Wolyer, D. Djurado, *Synth. Met.* 101 (1999) 724.