Shrinking Rate of Conducting Grains in HCl–Protonated Polyaniline, Polypyrrole, and Polypyrrole/Polyaniline Blends with Their Thermal Aging

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ABSTRACT: The dc electrical conductivity (σ) of HCl-protonated polyaniline, polypyrrole, and their blends was measured from 80 to 300 K for thermal aging times between approximately 0 and 600 h. The thermal aging took place at 70°C under room atmosphere. The change of σ with the temperature (T) and the decrease of σ with the thermal aging time (t) are consistent with a granular metal type structure, in which conductive grains are randomly distributed into an insulating matrix. Aging makes the grains shrink in a corrosion-like process. From $\sigma = \sigma(T)$ measurements the ratio s/d, where s is the average separation between the grains and d their diameter, as well as the rate $d(s/d)/dt$ of their decrease with t were calculated. These revealed that the conductive grains consist of a shell, in which aging proceeds at a decreasing rate, and a central core, which is consumed at a much slower rate. Our measurements not only permitted the estimation of the shell thickness, which lies between 0 and 5 Å, but also gave quantitative information about the quality of the shells and the cores from their aging rates. The shells are consumed with an average rate of $d(s/d)/dt = 6.6 \times 10^{-4}$ (h^{-1}), which is about 5 times greater than the more durable cores. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 117–122, 2005

Key words: conducting polymers; polyaniline; polypyrrole; blends; aging

INTRODUCTION

The thermal stability of conductive polyaniline (PANI) and polypyrrole (PPy) has been extensively studied, because the understanding of their aging, which is a complicated process involving the loss of dopant, chlorination of the rings, oxidation, hydrolysis, and crosslinking of the chains, may lead to the proper chemical modification of the polymer in order to delay this undesirable phenomenon.[1–3] As early as 1989, X-ray diffraction patterns in association with metallic Pauli susceptibility from HCl-protonated PANI led to the conclusion that in this polymer 3-dimensional conductive regions were formed that were separated by insulating unprotonated material.[4] Moreover, evidence supporting this granular metal type structure for PANI has been gathered from scanning tunneling and transmission electron microscopy, electron spin resonance, thermopower, and dc and ac conductivity.[5–8] Measurements of dc conductivity and thermal aging of PPy indicate that, like in PANI, this polymer also consists of conducting grains separated by insulating barriers and electronic conduction takes place by carrier tunneling through them.[9,10] Aging appears to be a process in which conducting grains are gradually consumed in a corrosion-like manner, advancing from their outer to central parts.[11–13]

The electrical conductivity in a material with the granular metal type structure is greatly reduced by the widening of the barrier thickness between the conducting grains. In an easily degrading material the rate of this widening with thermal aging would be expected to be higher than in a more durable one. This prompted us to investigate the aging rate of PANI and PPy for different thermal treatment times. Moreover, as in previous experiments on PPy/PANI blends, the conductivity of the nonaged samples and the time (τ), which characterizes the aging rate, as a function of the PPy/PANI ratio, exhibit a complementary wavelike behavior.[14] We extended our measurements in these blends as well to gain insight into the structure of their conducting grains.

EXPERIMENTAL

The conductive polymers, which varied from pure PANI to pure PPy with the content of the latter increasing in steps of 10% (w/w), were made from freshly distilled monomers (Merck) under a vacuum.

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They were mixed in the proper ratio and polymerized in the presence of FeCl$_3$ (Merck) as an oxidant in HCl acid–water solutions at pH 2.00 in an ice bath (monomers/oxidant = 1:1 mol/mol) under a nitrogen atmosphere. The polymers, obtained as black powders, were purified by Soxhlet extraction[15] for 36 h and then compressed in an IR press into disk-shaped specimens, which were 13 mm in diameter and about 1.5 mm thick. Because the chemical analysis of the solution above the precipitates revealed a negligible concentration of the monomers used initially, the blends must have the same PPy/PANI ratio as the monomers used at the beginning.

The thermal aging of the samples took place in an oven thermostated at 70°C under room atmosphere for times ranging from 0 to about 600 h. This temperature is very low for chemical degradation of the blends to occur, because it was confirmed by differential scanning calorimetry and thermogravimetry experiments that such a process takes place well above 150°C. The dc conductivity for temperatures ranging from 80 to 300 K was measured with a four-probe method in a cryostat filled with inert He gas.

RESULTS AND DISCUSSION

With the exception of PPy, the dc electrical conductivity (σ) of all the other polymers followed the relation

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/2}\right] \qquad (1)$$

which is consistent with a granular metal type structure, in which conductive grains are separated by insulating barriers, through which thermally excited carriers move by tunneling.[16] The parameter (T_0) directly depends on the ratio s/d, where s is the average distance between the conductive grains and d is the their average diameter, according to the relation[17,18]

$$\frac{s}{d} = \frac{kT_0}{16U} + \sqrt{\left(\frac{kT_0}{16U}\right) \times \left(\frac{kT_0}{16U} + 1\right)} \qquad (2)$$

where U is the energy of Coulomb repulsion between two electrons in a distance equal to the size of the monomer, which is estimated to be 2 eV from electron spin resonance measurements and remains practically constant with aging.[11] From eq. (2) it can be seen that from the values of T_0 for different thermal treatment times, the corresponding values of the s/d ratio can be deduced, so the increase of T_0 with thermal aging can be directly associated with the decreasing of the grain size.

For PPy the σ as a function of temperature followed the law

$$\sigma = \sigma_0 \exp\left[-\frac{T_1}{T_0 + T}\right] \qquad (3)$$

indicating that the conductive grains are so close together that the tunneling process is dominated by the thermal fluctuations of the carrier concentration across the insulating barriers.[19] From T_1 and T_0 the s of the conducting grains and the height (ΔE) of the energy barrier can be estimated for PPy, according to the relations[20]

$$\Delta E = kT_1 \text{ and } \frac{T_1}{T_0} = \sqrt{2m\Delta E}\,\frac{2s}{\hbar} \qquad (4)$$

Additional evidence supporting the granular metal type structure of the polymers used is that for all of them the thermal aging of the conductivity followed the law

$$\sigma = \sigma_0 \exp\left[-\left(\frac{t}{\tau}\right)^{1/2}\right] \qquad (5)$$

where τ is the time that characterizes the aging.[11]

Figure 1 shows the increase of the s/d ratios of 20/80 and 90/10 PPy/PANI as a function of the t of the thermal aging, where the 20/80 and 90/10 ratios indicate percentages. For the 20/80 PPy/PANI blend there is an initial stage of rapid decrease of the grain size (increase of the s/d ratio) with a continuously decreasing rate, although after about 100 h of heat treatment this rate is stabilized to a certain value. This behavior can be easily explained by the assumption that the conductive grains are surrounded by a shell, which has durability improving from the outside toward the interior, and a central part, the core, of better quality. The shell is consumed during the first 100 h of heat treatment and after that thermal aging affects the core, whose quality appears steady, as far as the aging goes after 600 h of treatment.

In contrast, the 90/10 PPy/PANI blend exhibits completely different behavior. As shown in Figure 1, the rate of the grain decrease remains constant throughout the thermal treatment and it is almost equal to that of the central part of the grains of the 20/80 PPy/PANI blend. This implies that the grains have no shell and they are of good quality to the depth at which they are consumed by the thermal aging after heating for ~600 h at 70°C.

For the conducting polymers examined in this study, from pure PANI to 60/40 PPy/PANI (included) the behavior was similar to that of the 20/80 blend, revealing the existence of a heterogeneous structure of the grains, consisting of an external shell and a central core of better quality. Conversely, in the 70/30, 80/20, and 90/10 blends, the grains have no shells. Thermal aging of pure PPy is accompanied by
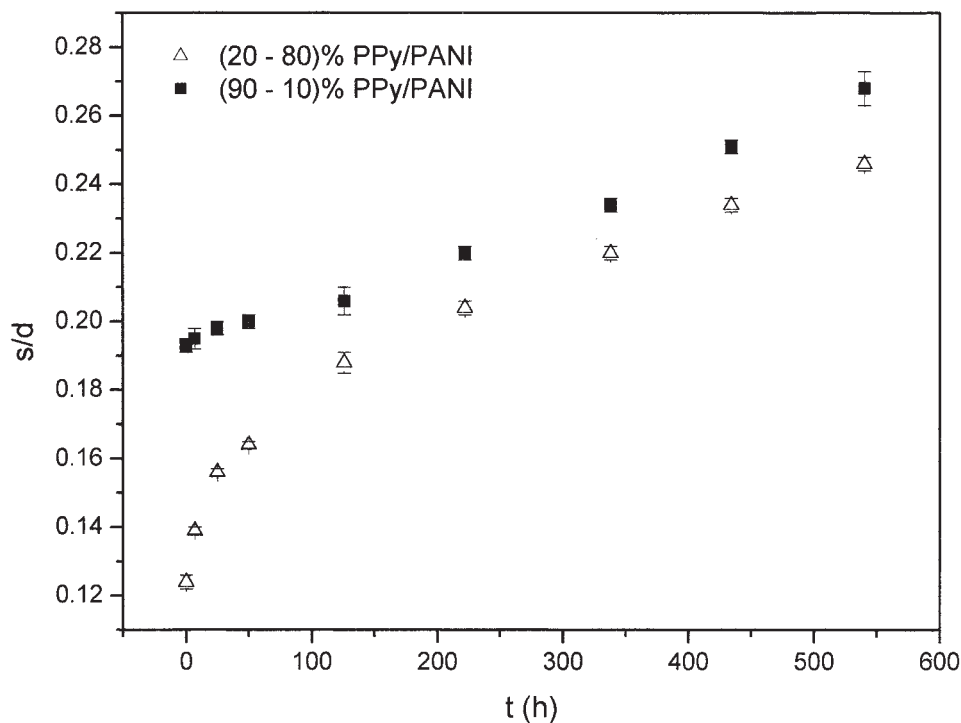
Figure 1 The change of the ratio of the average distance between the grains to the diameter (s/d) as a function of the thermal aging time (t) for the 20/80 and 90/10 polypyrrole/polyaniline blends. For the first sample, two regions with different slopes appear, which correspond to the shell and the core of the grain.

an initially rapid shrinking of the grains, followed by a slower contraction, revealing the existence of shells in this polymer as well.

From the s/d ratio and taking approximately $s + d \sim 200$ Å, the values of s and d can be calculated.[11,21] The thickness of the shell can be deduced as half of the difference between the average diameters of the grains at the two ends of the initial part of the $s/d = f(t)$ curve of Figure 1, which for the 20/80 PPy/PANI sample correspond to 0 and about 100 h of heat treatment, referring to the beginning and the ending of the consumption of the shell, respectively. The thickness of the shells for the polymers examined range between approximately 0 and 5 Å, as shown in Figure 2.

The rate $d(s/d)/dt$ of the thermal aging, deduced from the slopes of the graphs $s/d = f(t)$, such as the ones shown in Figure 1, give a measure of the quality of the shells and the central parts of the grains. The lower the rate $d(s/d)/dt$ is, the better the quality. From Figures 3 and 4, in which these slopes are shown for the shells and the central parts, respectively, for the different blends, it can be concluded that the quality of the shell is inferior to that of the central parts of the grains, because the aging rate of the former is on the average 6.6×10^{-4} (h^{-1}), which is 5 times greater than that of the latter, which is 1.3×10^{-4} (h^{-1}).

Starting from pure PANI, we see that a core of very good durability coexists with a shell of poor quality. The situation is reversed with the addition of only 10%

PPy, giving conductive grains with cores of greatly reduced quality and slightly improved shells. PPy, acting as a dopant, seems to significantly disturb the arrangement of the polymer chains in the central parts of the grains, although it improves the quality of the shell. Higher concentrations of PPy up to 60% improve the quality of the central part of the grains, which approaches that of pure PANI, although there is no systematic change of the shell quality. From Figures 2 and 3 it is evident that the conditions that lead to the formation of thicker shells do not favor their good quality.

The blends with PPy content between 70 and 90%, in which the grains are not surrounded by shells, are characterized by a similar slow rate of thermal aging, although their conductivities remain practically constant with the PPy content and take low values.[14] This is easily explained, because with the absence of shells, aging attacks the polymer of about the same good quality, as shown in Figure 4. At first sight the low conductivities are inconsistent with the good quality of the grains. However, from Figure 5, in which the s between the grains and the σ at room temperature as functions of the percentage of PPy are shown for the nonaged samples, blends with 70–90% PPy are characterized by longer distances between grains, which makes the tunneling of the carriers difficult.

For the blends with PPy contents between 10 and 60%, in which the grains are surrounded by shells,
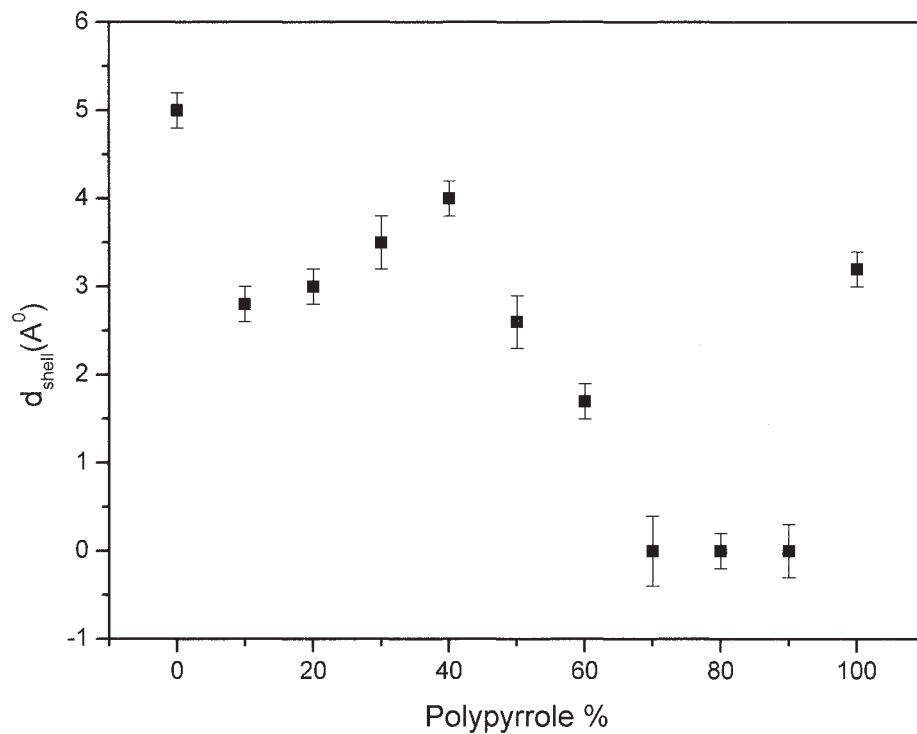
Figure 2 The calculated shell thickness for the different polypyrrole/polyaniline blends.
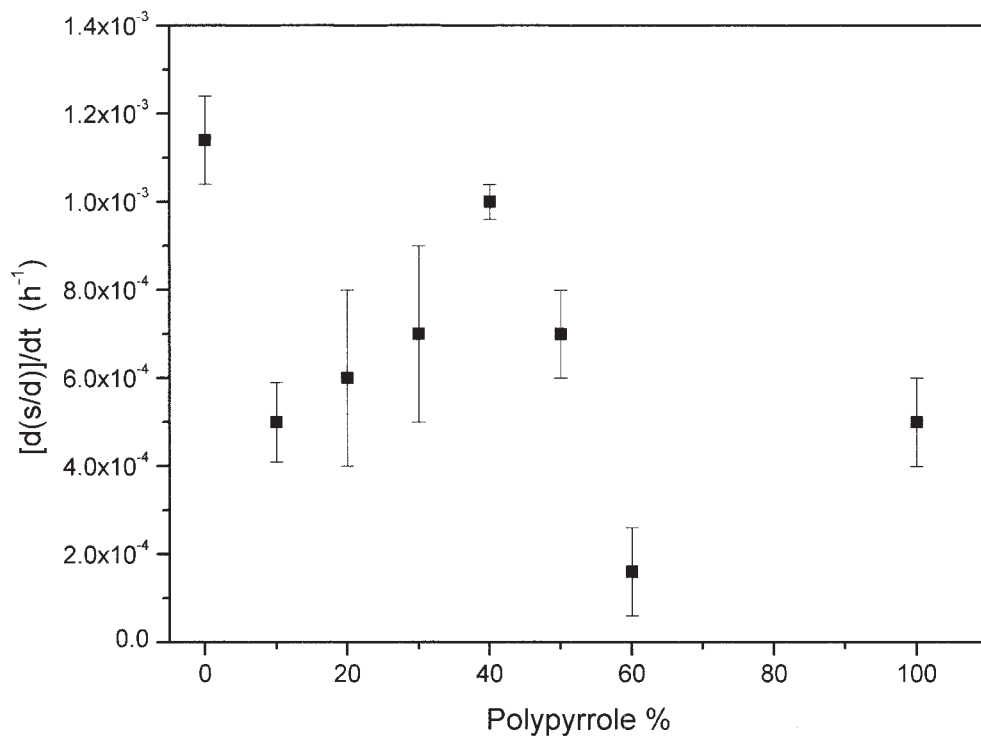

Figure 3 The average rate of change of the ratio of the average distance between the grains to the diameter (s/d) for the shells during their thermal aging for the different polypyrrole/polyaniline blends. The s value of the conductive grains increases as their d value decreases with aging. The higher this rate is, the worse is the quality of the shells. Blends with 70, 80, and 90% polypyrrole do not form shells.
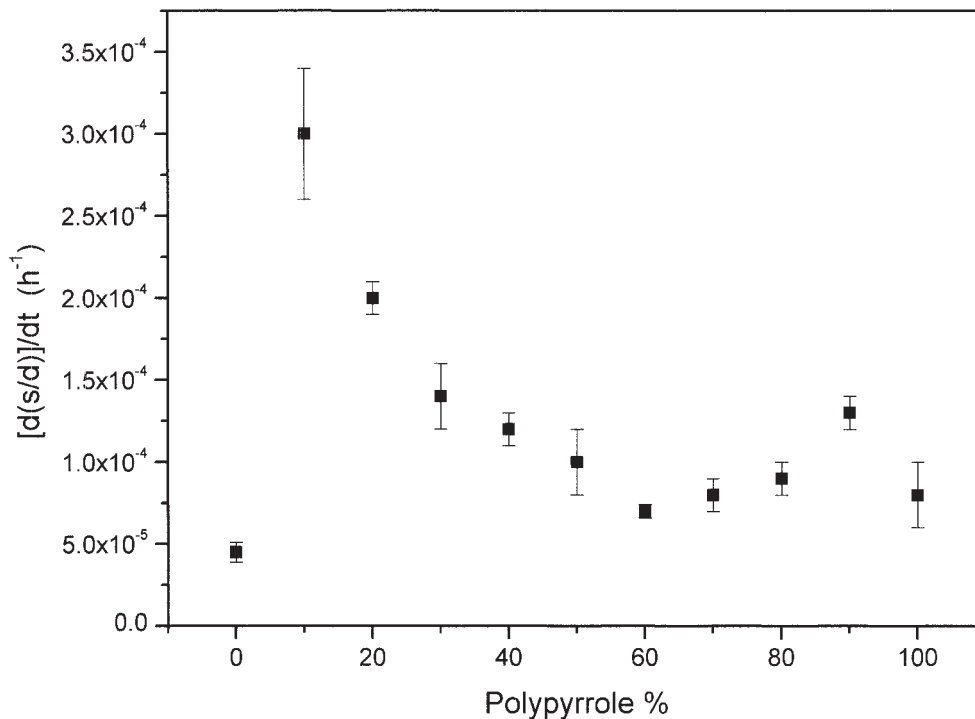
Figure 4   The rate of change of the ratio of the average distance between the grains to the diameter (s/d) for the cores of the grains, which gives a measure of their quality.

there is an increase of the aging rate. This is due to two reasons: the first is that now the shells, with their inferior quality, are attacked easier and the second is

that, as shown in Figure 4, the quality of the grain interiors is reduced. In addition, the overall influence of the shells on the aging is not as important as that of
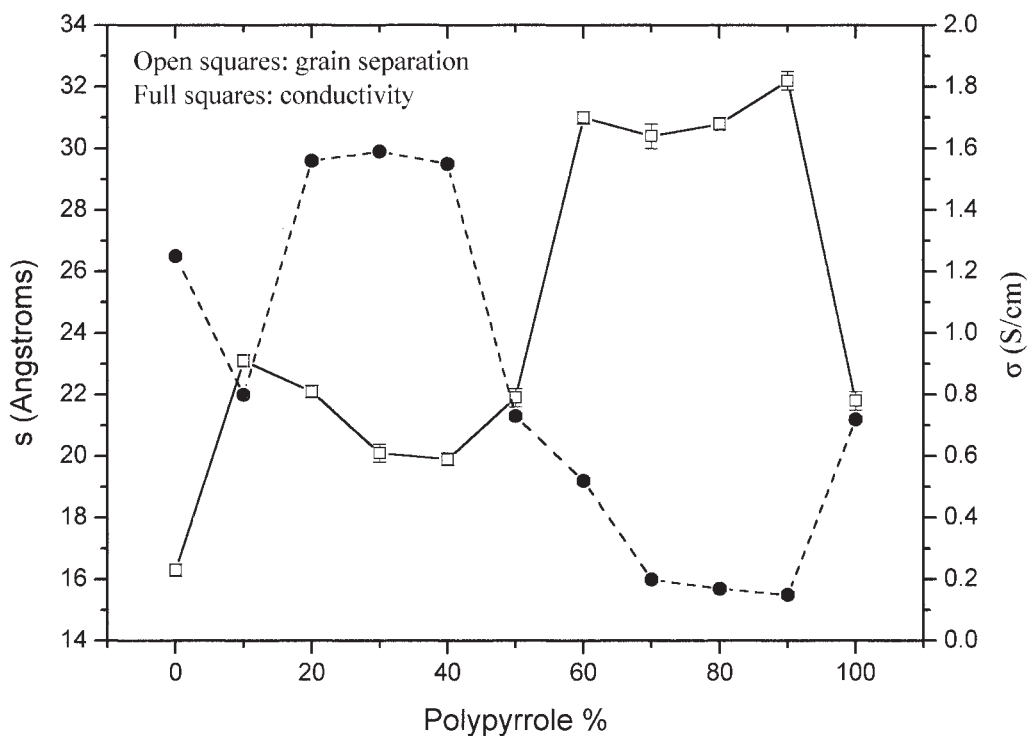

Figure 5   The average distance (s) between the conductive grains and the conductivities (σ) at room temperature of the non aged samples for the different polypyrrole/polyaniline blends.

the grain cores, because the aging of the shells changes them to insulating polymers after about the first 50–100 h of thermal treatment. The high conductivity of blends with contents from 20 to 40% PPy[14] can be explained by the short distance between the conductive grains, as shown in Figure 5, although it is combined with the polymer with reduced quality in the interior of the grains, in which the aging rate takes high values.

CONCLUSIONS

The study of the thermal aging of PANI, PPy, and their blends by dc conductivity measurements reveals a granular metal structure, in which the conductive grains, separated by an insulating polymer, consist of a shell of low durability to aging processes surrounding a core of better quality. Aging proceeds through the shell at a quicker rate than into the core, changing the conductive polymer into an insulating material. Moreover, our measurements allowed us to estimate the thickness of the shells, ranging from approximately 0 to 5 Å, as well as to find a measure of the quality for the shells and the cores of the conducting grains. The aging rates for the shells were on the average 6.6×10^{-4} (h^{-1}), although for the more durable cores of the grains they were 1.3×10^{-4} (h^{-1}), which is about 5 times lower.

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