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Dielectric properties of PANI/PSS blends obtained by *in situ* polymerization technique

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Summary

Polyaniline (PANI) was obtained by *in situ* polymerization in a polystyrene sulfonic acid (PSS) solution. We prepared a series of PANI/PSS blends with molar ratio of 1:2, and PSS sulfonated at the degrees of 13 mol%, 21 mol% and 30 mol%. A control sample of polystyrene, at an intermediate sulfonation degree of 21%, without polyaniline, was also considered. The impedance spectroscopy, scanning electron microscopy and X-ray diffraction of the blends were evaluated. Increasing sulfonation degree increases the conductivity of the blends. Scanning electron microscopy (SEM) images allowed us to correlate the electrical properties of the blends with their morphologic characteristics. The smoothness of the blends surface observed by SEM increased with the sulfonation degree. X-ray diffraction indicated the increasing order with the sulfonation. This can be associated with homogeneous phase distribution, which results in highly conductive material.

Introduction

Conducting polymers have attracted great scientific and technological interest due to their wide variety of applications [1]. In particular, the addition of conducting particles in an insulating polymer matrix increases their electromagnetic radiation absorption suggesting their use for effective electromagnetic interference shielding applications [2]. Intrinsically conducting polymers (ICP) are alternative materials to semiconductors, because of their high conductivity combined with low weight, low synthesis cost and easy processability. Among conducting polymers, polyaniline (PANI) presents remarkable conductivity, in the order of 10^2 $\mathrm{Scm^{-1}}$. It has received wide spread attention due to their industrial applications such as corrosion protection [3], electromagnetic interference shielding [2], environmental stability [3], moderate conductivity materials [3], interesting redox properties [4] and also to the economical efficiency. However, it presents the disadvantage of poor mechanical properties. This problem is related to its aromatic structure, interchain hydrogen bonds and effective charge delocalization in its structure [5]. A common method used to overcome the problems associated with the poor mechanical properties is the association of ICPs with thermoplastic polymers.

There have been some reports on the synthesis of polyaniline-polystyrene blends [6-10], poly(vinyl alcohol)–sodium polystyrene sulfonate blends [11], polystyrene-polyaniline-polystyrene sulfonic acid [12], polyaniline-poly(ethy1ene-copropylene-co-ethylidenenorbornene) [13]. According to reference [5] polyaniline-polystyrene was synthesized using emulsion method with HCl as doping agent and the effect of reaction conditions on the conductivity and morphology of the blends was investigated. Correlations between the electrical conductivity, homogeneity of PANI blends and synthesis conditions have been the subject of many works [7-10]. Indeed, the choice of chemical composition, the method of preparation and processing parameters influence the structural properties of the blends [14] and for this reason it is important to produce and investigate different PANI blends.

The transport properties of PANI associated with other polymers are quite different than the pure PANI. Interesting characteristics such as percolation thresholds have been reported, involving charge transport among PANI particles which typically occurs for concentrations in the order of 1-30% [10, 15-17]. Also the formation of a homogeneous dissolution phase with higher conductivity than that of thermoplastics prepared with PANI particles has been reported [9]. However, the microstructural features of the polymeric acid-doped PANI and the amount of polymeric acid groups that effectively dope the PANI are yet to be described properly [18].

In this work, we present dielectric properties of PANI polymerized inside PSS with different sulfonation degrees. We analyzed the complex impedance in the range 10 Hz to 30 MHz, and compared with the structural differences which depend on the sulfonation degree of PSS present in the prepared materials. The main result is that increasing sulfonation degree increases the conductivity of the blends. Scanning electron microscopy and X-ray diffraction were applied to investigate the correlation of the electrical properties to the morphological characteristics of the blends. The smoothness of the blend surface increased with the sulfonation degree, which implies in the homogeneity of phase distribution. This is consistent with the high conductivity observed for the highest sulfonation degree used.

Experimental

Synthesis

PSS was prepared using different amounts of commercial polystyrene (PS) $M_W = 33,000$ dissolved in CH_2Cl_2 in a three-neck round-bottomed flask (1 l) equipped with mechanical stirring, thermometer and separator funnel. The flask containing the solution was heated to 40°C in order to obtain total solubilization of PS and purged with Ar for 30 min. A freshly prepared acetyl sulfate solution was added using the separator funnel. The reaction mixture was maintained at 40°C under stirring for 2 h. The solution became clear yellow after addition the sulfonating agent. The reaction was interrupted by addition of excess of 2-propanol for 30 min and cooling to room temperature. Finally, the sulfonated polymer was isolated [19].

PANI/PSS conducting blends were prepared by *in-situ* polymerization technique with the PSS as dopant acid. The PSS was previously prepared at different sulfonation degrees. Then, PSS was dissolved in commercial ethanol at 50°C for solubilization.

After this, the temperature was decreased to 5°C and aniline monomers (1:2 molar ratios of PANI/PSS) were added and stirred for homogenization. Then a solution of ammonium persulfate ($(NH_4)_2S_2O_8$) used as oxidant agent in a monomer/oxidant ratio of 0.8 was dropped into the aniline-PSS solution. The reaction was finished after 2 h and the material was washed and dried. A characteristic green powder was obtained indicating the formation of conductive PANI. Different sulfonation degrees were obtained by the use of different volumes CH_2Cl_2 during the sulfonation process and determined by titration with a standard 0.01 $moll^{-1}$ NaOH solution in methanol [19]. All titrations were carried out by dissolving 150 mg of PSS in 15 ml of methanol. The sulfonation degree (x) is expressed as mole percent of the sulfonated styrene repeating units, PSSx%. In this work we used PSS21%, PANI/PSS13%, PANI/PSS21% and PANI/PSS30% which will be designated by A0, A1, A2 and A3 respectively.

Characterization

Scanning electron microscopy (SEM) was performed in a Hitachi-S4100 operated at 25 kV. The powder samples were carbon sputtered prior to measurements.

The structural characterization of all the powder samples were carried out by the X-ray diffraction (XRD) technique on a Rigaku Geigerflex-D/max-C diffractometer with nickel filter using Cu-Kα radiation (wavelength λ = 1.541 Å).

The powder samples were pressed into disc shaped samples with 8.0 mm diameter and 1.5 mm of thickness for the dielectric characterization. Dielectric measurements were carried out using a HP4285A LCR meter equipped with a HP16451B measuring contact cell for frequencies above 75 kHz, and an 850 Stanford Research lock-in amplifier for lower frequencies. The method consists in the measuring of the 'in phase' and the 'out of phase' components of the output signal, and these quantities were then used to calculate the values of effective resistance and capacitance in a parallel RC (Resistance-Capacitor) model of the sample. The experimental parameters were frequency range of 10 Hz to 30 MHz, without bias, and sinusoidal voltage amplitude of 1.0 V_{rms}. All the measurements were carried out at a constant temperature (23°C).

Results and Discussion

Figure 1 a, b, c and d presents SEM images of A0, A1, A2 and A3 respectively. The A0 image was obtained in a 100 times larger scale than the other ones. It can be seen that the powder particles are continuous, with flat and smooth surfaces and without observation of smaller particles. Comparing the morphologies of figure 1b to 1d, we can identify that the phase separation is clearly noticed in the A1 and A2 images, and for A3 there is no clear separation between PANI and PSS, indicating a homogeneous mixture of phases and a good compatibility. The morphology changes from a compact agglomerate of particles in Figure 1b, to a structure with large pores in 1c and to a uniform structure in 1d. The agglomeration of particles observed in figure 1b and 1c are characteristic of the emeraldine base PANI [10] powder which is absent in figure 1a, and which consists in PSS without PANI. This indicates that samples A1 and A2 did not present a homogeneous mixture of PANI and PSS.

The XRD patterns of the samples are presented in figure 2. They indicate that the samples have low crystallinity, with very broad diffraction peaks. As will be

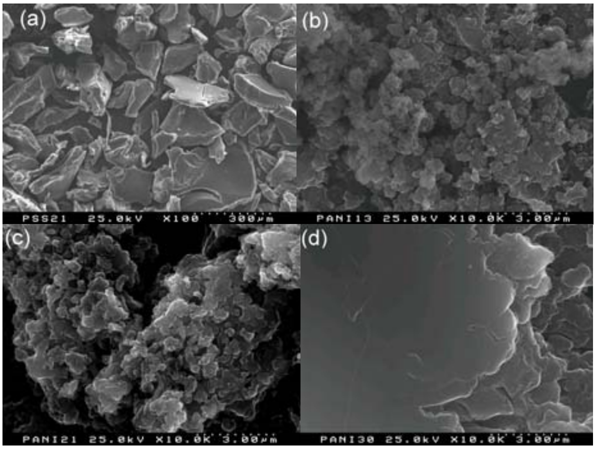

Figure 1 - SEM images of: (a) A0, (b) A1, (c) A2 and (d) A3.

demonstrated from the XRD analysis, our samples are more amorphous than that presented in reference [20]. Crystallinity and orientation of conducting polymers have been of much interest, because more highly ordered systems can display a metallic-like conductive state [21]. Table I summarizes the fitting parameters obtained from peak fittings of XRD measurements presented in figure 2. For each sample we present the peak position, the interplanar separation *d*, and the crystalline domain size *L*. Four distinct peaks were identified in all the samples, but with distinct characteristics. The *d* values were deduced from the angular position 2θ of the observed peaks, according to the Bragg formula

$$\lambda = 2d \sin\theta \qquad (1)$$

where λ is the X-ray wavelength.

For each peak, there is a defined value for *d* which does not vary significantly with doping, except for peak #1. For the other peaks we calculated values that sit around (4.5 ± 0.1) Å, (3.5 ± 0.4)Å, and (2.1 ± 0.2) Å for peaks #2, #3 and #4 respectively.

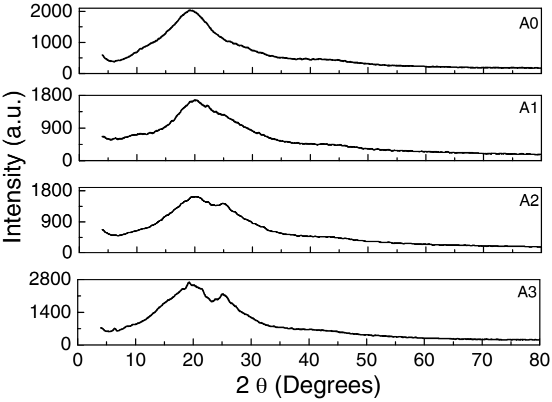

Figure 2 - XRD for the studied samples.

The crystalline domain size or the extent of order, L, were also estimated from the $\Delta(2\theta)$ (full width at half-maximum) according to the Debye-Scherrer equation

$$L = \frac{0.9\lambda}{\Delta(2\theta)\cos\theta} \tag{2}$$

Most L values are of the same order of d, indicating that the samples are highly amorphous. However, the peaks #2 and #3 show a clear tendency to increase with the doping reaching about 4 times their respective d values for the sample A3. Comparing our results with the HCl doped PANI results of reference [20], we can infer that two factors might influence the lower values of L observed for our samples. One is a lower effective doping of the PSS on the PANI, when compared to HCl doping. The second factor is that our PSS presented amorphous XRD characteristics, and since PANI was polymerized inside the PSS, it tends to accompany the PSS structure.

The dielectric response is described by the complex impedance as

$$Z^* = Z' - jZ'' \tag{3}$$

where Z' is the real and Z'' the imaginary parts of the complex impedance respectively.

Table I: Summary of the XRD fittings for all samples.

	A0			A1			A2			A3		
#	2θ (°)	d (Å)	L (Å)	2θ (°)	d (Å)	L (Å)	2θ (°)	d (Å)	L (Å)	2θ (°)	d (Å)	L (Å)
1	12	7.3	13	10	9.1	8.6	18	4.9	5.3	17	5.2	7.2
2	19	4.6	8.4	19	4.5	10	20	4.5	15	20	4.4	17
3	28	3.1	8.3	25	3.5	5.7	25	3.5	7.6	26	3.5	12
4	43	2.1	5.6	44	2.1	4.6	43	2.1	3.8	39	2.3	3.0

In figure 3, we present the real and imaginary parts of the complex impedance as a function of frequency, for two of the studied samples.

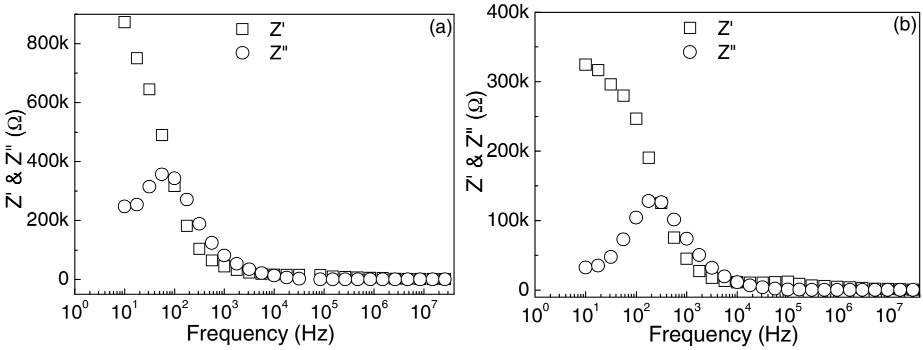

Figure 3 - Impedance spectroscopy of the samples: a) A2 and b) A3.

In order to analyse these data, we represent them in the form of Cole-Cole (Z'' vs. Z') plot, as is shown, as an example, in figure 4.

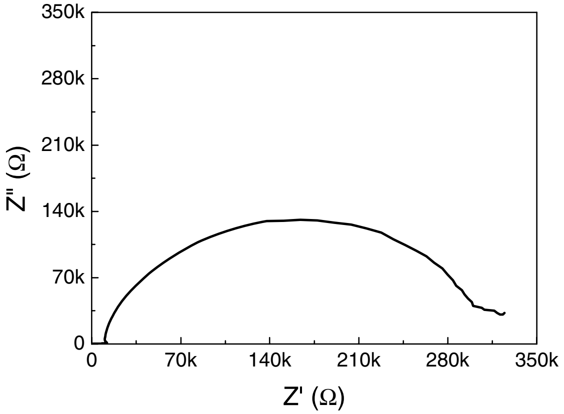

Figure 4 - Cole-Cole plot for the impedance of A3.

An asymmetry is visible further confirming that a single relaxation time equation of Debye cannot be used to explain the low frequency dielectric relaxation in these materials. We have, therefore, analysed the data from the point of view of Cole-Cole [22] function,

$$Z^*(\omega) = Z_\infty + \frac{\Delta Z}{1 + (i\omega\tau)^{1-\alpha}} \tag{4}$$

In this expression, which is an empirical modification of the Debye equation, Z_∞ is the high frequency resistance, ΔZ the relaxation strength, τ the relaxation time and α a parameter between 0 and 1 that reflects the dipole interaction. When α is close to 0, the material is more homogeneous, and the semicircle is practically centred in the x-axe. In table II we summarize the calculated relaxation parameters.

Table II: Relaxation parameters for all samples using the Cole-Cole model.

Sample	Sulfonation (%)	ΔZ (kΩ)	α	Relaxation frequency (Hz)
A0	21	960	0.70	23
A1	13	950	0.69	30
A2	21	859	0.62	51
A3	30	304	0.57	237

We can observe that the α decreases with the degree of sulfonation, indicating that the material becomes more homogeneous. Simultaneously, the relaxation time decreases, corresponding to an increase of the relaxation frequency. The relaxation strength decreases with sulfonation degree, due to the presence of the conducting particles.

Considering that A0 and A2 have the same sulfonation degree, and that A0 has no PANI, the conductivity is higher for A2, due to the presence of the conducting particles.

Comparing A1 and A2, we observe the increase of conductivity with the sulfonation degree, which is consistent with a better interaction between PSS and PANI and in the homogeneity of the phases. Associating these observations with the SEM images, we can infer that, since the morphology of samples A1 and A2 are very similar, the effect of the doping characteristic of the PSS on the PANI might have a higher effect on the observed changes from A1 to A2 on the dielectric characteristics than the morphology itself.

Increasing the sulfonation degree from 21% to 30%, we observe again the decrease in the impedance. For A3, the morphology changes, when compared with A1 and A2, as presented in figure 1d, with a smooth surface and no identifiable particle structures. In this case, besides a higher doping by the PSS due to a higher sulfonation degree, the homogeneous distribution of PANI leads to a higher conductivity since charge carriers can flow without the need of crossing PSS high resistive regions. The homogeneity distribution of PANI leads to a highly conductive material. This indicates that the sulfonation degree of PSS can be used as an efficient method to control the electrical characteristics of the PANI blends designed for this work in a similar manner than the PANI particle density in other blends [10,15-17]. The increase of conductivity evidences the doping character of the PSS on PANI through the SO_3H groups present in PSS that provide the protonation reaction for PANI.

A0 and A1 present similar conductivity characteristics. This indicates that the PSS itself, even at a sulfonation degree of 21% does not have significant conductivity and also that the PANI particles in the PSS matrix with the sulfonation degree of 13% are not doped enough to change the conductive characteristics of the combined material through percolation. The segregation of the PANI particles plays an important role on this matter. Since the SEM images of sample A0 and A3 presented in figures 1a and 1d are similar, this means that two effects are present in sample A3. One is the doping of PANI by the PSS and the other is the homogeneous distribution of PANI at the PSS matrix.

Conclusion

In summary, polyaniline was prepared by *in situ* polymerization method in a polystyrene sulfonic acid solution. Increasing sulfonation degree increases the conductivity of the blends. As the amount of SO_3H groups present in the polymeric acid content increases, it is expected that the doping level of PANI increases. The impedance measurements, SEM images and XRD patterns suggest good compatibility of PSS with PANI. SEM images and XRD allowed us to correlate the electrical properties of the blends to their morphology characteristics. The smoothness of the blend surface and the order increase with the sulfonation degree. For the highest sulfonation degree, we observe homogeneous phase distribution which results in highly conductive material.

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