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Analysis of Conducting Poly(*o*-methoxyaniline) Blends by Impedance Spectroscopy

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Summary: Impedance measurements were carried out in flexible, conducting and semi crystalline films obtained by casting poly(*p*-hydroxystyrene)-*b*-polyisoprene (PHS-*b*-IR) and *p*-toluene sulfonic acid (TSA)-doped poly(*o*-methoxyaniline) (POMTS) mixtures from N,N-dimethylformamide solutions. The measures *ac* were made in LCR Meter HP4284A equipment, in the range 10^2–10^6 Hz. The results were analyzed using a program in LabView platform for the attainment of the impedance arcs to obtain the conducting blends parameters. The obtained results had allowed evaluating some characteristics of studied conducting POMTS blends as conductivity *ac*, dielectric relaxation time, and capacitance. Analysis by optical microscopy (OM) allowed the observation of quasi-spherical particles dispersed morphology for blends with 5 to 50-wt% of POMTS. However, this morphology was not observed for blends presenting more than 50% of POMTS.

Keywords: conducting blends; impedance spectroscopy; poly(*o*-methoxyaniline)

Introduction

Polyaniline (PANI) and their derivatives, such as poly(*o*-methoxyaniline) (POMA), are attractives conducting polymers due to its good conductivity, easy synthesis route and good thermal stability. The main disadvantage for industrial use is due to their low processability and poor mechanical properties. A way of overcoming this problem is blending POMA with insulating polymers to obtain materials with good properties for practical applications.

The mixture of two or more polymers to produce a blend or a composite is an efficient industrial strategy for achieving a material with specific properties. The goal of conducting blends is to combine mechanical properties of insulating polymers and electrical conductivity of conducting ones. These blends can be prepared by chemical (solution casting or melting) or electrochemical methods.

Conducting blends of PANI with poly (methyl methacrilate) (PMMA),[1,2] polystyrene (PS),[3,4] polyethylene (PE)[5,6] and terpolymer ethylene-propylene-diene (EPDM)[7] were obtained and a great number of practical applications proposed.[8–10]

MacDiarmid and coworkers[11,12] reported the unfavorable effect of the primary dopant (counter ions), which can attract the opposite moving charges and decrease the conductivity and crystallinity of the polymers. These effects can be reduced through the introduction of the so-called secondary dopant, moreover further increase in conductivity may be

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obtained.[13] The PHS may behave as a polymeric secondary dopant (PSD) in blends with poly(*o*-methoxyaniline). The interaction between the poly(*o*-methoxyaniline) and PHS will control the blend miscibility and dictate the secondary doping effect and the resulting in an electrical conductivity. The variation of the electrical resistivity conductivity of the conducting polyblend depends not only on the composition of the poly(*o*-methoxyaniline), but also on the amount of PSD and the blend morphology.[12]

In this work we have prepared blends of synthesized diblock copolymers, poly (*p*-hydroxystyrene)-*b*-polyisoprene (PHS-*b*-IR) and a polyaniline derivative, poly (*o*-methoxyaniline) (POMA), which is highly soluble in organic solvents even when doped with organic strong acids. The aim of this paper is to characterize POMTS/PHS-*b*-IR blends obtained through the casting out technique by impedance spectroscopy. The results were analyzed considering chemical or physical interactions between the conductive material and insulating matrix.

Experimental

Deacetylation of Poly(*p*-Acetoxystyrene)-*b*-Polyisoprene (PASt-*b*-IR)

PASt-*b*-IR was prepared by nitroxide-mediated living radical polymerization, according to our previous work.[14] In the hydrolysis process catalyzed by KOH, 1.0 g of PASt-*b*-IR containing 0.468 g (2.89 mmol) of PASt block was dissolved in 30 ml of THF in a flask equipped with a condenser; a solution of 1.63 g (29.1 mmol) of KOH in 5 ml of methanol was added under strong stirring. The reaction mixture was heated to reflux for 29 h, during which time the polymer went into solution. The resulting mixture was slowly added under stirring to a large excess of 5% aqueous hydrochloric acid. After standing for several hours, the hydrolysis product poly (*p*-hydroxystyrene)-*b*-polyisoprene (PHS-*b*-IR) was isolated and washed with water several times, followed by drying in a vacuum oven at 60 °C overnight. Typical yield of the isolated PHS-*b*-IR was 78%. IR (neat) 3500–3200 cm^{-1} (OH), 3024 cm^{-1} (Ar–C–H), 3000–2850 cm^{-1} (CH_3), 1470 cm^{-1} (C=C). ^{13}C NMR (75 MHz, acetone-d_6): δ 16.04, 21.18, 26.43, 28.20, 30.72, 32.07, 38.29, 53.95, 111.29, 121.11, 134.98, 147.75. DSC: T_g's 194.2 °C (PHS)/ −60.7 °C (IR).

Doping of Poly(*o*-Methoxyaniline) (POMA) with *p*-Toluene Sulfonic Acid (TSA)

Doping was performed by mixing poly (*o*-methoxyaniline) with *p*-toluene sulfonic acid at 1:2.5 ratio in N,N-dimethylformamide (DMF). TSA-doped POMA (POMTS) thus prepared was used in polymer blends.

Polymer Blending

The blending of PHS-*b*-IR with POMTS was carried out in N,N-dimethylformamide (DMF) solution. The 1% POMTS and 1% PHS-*b*-IR DMF solution were prepared and mixed at different relative proportions in order to obtain controlled relative weight ratios of POMTS and PHS-*b*-IR in the polyblend. The polyblend solution was stirred for 24h, followed by casting on a glass plate and drying in a vacuum oven at 60 °C for 48 h.

Characterization

The poly(*p*-hydroxystyrene)-*b*-polyisoprene was confirmed using a Bruker NMR spectrometer, ^{13}C NMR (75 MHz) spectrum was obtained from acetone-d_6 solution with tetramethylsilane as an internal standard. IR spectra were collected by a Nicolet Magna-IR 560 FTIR spectrometer. Differential scanning calorimetry (DSC) analysis was performed using a Q-10 TA Instruments under N_2 atmosphere (20 °C/min). The morphology of the polymer blends were studied by optical microscopy (OM) equipment equipped with the "Went Worth 900" workstation. Impedances were measured by a LCR Meter HP4284A system, the frequency ranging from 10^2

to 10^6 Hz. The temperature was kept close to 25 °C.

Results and Discussion

The most commonly used experimental technique to analyze dynamics of charge carrier movement in conducting POMTS blends is complex impedance spectroscopy analysis.[14] Contributions of various microscopic elements can be identified by reference to an equivalent circuit, which contains ideal resistors, capacitors, perhaps inductances, and possibly various distributed circuit elements. The results of real (Z') and imaginary (Z'') parts of complex impedance data of conducting POMTS blends at different contents over the range of frequencies between 10^2 Hz and 10^6 Hz are shown in Figure 1a–c. In Figure 1a is observed that it was not possible to obtain a complete impedance arcs. For low frequencies the conducting POMTS blends impedance can be very high than 1 GΩ and the used equipment does not have resolution to operate in this impedance range. It can also be seen that there is a variation in the radius of the semicircles due the conducting blends polymer variable resistance.

The real (Z') and imaginary (Z'') parts of conducting blends complex impedance results data with 9% (Figure 1b), 90% and 100% (Figure 1c) of POMTS contents had been plotted separately due to great variation in the resistance, making possible the comparison of the obtained results.

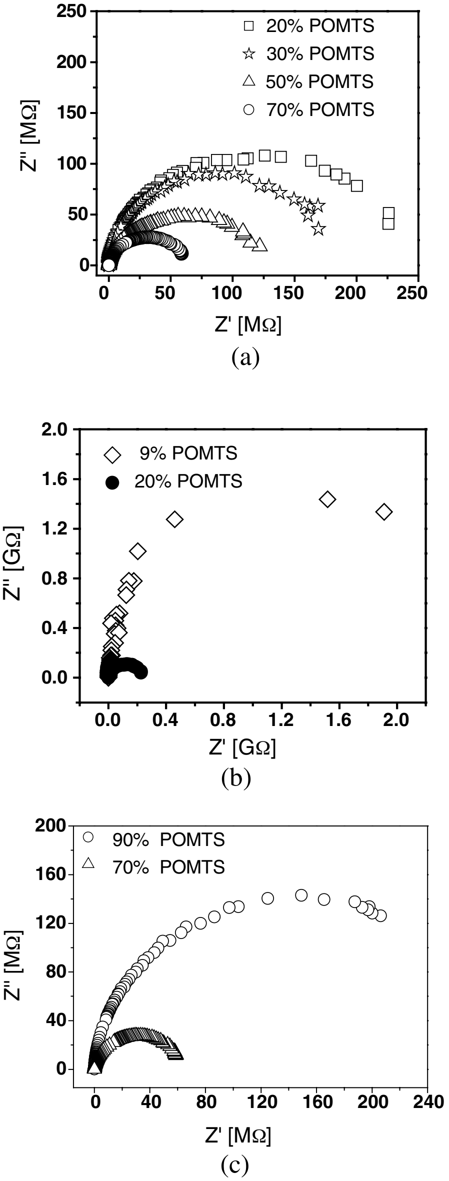


Figure 1.
Complex impedance plot of real (Z') and imaginary (Z'') of the conducting blends at different contents of POMTS.

Figure 2a–g shows the complex impedance plot of imaginary (Z'') versus real (Z') for the conducting blends at different contents of POMTS 9%, 20%, 30%, 50%, 70%, 90% and 100%, respectively. It can be seen from Figure 2a–g in Cole-Cole plots that the obtained adjustments had been very good, except the 9% POMTS content conducting blend that presented a high resistance and in low frequencies the combination with the capacitive effect produced noise results. These results permit to conclude that the arc center is displaced below the real axis due the presence of distributed elements that cause relaxation time distribution suggesting the presence of Constant Phase Element (CPE). Thus the electrical behavior (equivalent circuit) of conducting POMTS blends may have a CPE element in parallel with a resistance.

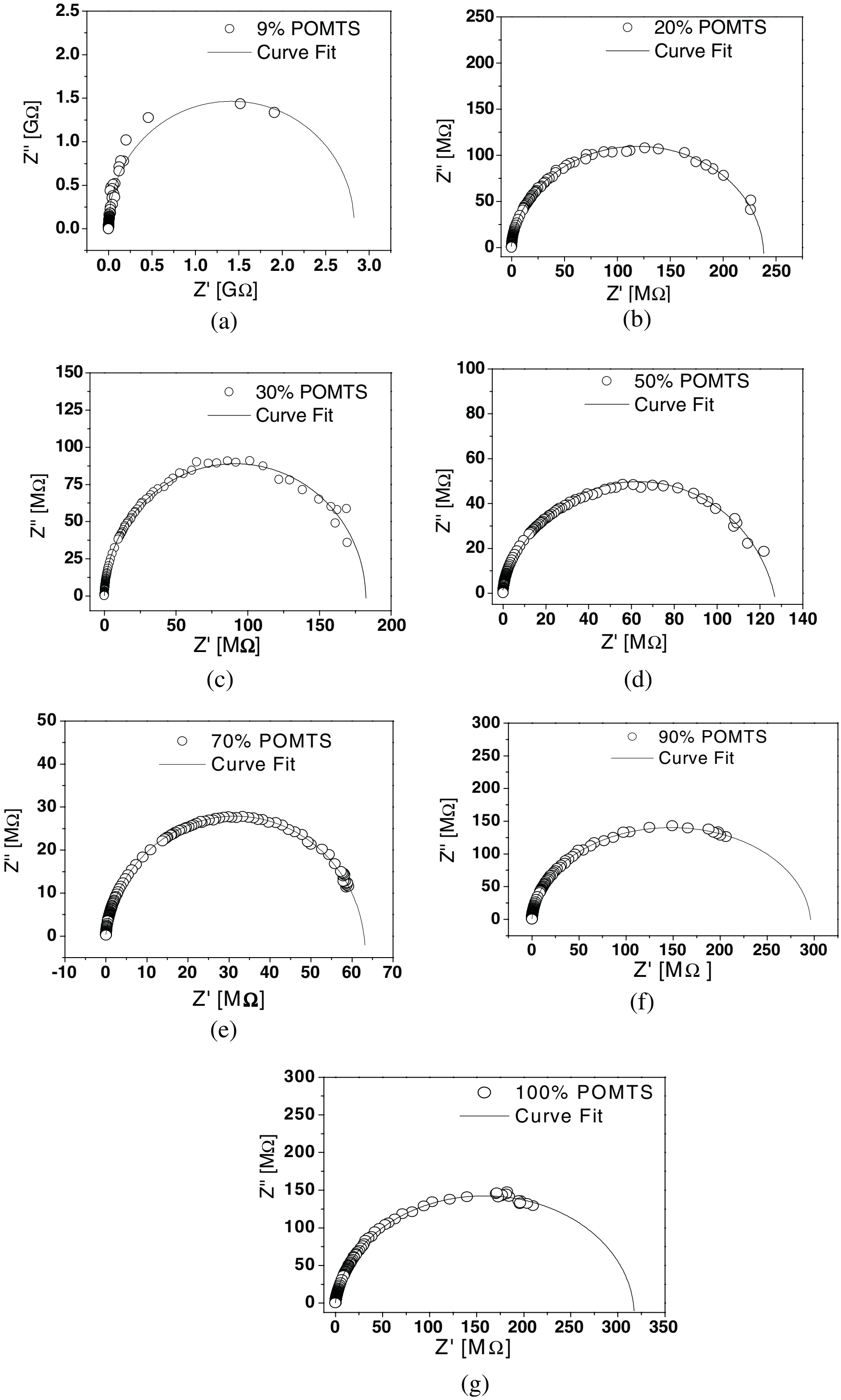
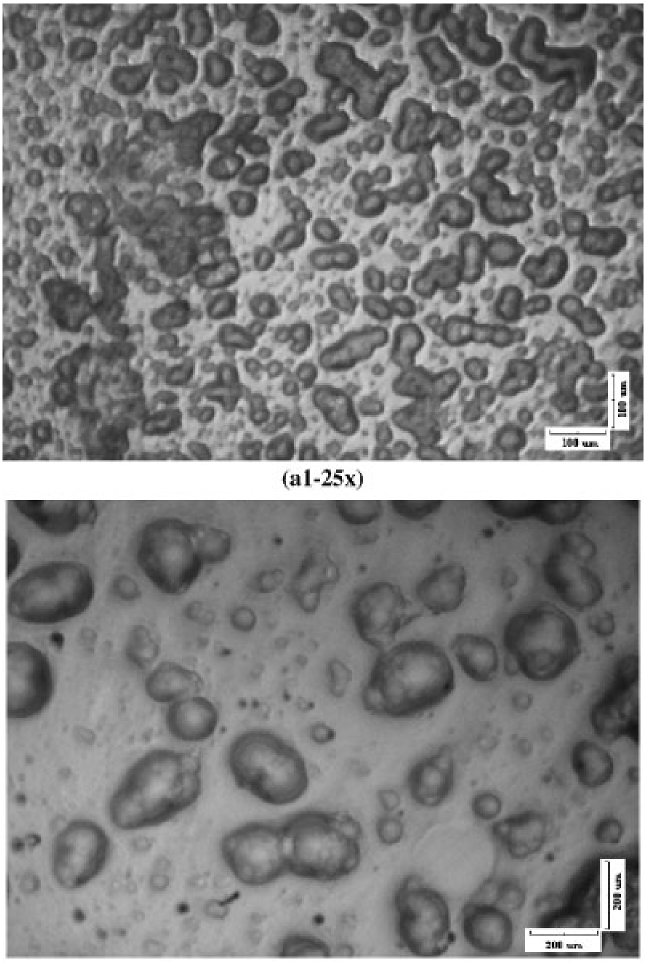


Figure 2.
Cole-Cole plots of the complex impedance of real (Z′) and imaginary (Z″) of the conducting blends at different contents of POMTS: a) 9%; b) 20%; c) 30%; d) 50%; e) 70%; f) 90%; g) 100%.

The prepared polymer films were flexible solids and translucent under visual inspections, and, accordingly, OM observations indicated phase separation in the blends (Figures 3–5). OM pictures of POMTS/PHS-*b*-IR blends with various compositions were taken at different magnifications: (a1–a2) 5/95, 25× and 80×; (b1–b2) 70/30, 25× and 80×; (c1–c2) 90/10, 25× and 80×.

Observed by OM, blends presented a light matrix (PHS-*b*-IR) and a dark dispersed phase (POMTS). Heterogeneous morphologies were observed for all samples, POMTS droplet dispersed phase in PHS-*b*-IR matrix for the 5/95 blend, while the 70/30 and 90/10 blends presented ever-increased dendritic structures and embedded isolated droplets were rarely observed. No phase inversion was observed for POMTS content over 50wt%, which remained as the dispersed phase. This behavior can be attributed to the POMTS lower solubility in DMF.

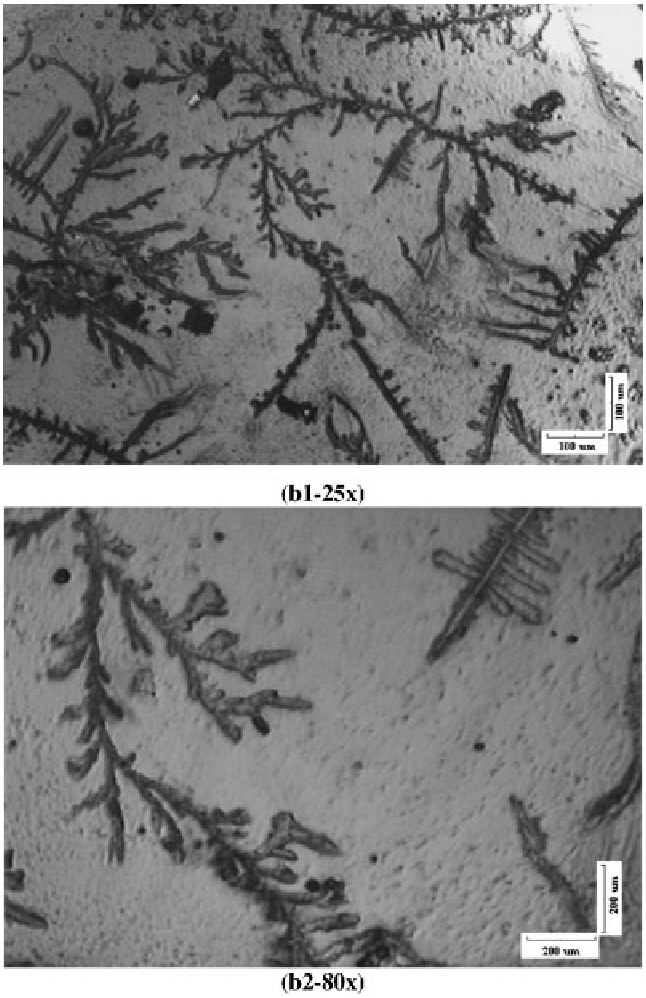
In Table 1 are presented the values of conductivity (σ), relaxation time (τ_R), capacitance (A_0) of the conducting blends at different contents of POMTS.



(a1-25x)

(a2-80x)

Figure 3.
OM pictures of POMTS/PHS-*b*-IR blend 5/95 at different magnifications.



(b1-25x)

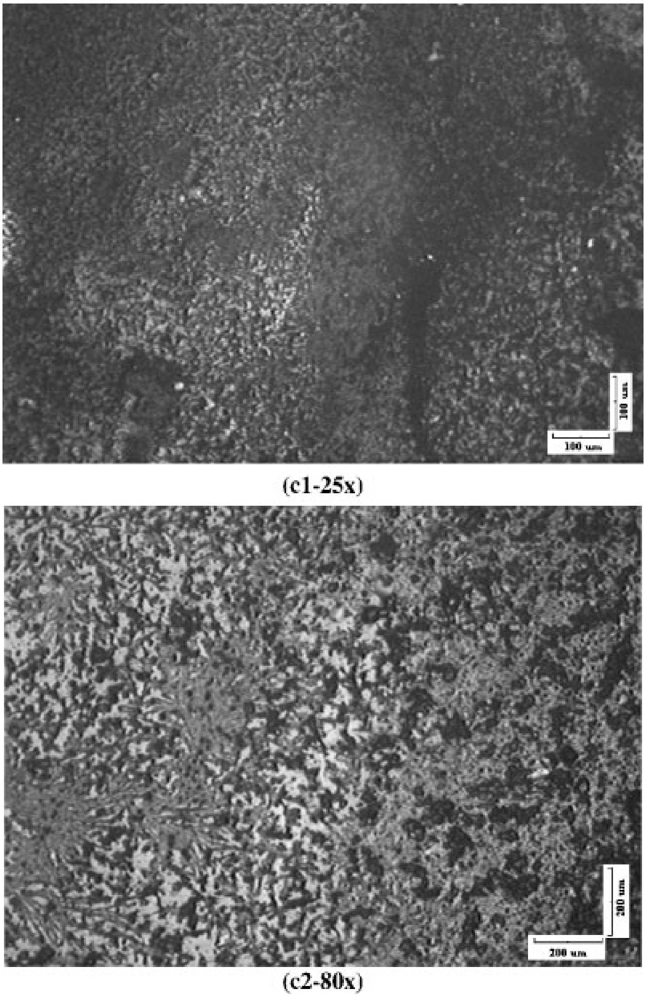
(b2-80x)

Figure 4.
OM pictures of POMTS/PHS-*b*-IR blend 70/30 at different magnifications.

A maximum point in the electrical conductivity was observed for 70% of POMTS, as shown in Table 1. The secondary doping, resulting from the PHS-*b*-IR, for low POMTS contents (<70%) is responsible for the conductivity increase. The obtained relaxation times (τ_R) decreased with increasing contents of POMTS, except the 50% content sample. This can be due to no homogeneity of the conducting blends as well as a bigger distribution of relaxation times. The average capacitance (A_0 - of the order of pF) was not influenced by the content of used doping.

Conclusions

A great amount of research has been done worldwide to produce blends with conducting polymers to increase the technological potential and versatility of these materials. It was demonstrated that flexible, free-standing films can be obtained by casting polyblends of POMTS and thermoplastic rubber PHS-*b*-IR. The OM pictures showed a heterogeneous morphology for all the POMTS/PHS-*b*-IR blends studied here. The impedance technique and the fitting procedure allowed evaluating the charac-



(c1-25x)

(c2-80x)

Figure 5.
OM pictures of POMTS/PHS-*b*-IR blend 90/10 at different magnifications.

Table 1.
Conductivity, relaxation time, and capacitance of blends at different contents of POMTS.

% POMTS in the blend	σ (S/cm)	τ_R (s)	A_0 (pF)
9	1.34×10^{-8}	1.57×10^{-3}	0.639
20	1.59×10^{-7}	1.91×10^{-4}	1.250
30	2.08×10^{-7}	1.40×10^{-4}	0.894
50	3.01×10^{-7}	1.80×10^{-4}	5.250
70	6.08×10^{-7}	7.20×10^{-5}	2.390
90	1.28×10^{-7}	2.17×10^{-4}	0.977
100	1.19×10^{-7}	2.90×10^{-4}	1.590

teristics of conducting POMTS blends such as conductivity *ac*, time of dielectric relaxation and capacitance.

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