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Studies of Optical, Morphological and Electrical Properties of POMA/PMMA Blends, Using Two Different Levels of Doping with CSA

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Abstract: Poly(o-methoxyaniline) (POMA) was synthesized by oxidative polymerization of the monomer o-methoxyaniline. POMA/poly(methyl methacrylate) (PMMA) blends were produced by dissolving both polymers in chloroform ($CHCl_3$).The amount of camphor sulfonic acid (CSA) used as dopant of POMA was different, providing two methods for preparation of the blends. Solutions were analyzed by Fourier transform infrared spectroscopy (FTIR) and then deposited on glass substrate by spin coating for characterization by atomic force microscope (AFM) and current versus voltage (I × V) curves. FTIR spectra of solutions were similar as expected. In the AFM images a reduction and/or loss of globules common in conducting polymers (CP) such as polyaniline (PANI) and its derivatives was observed. Films produced with different amounts of CSA presented distinct, linear and non-linear I × V curves.

Keywords: *POMA, CSA, PMMA, morphological, optical, electrical.*

Introduction

Conducting polymers (CP) are also known as "synthetic metals" because they have electrical, electronic, magnetic and optical properties similar to metals[1]. In recent years the study of CP has grown significantly due its promising applications in electronic devices, including gas sensors[2], electrochemical sensors[3], chemical sensors, diodes, and transistors[4]. A recent paper[5] investigated the use of nanostructured films of poly(o-etoxyaniline) (POEA) prepared with different doping acids in the fabrication of chemical sensors to distinguish sucrose, NaCl, HCl and caffeine solutions.

A "synthetic metal" can change from insulating to conducting by adding a dopant. These dopants, called in analogy to inorganic semiconductors, are charge transfer agents and their use leads to changes in the properties of polymers. It is possible to model the conductivity of material by controlling the amount and type of dopant[1].

CP can be classified as type 1, type 2 and type 3 by oxidation (p-doping). In polymer type 1 the protonic/eletronic doping involves proton and anion in the polymer chain, e.g., polyaniline (PANI). Type 2 has as example polypyrrole (PPY) and polythiophene (PT) and electronic doping occurs with incorporation of the anion in the polymer. Doping made with the expulsion of a cation or an acid group covalently bonded classifies type 3 and is represented by sulfonated polyaniline[6].

Among the CP, the PANI has been widely studied; it has good electrical properties and chemistry stability upon dopant. Poly(o-methoxyaniline) (POMA) is derived from PANI and both have similar characteristics, but the POMA is more soluble than the original polymer[7].Although the POMA has lower electrical conductivity than the salt PANI-HCl, its higher solubility in organic solvents raised the interest of many researchers, due to its increase in processing capacity[8]. The improvement in the solubility of substituted polyanilines can be explained by the incorporation of flexible groups in the polymer chains. These groups reduce the stiffness of the polymer backbone and/or the presence of polar substituent increases the polarity of the polymer chain[9]. The disadvantage of the presence of substituent on the polymer chain is the steric effect caused by them, which can result in twisted chains, causing a negative effect on the electrical properties of polymer[9].

The optical properties of PANI and its derivatives have also attracted great interest of several research groups. Melo et al.[10] showed that the POMA can be used to produce light-emitting heterostructures by self-assembly technique. For the optical characterization of POMA/poly(p-phenylenevinylene) (PPV) films, it was observed that the CP can be used as an optical window for the PPV.

According to literature, solutions or layer by layer (LBL) films of POMA presented peaks of absorption at 770-820 nm and a shift to longer wavelengths increasing the concentration of POMA[11]. The disadvantage of CP is that it does not have good mechanical properties. Several attempts were made to combine the mechanical properties of insulating polymers with CP, involving composites and blends, such as PANI mixed with epoxy resin, to produce materials with anti-corrosion properties[12]; blends of PANI and lignin to study modification in the thermal properties of CP[13] and PANI with polystyrene (PS) to investigate electrical and thermal properties[14]. The mixing of CP with insulating polymers presents the advantage of producing materials with good mechanical properties associated with attractive electrical properties[15].

In this work, the POMA was doped with camphor sulfonic acid (CSA) and POMA/poly(methyl methacrylate) (PMMA) blends were prepared with two levels of doping and its optical, morphological and electrical properties were analyzed.

Experimental

The monomer o-methoxyaniline, PMMA and CSA were purchased from Aldrich Co. POMA was synthesized by oxidative polymerization of o-methoxyaniline (freshly distilled) with ammonium peroxydissulfate (APS) in an aqueous solution of HCl (1 $mol.L^{-1}$) near to 0 °C. After 4 hours of polymerization,

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the POMA was filtered with Whatman 41 filter paper and washed with acetone until the filtrate becomes colorless. Dedoping was performed with a solution of NH_4OH (0.1 mol.L^{-1}) for 16 hours at room temperature to yield a polymer in the emeraldine base [EB] form. Again, the polymer was filtered and placed in a drying vacuum for 48 hours[16].

POMA/PMMA blends were prepared by mixing the two polymers in chloroform, using two different methods.

In method 1, 0.2 g of POMA was dissolved in 40 mL of chloroform. CSA was added to obtain a green solution, which corresponded to 5.1 mmol of dopant. As the amount of CSA was small, the solubility of the POMA-CSA in chloroform was not complete. So, the solution was kept under magnetic stirring for 6 hours and then placed in an ultrasonic bath for 3 hours. After, it was filtered leading to a solution of POMA-CSA with a final concentration of 7.5×10^{-4} g.mL^{-1}. This solution was divided into four parts: P1, P2, P3 and P4. The P1 solution was considered as POMA stock solution, while in the solutions P2, P3 and P4, PMMA was added and submitted to magnetic stirring for 1 hour, obtaining mixtures with 10:90, 30:70 and 50:50 (wt/wt %) POMA/PMMA.

In method 2, four solutions of POMA were prepared (S1, S2, S3 and S4). Solutions S1 and S2 had the same concentrations (0.01 g.mL^{-1}) and the solutions S3 and S4 had concentrations of 0.006 g.mL^{-1} and 0.003 g.mL^{-1}, respectively. The mass of CSA was calculated as a function of the tetramer number of mol of POMA[17]. In these conditions the POMA-CSA was completely soluble in chloroform. The S1 solution was kept as a stock solution, while in S2, S3 and S4 solutions PMMA was added and submitted to magnetic stirring for 1 hour, producing solutions with 25:75, 50:50 and 75:25 (wt/wt %) POMA/PMMA concentrations.

To better understand the influence of doping on the morphology of the POMA, a sample of POMA was weakly doped with HCl (1 mol.L^{-1}) in the presence of $CHCl_3$. The solution was kept under agitation for 6 hours, followed by an ultrasonic sound bath for 3 hours. Finally, the sample was filtered and deposited on glass substrate.

Solutions were analyzed by Fourier transform infrared spectroscopy (FTIR) and recorded on a Michelson Bomem & Braun FTIR spectrometer in the range 400-4000 cm^{-1}.

The solutions were deposited on glass substrates (1.0 × 2.5 cm), covered with fluorine tin oxide (FTO), with planar resistivity in the order of 30 Ω cm by technical spin coating with a rotation of 2000 rpm.

Samples were analyzed by atomic force microscopy (AFM) of the Veeco Innova (Instruments) microscope, in the contact mode (512 × 512 pixels) and by electrical measurements at room temperature using a Keithley 2400 programmable semiconductor measuring system, obtaining current versus voltage (I × V) curves. A stainless steel tip test of the Keitley equipment was placed directly on the polymeric films separated by a distance of 1 cm. No special electrode was used to made contact. Electrical measurements were obtained in quadruplicate and subsequently an average of curves was made by the program Matlab.

Results and Discussion

FTIR spectra of POMA doped with CSA (P1) (method 1), PMMA and POMA/PMMA blends (P2, P3, P4) are presented in Figure 1.

Figure 2 shows the FTIR spectra of POMA doped with CSA (S1) (method 2), PMMA and POMA/PMMA blends (S2, S3, S4).

Both spectra exhibited bands with similar characteristics in the range of 3500-600 cm^{-1}. The peaks observed at 2830 and 2923 cm^{-1}occurred due to C-H stretching of the -OCH_3 group in the polymeric chain[18-21] and CH_3, CH_2 groups belonging to CSA[21].

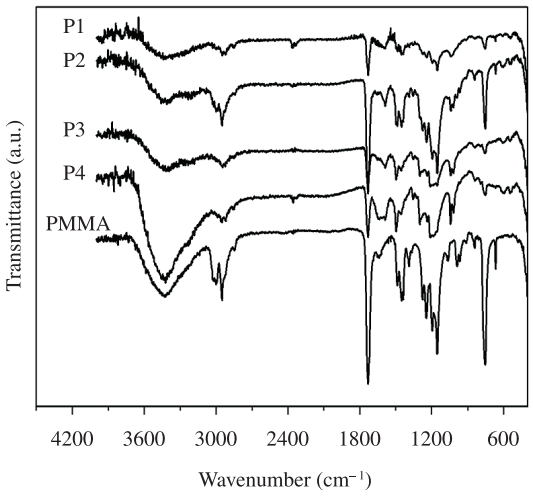

Figure 1. FTIR spectra of: POMA doped with CSA, by method 1 (P1); POMA/PMMA blends (P2, P3, P4) and PMMA.

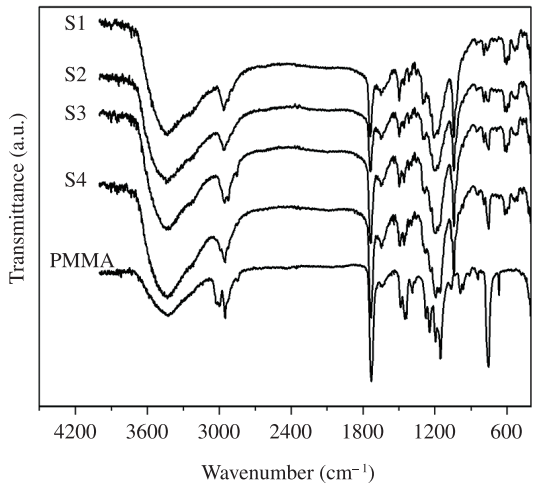

Figure 2. FTIR spectra of: POMA doped with CSA, by method 2 (S1); POMA/PMMA blends (S2, S3, S4) and PMMA.

The vibration at 3443 cm^{-1} can be attributed to N-H stretching of CP[19-22]. However, it may have been masked by the presence of a small amount of water in the samples[20] and by overtones of $\nu_{(CO)}$ PMMA ester group[23]. Bands at 1242 and 1040 cm^{-1} are a contribution of the C–O–C stretching of an alkyl aryl ether linkage[23]. Bands observed at 1047, 789, 712, 602 cm^{-1} are associated with o-substituted aromatic rings[18]. Peaks at 1588 and 1495 cm^{-1} were attributed to C=C stretching vibrations of the quinoid and benzenoid rings, respectively[19,21], indicating that CP possess imine and amine groups in the polymeric structure[19]. However, other papers report that the peak of quinoid rings can also appear at 1568 cm^{-1}[22] or 1610 cm^{-1}[24].

Samples prepared by method 2 showed a well defined peak at 1650 cm^{-1} characteristic of deformation in the N-H bonds[25]. A possible explanation for this peak arises at 1650 cm^{-1} in these samples and is likely due to the oxidation degree (X*) of the CP utilized in the preparation of blends, where $*X+X/(I_{1,615}/I_{1,495}) = 1$[25]. The intensity ratio ($I_{\sim 1615}/I_{\sim 1495}$) revealed that the POMA doped by method 2 was oxidized 53%, approximately, i.e., the POMA is in the emeraldine form provided, while a POMA doped by method 1 possesses an oxidation degree close to 50%.

Previous studies related a band at 1742 cm^{-1} related to C=O stretch of the dopant[19,20] revealed that the CSA is incorporated in the polymer backbone[20]. This band appears strong and well defined at 1738 cm^{-1} in FTIR spectra of samples analyzed and it can be overlapped on the band at 1728 cm^{-1} of the PMMA ester group[25].

PMMA spectrum shows bands at 2954 cm^{-1} attributed symmetric bend of C–H, and at 1150 cm^{-1} due to axial asymmetric bend of C–C=O[26,27]. Bands between 960 cm^{-1} and 667 cm^{-1} are associated with C-H bending[28].

AFM images of POMA doped with HCl and CSA by two methods (1 and 2) are shown in Figure 3.

The polymer doped with HCl possesses numerous and rounded globules (Figure 3a). However, AFM images of the POMA doped with CSA by method 1 (P1) and method 2 (S1) (Figures 3b, c, respectively) showed the presence of flattened cells and destruction of globules, principally the POMA doped by method 2. It is known in literature that different dopants can modify the morphology of CP depending on preparation conditions[29].

Figure 4 presents AFM images of the POMA, POMA/PMMA blends prepared by method 1 and PMMA.

AFM image topographic of PMMA (Figure 4e) shows, apparently, globules larger but in smaller quantities than in the POMA/PMMA blends images and it does not present flattened globules as was revealed in the image of pure POMA (Figure 4a). AFM images of POMA/PMMA blends (Figures 4b-d) showed that the increase of PMMA concentration in the blends provides a decrease in flattened globules. This is best observed in Figure 4b. The amount of flattened globules in the POMA and in its blends is related to the amount and type of dopant utilized to prepare the samples (Figure 3).

It was possible to observe that the increase in the amount of CP improved the roughness in the host matrix (PMMA) (Figure 5a). Through Figure 5b it was possible to confirm that the roughness of blends was higher than the roughness of PMMA and also greater than the CP, except for sample S4. This increase in roughness in these materials compared with the material prepared by method 1 can be explained by the presence of recrystallized CSA crystals after solvent evaporation. These same crystals of CSA on the surfaces of blends are responsible for the growth of the random roughness in these materials (Figure 5b).

AFM images of the pure POMA and POMA/PMMA blend 25:75 (S2), produced by method 2 (Figures 6a, b), presented surfaces with flattened globules and a region with prominences.

In the surface of blend 50:50 (S3) (Figure 6c) it is possible to observe the destruction of globules with traces of recrystallized dopant, whereas the samples 75:25 (S4) (Figure 6d) presented a surface with globules partially destroyed and again with prominences.

I × V curves of the blends produced with POMA obtained by method 1 (Figure 7) indicated that the materials have the behavior

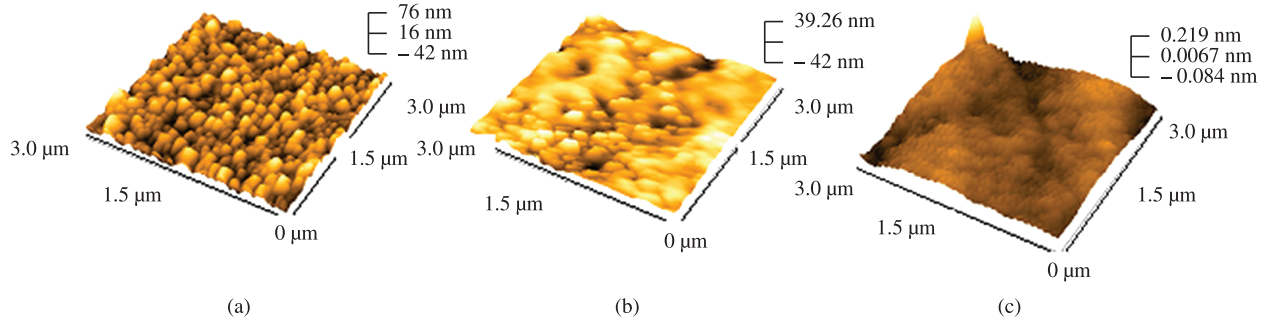

Figure 3. AFM images of (a) POMA doped with HCl; POMA doped with CSA by (b) method 1 (P1) and (c) method 2 (P2). Scanning area: 3 × 3 µm.

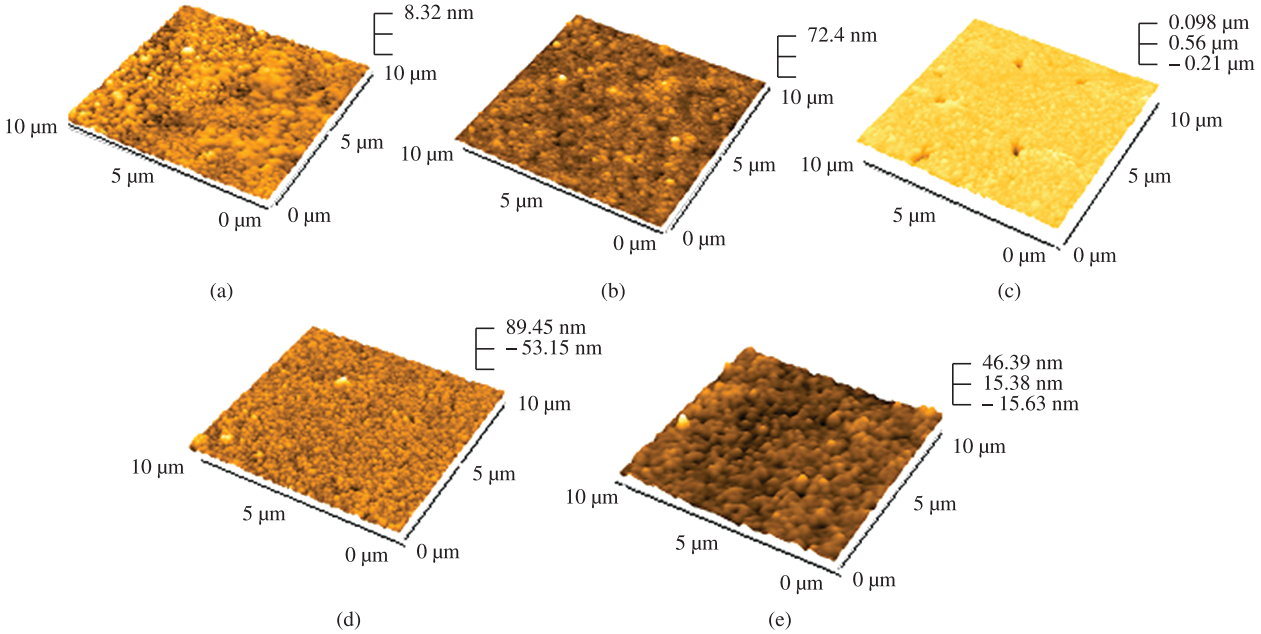

Figure 4. AFM images of (a) pure POMA, POMA/PMMA (b) 10:90 (P2), (c) 30:70 (P3), (d) 50:50 (wt/wt) (P4); and (e) PMMA. Scanning area: 10 × 10 µm.

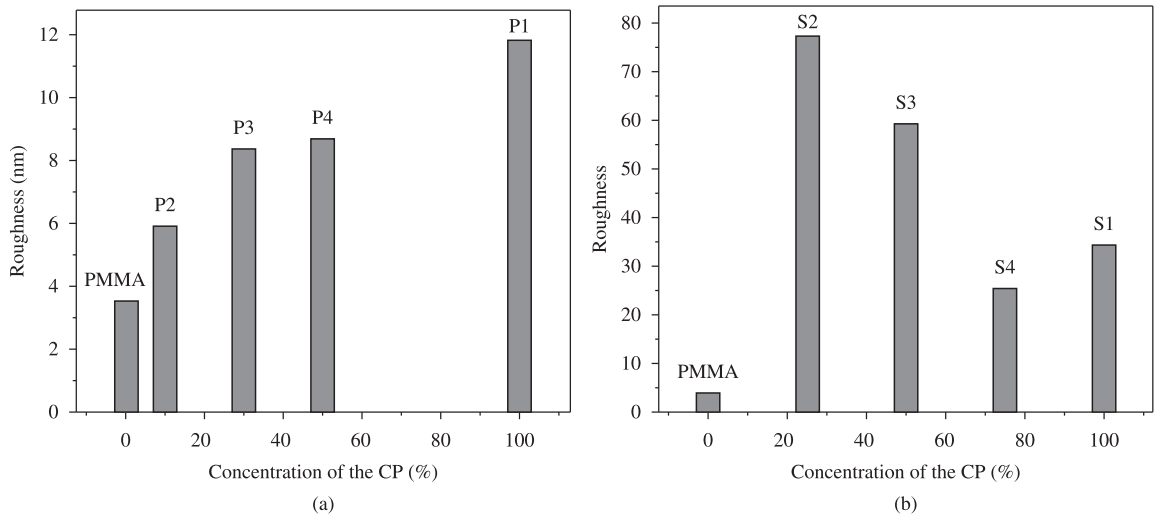

Figure 5. Surface roughness of blends prepared by (a) method 1; (b) method 2.

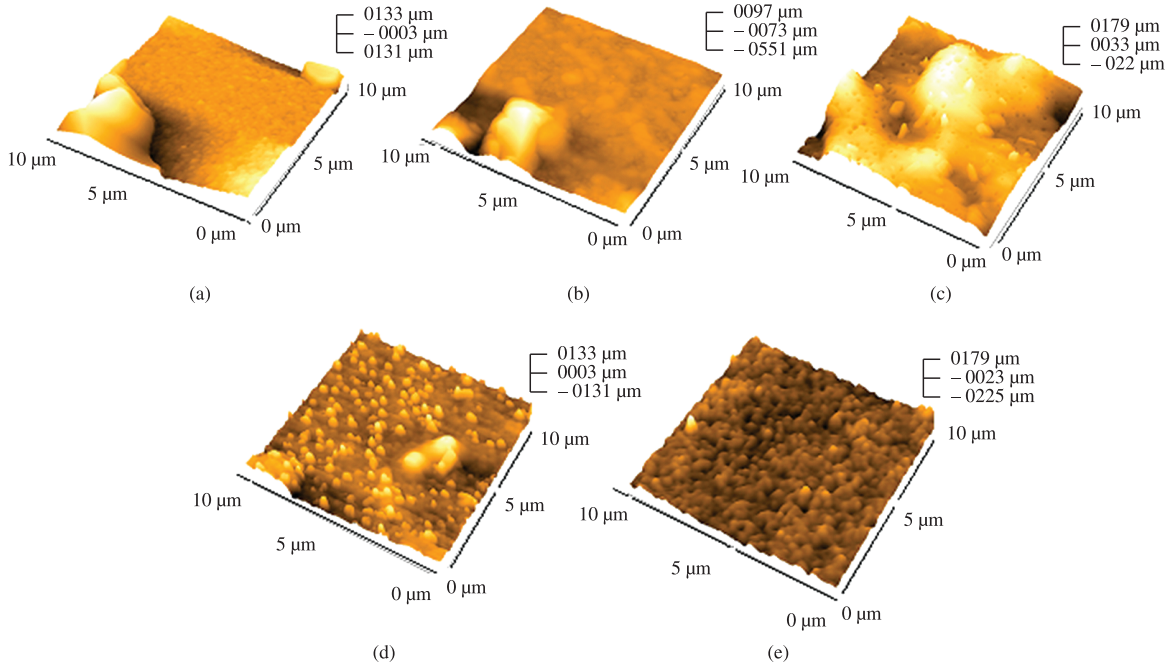

Figure 6. AFM images of POMA/PMMA: (a) 25:75 (S2), (b) 50:50 (S3), (c) 75:25 (wt/wt) (S4); and (d) PMMA. Scanning area: 10 × 10 µm.

of a linear device (i.e, resistor). Paul et al.[30] found this linear behavior in films of the POMA prepared by Langmuir-Blodgett (LB) technique.

I × V curves of the films produced with the pure POMA (P1) solution and POMA/PMMA30:70 (P3) showed smaller resistance than the blend with 10% of POMA (P2). It was possible to observe that a small quantity of CP in the blend composition is enough to produce electrical properties in the insulating material (PMMA). These data are in agreement with literature[29]. Rocha et al.[31] concluded that low contents of POMA are sufficient to affect the crystallization, morphology and electrical properties of blends with poly(vinylidene fluoride) (PVDF).

The morphology of blends prepared by method 1 was similar to pure POMA (Figure 4a) and PMMA (Figure 4e). The PMMA electrical characteristics were changed with the addition of CP; all blends begin to have the behavior of pure POMA with the same order of magnitude of current, close to 20 mA. However, the

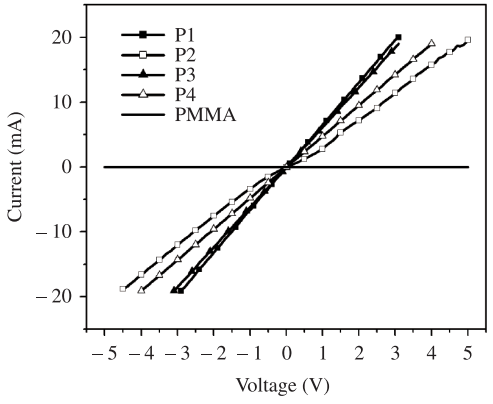

Figure 7. I × V curves of films: POMA (P1), POMA/PMMA blends (P2, P3, P4) and PMMA.

morphological properties were not affected significantly. Overall, there is the formation of globules, some more flattened and others more spherical.

Figure 8 shows I × V curves of POMA films, doped by method 2, and of its blends with PMMA.

I × V curve of POMA also presented behavior of a linear device with an electrical current value approximately 20 mA (Figure 8a), as was seen in Figure 7. However, when PMMA was added, I × V curves showed a nonlinear device behavior (Figures 8b-d), with a decrease in current (Figures 8b, c). I × V curve of POMA/PMMA blend with 75% of POMA (S4) (Figure 8d) presented a form similar to the pure POMA curve, however with some non-ohmic regions caused, probably due to the presence of PMMA. This little amount of insulating polymer was not enough to drastically affect the electrical properties of the materials, keeping the current values of near 17 mA. The 50% sample (S3) revealed diode behavior of with a maximum electrical current of 68 μA at a voltage of 4.7 V (Figure 8c), while blends with 25% of POMA (S2) (Figure 8b) showed an increase in the current with a rise in the voltage value, reaching a current of 8 nA at 4.7 V.

The morphology of materials with 25% and 50% (S2 and S3, respectively) was extremely affected; the globules were reduced in size (S2) and destroyed (S3). The electrical properties of these materials were fully modified.

Although, the methods used have different concentrations, it is expected that method 2 produces conducting blends with better electrical characteristics than the electrical characteristics of blends obtained by method 1, because the doping level is higher (observed by color of the solution). This can be better analyzed between samples of the same concentration (50:50 wt/wt %) that possess different electrical current values with the same voltage values. In a bias of 4.0 V, POMA/PMMA blends (50:50 wt/wt %) prepared by method 1 present a 19 mA current, while blends with the same concentration prepared by method 2 showed a current of approximately 45 μA.

In analyzing the polymer structures, it is possible to observe that they did not react resulting in new compounds at room temperature. A possible explanation for the blends prepared by method 2 presenting a current 400 times smaller than that obtained by method 1 is the possibility that PMMA caused a twisting of the POMA chains. This twisting can have a negative effect on the electrical properties[9].

So, the possibility is evident for preparing the same material with different electrical properties simply by changing, the concentration of the dopant. In this case, method 1 was better in relation to electrical characteristics, however, method 2 produced remarkable materials with diode properties.

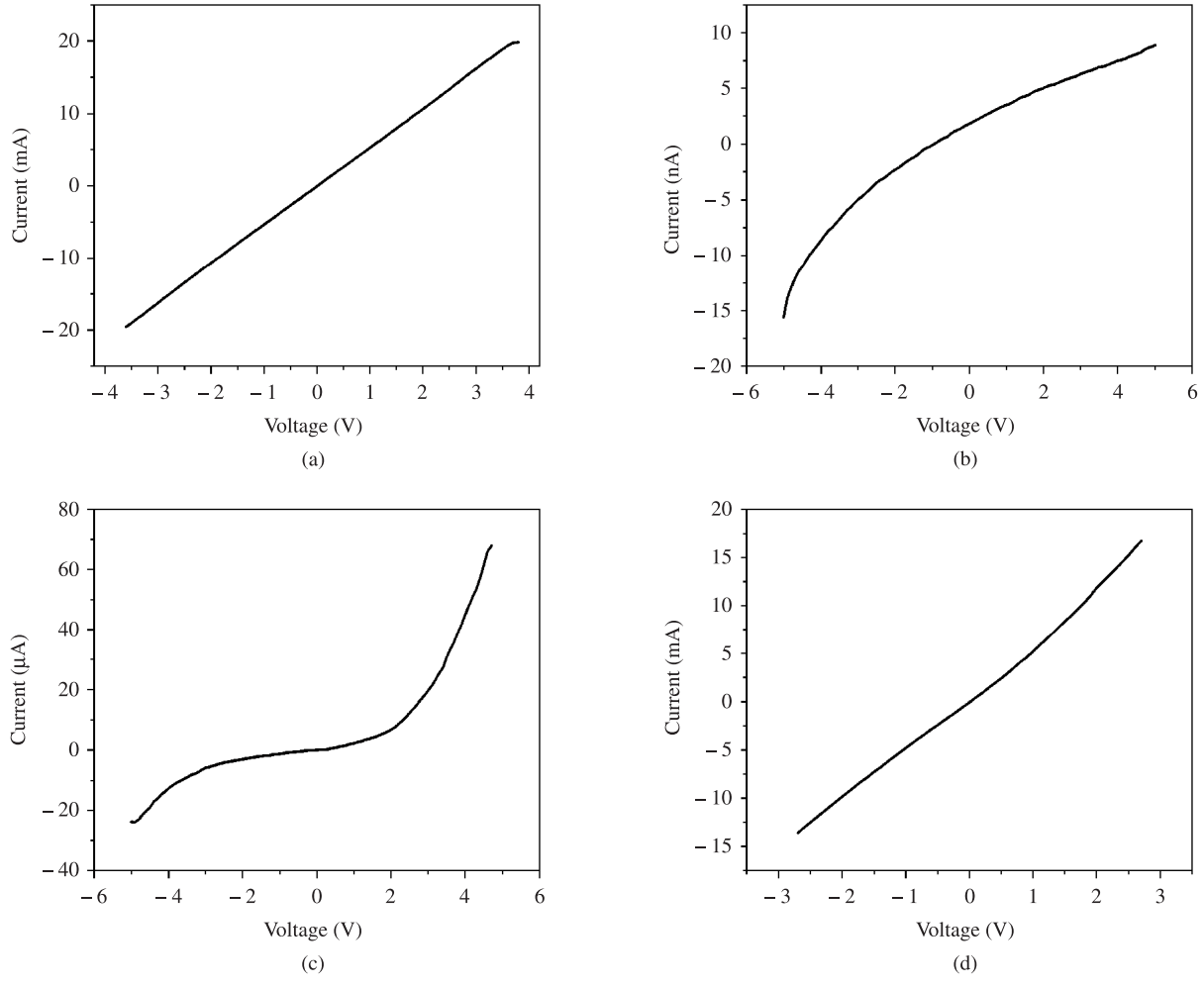

Figure 8. I × V curves of films: (a) POMA (S1) and POMA/PMMA blends (b) S2, (c) S3 and (d) S4.

Conclusions

POMA/PMMA blends produced using POMA, with different levels of CSA, presented promissory results. FTIR spectra of blends were similar. Globules observed in the AFM images of POMA/PMMA blends prepared by method 1 were reduced and/or destroyed in POMA/PMMA blends prepared by method 2. AFM images showed that blends produced with P2, P3 and P4 solutions reduce the number of flattened globules with the increase of PMMA. Images of films produced by S2, S3 and S4 solutions revealed surfaces with globules flattened (S2), destroyed and with traces of recrystallized CSA after evaporation of the solvent (S3); and finally with globules partially destroyed as in sample S4. I × V curves of blends obtained with POMA prepared by method 1 presented linear device behavior, while I × V curves of blends produced with the POMA obtained by method 2 showed nonlinear device behavior and with a lower current compared to samples produced by method 1. The exact reason why the material has its electrical properties affected by the addition of PMMA is still a subject that deserves more research and discussion.

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