Electrical, Spectroscopic, and Thermal Properties of Blends Formed by PEDOT, PVC, and PEO

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ABSTRACT: This study describes the preparation of blends between an amorphous polymer (PVC) and a crystalline polymer (PEO), with a third polymeric part that presents electronic conduction capacity (PEDOT-PSS). Binary (PEO/PVC, PEO/PEDOT-PSS, PVC/PEDOT-PSS) and ternary (PVC/PEO/PEDOT-PSS) blends were prepared by changing the concentrations of the constituents and were analyzed by electronic conductivity, Raman spatial resolution, infrared spectroscopies, and thermogravimetric analysis. The Raman and FTIR analyses showed the incorporation of PEDOT-PSS within the blends. The higher conductivity

presented by the ternary blend was 8.6 \times 10⁻⁶ Scm⁻¹, composed of 24% of PVC, 16% of PEO, and 60% of PEDOT-PSS. For binary blends the conductivity was proportional to the PEDOT-PSS content. The thermal stability could be observed through the TG curves of the blends that presented an increase of 19 K in the weight loss temperature at the 10% level when compared to the pure components. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1710-1715, 2005

Key words: PVC; PEO; PEDOT-PSS; blends; conducting polymer

INTRODUCTION

Both the engineering and material sciences have made technologically important progress in the last decades. The development of new materials has allowed great evolutions in several fields, from the medical area to aerospace projects. Among the different areas of the material sciences, it can be observed in modern daily life that polymeric materials play important roles. In the twentieth century the "kingdom of the plastics"¹ arose, where plastics substituted for traditional materials such as glass, metals, and minerals, in domestic articles, automobile parts, etc.

A number of materials with specific mechanical, thermal, and morphologic properties can be obtained by physical mixtures of two or more polymers, creating the polymeric blends. Polymer blending is a useful method for designing materials with a variety of properties. The polymeric blends often exhibit properties that are superior compared to the properties of the individual components (a synergic effect). The blends can be tailor-made and, in many cases, provide new materials without investments in new synthesis routes, which is economically viable due to cost reduction. Conductive polymer blends are prepared by combining an insulating polymer with an intrinsically

conductive polymer. The most common conductive polymers are polypyrrole, polythiophene, polyaniline(PANI), and their derivatives. Preparation methods include mechanical mixing, casting of a solution containing the components of the blend, or polymerization of one polymer into the other.²

The final properties of polymeric blends will depend, mainly, on the properties of the pure components, on the specific interactions occurring between chemical groups of the different polymers, and also on the processing involved during the mixture. Mixing polymers on the molecular scale can induce certain properties that promote an increase in specific interactions involving groups or polymer segments that lead to a decrease in the Gibbs energy of mixing, thus, presenting a single phase. The immiscible blends tend to separate phases, forming a heterogeneous mixture. The conditions causing phase separation are due primarily to differences in molecular geometry, molar mass, and incompatibility of functional groups.³ However, some partially miscible blends, such as PANI/ PMMA and PANI/PE,4 PANI/PVAc,5 PANI/aliphatic copolymers,⁶ PANI/EVA,⁷ and PANI/polyester-polyether block copolymer,⁸ can exhibit good mechanical properties and are mechanically compatible.

Poly(vinyl chloride) (PVC) possesses vast applications in several areas of the materials industry, such as in flexible or rigid plastic molds, fibers, films, laminates, etc., and its main properties are degradation

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resistance and low flammability.9 Poly(3,4-ethylenedioxythiophene) (PEDOT) has been extensively studied in recent years.¹⁰⁻¹⁶ It presents high environmental stability, good solubility in organic solvents, high electrical conductivity (200-600 Scm⁻¹),¹⁷⁻¹⁹ and low gap energy, ca. 1.6 eV.²⁰ This low gap energy makes this material useful in the optical and electronics industries.^{21,22} Intrinsically conducting polymers (ICP) can be applied in a number of areas. They possess transparency and flexibility,²³ being used for capacitors and photodiodes,^{24,25} photoelectrochemical cells,^{26–28} antistatic coatings,^{29,30} and electrochromic windows.^{31–33} Recently, PEDOT has appeared as one of the important materials in the preparation of conductive blends. This is due to its low gap energy and good processability, as observed for several polymers of the polythiophenes family.⁹ These materials show excellent transparency, stability in the oxidized state,¹⁹ and high mobility of carriers.34,35 According to the literature, the solubility presented by poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS) is high in polar solvent, as well as the poly(ethylene oxide) (PEO). Thus it was possible to propose the formation of PEO/PEDOT-PSS blends, due to their mutual solubility and molecular structure. PEO has also been blended with PEDOT-PSS to increase the ionic mobility in the final product.³⁶ In addition, PE-DOT-PSS has been used as the conductive component in the PEO polymeric matrix presenting similar conductivity to the carbon-graphite.³⁷

One of the great problems in the electronic conducting polymer industry is the processing difficulty. To circumvent this problem, much research is being carried out to prepare new monomers or blends between ICP and conventional polymers. In blends constituted of heterogeneous components, the level of electronic conductivity depends mainly on the concentration and the geometry of the conducting particles.³ The conductivity presented by the polymers is strongly dependent on the morphology, the chemical structure, and especially on the degree of crystallinity.³⁸

According to Reynolds and co-workers,³ the conductivity presented by poly(vinyl alcohol) or poly(ethylene oxide) mixed with PEDOT-PSS is dependent on the morphology and crystallinity presented by the pure components. The authors reported that the electrical conductivity depends on the blend composition and is higher with crystalline PEO. The studies of PEDOT blends with other construction polymers are of current interest, and the present article describes the preparation of blends between PEDOT-PSS and insulating conventional polymers (crystalline and amorphous, PEO and PVC, respectively), and their electrical, spectroscopic, and thermal characterization. This article contributes to the studies for industrial and technological applications, such as the manufacture of printed circuits, coatings for corrosion protection, and

Sample	PEO (wt)	PVC (wt)	PEDOT-PSS (wt)
Blend 1	0.32	0.08	0.60
Blend 2	0.24	0.16	0.60
Blend 3	0.20	0.20	0.60
Blend 4	0.16	0.24	0.60
Blend 5	0.08	0.32	0.60
Blend 6	0.50	0.50	_

antistatic coating materials, besides the possibility of producing conductive layers with pre-established properties, resistant to, for example, heat.

EXPERIMENTAL

Poly(ethylene oxide) (PEO) (molar mass 200,000 gmol⁻¹, Aldrich) and poly(vinyl chloride) (PVC) (molar mass 100,000 gmol⁻¹, Aldrich) were used. These polymers were kept in vacuum at 323 K for 24 h before use. The poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS) (Baytron-P[®]) was obtained from Bayer (Brazil). N,*N*-dimethyl acetamide (DMAc, Aldrich) was used as solvent.

Initially, solutions of PEO and PVC at 5% (wt/wt) were prepared. These solutions were mixed with a dispersion of Baytron-P®/DMAc (5% of Baytron-P®) to prepare the blends. Other organic solvents, such as dimethyl sulfoxide, N,N-dimethyl formamide, or tetrahydrofuran, can also be used.²³ Each polymeric solution was stirred for 24 h with slight heating, to obtain a homogeneous solution. The blends were prepared by slowly pouring the PEDOT-PSS/DMAc solution into the other polymeric solutions with vigorous stirring to ensure that the mixture was homogeneous. The blends were prepared from different ratios of the solutions and the mixtures were stirred for 30 min; afterward, the films were prepared by casting in polytetrafluoroethylene plates (5.0 cm diameter). The volume of the solution in each plate was controlled, maintaining the blends with an average thickness of 60 μ m. They were dried by heating at ~ 313 K, using saturated atmosphere to avoid the fast evaporation of the solvent. The PVC/PEDOT-PSS blends were prepared following the same procedure used for the preparation of the PEO/PEDOT-PSS blends, changing the percentages of PVC and PEDOT-PSS, in the same ratios used above.

For the preparation of the PEO/PVC/PEDOT-PSS blends, the amount of PEDOT-PSS was fixed at 60% and the PEO/PVC ratio was varied within the remaining 40%. These ratios are defined in Table I. Blend 6 is composed of PEO and PVC without PEDOT-PSS, and the procedure used in the preparation of this blend was the same as the one used previously. After drying,

the films were placed in a dynamic vacuum chamber at *ca*. 318 K for 72 h to remove the remaining solvent.

Electrochemical impedance spectroscopy (EIS) measurements were used to determine the conductivity of the samples. The EIS was performed in a potentiostat/ galvanostat AUTOLAB, model PGSTAT 12, with a FRA (frequency response analyzer) module. To confirm the results, dc conductivity measurements were also made using the four-point probe method by using a Keithley programmable voltage source, model 230, a Keithley programmable electrometer, model 617, and a Keithley Source Measure unit, model 236. The room temperature was ca. 297 K and the relative humidity 54%. The films were characterized by spatial resolution Raman spectroscopy in a Renishaw Raman Imaging Microprobe System 3000, with a He-Ne laser with excitement source emitting in 632.8 nm, coupled to an optical microscope, with spatial resolution of 1.5 microns. The Raman spectra were obtained with 8 mW, in the interval of $200-2000 \text{ cm}^{-1}$ (with 5–10 scans) and the infrared spectra in a Bomen, model MB-100, spectrophotometer. The thermogravimetric analyses (TGA) were carried out using a TGA Shimadzu, model 50.

RESULTS AND DISCUSSION

The results using the electrochemical impedance spectroscopic (EIS) method agreed with the four-point probe method results. Thus, only the EIS results are shown. All the results agree with data in the literature.³ The conductivity for the binary blends, PEO/ PEDOT-PSS and PVC/PEDOT-PSS. obtained by the EIS³⁹ method is displayed in Figure 1a. This technique allows us to investigate the dependence of the bulk conductivity on the conducting polymer concentration. According to the data in the literature, the result suggests a percolation threshold present in the 0 to 0.2 PEDOT-PSS content range.³ The largest conductivity range is presented by the blends prepared with amorphous PVC, changing from *ca.* 10^{-11} (pure PVC) to 10^{-5} Scm⁻¹ (blend 9, see Fig. 1a). The same variation was not presented by the PEO/PEDOT-PSS blends, which changed from 10^{-9} (pure PEO) to 10^{-5} Scm⁻¹ (blend 9). However, in both cases the maximum conductivity was ca. 10^{-5} Scm⁻¹.

The PEO/PEDOT-PSS blends presented a phase separation in low PEDOT-PSS ratios, as well as lower electrical conductivity. The conductivity is lower due to the morphology presented by PEO, that is, it presents an appreciable crystallinity, inducing immiscibility, which directly affects the charge transport properties of the blend. In addition, the conductivity of the PEO/PEDOT-PSS blend does not present significant variation from 20 to 40% of PEDOT-PSS. This is also due to the morphology presented by PEO, which is not affected by the conducting polymer presence in



Figure 1 (a) Conductivity as a function of the PEDOT-PSS content. (b) Conductivity of the PEO/PVC/PEDOT-PSS blends with 60% PEDOT-PSS.

these ratios; hence, significant effects are not introduced on the PEO crystallinity. In higher weight PE-DOT-PSS fractions, the increasing conductivity is due to the increasing concentration of the conducting polymer, and above 40% the PEDOT-PSS tends to hinder PEO crystallization.

The conductivity of the PVC/PEDOT-PSS blend shows a linear dependence on the PEDOT-PSS content. This behavior is acceptable due to the miscibility existent between the components of the blend (PVC and PEDOT-PSS). However, a reproducible interruption in this linear behavior at the weight fraction 0.40PVC/0.60PEDOT-PSS was observed, because the conductivity did not respond as expected. This was probably due to interactions occurring in this weight fraction, which influenced the PVC crystallinity.

The conductivity measurements of the PEO/PVC/ PEDOT-PSS ternary blends are showed in Figure 1b. The higher conductivity value ($8.6 \times 10^{-6} \text{ Scm}^{-1}$) was obtained by the ternary blend formed by 60% of PE-DOT-PSS, 16% of PEO, and 24% of PVC. The conductivity was proportional to the PVC weight fraction up





Figure 2 (a) Micrograph of the PEO/PEDOT-PSS sample. (b) Raman spectra of the prominent areas in the micrograph.

to 0.24PVC/0.16PEO (Fig. 1b). After this point a sharp decrease in the conductivity is observed. This occurs due to a great miscibility between PVC and PEO up to the ratio 60/40, respectively. This hypothesis is reinforced by the Hoffman–Weeks theory reported for the PVC/PEO mixture.⁴⁰

The Raman spectroscopy results are presented in Figure 2. According to the literature,³ it was possible to confirm the hypothesis of the partial migration of PEDOT-PSS outward from the PEO spherulite. This phenomenon was assigned to a crystallization-induced phase separation occurring in the PEO host. Raman spatial resolution Raman spectroscopy was used to confirm this fact. Figure 2a shows three different regions (1, center of the spherulite; 2, triple point among three spherulites; and 3, interface between two spherulites). These regions were used to monitor the conducting polymer presence in different places of the spherulites generated by the PEO/PE-DOT-PSS blends. In Figure 2b, the three curves present characteristic peaks of PEDOT-PSS. suggesting a homogenous mixture although the conducting polymer seems to be moved. According to the literature, these results confirm that the PEDOT-PSS are excluded from the PEO spherulites during crystallization,³ but we suggest that they lie on its surface and in the interspherulitic regions, maintaining chemical interactions with the host polymer and the interspherulitic PEDOT-PSS. Regarding the conductivity measuring type, that is, bulk measurements with EIS, the conductivity data confirmed this hypothesis, showing an increasing value as the PEDOT-PSS content increased in the blend, certainly due to a larger amount of the conductive polymer on the spherulitic surfaces.

Due to the low crystallinity degree of the PVC, the expulsion does not occur in the PVC/PEDOT-PSS blends, leading to completely miscible mixtures. In ternary blends formed by PEO/PVC/PEDOT-PSS, the spherulite formation was not observed, even in PEO high ratios, and this fact is probably due to chemical interactions among the polymers that prevent the spherulitic from growing.

Figure 3 presents the Raman spectra for the components of the ternary blend. Pure PVC possesses signals at 616 and 686 cm⁻¹, and these bands are characteristic of the stretching C-Cl bond and the peak observed at 1098 cm⁻¹ assigned to CH₂ stretching.⁴¹ The PEO spectrum shows signals at 357 cm⁻¹ due to OCC vibration. The peak at 839 cm⁻¹ is characteristic of the twisting vibration generated by CH₂, and the peak at 1474 cm⁻¹ was attributed to the scissoring vibration existing in the CH₂ group. In the spectrum of the blend, it was possible to identify the characteristic signals of PEDOT-PSS, presented at 1430 cm⁻¹, attributed to the asymmetrical C = C stretching existent in the thiophene ring.¹² At 1251 cm⁻⁻¹ a signal of the stretching S-CH was observed. The peak at 985 cm⁻¹ was also considered to be sulfur-carbon bonding, characteristic of (S-C=C). Another peak characteristic



Figure 3 Raman spectra for the samples of pure PVC, pure PEO, and blend 3 (60% PEDOT-PSS, 20% PVC, and 20% PEO).



Figure 4 FTIR spectra for the samples of pure PVC, pure PEO, pure PEDOT-PSS, and the blends 1 (60% PEDOT-PSS, 32% PVC, and 8% PEO), 5 (60% PEDOT-PSS, 32% PEO, and 8% PVC), and 6 (50% PEO and 50% PVC).

of the conducting polymer lies at 439 cm⁻¹, attributed to the asymmetrical stretching of the dioxide (C-O-C) existent in the ring.^{42,43}

Figure 4 shows the FTIR spectra obtained for the pure polymers and for the blends. The pure PVC spectrum shows several absorption peaks between 500 and 1500 cm⁻¹. The stretching vibrations for C-Cl valence bonds lie at *ca.* 650 cm⁻¹.^{44,45} The spectrum of PEDOT-PSS presents a signal at *ca.* 1050 cm⁻¹, assigned to the R-SO₃ present in the dopant (PSS).²⁰ In the pure PEO spectrum, absorption bands of the stretching CH at 2890 cm⁻¹ and the relative absorptions to the asymmetrical stretching C-O-C at 1250 cm⁻¹ were observed.⁴⁶ The spectra of the blends showed an enlargement in the peaks at *ca.* 2885 cm^{-1} , and the most pronounced enlargement had an increase in the PEO weight fraction. The appearance of a wide band at 3500 cm⁻¹ for the blends was also observed, corresponding to the stretching O-H from molecules derived from R-SO₃H.⁴⁷ The peaks at ca. 1311 cm⁻¹ are assigned to sulfonic groups, as well as a small deformation at *ca.* 1600 cm^{-1} originating from SO_3^{-} , related to the interactions between the components of the PEO/PVC/PEDOT-PSS blend.

Thermal stabilities are illustrated in the weight loss curves, Figure 5. It was verified that the sample of pure PEO presented a single weight loss process of *ca.* 95% of the total material between 591 and 699 K. The weight loss temperature at a 10% level was 641 K. In pure PVC, the weight loss began at 388 K, probably due to remaining solvent in the polymeric film. This weight loss corresponded to approximately 3% of the total material, and it was not related to HCl liberation since it should correspond stoichiometrically to 58.4% of the total weight.⁴⁸ The weight loss temperature around 10% for the PVC occurred at *ca.* 553 K. For

blend 3 the curve of weight loss began at *ca*. 507 K, and the decomposition temperature at the 10% level was 572 K. Thus, it was observed that blend 3 presented an intermediate performance between the curves of pure PEO and pure PVC. The thermal stability of the blend is approximately 19 K higher compared to the weight loss temperature at the 10% level for PVC. This was probably due to the fact that PVC induced PEO decomposition.

In other words, by increasing the amount of PEO the blend tended to perform similarly to this pure polymer. In addition, although PEO was present in small amounts, it was enough to delay the liberation of HCl from PVC. Therefore, the enhancement stability in the blends was due to the existence of a synergic effect caused by PEO, on PVC and PEDOT-PSS. The weight loss temperature at the 10% level for pure PEDOT-PSS occurred at *ca.* 443 K.³⁰ Our results showed that PEDOT-PSS did not influence the thermal stability of the blends.

CONCLUSIONS

The blends showed enhanced electrical and thermal properties compared to the pure insulating polymers. The values obtained in the conductivity measurements for the binary and ternary blends were sufficient to consider these materials as semiconductors. Electrical conductivity is due to the conducting polymer presence, and the thermal stability is due to the synergism caused by PEO.⁴⁹ Flexibility properties were not lost due to the presence of PEDOT-PSS, and further mechanical analyses are in progress.

Raman and infrared spectroscopies confirmed the presence of PEDOT-PSS in the blends. In addition, the spectroscopy results suggested a chemical interaction



Figure 5 TG curves for pure PVC, pure PEO, and blend 3 (60% PEDOT-PSS, 20% PEO, and 20% PVC). Heating rate 10° C/min and N₂ flow rate 50 cm³/min.

between the polymers. The spatial resolution Raman analyses indicated that the conducting polymer could be expelled from the spherulite interior but remained on the spherulite surface, maintaining a pseudohomogenous mixture.

The thermal stability of the ternary blends increased as the concentration of PEO increased. It was also observed that the presence of PEDOT-PSS in binary blends did not change the thermal stability. The stability effect was assigned to PEO. Concerning their visual and physical characteristics, the blends presented a continuous morphology, transparency, and became bluer in color as the PEDOT-PSS concentration increased. This may prove important for applications in which optical transparency is desired, and conductivity is retained.

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