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Improved conductivity of films of ultra high molecular weight polyethylene and polyaniline blends prepared from an *m*-cresol/decaline mixture

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Abstract

Blends of polyaniline (PANI) doped with camphor sulfonic acid and ultra high molecular weight polyethylene were prepared using a mixture of *m*-cresol and decaline under conditions that promote specific interactions between the polymer, dopant and solvent mixture, leading to films with improved electrical conductivity. Such interactions are in agreement with the formation of supramolecular structures based on hydrogen bonding and phenyl stacking reported in the literature for similar systems. The results from the blend characterization by tensile strength and electrical conductivity measurements, differential scanning calorimetry, UV–Vis spectroscopy, X-ray diffraction and scanning electron microscopy are presented and discussed. Low percolation threshold and high conductivity were obtained, for instance, 10^{-6} and 10^{-2} S/cm, for blends containing 1 and 5% of PANI, respectively. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Conducting polymers; Polyaniline; Blend

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1. Introduction

The goal of combining the mechanical properties characteristic of polymers with the electrical properties of metals can be finally achieved by the preparation of blends of conducting and conventional polymers [1]. Although polyacetylene and other conducting polymers had, in principle, such potential they did not exhibit properties, such as flexibility, tensile strength, elasticity and processability peculiar to high performance polymers. The possibility of processing conducting polymers in the form of blends with commercial polymers [1–5] has opened a wide range of application and increased the technological potential of these materials since the most desirable features of both the conducting and conventional polymers can be combined in a synergistic matter.

The challenge of producing blends and composites with conducting polymers has been studied by many researchers in the last years. Several alternative strategies have been used to prepare these blends such as, electrochemical deposition [6,7], in situ chemical polymerization [8,9], powder dispersion [10–12], melt blending [13–17] and solution blending [1,3,4,17–22]. Among the conducting polymers, blends with polyanilines (PANIs) have obtained the greatest technological importance due to the remarkable properties of such conductive polymer namely, ease of synthesis and doping, environmental stability, solubility and processability.

Although a great number of blends of conducting polymers have been investigated, little has so far been done to characterize the materials produced, as well as to optimize the blends properties as a function of preparation conditions. It is known [14,17,21], for instance, that the solvent, co-solvent and dopant are of key importance for determining the structure, morphology, electrical and other properties of PANIs.

The aim of this paper is to characterize blends of PANI and ultra high molecular weight polyethylene (UHMW-PE) produced using a solvent mixture under conditions for which improved conductivity is achieved.

2. Experimental

2.1. Blend preparation

Parent PANI was synthesized as described elsewhere in

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Table 1
Tensile properties for blends of PANI (doped with CSA) and UHMW-PE prepared from *m*-cresol/decaline mixtures

PANI content in the blend (%)	Tensile strength (MPa)	Elongation at break (%)
0	3.3 ± 0.1	400
5	3.2 ± 0.1	5
10	3.3 ± 0.1	80
20	<0.5	<1

order to have a Mw of about 50 000 g/mol [23]. The polymer in the emeraldine base form was dissolved in *m*-cresol (≈ 1%) and then protonated with camphor sulfonic acid (CSA) to a doping degree of 50% PANI $(CSA)_{0.5}$. UHMW-PE was dissolved in decaline (≈ 5%) at 120°C and added to the conducting polymer solution in order to obtain the desired composition, maintaining the *m*-cresol to decaline ratio at 1:2.4 v:v, according to our previous work on PANI blends [18,22]. Under such conditions homogeneous and flexible films were obtained after drying for 96 h at room temperature plus 24 h at 60°C, when no significant *m*-cresol residue was detected.

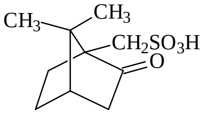
2.2. Characterization

Electrical conductivity data were obtained using the four-probe method, doing five measurements in three different samples of each composition, the standard deviation being always less than 1%. Tensile properties were obtained from an Instron machine model 1127 in at least five samples (5 × 50 mm large and 20 μm thick) of each composition, with standard deviation below 4% for tensile strength and 10% for elongation. The UV–Vis absorption spectra was obtained using a Perkin–Elmer model Lambda-9 Spectrophotometer. Scanning electron microscopy (SEM) were performed in a Zeiss microscope model DSM 960 operated at 20 kV, on samples coated with a thin layer of gold. Thermal analysis was done in a differential scanning calorimeter Du Pont model 2000, at a scan rate of 10°C/min in nitrogen atmosphere. X-ray diffraction patterns were taken on a Rigaku RU-200B diffractometer, using Cu K_α radiation and a Ni filter.

3. Results and discussion

Blends of PANI and UHMW-PE were successfully produced from solution using an appropriate solvent mixture consisting of decaline and *m*-cresol and CSA as the dopant. The idea of a functionalized acid, such as CSA, was firstly used by Cao et al [1] for the preparation of blends of PANI and several commercial polymers. They proposed that the dopant counter-ion induced solubility in organic solvents allowing the preparation of blends from solution. It should be pointed out that, in our case, if lower amounts of *m*-cresol were used the blend started to present a macro-phase separation because the hydrogen-bonding strength of the solvent mixture was reduced. Such observation is in agreement with the recent work of Ikkala et al. [14,17], which demonstrated the importance of finding a sufficiently strong specific interaction, based on hydrogen bonds between acidic solvents and PANI, to have high solubility. Therefore, the solvent mixture had two roles: (i) to solubilize the two different polymers—(decaline for PE and *m*-cresol for PANI) and (ii) to promote specific interactions that lead to improvement in solubility and conductivity of the blend. Similar synergistic effects of solvent mixtures were also observed for PANI–CSA/SEBS (block copolymer of styrene–ethylene/butylene–styrene) blends [18,22].

The CSA dopant used in this work is a functionalized protonic acid whose chemical structure is



where the acid group, SO_3H, dopes PANI by preferential protonation of its imine units. Additionally, CSA provides specific interactions, which improves the solubility and conductivity as demonstrated recently in literature [14,17,21]. The recent work of Ikkala [17], for instance, showed that for this same system a steric match leading to supramolecular structures can be obtained due to a combination of three simultaneous interactions: firstly, the sulfonic acid is bonded to PANI due to proton transfer; secondly, the hydroxyl group in *m*-cresol is hydrogen bonded to the carbonyl group of the CSA molecule; and lastly, the phenyl groups of the *m*-cresol and PANI are stacked, thus yielding enhanced mutual dispersion forces. They also showed that such specific interactions are possible because the molecular dimensions and steric details simultaneously allow the specific interactions described (charge transfer, phenyl stacking and hydrogen bond), thus providing the requirement of what was called molecular recognition. Such interactions promote a more extended conformation of the PANI chains [24], which leads to the improvement in solubility and conductivity observed, consistent with the present study. It has also been shown [24] that the improvement in conductivity persists even after eliminating the residual *m*-cresol, after the film preparation.

It is important to stress that the preparation conditions used in the present work were very critical for obtaining a high quality film, since a change in the solvent mixture proportions or in the dopant would result in a non-cohesive

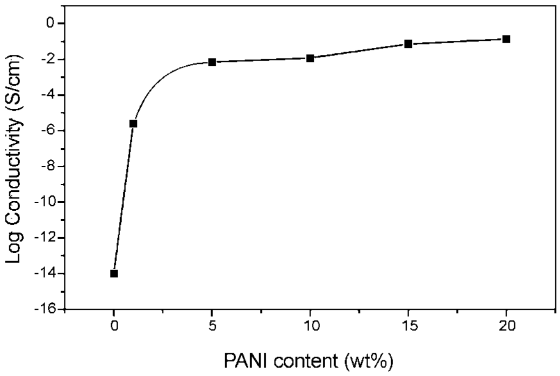


Fig. 1. Electrical conductivity as a function of PANI content (doped with CSA) in blends with UHMW-PE prepared from *m*-cresol/decaline mixtures.

or a very brittle film. As demonstrated in Table 1 the tensile strength of the UHMW-PE film (3.3 MPa) could be maintained in the blend up to the addition of 10% of PANI, after which it was drastically lost. The elongation at the break of UHMW-PE, which is usually above 400%, was significantly decreased by the addition of PANI to the blend. This was expected since PANI possesses a very stiff polymer backbone owing to the presence of the aromatic rings and the double bonds that result usually in an extremely brittle polymer, unless a plasticizer is used [14,17], which it was not our case. It should be noted that, surprisingly, the elongation at break of the blend containing 5% of PANI is lower than that with 10% of PANI, suggesting the occurrence of phase separation due to the saturation of PANI in the blend, as it will be further supported by electrical conductivity measurements and SEM analysis.

Fig. 1 shows that electrical conductivity as high as 10^{-1} S/cm was obtained by blending UHMW-PE and PANI–CSA. Remarkably a very small percolation threshold is observed, where, for instance, the addition of only 1% of PANI into the UHMW-PE promotes eight orders of magnitude increase in conductivity, going from 10^{-14} to 10^{-6} S/cm. For PANI contents above 5% the conductivity tends to be a constant value, consistent with the saturation observed in the mechanical properties data previously discussed. The conductivity achieved for the undrawn blend containing 5% of PANI (10^{-2} S/cm) is well above those reported in literature [1], 10^{-6} and 10^{-4} S/cm, respectively for undrawn and drawn samples containing the same amount of PANI. Such behavior is attributed to the more appropriate solvent mixture used in the present work. Moreover, the dopant used in that study [1], dodecyl benzene sulfonic acid (DBSA), had to be in excess in order to plasticize PANI and render it soluble in decaline, without *m*-cresol addition. In the present case the dopant used was CSA, which did not need to be in excess to render PANI soluble in the solvent used, *m*-cresol. In addition *m*-cresol, used as a co-solvent, presents the advantage of having specific molecular recognition interactions with PANI and CSA due to hydrogen bonding and phenyl stacking, which account for the conductivity improvement, as has been discussed in this paper, based on the study previously reported for PANI alone [14,17,21]. UV–Vis electronic absorption spectra confirms that PANI is in the doped conductive emeraldine salt state, as indicated by the absorption band at around 800–850 nm, even for small contents of PANI in the blend as shown in Fig. 2.

Thermal analysis by DSC (Fig. 3) indicates a decrease in the heat of fusion (ΔH) and melting temperature (T_m) of the polyethylene crystals [25] upon blending from 39.7 J/g and 144.8°C to the ranges 10.9–16.0 J/g and 135.4–137.6°C, respectively for UHMW-PE and the blends containing up to 20% of PANI. No melting peak was observed for PANI, since it is known from literature that although it can exhibit some crystallinity, the degradation temperature is lower than the melting temperature. The decrease in T_m and ΔH observed are consistent with some degree of miscibility of the PANI + (dopant counter-ion) with the UHMW-PE. X-ray diffraction analysis corroborates the DSC results. The

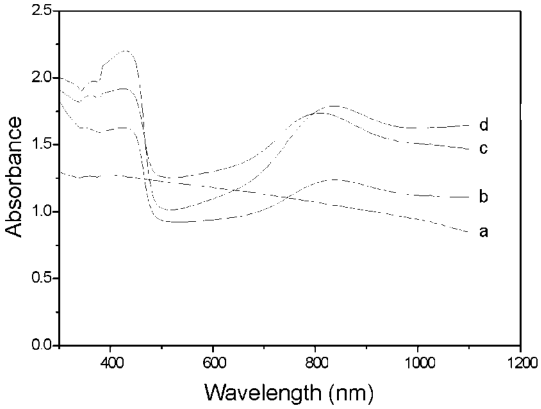


Fig. 2. UV–Vis spectra of blends of PANI (doped with CSA) UHMW-PE prepared from *m*-cresol/decaline mixtures: (a) UHMW-PE blends with PANI content of (b) 5%; (c) 10%; and (d) 20%.

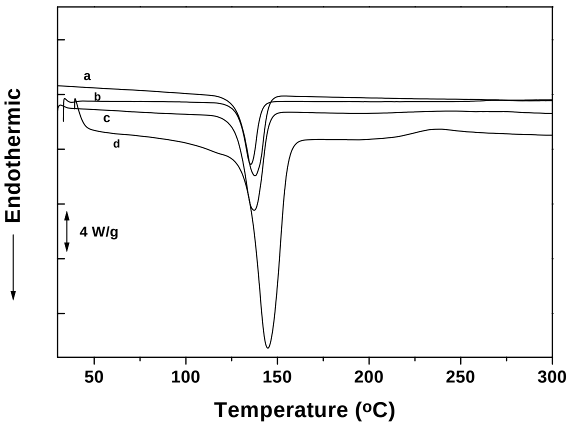


Fig. 3. DSC of blends of PANI (doped with CSA) and UHMW-PE prepared from *m*-cresol/decaline mixtures. Blends with PANI content of: (a) 1%; (b) 5%; (c) 20%; and (d) 0%.

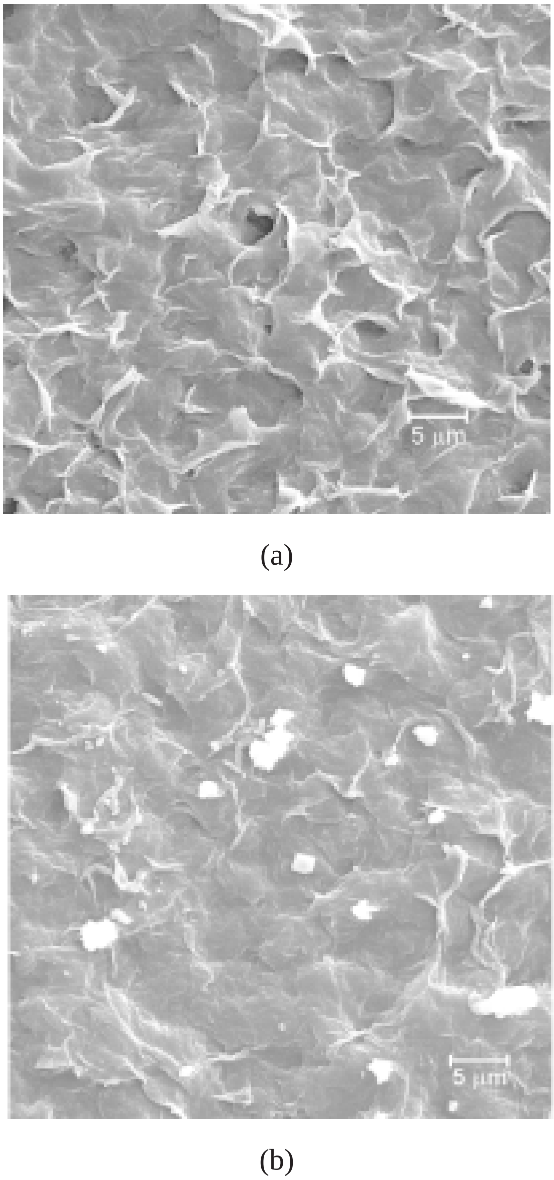


Fig. 4. Scanning electron micrographs of: (a) UHMW-PE; and (b) blends of UHMW-PE containing 10% of PANI (doped with CSA) prepared from *m*-cresol/decaline mixtures.

position of the main diffraction peaks characteristic of UHMW-PE [25] ($2\theta = 21$ and 24°) did not change, but their intensity was decreased upon blending. Furthermore, from preliminary SEM investigations (Fig. 4) one can observe the formation of agglomerates only for compositions above 10% of PANI, which is consistent with the occurrence of some phase separation of PANI due to its saturation into the UHMW-PE blend. For blends containing 1 and 5% of PANI the morphology obtained was basically the same as that seen for PE. Further work is in progress to study the structure and morphology of these blends more deeply by atomic force microscopy studies.

4. Conclusions

The present work has shown that blends of PANI doped with CSA and UHMW-PE can be successfully prepared using a mixture of *m*-cresol and decaline under conditions which promote specific interactions between the polymer, dopant and solvent mixture, leading to improved electrical conductivity. Higher conductivity and lower percolation threshold than those reported in the literature were obtained, for instance, 10^{-6} and 10^{-2} S/cm for blends containing 1 and 5% of PANI, respectively.

Acknowledgements

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