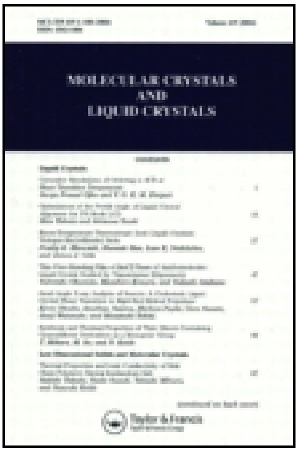

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Conductive Blends of Polyaniline and Poly(Amide-Imide)

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Among the studied conductive polymers, polyaniline (PAni) is the most promising one, due to its relatively good solubility and environmental stability. In this work we prepared a poly(amide-imide) and polymer blends with PAni by solution of both polymers in NMP. These polymers were able to form blends in any proportion and characterized by DSC, TGA, FTIR and microscopy techniques (optical and AFM). The glass transition temperatures (Tg) of the blends showed a decrease with PAni contents, indicating that no phase separation occurred in the blends. The microscopy techniques showed that the blend is completely compatible, and the FTIR spectra indicating strong interactions between the components. Preliminary conductivity evaluations showed a conductivity of 10^{-3} S/m for blends with 60% PAni. The films may be also selectively crosslinked by thermal treatment, yielding a completely insoluble, extremely flexible, resistant and, depending on the PAni content, very clear and transparent material.

Keywords: polyaniline, blend, poly(amide-imide), thermal analysis

INTRODUCTION

Among the studied conductive polymers, polyaniline (PAni) is the most promising one, due to its relatively good solubility and environmental stability. However despite its advantages, some physical properties, such as brittleness and thermal stability, are so far from most used polymers to not permit the increase on the applications of these polymers. Blends with other polymers have been used to increase the processability and stability of PANI. The process most used is the solution blending, where thin films are obtained by casting from the solution of the polymer mixture. The feasibility of these blends depend on two main factors: (a) The disposability of a common solvent for both the polymers to be used and PAni. (b) The compatibility (or even miscibility) of the polymers blended. Good solvents for polyaniline are strong polar solvents as N-methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide, thus the polymer to be blended with PAni need to be soluble in these solvents. Most of the PAni blends that appear in the published works are not miscible [1-6], but polyimides and some other polymers[7-10] could form miscible blends. Polyimides are one of the mostly high temperature resistant polymers and have very good mechanical properties. However polyimides are very expensive, and are soluble only in its precursor form (polyamic acid), have short shelf life even when stored at low temperatures and are difficult to be obtained in a thermoplastic version. Another high performance resistant polymer class more economical, easier to be processed, and that can be obtained in the thermoplastic form are the polyamide-imides (PAI). In the electro-electronic industries [11] the PAIs are used in applications where high mechanical resistance and/ or temperatures are required, conjugated with easy processability in solution or as a thermoplastic.

EXPERIMENTAL

Polymers synthesis: Polyaniline (PAni) in the emeraldine base form was synthesized by oxidative polymerization of freshly distilled aniline with ammonium peroxydissulfate in 1.0M hydrochloric acid aqueous solution, according to conventional methods [12], followed by deprotonation of PAni hydrochloride with 0.1M ammonium hydroxide aqueous solution. Poly(amide-imide) (PAI) was prepared by the solution copolymerization of 4,4'-diphenylmethanediisocyanate (MDI) and trimellitic anhydride in N-methyl-2-pyrrolidone(NMP) at 80 °C

Blend preparation: Solutions of PAI (0.04% w/v) and PAni (0.07% w/v) in N-methyl-2-pyrrolidone were mixed in the appropriate proportions, and magnetic stirred for 1 hour prior to casting onto glass substrates and drying at 50 °C for 6 hours to yield the free standing films

Film Analysis: The PAni/PAI films were characterized by thermal analysis (Differential scanning calorimetry, DSC, and thermogravimetric analysis, TGA), Fourier Transform Infrared Spectroscopy (FTIR) and microscopy techniques (optical and AFM). Thermal analyses were performed in a Shimadzu Twi-50 system, under nitrogen and at a heating rate of 10°C/min. The weight losses in TGA experiments were recorded from ambient temperature to 950°C. The infrared spectroscopy analyses of the films were performed in a Nicolet Avatar 360, in the Total Attenuation Reflection mode (ATR) using zinc selenide crystal. Atomic Force Microscopy observations were made with a Digital III system, in the tapping mode.

RESULTS AND DISCUSSION

The DSC thermograms of the PAni/PAI blends are shown in figure 1.

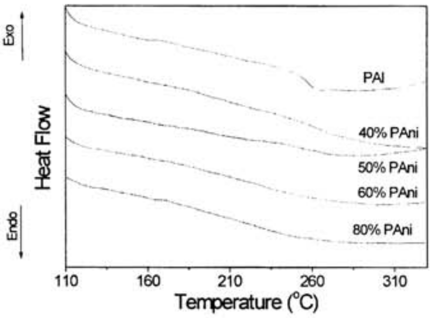

FIGURA 1 – DSC thermograms of some PAI/PAni blends.

The onset of the Tg transitions of the blends showed a decrease with PAni contents, indicating that no phase separation occurred in the blends. The temperature of initial decomposition (T_{id}), determined by TGA thermograms (fig 2), decreased as the PAni content increased and the first weight loss around 200 ^{O}C, attributed to the PAI crosslinking, also decreases with PAni content.

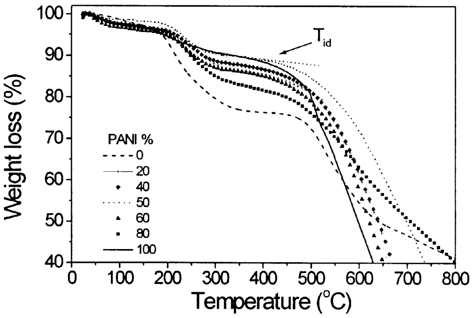

FIGURA 2 – TGA thermograms of some PAI/PAni blends.

The microscopy techniques showed that the blend is completely compatible, since only a single and extremely homogeneous phase could be visualized.

The FTIR spectra of some PAni/PAI blends and also of PAni and PAI polymers are shown in Figure 3. PAni spectrum presents broader bands than PAI and there is some band superposition between the spectra of the pristine polymers in the region of 1750-1400 cm^{-1}. In order to infer if there is some degree of interaction between the components, the sum of PAI and PAni spectra was calculated and compared to the blend 50/50 spectrum (Fig. 4).

As it can be clearly seen in figure 4, strong interactions between the blend components [13] occur, as evidenced by the shifts and broadening of some bands and also by the changes in the relative intensity of the absorption bands.

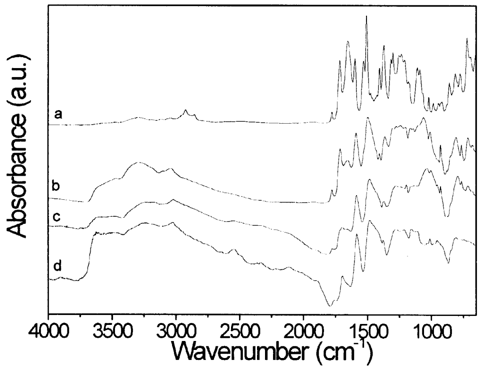

FIGURA 3 – FTIR spectra: (a)PAI; (b) PAni/PAI 40/60; (c) PAni/PAI 80/20 and (d) PAni.

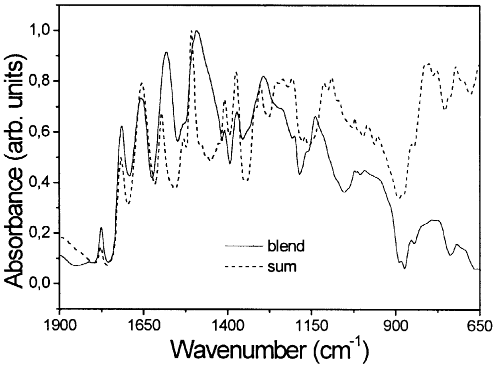

FIGURA 4 – Comparation between FTIR spectrum of PAI/PAni 50/50 blend and the sum of the spectra of PAni and PAI.

Blends form thin free-standing films with visually better quality than the pure PAni. Homogeneous blends could be formed in any proportion of PAni/PAI. Preliminary bulk conductivity evaluations [14] showed conductivity values of 10^{-3} S/cm for blends with 60% PAni after HCl doping. This low value is consequence of the doping process with aqueous solutions, which cannot wet the blend surface. The optimizing of the doping method is being carried out in order to increase the conductivity values. The films may be also selectively crosslinked by thermal treatment, yielding a completely insoluble, extremely flexible, resistant and, depending on the PAni content, very clear and transparent material.

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