Preparation and Characterization of Castor Oil-Based Polyurethane/Poly(*o*-methoxyaniline) Blend Film

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ABSTRACT: Blends made up of castor oil-based polyurethane (PU) and poly(*o*-methoxyaniline) (POMA) were obtained in the form of films by casting and characterized by FTIR, UV-Vis-NIR spectroscopy, and electrical conductivity measurements. Doping was carried out by immersing the films in 1.0*M* HCl aqueous solution. Chemical bonds between NCO group of PU and NH group of POMA were observed by means of FTIR spectra. The UV-Vis-NIR spectra indicated that the presence of the PU in the blend does not affect doping and formation of the POMA phase. The electrical conductivity research was in the range of 10^{-3} S/cm. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 706–709, 2007

Key words: poly(*o*-methoxyaniline); polyurethane; castor oil; conducting polymer; blends

INTRODUCTION

Polyaniline (PANI) is one of the most interesting conducting polymers in view of the fact that it has attracted considerable attention owing to its good environmental stability, control of electronic and optical properties via the level of oxidation and protonation, low cost of raw material, and ease of synthesis.[1] The main disadvantage of parent PANI is poor processability, both in melt and solution, because of the stiffness of its polymeric backbone. To overcome this disadvantage substitution of alkyl chain on the aromatic ring can be executed, thus improving the solubility in various organic solvents.[2]

Accordingly, the poly(*o*-methoxyaniline) (POMA) has received considerable attention,[3–5] since the presence of the *o*-methoxy group (—OCH$_3$) increases the solubility in various organic solvents, when compared with that of parent PANI, while maintaining similar optical and electronic properties.[6] The conductive forms of PANI, as well as its derivatives, lead to very brittle materials with low mechanical properties, and on account of this reason they are mostly used in blends with common insulating polymers.[7–12]

In the present work, Polyurethane (PU)/POMA blend films were prepared and morphological, optical, and electrical properties were investigated using FTIR and UV-Vis-NIR spectroscopy and electrical conductivity measurement. The choice for POMA was because this polymer is easily soluble in volatile organic solvent,[13,14] which allows thin films to be obtained by spin coating technique, with strong interaction between the blend components.

EXPERIMENTAL

Polymer synthesis

POMA was chemically synthesized with ammonium peroxydisulfate (NH$_4$)$_2$S$_2$O$_8$ in aqueous 1.0*M* HCl at 0°C, as described elsewhere.[15,16] Dedoping was performed by treatment with 0.1*M* ammonium hydroxide for 16 h at room temperature to yield the polymer in the emeraldine base form (EB). The polymer was then dried under dynamic vacuum for 24 h at room temperature.

Blend preparation

PU based on castor oil was prepared using the prepolymer F-329 and polyol 21 L supplied by Grupo de Química Analítica e Tecnologia de Polímeros-GQATP-USP (Brazil) and purchased from Poliquil Araraquara Polímeros Química LTDA (Araraquara, SP, Brazil). Stock solutions of POMA dissolved in chloroform with different concentrations were
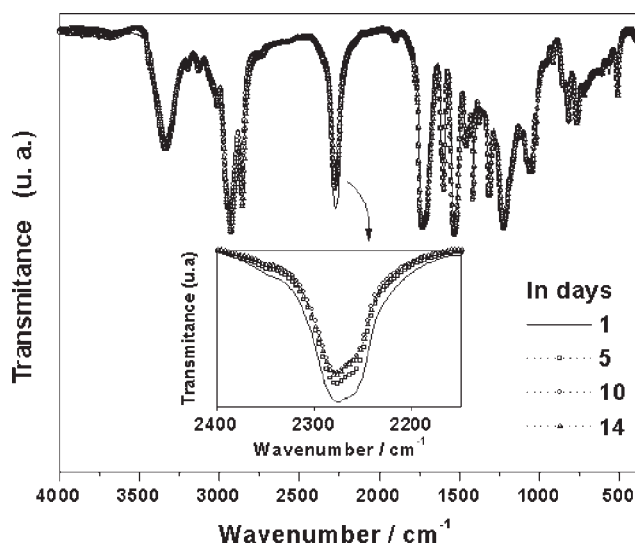
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Figure 1 Infrared spectra of PU taken at different days. The inset highlights the NCO (2270 cm^{-1}) band.

prepared separately. These POMA solutions were mixed at the desired proportions with the polyol and then with the prepolymer that was previously diluted in chloroform. Films (20–170 µm thick) were prepared by casting these solutions onto glass slides placed in an oven with air circulation, at room temperature. After solvent evaporation the films obtained were removed from the glass surface by peeling them out. The prepolymer/polyol weight rate was always kept at 1/0.7. Doping of the blends was carried out by immersing the films in 1.0M HCl aqueous solutions. PU films were obtained from the mixture of prepolymer and polyol previously diluted in chloroform. The sample in this case is called PU/Ch.

Characterization

FTIR spectra were recorded with a NEXUS 670 spectrophotometer from Nicolet Instrument Corp. The samples for FTIR analysis in film form were obtained by casting the blend solution on the disc surface of KBr. Thermal analysis was performed in a MDSC TA Instruments model 2920 at a scan rate of 10°C/min in nitrogen atmosphere. Electrical conductivity was performed using the two and four-probe method at room temperature. UV-Vis-NIR spectroscopy analysis was executed in thin films deposited on glass substrate by spin coating with a Cary 50 spectrophotometer fabricated by Varian.

RESULTS AND DISCUSSION

The PU is characterized by —NH—CO—O groups that are obtained by the reaction of isocyanate (NCO) and hydroxyl (OH) group. The isocyanate band in
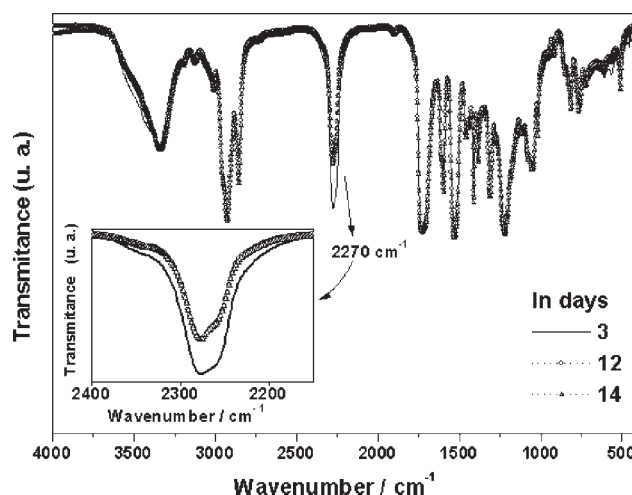

Figure 2 Infrared spectra of PU/Ch taken at different days. The inset highlights the NCO (2270 cm^{-1}) band.

FTIR spectroscopy occurs at 2270 cm^{-1} and the cure time of PU can be investigated considering the isocyanate band as function of time. Figure 1 shows the FTIR spectra of PU taken at different times subsequent to mixing polyol with prepolymer. The isocyanate band intensity decreased until the 10th day, maintaining constant after this period, thus indicating that the reaction proceeded to its completeness. The same behavior was observed when the prepolymer and polyol were diluted in chloroform prior to mixture, as shown in Figure 2. The presence of the same band can be observed in pure PU, indicating that there are no chemical reactions between PU and chloroform.

Figure 3 shows the FTIR spectra of PU, de-doped POMA, and corresponding de-doped PU/POMA at different POMA content in the blend. The main absorption band for POMA is associated with the
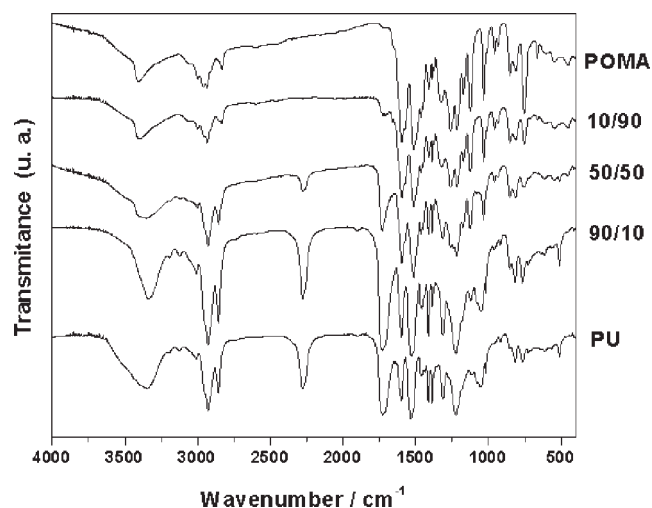

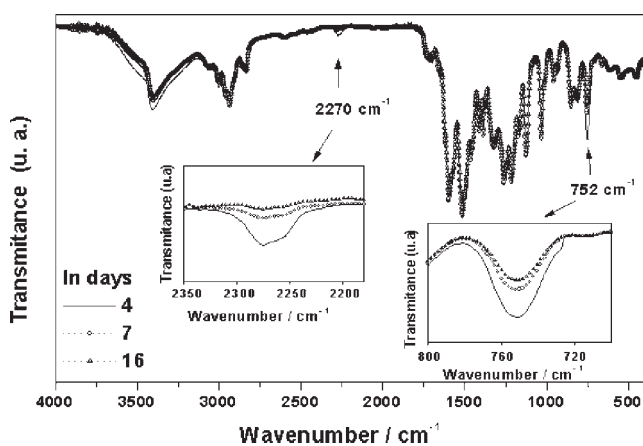**Figure 3** Infrared spectra of PU/POMA blend for different POMA content.

Figure 4 Infrared spectra of the blend PU/POMA (10/90) taken at different days. The inset highlights the NCO (2270 cm^{-1}) and N—H (752 cm^{-1}) band.

stretching vibration of N—B—N and N=Q=N, which appears around 1512 and 1595 cm^{-1} (where —B— and =Q= stands for benzenoid and quinoid moieties in the POMA backbone), C—O stretching vibration of the —OCH$_3$ (1029 cm^{-1}) and N—H angular deformation out of plane (752 cm^{-1}), in agreement with the literature.[17,18] The PU/POMA blends show the characteristic peaks for both PU and POMA, becoming more similar to PANI with the POMA content increasing in the blend. Looking closely at blend FTIR spectra, taken at different days after components mixture, it can be observed that the band at 752 and 2270 cm^{-1} decreased, as shown in Figure 4. This variation stops fourteen days after the mixture of components. The same behavior was found with POMA and prepolymer films, as shown in Figure 5. In this case, the POMA dissolved in chloroform was mixed with the prepolymer and
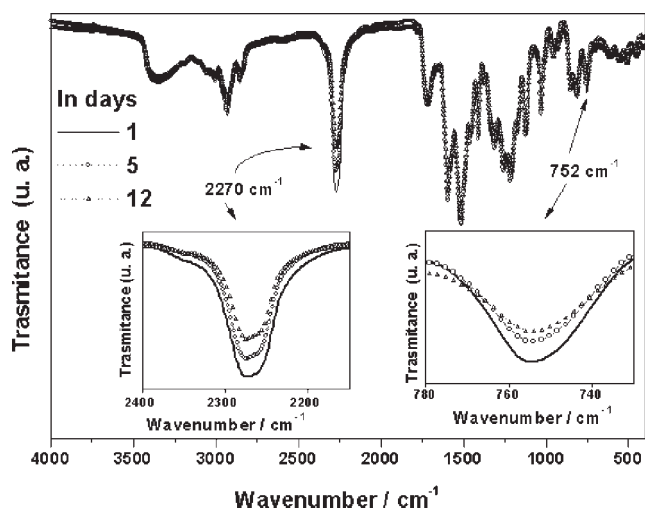

Figure 5 Infrared spectra of prepolymer/POMA taking at different days. The inset highlights the NCO (2270 cm^{-1}) and N—H (752 cm^{-1}) band.
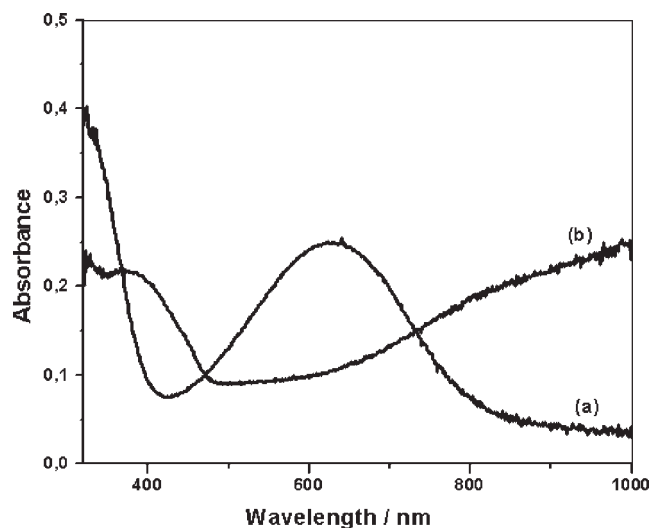

Figure 6 UV-Vis-NIR spectra of PU/POMA films (50/50) (a) undoped and (b) doped with 1.0M HCl solution.

casted on KBr disc surface. These results suggest that a chemical reaction occurs between NCO PU and N—H POMA groups. The same result was reported recently in the literature for NCO terminated PU and PANI emeraldine base.[19,20]

The UV-Vis-NIR absorption spectra of undoped PU/POMA and PU/POMA doped with 1.0M HCl is shown in Figure 6. The films were obtained on the glass substrate by casting and doped by immersion in 1.0M HCl aqueous solutions. The undoped PU/POMA shows a peak at 625 nm, characteristic of POMA, corresponding to molecular exciton transition, as described in the literature.[21] The band at 390 nm and the free carrier tail above 600 nm, related to the doping process, are assigned as polaron bands that are responsible for the polymer conductivity. The free carrier tail is indicative of secondary doping effects, which result from a more extended chain conformation,[22] allowing a more delocalized polaronic band. The spectra of doped and undoped PU/POMA blend are similar to the neat POMA,[21] indicating that the POMA conjugation structure is not destroyed by the presence of the PU matrix.

Figure 7 shows a dependence of electrical conductivity of the PU/POMA as function of POMA content. The conductivity increases from a value of 1.0 × 10^{-14} S/cm (pure PU), up to 1.0 × 10^{-3} S/cm to 50% of POMA content in the blend. To 30% of POMA content the conductivity is around 5.6 × 10^{-5} S/cm, one order lower than described in literature for PU/PANI network.[19] In the literature[13] we found that the electric conductivity of POMA film on a glass sheet, doped by p-toluene sulfonic acid (TSA) obtained from different solvent, is in the order of 10^{-3} S/cm as found in our blend. To free-standing POMA films obtained from 1-methyl-2-pyrrolidine
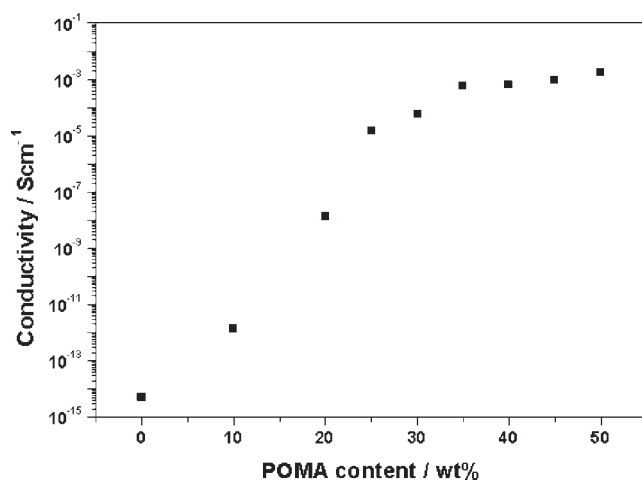
Figure 7 Electrical conductivity of the PU/POMA films versus POMA content doped with in 1.0*M* HCl solution.

(NMP) casting solution, doped in HCl solution the conductivity is around 1.3 S/cm three orders of magnitude higher than what is found in this work. We believe that the low conductivity, mainly for low POMA content in the blend, can be related to difficulties of diffusion of ion because of PU matrix causing a non efficient POMA doping. Although blends exhibiting higher conductivity can be found in literature,[23–27] they usually use high boiling point solvents. In our case, the use of a PANI derivative, POMA, made possible the preparation of blends from a very volatile solvent, which is very convenient for the preparation of ultra-thin films for sensor application, as it is currently being studied in our laboratories and will be the subject of another publication.

CONCLUSIONS

Flexible and free-standing films of blends of PU and POMA with different POMA content were obtained by casting and doped by immersion in 1.0*M* HCl aqueous solution. Chemical reaction between NCO PU groups and N—H POMA groups were observed by FTIR analyzes. The UV-Vis-NIR spectra of the blend show the same behavior found for pure POMA films indicating that POMA conjugation

structure is not destroyed by the presence of the PU matrix. The electrical conductivity increased as a function of POMA content in the blend reaching 10^{-3} S/cm.

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