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Polymer 44 (2003) 6891–6899

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Networks and blends of polyaniline and polyurethane: correlations between composition and thermal, dynamic mechanical and electrical properties

Paula C. Rodrigues[a], Leni Akcelrud[a,b,*]

[a]Departamento de Quimica, Universidade Federal do Parana, Curitiba-PR, CP 19081, CEP 81531-990, Brazil
[b]Instituto Tecnológico para o pesenvoluimento (LACTEC), Curihba-PR, CP 19067, CEP 81531-990, Brazil

Received 7 July 2003; received in revised form 6 August 2003; accepted 13 August 2003

Abstract

The combination of the electrical conducting properties of polyaniline (Pani) with the mechanical performance of polyurethanes (PU) was accomplished through the interconnection of the two polymers via condensation of a NCO terminated PU prepolymer and the amine groups of polyaniline. The crosslinking density of the resulting networks was set by the proportion between the two components, since the PU length was kept constant ($M_w = 40,000$, $M_n = 23,000$). The composition range Pani/PU spanned from 1 to 30%. Blends of the same composition were prepared for comparison purposes. Taking into account the IR absorption shifts, DMTA spectra, electrical conductivity results and computer generated optimized chain conformation, a morphological interpretation is proposed in which Pani chains form a continuous percolating phase dispersed in a polyurethane matrix, linked together by an interphase, with a certain degree of miscibility. This interphase would be responsible for the connectivity between the two components and the good mechanical properties observed. Electrical conductivity of the networks was in the 10^{-4} S/cm range.

Keywords: Polyaniline; Polyurethane; Networks

1. Introduction

Since their discovery conducting polymers have been employed in a wide variety of applications, such as rechargeable batteries, electromagnetic shielding, dielectric metallization, anti-static coatings [1], anodes in light emitting diodes [2], corrosion inhibitors [3] and sensors [4]. Among these polymers polyaniline is unquestionably the most explored, due to its environmental stability, ease of preparation, and the possibility of controlling the electrical conductivity through a unique doping process (protonic). However, the chain stiffness renders processing difficult, since the polymer in its doped form is insoluble in common organic solvents and the mechanical properties are not so good as desired for many applications. Extensive work has been devoted to circumvent this problem, and in a general way the main efforts can be described as: insertion of substituents in the chain; copolymerization and the blending with ‘conventional’ polymers. The insertion of lateral groups either on the ring [5–8] or in the nitrogen atom [9–11] results in more soluble materials, but the chain torsion brought about significant decreases in conductivity. Examples of copolymers containing aniline include the graftization of polyethylene glycol [12] or polyacrylic acid [13] onto a polyaniline backbone and blocked structures as polyurethane–polyaniline octamer [14]. Recent advances report the synthesis of tetraaniline-terminated starburst polyurethane–urea, utilizing a fullerenol as a molecular core [15,16] and light emitting-hole transporting block copolymers of polyaniline–polyfluorene [17].

The blending of polyaniline with other polymers is a very active area, with an abundant number of publications in the last few years [18] aiming to combine good mechanical properties with low electrical resistance. The low miscibility of the conjugated chains with the hosting plastics, leading to a variety of morphologies is, as expected, of

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[*] Corresponding author. Tel.: +55-41-361-6221/336-7507; fax: +55-41-266-3582.

E-mail address: akcel@onda.com.br (L. Akcelrud).

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doi:10.1016/j.polymer.2003.08.024

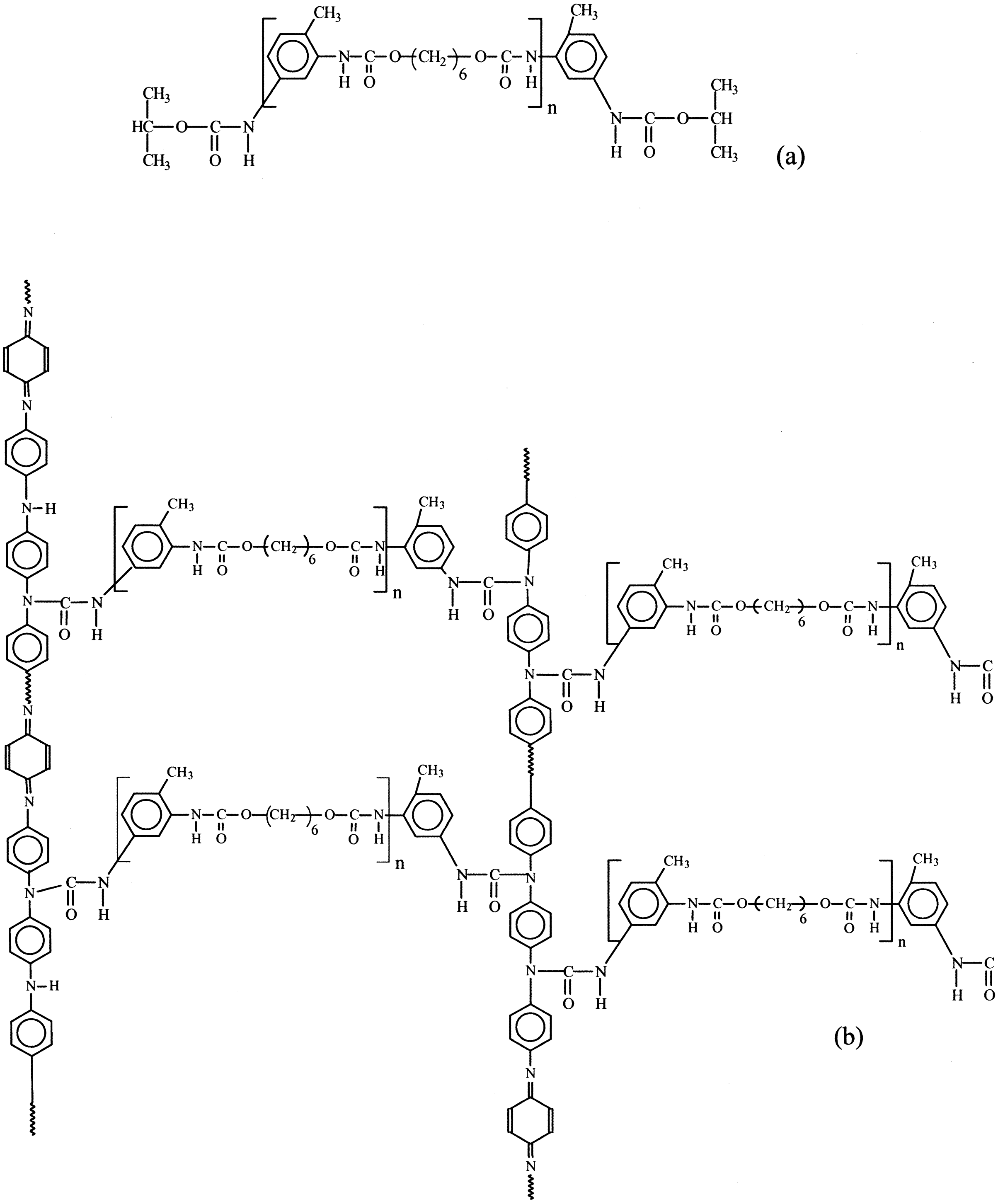

Fig. 1. Chemical structure of (a) PU model compound and (b) Pani/PU network.

prime importance in the general physical behavior of these materials. One elegant way to improve the miscibility was to insert counter ions among the chains [19] making it possible to blend conductive polyaniline with some conventional polymers. Similar results were obtained with the use of phosphoric diesters to protonate and plasticize polyaniline [20].

Finally, conducting IPN's built by Pani and polyvinyl alcohol [21] or carboxy methyl cellulose [22] can be cited as resources to achieve the desired set of physical properties.

In this contribution we report and discuss the electrical, thermal and spectroscopy properties of a network consisting of Pani chains interconnected through covalent links to polyurethane segments (PU). The length of the PU segment was kept constant ($M_w = 40,000$, $M_n = 23,000$) and therefore the degree of crosslinking was set by the distance between each point of interconnection between Pani and PU segments. This type of molecular architecture was not reported before, to our knowledge. Blends of the same composition as the networks were prepared for comparison purposes, using a PU model compound. The chemical structure of these materials is depicted in Fig. 1.

2. Experimental

2.1. Materials

Aniline (Vetec, Brazil) was distilled twice in the presence of metallic zinc (reducing agent) under vacuum (5 mmHg) and stored at 5 °C. 1,6 Hexanediol, HDO (Aldrich), was treated with calcium hydride and distilled under vacuum (5 mmHg). Tolylene diisocyanate, TDI (Bayer Brazil, mixture of 2,4/2,6 isomers in the 80/20 ratio) was distilled under vacuum (5 mmHg) and stored at 5 °C. *N*-methyl pyrrolidone, NMP (Vetec, Brazil), was dried firstly with anhydrous $MgSO_4$ and in a second step with calcium hydride. After distillation under vacuum, NMP was stored under molecular sieves (4 Å). Ammonium persulfate, hydrochloric acid, ammonium hydroxide (Merck, PA), *m*-cresol and camphorsulfonic acid, HCSA (Acros, PA) were used without further purification.

2.2. Polymerization procedures

2.2.1. Polyaniline

Polyaniline was synthesized through the aniline chemical oxidation in acid medium, according to published procedure [23].

2.2.2. Polyurethane prepolymer

Polyurethane prepolymer (PU) was synthesized as described elsewhere [24,25]. Briefly, HDO (1 mol) dissolved in NMP reacted with an excess TDI (free NCO content 5%), at 65 °C, under nitrogen, during 3 h.

The model compound was prepared by end capping the NCO terminated PU with isopropanol (Fig. 1(a)).

2.2.3. Network preparation

The Pani/PU networks (Fig. 1(b)) were prepared through the reaction between the NCO terminated PU chains and Pani-BE in NMP solution, at 65 °C, during 24 h, under nitrogen. After that the mixture was poured over a Teflon plate and allowed to cure at 75 °C during 72 h. The Pani/PU ratios (w/w) were the following: 1/99, 5/95, 10/90, 15/85, 20/80, 25/75, 30/70, 50/50. Doping was made by adding camphorsulfonic acid before curing.

2.2.4. Blend preparation

The blends were prepared by mixing the NMP solutions of the Pani and the PU model compound in order to obtain the same Pani/PU (w/w) ratios as in the networks. After 24 h under magnetic stirring at room temperature, the solutions were cast over Teflon plates and dried in an oven kept at 75 °C, during 72 h. The doping was made the same way as described for the networks.

2.3. Equipment

2.3.1. GPC

M_n and M_w were measured using a gel permeation chromatograph (HPLC Agilent 1100), PL gel mixed C and B packed columns connected to a RI detector. The PU was dissolved in THF at 30 °C and the calibration was based on PS standards.

2.3.2. IR

Polymeric films for FTIR measurements were cast onto KBr disks. Spectra were carried out in a Bomem MB 100 FTIR Spectrophotometer.

2.3.3. Thermal analysis

The TG 209 and DMA 242 coupled modules of Netzsch-Thermisch Analyse were used to perform the thermal analyses. For the thermogravimetric tests (TGA) a heating rate of 20 °C/min was used with a nitrogen flow of 15 ml/min from room temperature to 450 °C. A heating rate of 20 °C/min was also used, to compare with DMA results.

The mechanical dynamic characterization (DMA) was performed in the tension mode, under a steady load of 1.78 MPa and a dynamic stress of 1.98 MPa, under a nitrogen flow of 50 ml/min. The sweepings were made in the temperature interval of − 150 to 250 °C at a heating rate of 2 °C/min at a frequency of 5 Hz. The dimension of the samples used in the characterization by DMA was (4.8 × 10.0 × 0.65) mm.

2.3.4. Electrical measurements

The conductivity of films was measured at room temperature (26 °C) by the standard spring-loaded pressure contact four probe method.

2.3.5. Computer modeling

For the simulation of the Pani, PU and Pani/PU network structures the HYPERCHEM PRO-6 program using AM1 semiempirical Hamiltonian was used.

3. Results and discussion

3.1. Network structure

The composition of the networks varied systematically in the following order Pani/PU (w/w): 1/99, 5/95, 10/90, 15/85, 20/80, 25/75, 30/70, 50/50. The same ratios were used to prepare the blends. When the concentration of Pani in the networks was greater than 30% the resulting films

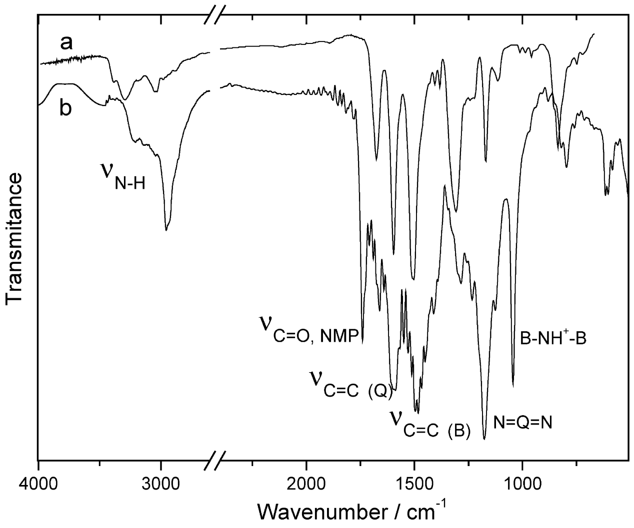

Fig. 2. Infrared spectra of (a) Pani emeraldine base (Pani EB) and (b) Pani emeraldine salt (Pani ES). (B): benzenoid ring and (Q): quinoid ring.

were brittle, but for lower concentrations the films were easily manipulated and had a glossy surface. On the other hand, the blends were always very fragile materials, even when the concentration of Pani was kept low. We have restricted our study on networks with Pani amounts limited to 30% (w/w). Virtually complete crosslinking was achieved, since only negligible amounts of soluble materials could be removed by solvent extraction.

3.2. Infrared spectroscopy

3.2.1. Polyaniline

The assigned infrared spectra of Pani emeraldine base (Pani EB) and Pani emeraldine salt (Pani ES) are shown in Fig. 2(a) and (b), respectively. Pani cast films from NMP solutions always contain a certain amount of residual solvent [26], which was detected by the absorption at $1670\ \text{cm}^{-1}$ and also by TGA of the free standing film, as discussed further on. The main features observed in the spectrum of doped and non-doped Pani are in agreement with published data [27,28].

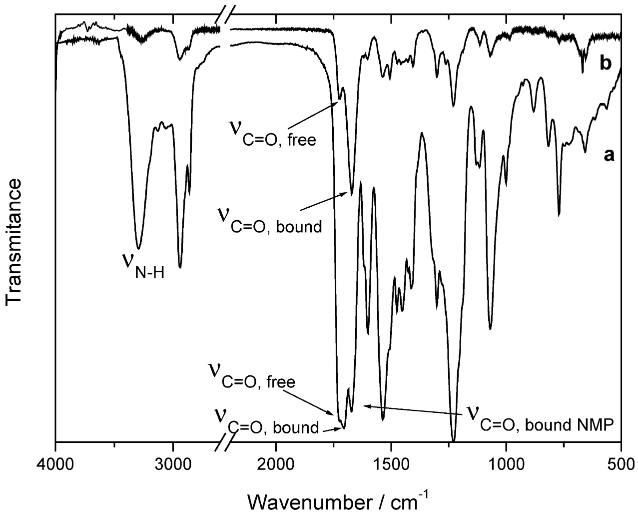

Fig. 3. Infrared spectra of (a) PU model compound in solution and (b) in film form.

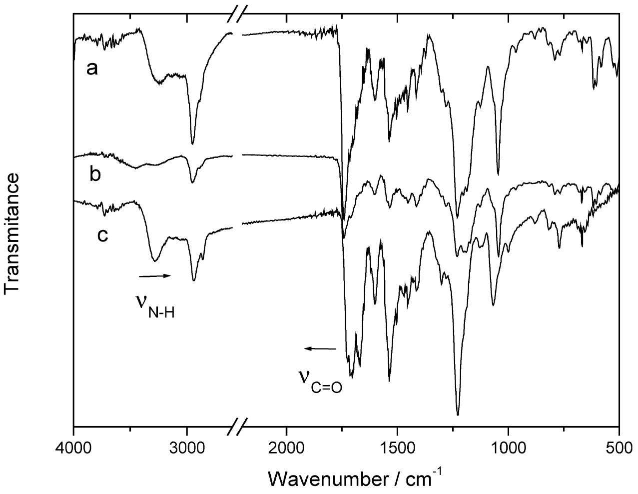

Fig. 4. Infrared spectra of the doped Pani/PU networks. Pani/PU compositions: 30/70 (a), 10/90 (b) and 1/99 (c). The arrows show the shifts of absorption of bands (C=O and N–H) with increasing Pani concentration.

3.2.2. Polyurethane

Infrared spectroscopy has been used to characterize phase separation in polyurethanes [29]. The method is based in the existence of absorption bands sensitive to miscible or immiscible states. It has been reported that the carbonyl and N–H groups undergo shifts in the range of $20–25\ \text{cm}^{-1}$ going from the linked state (through H bonds) to the free state. Considering that the stronger intermolecular forces lead to absorption at lower frequencies, the shifts can vary with the interaction strength. In order to determine the extent of hydrogen bonding and the related absorption shifts in our system, we have prepared a model compound of the PU segment (see Fig. 1(a)) by reacting isopropanol with the NCO end groups of the prepolymer.

The solution and film spectra of the PU are shown in Fig. 3(a) and (b). Considering the –NH– absorption, going from solution to film, a shift of $24\ \text{cm}^{-1}$ was detected, indicating that the intermolecular forces are stronger than the polymer-solvent interactions. Two peaks were observed for the carbonyl absorption in the film spectrum: at 1724 and $1671\ \text{cm}^{-1}$, which were assigned to the free form and to the bound form (more intense). In the solution three carbonyl absorptions were seen: at 1716 and $1708\ \text{cm}^{-1}$, attributed to the free and to the bound carbonyl groups, respectively, and another one at $1670\ \text{cm}^{-1}$ assigned to the solvent bound to the N–H groups of the polymer.

3.2.3. Pani/PU networks

The infrared spectra of the doped Pani/PU networks shown in Fig. 4, presented significant shifts of the –NH– and carbonyl stretching bands as compared to those of the

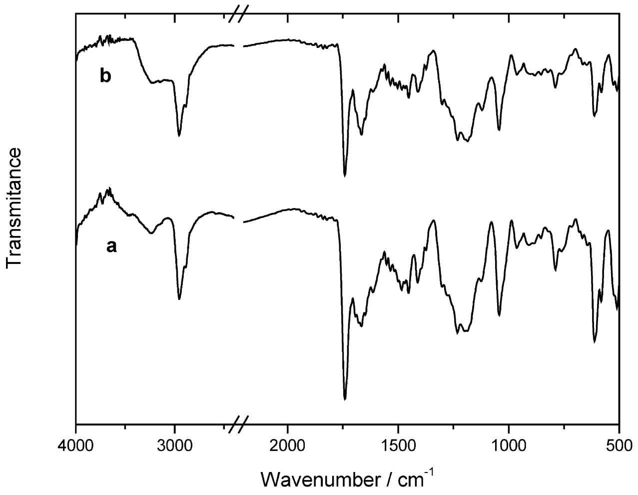

Fig. 5. Infrared spectra of the doped Pani/PU blends. Pani/PU compositions: 30/70 (a) and 20/80 (b).

pure components. The –NH– peak is shifted from 3292 cm^{-1} (either for pure Pani or PU, Figs. 2 and 3, respectively) to lower frequencies: 3290, 3268 and 3259 cm^{-1}, for Pani/PU ratios of 1/99, 10/90 and 30/70, respectively. This indicates that a certain degree of mixing was achieved and also that the carbonyl group of the PU interacts more strongly with of the –NH– group of the Pani than with the –NH– group of the parent molecule. Of course not all the –NH– groups were influenced by the presence of the other component, since the PU was preponderant in the system. The broadness of the –NH– peak reflects the presence of diverse environments. The same way, the changes in the absorption of the PU carbonyl were assigned to the influence of nearby Pani molecules to some extent. The interpretation of the spectral changes observed in the region 1670–1720 cm^{-1} is not straightforward, since a number of absorptions overlap in a relatively narrow range: such as those of the free carbonyl groups, those bonded to –NH– groups of the parent PU or to the Pani –NH– groups, those belonging to the new urea type bond formed between Pani and PU segments [15,16] and finally those with remaining solvent molecules. A shift to higher frequencies was observed in the PU carbonyl absorption in the networks as compared with the free PU: from 1716 cm^{-1} (Fig. 3) to 1740 cm^{-1} (Fig. 4(a) and (b), respectively). This could be assigned to the interruption of some interchain interactions in the PU, due the interspersed Pani chains.

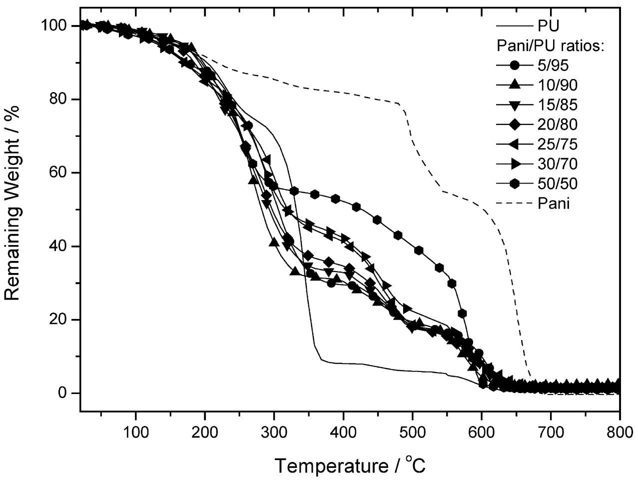

Fig. 6. TGA thermograms for Pani, PU and Pani/PU networks.

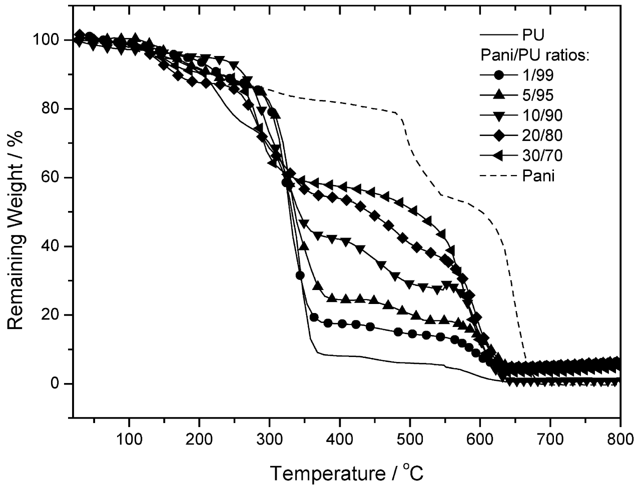

Fig. 7. TGA thermograms for Pani, PU and Pani/PU blends.

The same trend was observed for Pani/PU blends as observed in Fig. 5. It is noteworthy that the relative intensity of the 1740 and 1660 cm^{-1} absorptions in the blends is changed as compared to the networks: in the blends the latter is less intense than in the networks. This result was attributed to the inclusion of the absorption of the carbonyl group resulting from the new urea type bond Pani/PU in the networks.

3.3. Thermogravimetric analysis

The thermogravimetric analysis (TGA) traces of Pani and PU are shown in Fig. 6. Pani presents three main regions of mass loss: the first, in the 25–120 °C range ($\Delta m = 5.2\%$) is related to the evaporation of water molecules in the film [30–32]. The second, in the range 120–250 °C is attributed to solvent loss and possibly to a water/NMP azeotrope evaporation; and the last one is due to the loss of NMP molecules linked to the amine groups of Pani through hydrogen bonds, at 250–360 °C [26]. Above 470 °C the mass loss is about 24.4% and complete decomposition occurs at temperatures above 680 °C under oxygen atmosphere. Computing the second and third mass losses the residual NMP in the films was estimated to be around 16%.

The PU thermal decomposition (Fig. 6) is characterized by a mass loss of about 21%, in the range 25–240 °C, due to the evaporation of residual solvent. For washed films this loss is reduced to 2%. It was observed that above 240 °C the PU film containing residual solvent was more degradable.

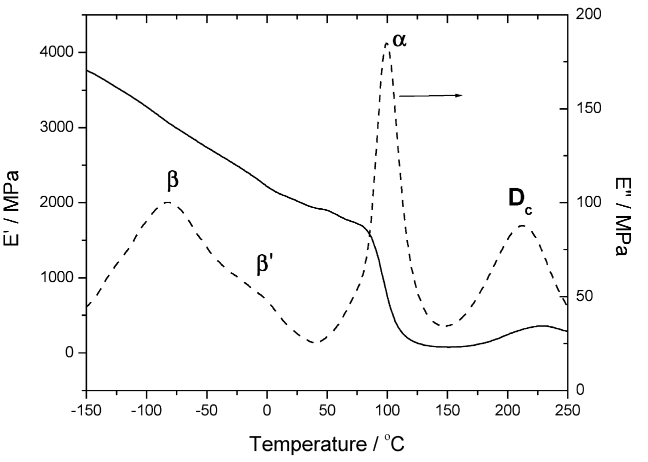

Fig. 8. DMTA spectra of Pani film.

This is probably due to the enhanced chain mobility that facilitates interchain reactions such as those leading to biuret and alophanate linkages. Those are formed around 120 °C and are not stable, leading to a faster decomposition.

The main feature of the decomposition pattern of the Pani/PU networks is a greater mass loss than the pure PU in

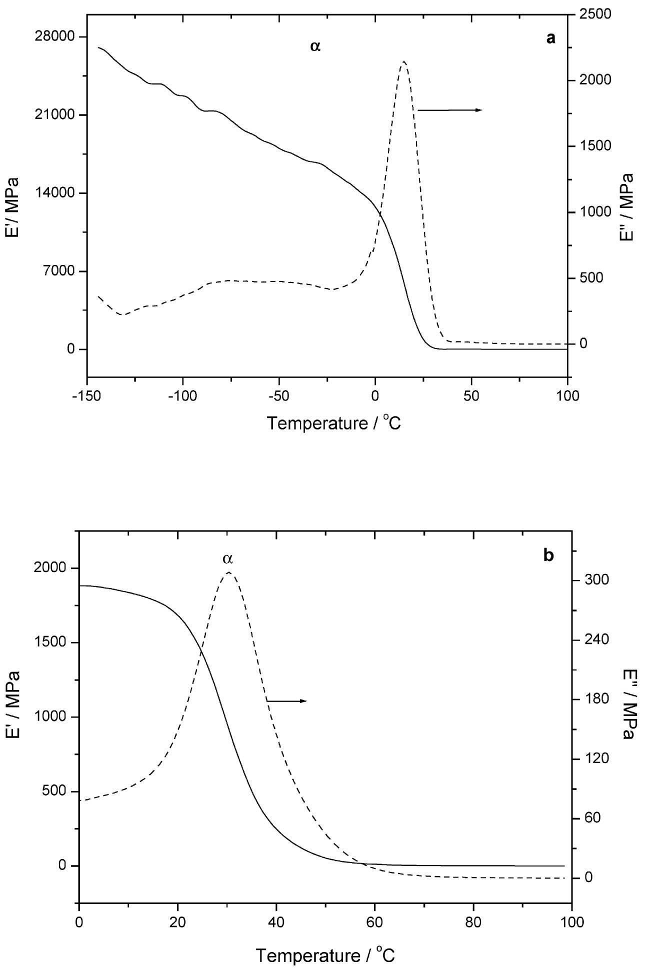

Fig. 9. DMTA spectra of PU films: (a) containing residual NMP (~20%) and (b) containing no residual solvent.

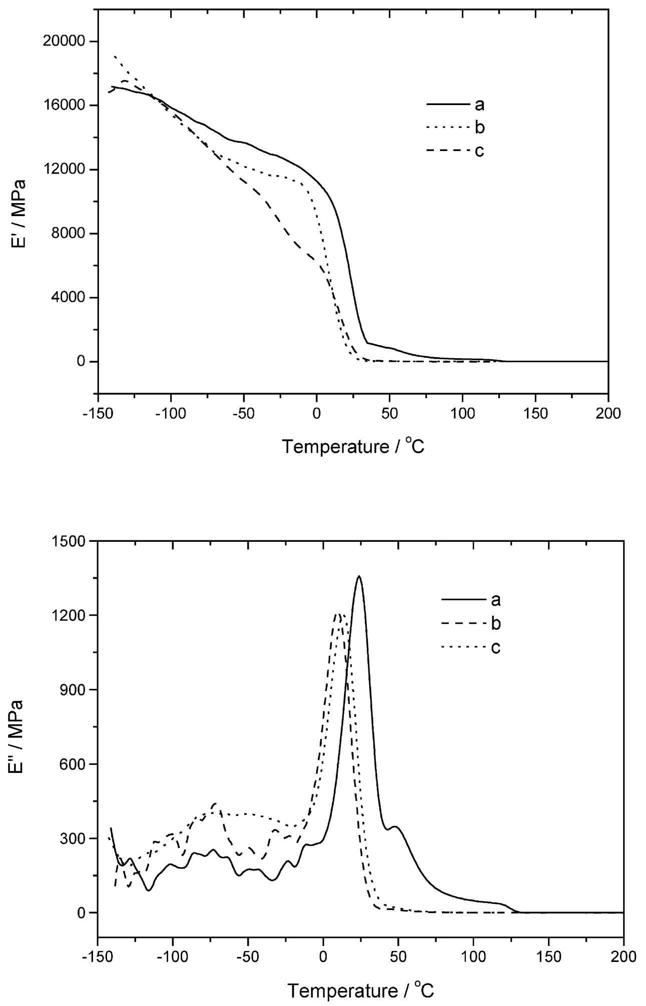

Fig. 10. DMTA network spectra recorded for Pani/PU ratios of 25/75 (a), 20/80 (b) and 5/95 (c).

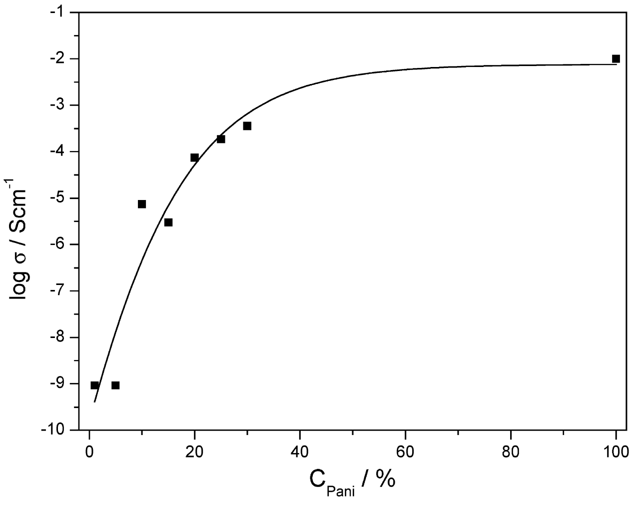

Fig. 11. Electrical conductivity of the doped networks.

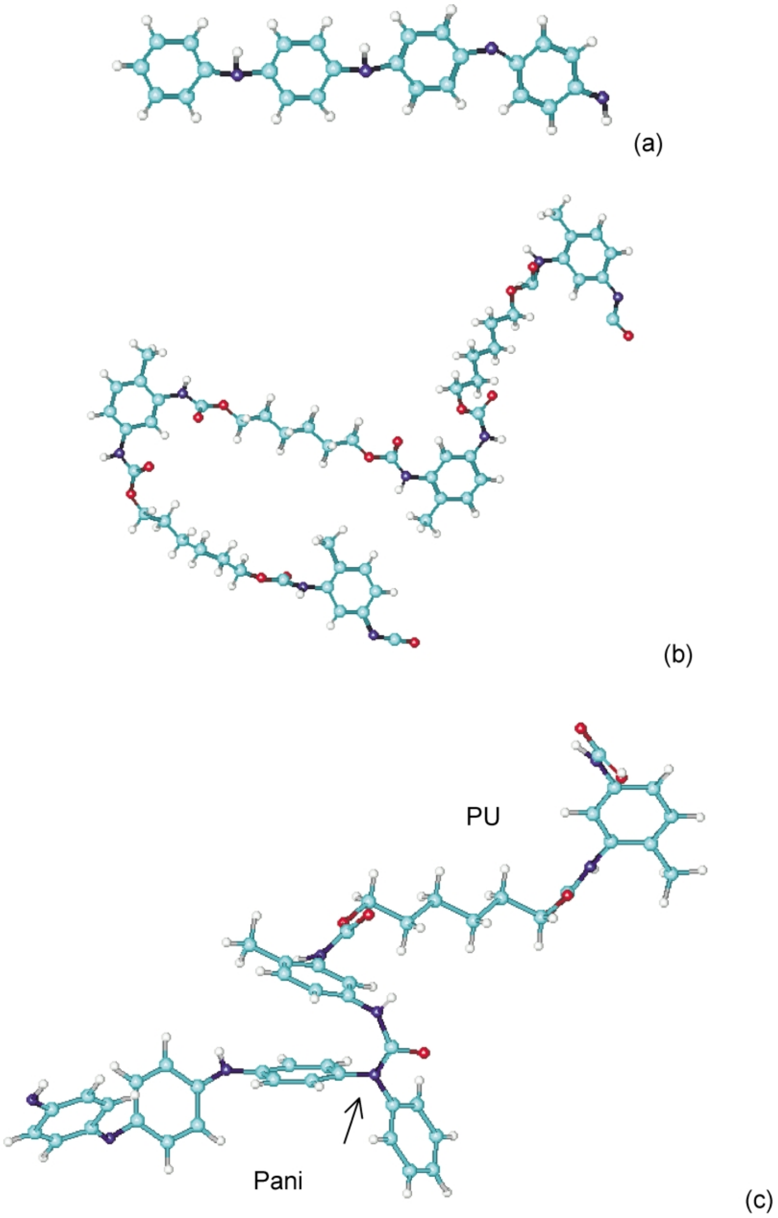

Fig. 12. Minimum energy conformations for Pani tetramer (a), PU trimer (b) and structural unit of a network (c).

the 25–300 °C range. This was attributed to a lower thermal stability of the new urea type linkages between polyaniline and polyurethane as compared to the pure components. Above 300 °C the mass loss is determined by the Pani content, decreasing with increasing Pani concentration.

The thermograms of the blends, shown in Fig. 7, confirm the previous assignment of the lower thermostability of the networks, due to the chemical linkage between Pani and PU segments, since the mass losses in the blends are intermediary between those of the pure components.

3.4. Dynamical mechanical thermal analysis

3.4.1. Polyaniline

The dynamical mechanical thermal analysis (DMTA) spectrum of the pure Pani is shown in Fig. 8. Four relaxation processes were detected: a peak at -82.5 °C (β), a shoulder (β'), the glass transition (α) at 99.3 °C and D_c at 212.7 °C. The widths of β and β' are related to different degrees of water or NMP solvation in the film and were attributed to the relaxation of aromatic rings and/or of solvent molecules bound to the polymer chain. The notation used is the same we used in our previous publication on Pani relaxations [26]. The location of T_g is in accordance with reported data for Pani plasticized with NMP [30]. D_c is related to crosslinking and thermal decomposition.

3.4.2. Polyurethane

The effect of residual solvent in the DMTA spectra of PU films is shown in Fig. 9. The main peak at 14 °C in Fig. 9(a) was attributed to the glass transition of the film containing residual NMP (~20%) since an abrupt decrease in storage modulus occurred in this region. The glass transition of the film containing no residual solvent (Fig. 9(b)) was significantly shifted to 30.4 °C. The plasticized and non-plasticized films began to flow at 50 and 70 °C, respectively, and no further transitions could be detected. Both samples had a secondary transition around −70 °C, related to the $-CH_2-$ motion of the hexamethylene sequences of the PU segments.

3.4.3. Pani/PU networks

The network spectra were recorded for Pani/PU ratios of 25/75, 20/80 and 5/95 (Fig. 10(a)–(c)). In the spectra of the last two, the location of the PU glass transition remained unchanged, and after that temperature, the samples flowed completely. For the 25/75 network the PU glass transition shifted from 14 °C (pure PU, Fig. 9(a)) to 24 °C, and a peak at 48 °C and a shoulder and 109 °C appeared in the spectrum. Thus three new features were introduced in the spectrum of this network: the 10 °C increase of the T_g of the PU, as compared with the pure component, a new peak at 48 °C, and the shoulder at 109 °C. The first finding was indicative of a certain degree of phase mixing, in accordance with the previously described carbonyl shifts observed in the infrared spectra of the networks. The shoulder at 109 °C was assigned to the glass transition of Pani, which was shifted to higher temperatures as compared with the free Pani, due to crosslinking. The new peak at 48 °C was ascribed to the relaxation of an interphase formed between PU/Pani components.

3.5. Electrical properties

The electrical conductivity of the doped networks is shown in Fig. 11 for the various Pani/PU ratios. It can be observed that the incorporation of only 10% Pani in the networks was able to raise the conductivity by around four orders of magnitude. Further increases in conductivity were obtained with increasing Pani concentration, reaching values as high as 4×10^{-4} S/cm for the 30/70 Pani/PU ratios. These results indicate that although crosslinked through PU segments, Pani is still a semi-conducting polymer. The results from the IR, TGA and DMTA techniques discussed so far, together with our previous results from UV–Vis studies [33], lead to the conclusion that above a threshold of about 5%, the Pani chains are interspersed in the PU matrix forming a conductive phase, probably in a co-continuous phase. A certain degree of mixing exits in the boundary of the two phases, which could be responsible for the good interphase adhesion and cohesive properties of the resulting materials.

Preliminary adhesion tests of the networks onto steel showed promising results, forecasting the application of these materials as anti-static coatings and corrosion inhibitors.

3.6. Optimized molecular conformation

In Fig. 12 the conformations of minimum energy for Pani tetramer (a), PU trimer (b) and a structural unit of a network are presented (c). Pani EB is essentially planar, allowing the overlap of the π orbitals of the aromatic rings with the nitrogen atom. In the PU there is a tendency to chain coiling, resulting in a non-planar conformation. When linked through PU bridges, the Pani chains undergo a torsion and the aromatic rings are forced out of planarity (see arrow). The observed conductivity, however, seems to indicate that this torsion is localized near the interconnection, and is leveled out along the Pani chains, allowing electronic delocalization.

4. Conclusions

The interconnection of Pani chains through PU segments has originated a series of new semi-conducting materials with good mechanical properties. The chemical link between the two components was verified by several techniques, including new decomposition patterns in TGA. The new urea type linkage was responsible for a certain degree of torsion of the Pani chains, as demonstrated by computer modeling. Nevertheless, the conductivity values suggested that this torsion should be leveled out along the conducting chains.

Shifts of the carbonyl and –NH– absorption in the infra red, along with the presence of a new relaxation in the DMA spectra strongly suggested the presence of an interphase, which would be responsible for the connectivity between the Pani and PU phases and for the resulting good mechanical properties. The application forecast for the new materials include anti-static coatings and corrosion inhibitors.

Acknowledgements

The authors wish to acknowledge Drs Debora Baloghi, Renê Robert, Marilda Munaro, Gabriel Pinto de Souza and Cleuza Maria Wasilkoski for the help in GPC, TGA, DMA and electrical analyses and also to CNPq, CAPES and LACTEC for financial support.

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