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Polyaniline/polyurethane networks. II. A spectroscopic study

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Abstract

The interconnection of polyaniline (Pani) chains through polyurethane (PU) blocks of the same length but with different spacing has originated a series of new semi conducting networks of varying crosslinking density, with good mechanical properties. FTIR, UV–Vis–NIR, XPS and EPR were used to probe the molecular features of the conducting species, and to test the morphological model proposed in a previous publication, where a continuous Pani phase percolates a PU matrix, linked together by a mixed interphase. Blends with the same composition of the networks and a model structure of crosslinked Pani were also prepared for comparison purposes. The proposed morphological model was confirmed by the new findings obtained by the spectroscopic techniques. The differences between the blends and networks of the same composition were discussed in terms of the morphology presented by each of these systems.

Keywords: Polyaniline; Polyurethane; Networks

1. Introduction

In the class of conducting polymers, polyaniline (Pani) has been the most explored due its ease of preparation, chemical and thermal stability and simple non-redox doping with protonic acids. The increase in electronic conductivity that occurs after the transition emeraldine base (EB) to emeraldine salt (ES), involves a doping mechanism different from those commonly observed with conducting polymers: the addition of a proton to the polymer chain, instead of the partial oxidation of the polymer's π system, as is the case of 'p' doping in other conducting polymers [1–3]. However the processability of ES is somehow complicated due to its poor solubility in common organic solvents (only concentrated sulfuric acid and 80% acetic acid [4] can dissolve it) and the salt is not fusible as well. To overcome this problem, different strategies have been approached, like insertion of lateral groups to the chain, block copolymerization and blending with other polymers. In a general way, the materials thus obtained do not present the same level of conductivity of the pure ES. The insertion of substituent, for example, either in aromatic ring [5–8] or in the nitrogen atom [9–12] can improve solubility, but impairs the conductivity due to the chain torsion imposed by steric effects that decrease the effective conjugation length. The combination of Pani segments with blocks of another polymer has been recently reported, like the grafting of polyethylene glycol [13] or polyacrylic acid [14] onto a Pani backbone, a block copolymer polyurethane/Pani octamer [15], and the most interesting case of combining the light emitting properties of fluorene blocks and the Pani hole transporting capacity, thus obtaining an improved light emitting device [16]. The blending of conducting and conventional polymers has recently been an active area, with a large number of publications in the last decade [17–18]. This interest is based in the possibility of combining good mechanical properties and processability with low electric resistance. However, the low miscibility of the conjugated chains in the host matrix leads to a variety of morphologies, which are crucial for the comprehension of the physical properties observed. To render these systems more compatible an elegant technique was introduced by Cao et.al. [2], through the inserting of counter ions among the chains, enabling the doping of Pani and at the same time plasticizing the material. Commercial examples applying

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this technique include melt processable materials made with phosphoric diesters [19]. Finally, interpenetrating polymer networks can be cited as means to circumvent the miscibility problem, as reported for Pani as a component in PU/PMMA [20] or carboxy methyl cellulose [21] systems.

Polyurethanes (PU) are a large class of polymers, displaying all kinds of mechanical behavior, from hard plastics to soft rubbers, including various kinds of foams, coatings, etc. This is due to the different chemical compositions that can be achieved, by simply linking the chain components by the urethane linkage (–NHCO–O–). Segmented polyurethanes can be previously designed in such way that chemically different blocks can be bound by joining one –OH terminated segment with an –NCO terminated prepolymer with no by products [22].

In a recent publication [23], we reported on the synthesis and properties of a series of PU/Pani networks with systematic variation in the components ratio. The length of the PU segment was kept constant, and linking the Pani chains at different distances, thus varying the crosslinking density. This was the first publication on the association of Pani with another polymer with this type of molecular architecture. The materials had an electrical conductivity in the 10^{-4} S/cm range and good mechanical properties. It was proposed a morphological model in which Pani chains form a continuous percolating phase dispersed in a PU matrix. A mixed interphase of both components was also detected, and was probably involved in the phase connectivity, mechanical resistance and ease of handling presented by the networks.

As the PU component can be built in a variety of compositions, the method can be used to design conducting materials in a full range of physical properties. This paper is a continuation of that project, utilizing various types of spectroscopy to gain further insight in the configuration and morphology of these networks. For comparison purposes, blends were prepared with the same composition as the networks. Fig. 1 displays the molecular structure of a hypothetical PU/Pani network.

2. Experimental

2.1. Materials, polymerization procedures, networks and blends preparation

The detailed experimental description concerning these items was given in our previous paper [23]. To complement the information given by the spectroscopy data, we have synthesized a new crosslinked material, a model structure for the networks without the hexamethylene bridge and urethane groups, thus containing only urea bonds linking the two kinds of polymeric chains. This was done by reacting toluene diisocyanate (TDI) with Pani-EB in NMP. The NCO/NH ratio was set in 1.0, resulting in a highly crosslinked material, which was called crosslinked Pani, (see Fig. 2).

2.2. Equipment

2.2.1. Gel permeation chromatography (GPC)

A HPLC Agilent 1100 equipment with columns PL gel (mixed C) was used. The columns were connected to a refraction index detector, using THF as solvent, and the calibration was based on PS standards.

2.2.2. Electronic paramagnetic resonance (EPR)

EPR experiments were carried out at room temperature on a Bruker ESP 300E spectrometer operating at X-band frequency (9.5 GHz) with 100 kHz field modulations. A weak pitch standard from Bruker ($g=2.0028$) was used as reference. The samples were placed in a tissue cell oriented in the parallel or normal direction to the magnetic field, in order to observe the presence of any anisotropy.

2.2.3. Infrared spectroscopy (FTIR)

A Bomem spectrofotometer model MB 100 was used. The polymer films were prepared by solution casting onto KBr disks and dried at 75 °C, 10 mmHg, overnight.

2.2.4. Electronic spectroscopy (UV–Vis and UV–Vis–NIR)

A Shimadzu spectrophotometer, model UV-2401PC, was used for the UV–Vis region and a Cary equipment for near infrared (UV–Vis–NIR). The polymer films were cast onto quartz substrates and dried at 75 °C, 10 mmHg, overnight. The thickness of the films was kept constant in the range of 200 nm.

2.2.5. X-ray photoelectron spectroscopy (XPS)

The XPS spectra were taken using a VG ESCA 3000 system with a base pressure of 2×10^{-10}mbar. The spectra were collected using Mg Kα radiation and the overall energy resolution was approximately of 0.8 eV. The energy scale was calibrated using the Fermi level and C 1 s peak at 284 eV. The spectra were normalized to the maximum intensity after a constant background subtraction.

3. Results and discussion

The composition of the networks and blends 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 molecular weight of the PU segment was M_n 23.000, M_w 40.000, polydispersity 1.7, which is consistent with the free NCO content set for the PU preparation (5%). The network cast films were easily manipulated and had a glossy surface, whereas those cast from the blends were brittle and fragile.

Crosslinked Pani contained only urea type carbonyls, as noted, and was used as a model compound to detect the urea

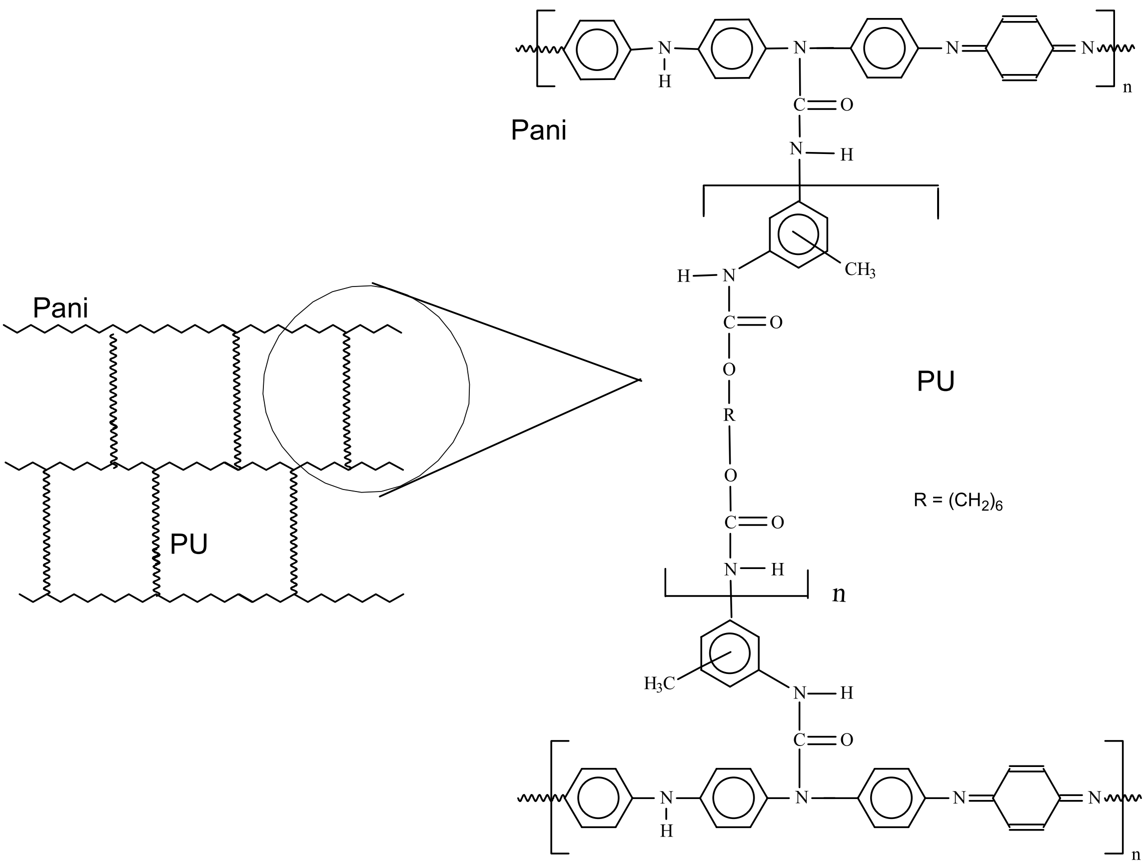


Fig. 1. Schematic representation of the crosslinked Pani/PU networks.

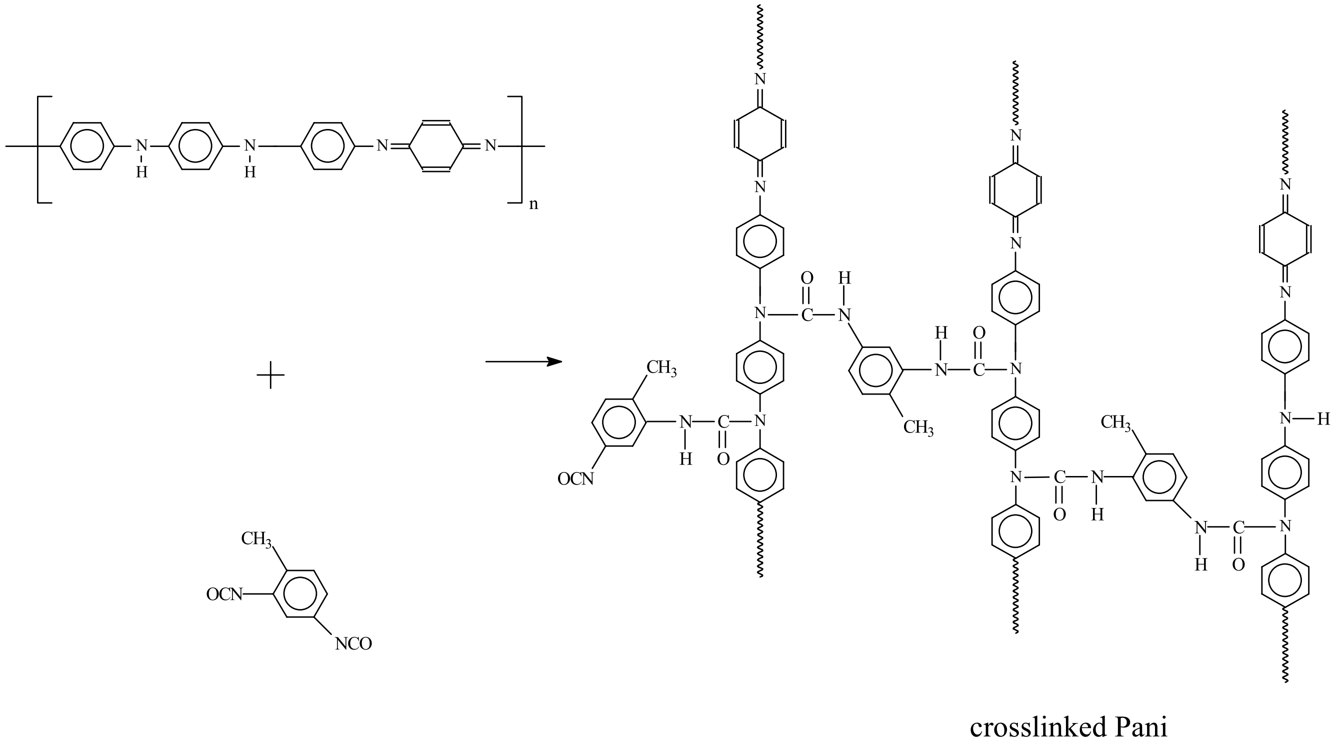


Fig. 2. Schematic representation of crosslinked Pani.

type carbonyl in the networks in all the analytical methods employed.

3.1. Infrared spectroscopic (FTIR)

The carbonyl group of crosslinked Pani, appears at 1656 cm^{-1} (Fig. 3(a)), and represents the absorption of the urea-type linkage between Pani and PU, without the interference of the urethane carbonyl group. The PU spectrum (Fig. 3(b)) is more complex due to the presence of hydrogen bonded and non-bonded urethane carbonyls [24,25], and to the absorption of some remaining solvent (*N*-methyl pyrrolidone, NMP). These effects were discussed in detail elsewhere [23]. The networks spectra (Fig. 3(c)) are further complicated by the hydrogen bonding between the PU carbonyls with the amine groups of Pani, which shift the absorption to higher frequencies (from 1716 cm^{-1} for pure PU to 1740 cm^{-1}, for the networks) and to the presence of the new urea type bond, linking the Pani segments to the PU chains, formed in the crosslinking reaction. All these carbonyl absorptions result in the broader spectrum shown in Fig. 3(c).

At the same time the band at 2250 cm^{-1}, characteristic of the NCO group was absent, indicating that the reaction went to its completeness. As discussed earlier [23] the –NH– stretching band in the networks presented significant shifts as compared to the pure components, indicating the occurrence of a certain degree of mixing due to hydrogen bonding. The –NH– absorption shifted from 3292 cm^{-1} (either for pure Pani or PU) to lower frequencies: 3290, 3268 and 3259 cm^{-1}, for Pani/PU ratios of 1/99, 10/90 and 30/70, respectively. The same trend was observed in the

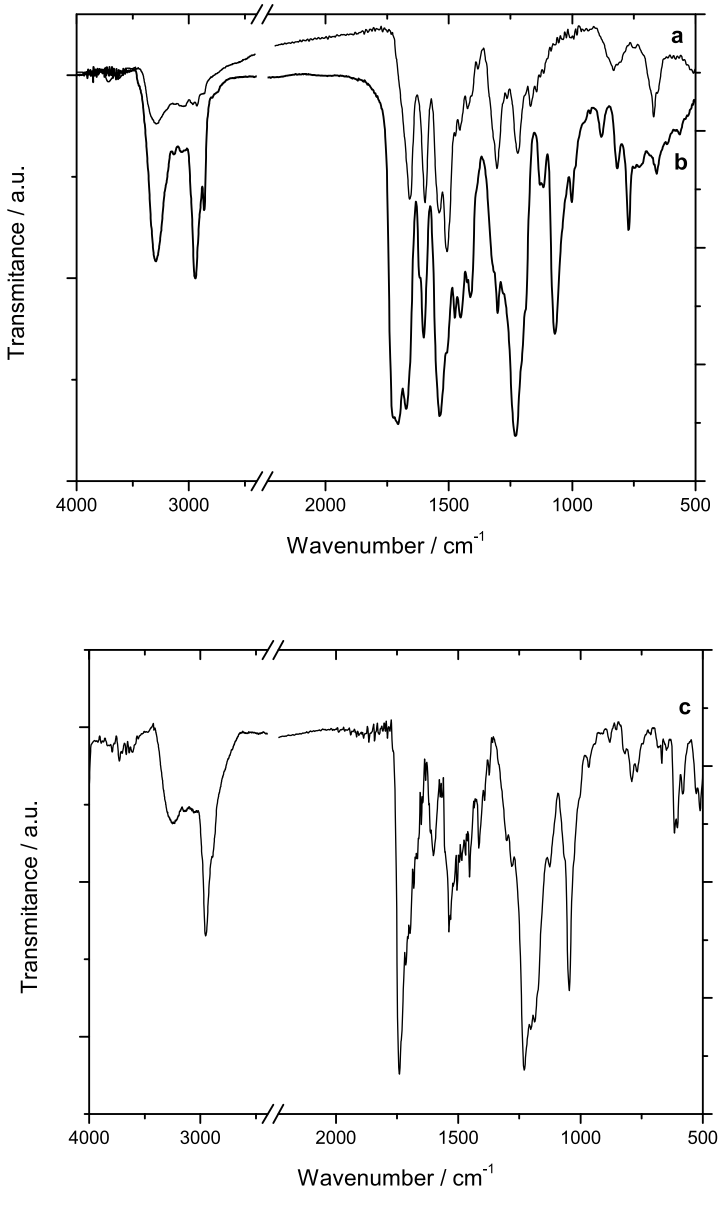


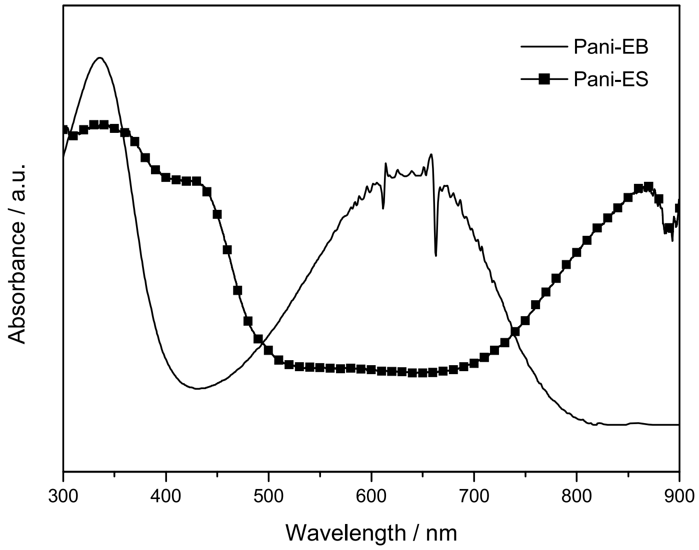
Fig. 3. Infrared spectra of (a) Crosslinked Pani, (b) PU and (c) Pani/PU network.

crosslinked Pani, the NH– stretching band was shifted from 3292 to 3250 cm^{-1}. The XPS results agree with these findings, as discussed further on Section 3.3.

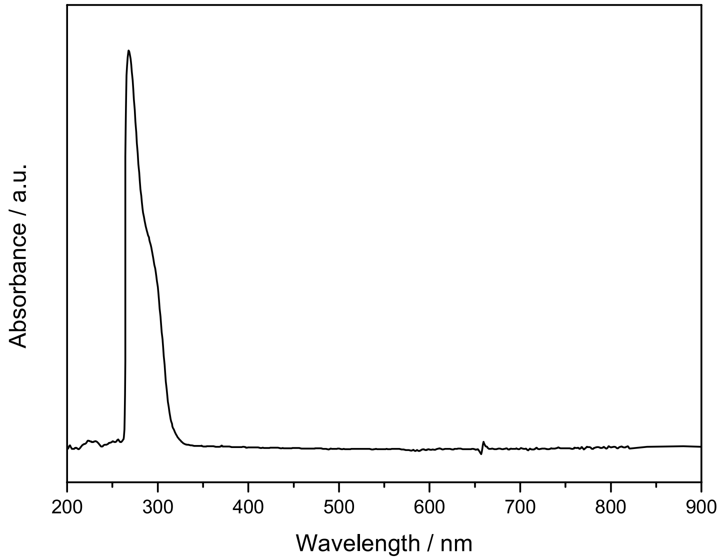
3.2. Electronic spectroscopy (UV–Vis and UV–Vis–NIR)

UV–Vis spectroscopy is an extremely valuable tool for the characterization of conducting polymers, since it can forecast the electrical behavior of a polymer (insulating or conducting) and to a certain extent its morphological features. The localization and shape of the absorptions of the conjugated polymer can disclose the level of the electronic delocalization.

In the Pani-EB spectrum (Fig. 4(a)) two bands were observed: one at 328 nm (π–π^* transition) and another at 640 nm (n–π^* transition). The doping of Pani-EB with camphorsulfonic acid (CSA) suppresses the second band (640 nm), since this absorption is related with the transitions in the quinoid rings, which are no longer present in the ES form, due to the conversion of these segments into polysemiquinone cation-radicals. In the doped Pani films, two bands are seen, which are related to polarons absorption, at 420 nm and at 860 nm, indicating that the sample is a conducting polymer [26–28]. The comparison of the two spectra, (EB and ES) shows that some localized polarons are still present in the doped form, and this is probably due to the fact that the films were prepared from NMP solutions, which is not a secondary dopant and hence



(a)



(b)

Fig. 4. UV–Vis spectra of (a) Pani (EB and ES) and (b) PU.

the Pani chains keep their coiled conformation after the solvent removal [26,29]. The PU spectrum (Fig. 4(b)) presents only one peak at 266 nm and a shoulder about 288 nm, both related to transitions in the benzene ring. Comparing the UV spectra of a Pani/PU network with non-doped Pani, in Fig. 5, one can observe that the electronic transitions of Pani were not affected by the crosslinking with PU.

The UV–Vis spectra of the doped networks are shown in Fig. 6(a). The intensity of the Pani polaronic species increases with the concentration of Pani in the networks. It is noteworthy that these transitions were detected even with concentrations of Pani as low as 1%. The same way as noted in the non-doped networks, the bands were not altered in position in relation to pure Pani.

The blends spectra also showed that a small amount of Pani is capable to display the polaronic bands (Fig. 6(b)). In the blend 10/90 Pani/PU, the transition ($\lambda = 840$ nm) is shifted up to 21 nm, in relation to the pure Pani ($\lambda = 861$ nm), whereas in the networks with the same compositions, no significant shift was noted. This could be due to a more extended conformation of the Pani chains in the networks than in the blends, due to the covalent linkages with the PU and/or to a more interconnected Pani phase allowing a larger polaronic delocalization. The same effect was detected in the XPS and EPR analyses, as shown further on.

In order to verify the influence of a possible secondary doping [26,29], the doped films of the pure polymers, networks and blends were exposed to *m*-cresol vapors during seven days. Before the exposure to the secondary dopant the absorption profile of all samples showed a localized polaron absorption around 840 nm as shown in Fig. 7(a). After the exposure, this band disappears. However, the increase in absorption above 1000 nm is not as pronounced as that observed in films directly cast from *m*-cresol. It is known that NMP Pani cast films always contain an amount of residual solvent (of about 16%) [30]. In the present case, the secondary dopant was not capable to uncoil the chains to their full extent because the residual NMP strongly interacts with Pani thus maintaining a certain degree of coiling. The same behavior was more pronounced in the networks, the absorption in this region is more visible, indicating incomplete uncoiling of the Pani segments in the networks. Nonetheless, the *m*-cresol molecules were able to penetrate the network, solvating and plasticizing the system. The resultant conformational changes rendered the Pani chains more extended as compared to crosslinked Pani (Fig. 7(b)), decreasing the conjugation defects, and this way increasing the effective conjugation length, in a similar fashion as reported for binary systems containing Pani as a component [31]. It is likely that the PU matrix could assist this uncoiling effect, since the swelling brought about by the *m*-cresol forces all the chains to extend. Therefore, in spite of being 'tied' to the PU, the Pani chains in the networks are still able to uncoil, as in the pure polymer. The blends behavior could not be observed, since these dissolved when exposed to the *m*-cresol vapors.

3.3. X-ray photoelectronic spectroscopy (XPS)

Fig. 8(a) and (b) present the XPS (N1 s) spectra of Pani-EB and PU in film form. The Pani EB displayed four peaks, which were assigned to the imine nitrogen (398.5 eV), amine nitrogen (399.9 eV) e charged nitrogen –N^+– (401.5 and 402.5 eV). These values are in agreement with the corresponding data published for Pani [32–34]. The ratio of the imine to amine nitrogens is close to the unity, indicating that Pani is in the emeraldine form (base). The remaining nitrogens (5.51%) were attributed to the presence of N^+, which were originated from the partial oxidation of the film's surface or from weakly complexed oxygen atoms

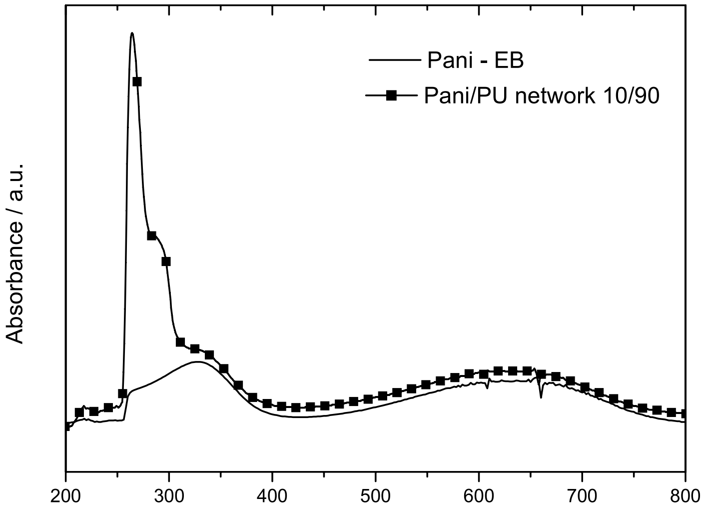
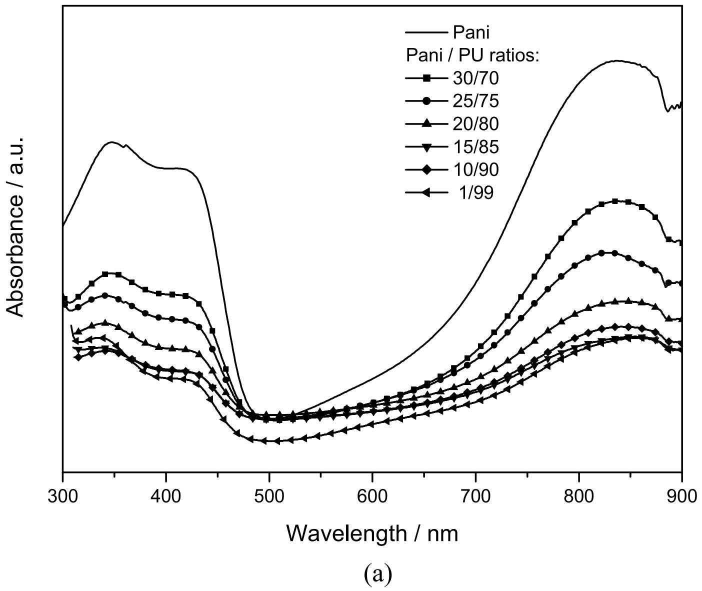


Fig. 5. UV–Vis spectra of Pani and Pani/PU network in emeraldine base form.



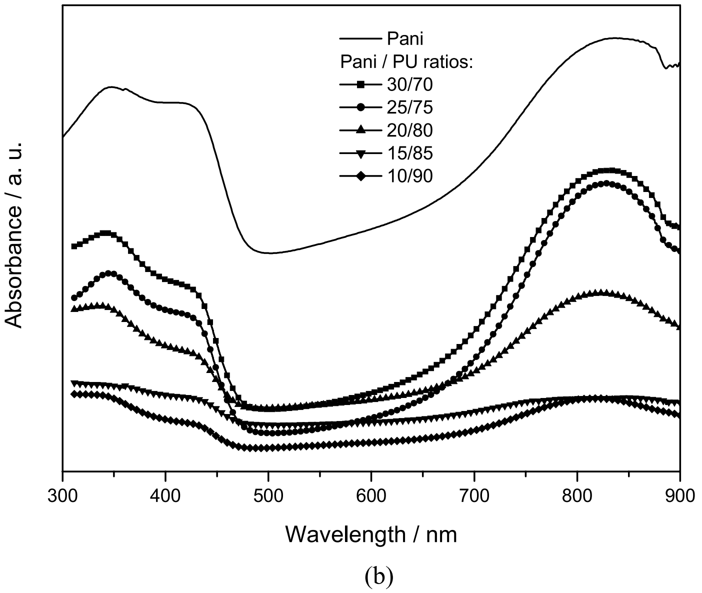


Fig. 6. UV–Vis spectra of system Pani/PU in doped form: (a) network and (b) blend.

[33–34]. The PU displayed one peak only, corresponding to the –NH– (398.9 eV) of the urethane linkage (Fig. 8(b)) [32]. The Pani/PU network films presented one more peak in addition to those above mentioned, localized at 397 eV (Fig. 8(c)). This new nitrogen species belongs to the urea type group formed by the reaction of Pani with PU, and its assignment was confirmed by the spectrum of crosslinked Pani (Fig. 8(d)), which shows the existence of a nitrogen atom in a different chemical environment. It was also noted that the –NH– groups belonging either to Pani or PU are enveloped in the same peak at 400 eV. The significant increase in the area relative to the =NH– groups can be assigned to the inclusion of hydrogen bonded nitrogen atoms from Pani and PU in this peak. The fact that hydrogen bonds of Pani with other compounds shift the –NH– to lower energy levels and are enveloped in the imine peak was proposed in earlier works [35]. The strong tendency of Pani and PU to form hydrogen bonds has been previously verified in this system through FTIR [23]. It seems that the same effect is operating in the blends, since the imine peak in these materials is similar to that of the networks (Fig. 8(e)). The Pani chains are capable of breaking the hydrogen bonds among PU segments forming new Pani–PU hydrogen bonds. This interaction is responsible for a certain degree of miscibility between the two components, and was confirmed through DMTA along with the already mentioned FTIR [23].

Fig. 9 presents the XPS spectra of the samples doped with camphorsulfonic acid. The Pani spectrum (Fig. 9(a)) shows a decrease in the intensity of imine nitrogen peak

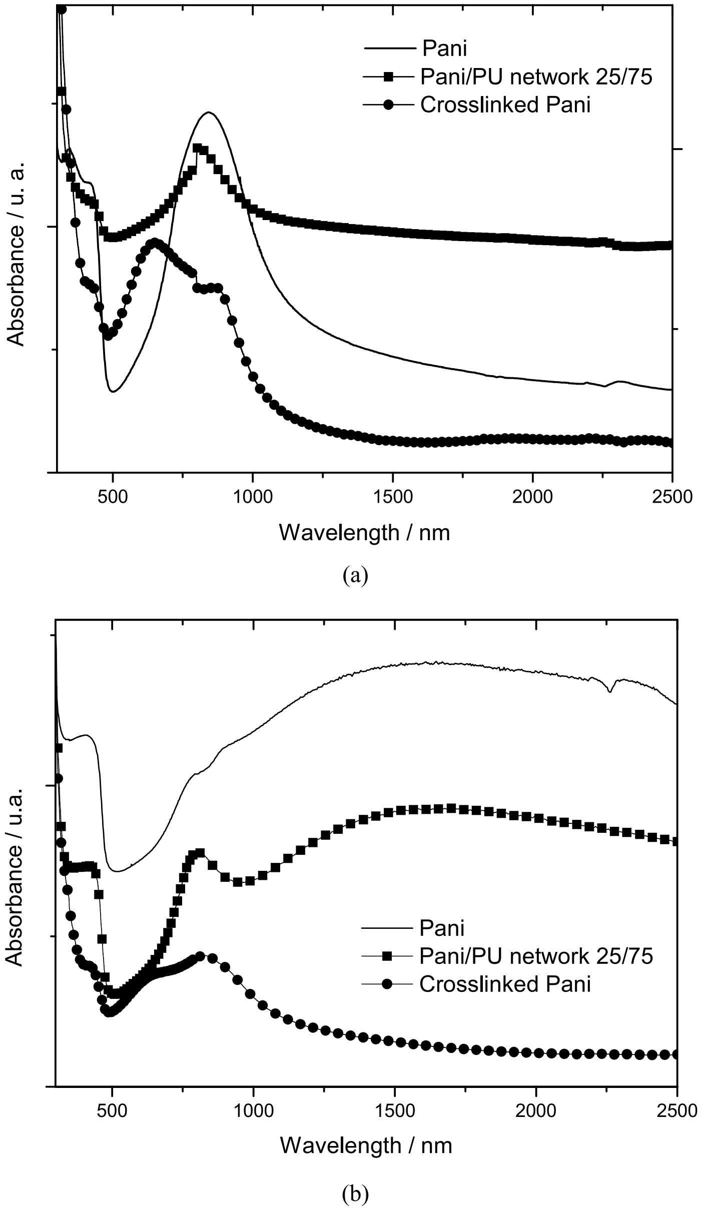


Fig. 7. UV–Vis–NIR spectra of the samples doped with CSA (a) before and (b) after *m*-cresol exposure.

(397.9 eV) and an increase of peaks corresponding to the charged nitrogen atoms (401.5 and 402.5 eV). This result is consistent with the assumption that the protonation site is the imine nitrogen [34]. The determined degree of protonation was 64%, which includes the protonated amine nitrogen (14%). In the PU spectrum (Fig. 9(b)) the intensity of the peak related to the –NH– groups decreased, due to the protonation of the nitrogen atom, as suggested by the appearance of a new peak at 400 eV, attributed to the protonated species. The determined degree of PU protonation was 76%. In the networks (Fig. 9(c)) and blends (Fig. 9(d)) spectra, the N^+ species were also present, originated either from the Pani or PU component. For compositions of 25/75 Pani/PU the determined protonation degree for the networks was 36% (the distinction between protonated species from PU or Pani was not feasible) and 14% for the blends. The fact that the networks were easier to protonate indicates that in the networks the imine groups are more available to protonation than in the blends (Fig. 7) and also to the higher interconnection of the Pani domains, as compared to the blends, as noted previously.

3.4. Electronic paramagnetic resonance (EPR)

The electronic paramagnetic resonance (EPR) technique permits to verify the existence of unpaired electrons in a sample. Since doped Pani is a paramagnetic material, containing poly(semiquinone) cation radicals in its structure, it was possible to observe the effects brought about by covalently binding the polymer as a segment in a network.

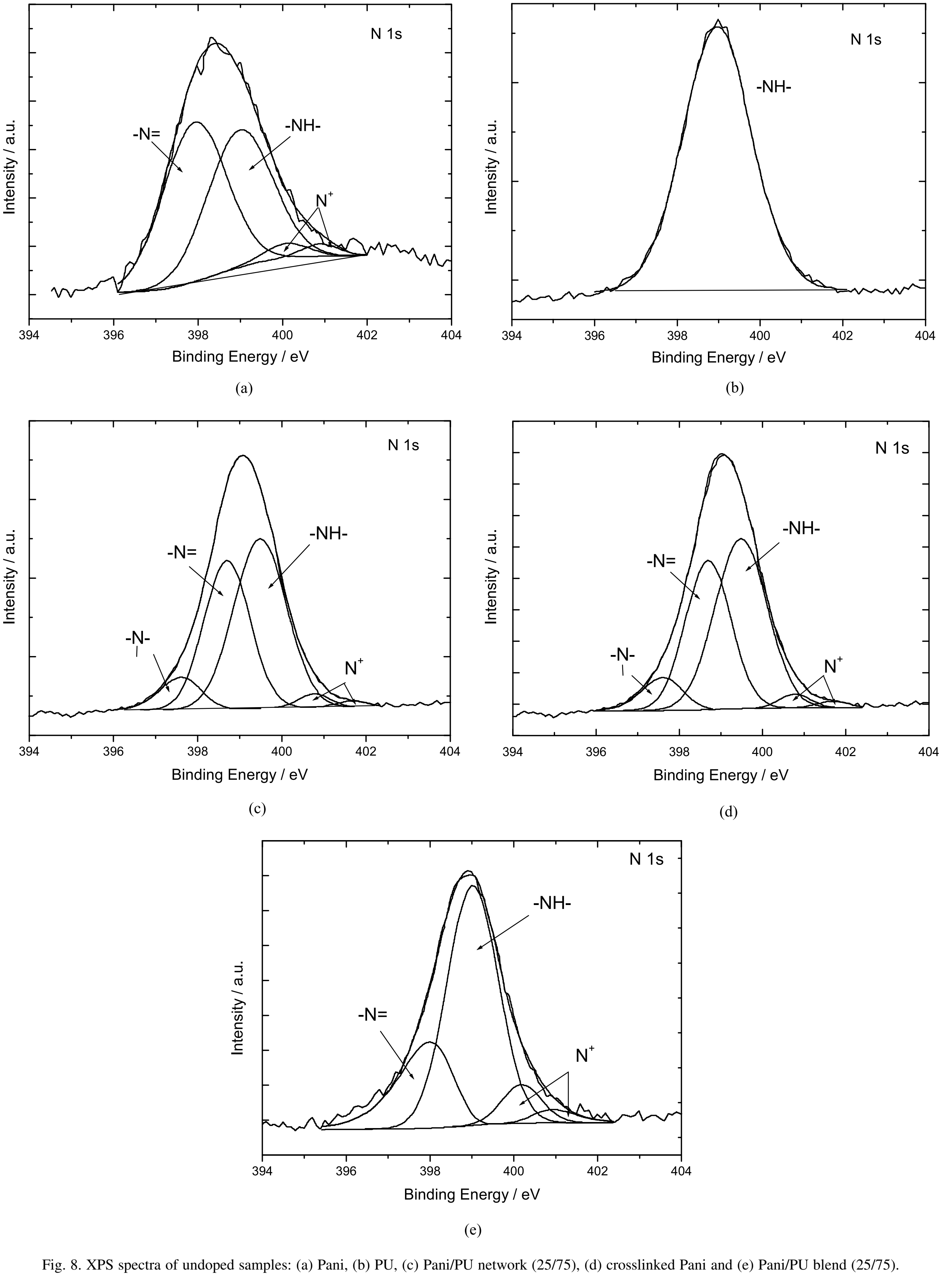
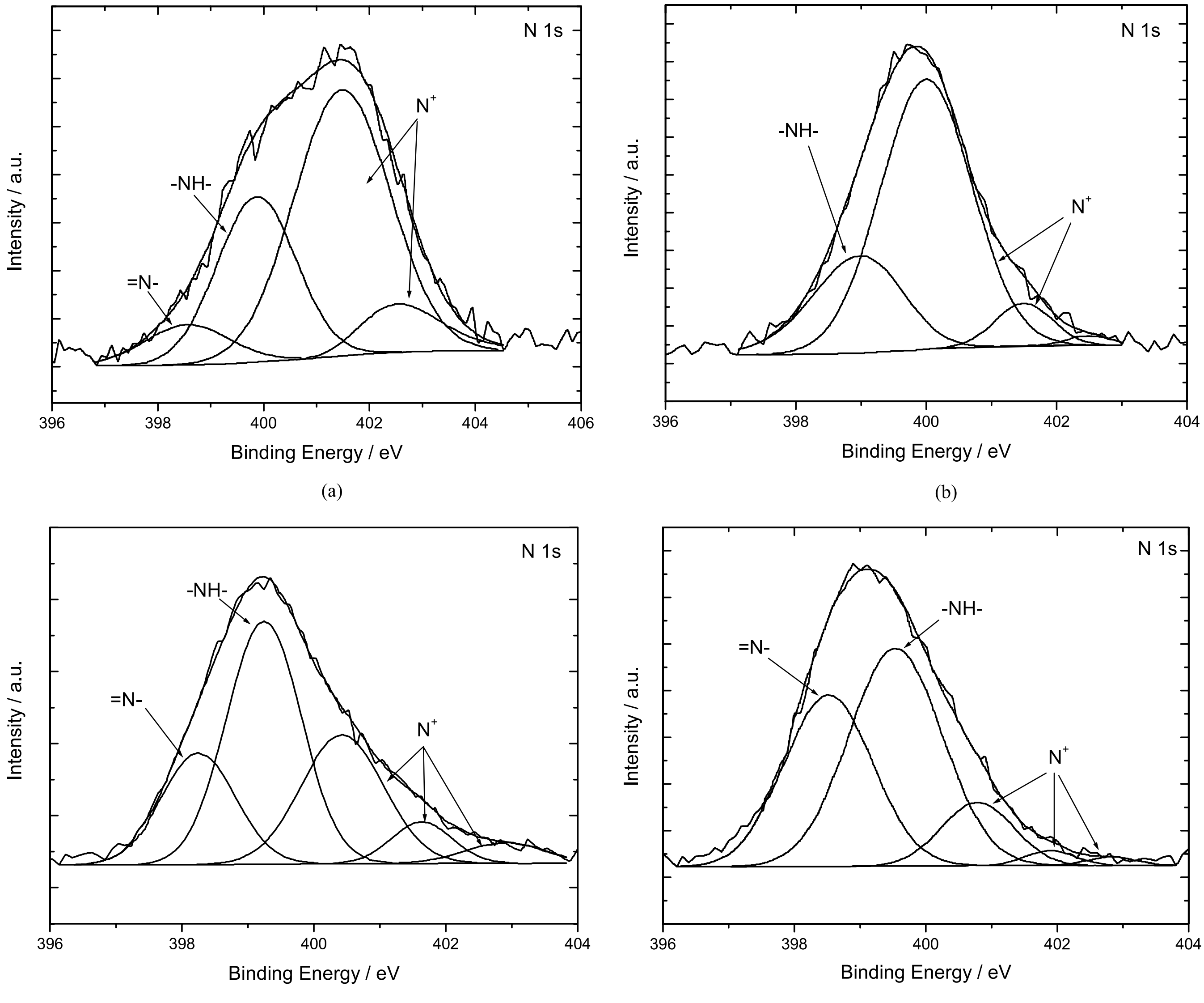


Fig. 8. XPS spectra of undoped samples: (a) Pani, (b) PU, (c) Pani/PU network (25/75), (d) crosslinked Pani and (e) Pani/PU blend (25/75).



(a) (b) (c) (d)

Fig. 9. XPS spectra of CSA doped samples: (a) Pani, (b) PU, (c) Pani/PU network (25/75) and (d) Pani/PU blend (25/75).

The EPR spectra, at ambient temperature of doped networks, blends and pure Pani revealed only one signal, without hyperfine structure.

Representative EPR spectra of these materials are presented in Fig. 10. The *g* parameter of all samples was identical ($g = 2.0028$), indicating that the same type of radical was present in the samples. This value is characteristic of the emeraldine salt [36].

By observing the values of ΔH_{pp} shown in Table 1, it was possible to get an idea of the degree of delocalization of the cation radical, since charge confinement increases this value [37–38]. It was found that ΔH_{pp} is larger for the crosslinked Pani than for pure Pani, indicating that the effective conjugation length was decreased in this material, probably associated with some torsion of the Pani chains, mainly near the urethane connecting junctions.

The same behavior was observed for the 5/95 networks and 5/95 and 25/75 blends. In the 5/95 network, we believe that the increase in ΔH_{pp} was due to chain torsion, as in crosslinked Pani, and also to the larger distance imposed among Pani chains, since the crosslinking connections are much more far apart. When the Pani concentration in the networks was increased, as in 25/75 sample, the ΔH_{pp} value equals that of pure Pani, indicating the existence of a pure Pani domain. The existence of a pure Pani phase was already verified by DMTA, where three transitions were detected and attributed to the pure components (Pani and PU) and to a mixed interphase of both [23]. The mechanical fragility of the blends was indicative of coarse phase separation. Definitive information about the existence of interconnection among Pani domains could be provided by electrical conductivity measurements, which was not feasible due to the poor mechanical strength of these materials. ΔH_{pp} values are useful to gain insight in the

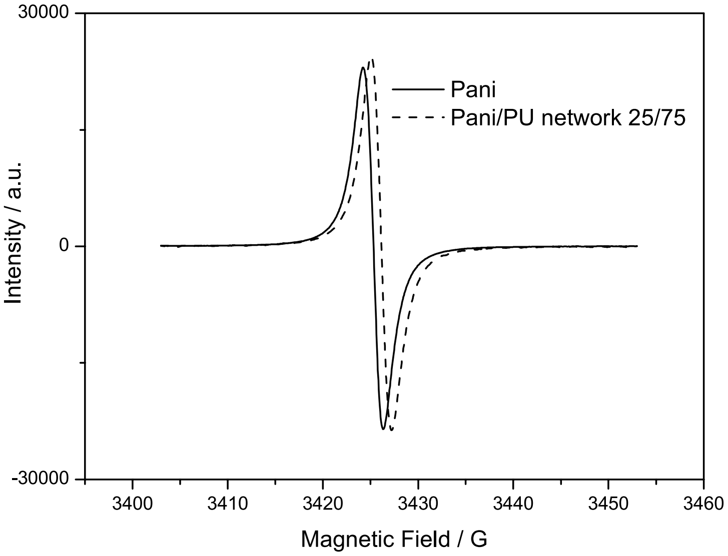


Fig. 10. EPR spectra of Pani and Pani/PU networks.

degree of charge delocalization, but do not inform about phase separation. The electronic delocalization in the blends, in a general way, was less than in the networks of the same composition, as shown in Table 1, confirming the assumptions resulting from UV–Vis (Section 3.2) and XPS (Section 3.3) analyses. In principle, if Pani forms a separate domain in the blends, ΔH_{pp} should be the same either in pure Pani or in the blends. Nevertheless, we observed variations in charge delocalization in all measurements, when comparing Pani in pure and blended forms, indicating a more compact chain arrangement. A plausible reasoning for these findings is that during pure Pani film formation the chains were in contact with only solvent molecules, whereas in the blends, the chains were in a medium containing apart from the solvent, a great amount of a thermodynamically immiscible second component, and due to repulsion, tended to coiling with solvent evaporation.

It was also verified by EPR that none of the tested materials was anisotropic.

4. Conclusions

In a previous work, we presented the synthesis and the thermal, dynamic mechanical and electrical properties of Pani/PU networks, which presented a semi-conducting behavior associated with mechanical resistance. A morphological model was proposed in which a percolating Pani phase was embedded in a PU matrix through an interphase that was responsible for the material's connectivity. In this paper we have found further evidence of these statements, based on different analytical methods: UV–Vis–NIR, XPS and ESR. New results were obtained as well. A model structure was synthesized for comparison purposes, where the bonds between Pani and PU were only urea type, without the interference of urethane linkages. Using this compound, the formation of the covalent link between Pani and PU was confirmed by FTIR and XPS.

Table 1
$\Delta H_{pp} H_{pp}$ of the Pani/PU networks

Sample	ΔH_{pp}/G
Pani	2.14
Crosslinked Pani	2.36
Pani/PU network 5/95	2.50
Pani/PU network 25/75	2.14
Pani/PU blend 5/95	2.71
Pani/PU blend 25/75	2.50

The UV–Vis spectra showed that the crosslinking of Pani with PU did not affect the electronic transitions of the conducting polymer, either in the doped or non-doped states, whereas those of the blends shifted up to 21 nm, as compared to pure Pani. This indicated that the Pani chains were more extended in the networks than in the blends, due to the covalent linkages with the PU. Secondary doping of the networks with *m*-cresol was achieved, and probably assisted by the network swelling as whole by the solvent.

XPS spectra showed that the hydrogen bonds of Pani with PU shift the –NH– to lower energy levels, close to the =NH– peak. This peak (398 eV), enveloping the contribution of both H bonded amine and imine groups, was present either in the networks or in the blends. The degree of protonation determined by XPS for CSA doped Pani was 64%, which includes the protonated amine nitrogen (14%), and that of the PU was 76%. For Pani/PU 25/75 network the protonation degree was 36 and 14% for the corresponding blends.

The EPR spectra of pure Pani, networks and blends presented the same *g* value, indicating that the paramagnetic species was the same in all these materials. When the Pani concentration in the networks was increased, as in 25/75 network, the ΔH_{pp} value reached that of pure Pani, indicating the existence of a pure Pani domain.

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