



Journal of the Mexican Chemical Society

ISSN: 1870-249X

editor.jmcs@gmail.com

Sociedad Química de México

México

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Journal of the Mexican Chemical Society, vol. 53, núm. 4, octubre-diciembre, 2009, pp. 248-252

Sociedad Química de México

Distrito Federal, México

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Characterization of Copolymer Based in Polyurethane and Polyaniline (PU/PANI)

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Received September 12, 2009; accepted January 28, 2010

Abstract. The present work describes the synthesis and characterization of polyurethane (PU), polyaniline (PANI) and three IPNs (90/10, 80/20, 70/30) ratios were characterized by Fourier transformed infrared (FTIR) to analyze the generated functional groups of the synthesis. The combination PU/PANI was accomplished through the interconnection of the two polymers via condensation of PU prepolymer terminal NCO groups and the amine groups of PANI. DMA studies indicated that the PU had higher glass transition temperatures (T_g) with the increase of PANI. SEM micrographics were obtained to 1000X of the PU, PANI and the ratios 90/10, 80/20 and 70/30 of PU/PANI. A morphological interpretation was proposed in which PANI chains formed a phase dispersed in a PU matrix, linked together by an interphase, that could be responsible for the connectivity between the two polymers and determine excellent mechanical properties.

Key words: Polyurethane, Polyaniline, IPN, FTIR, DMA, SEM.

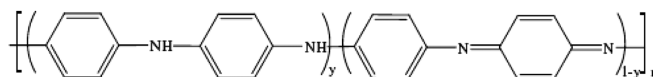
Resumen. El presente trabajo describe la síntesis y caracterización del Poliuretano, (PU), Polianilina (PANI) y tres IPNs (90/10, 80/20, 70/30). Estos materiales fueron caracterizados mediante espectroscopia de infrarrojo por transformadas de Fourier (FTIR) para analizar los grupos funcionales generados de la síntesis. La combinación PU/PANI se llevó a cabo a través de la interconexión de los dos polímeros vía condensación de grupos de NCO terminales del prepolímero de PU y las aminas de la PANI. Los estudios de DMA indicaron que el PU presentó temperaturas de transición vítreas (T_g) mayores con el incremento de PANI. Se obtuvieron las micrografías de SEM a 1000X del PU, PANI y las relaciones 90/10, 80/20 y 70/30 de PU/PANI, en donde, las cadenas de PANI formadas se dispersaron en la matriz de PU, se produjo una interfase, la cual fue la responsable de la conectividad entre los dos polímeros y determinaron excelentes propiedades mecánicas.

Palabras claves: Poliuretano, polianilina, IPN, FTIR, DMA, SEM.

1 Introduction

Conductive polymers are widely studied because of their foremost properties such as high conductivity to weight ratio, corrosion resistance and facile processability. Conducting polymers exhibit special properties compared to metals in the sense that they do not only reflect but also selectively absorb electromagnetic radiations. Various conductivities with radiation frequency have made them useful in radar absorbing materials. Conducting polymer as molecular wires is an excellent choice because of their long π -conjugation length as well as their high metal conductivity [1]. In recent years, polymer-polyaniline (PANI) conductive polymeric composites have received considerable attention because of their potential applications in electrodes, biosensors, batteries, antistatic coatings, gas sensors, membranes and light emitting diodes [2-14] PANI is a conducting polymer [15] which has been extensively studied due to its relatively high conductivity and potential application in electronic devices. The general formula for ideal PANI materials in their base forms consists in three ($-C_6H_4-NH-$) benzenoid units and one ($-N=C_6H_4=N-$) quinoid unit [16].

The y value accounts for the oxidation state of the polymer. Leucoemeraldine base (LEB), emeraldine base (EB)



and pernigraniline base (PNB) correspond to the completely reduced ($y = 1$), half oxidized ($y = 0.5$) and completely oxidized ($y = 0$) states, respectively. Whereas the three bases are insulating materials, base protonation leads to the corresponding salts.

Emeraldine salt (ES) is the only one exhibiting high electric conductivity and has consequently received considerable interest [16-17]. With PANI emeraldine salts a range of anions, including polyelectrolytes and functional molecules, can be incorporated as dopants. However, the range of dopants that can be directly incorporated is limited due to the fact that an acidic environment must be used to induce aniline solubility in aqueous media and to maintain the polymer in the conductive emeraldine salt form during growth [18]. A conducting polymer blend with PANI and conventional polymer can exhibit good mechanical properties associated with interesting electrical properties. However, blending has very little effect on the environmental stability of the conducting polymer itself. One of the major limitations of the blending is that it almost

always produces a highly heterogeneous two-phase morphology. Therefore, it may be more effective to prepare a conducting polymer with improved processability and mechanical property by the chemical synthesis approach. The combination of PANI segments with blocks of another polymer has been recently reported, such as the grafting of polyethylene glycol or polyacrylic acid onto a PANI backbone, and a block copolymer consisting of PU and PANI oligomer, etc. The use of a thermoplastic elastomer with conducting polymers is very attractive due to the combination of mechanical properties and a processability which does not require vulcanization [16]. The reason why PU is chosen is due to its balanced flexibility and hardness, good film forming property and resistance to solvent. Moreover, the interaction between NH in PANI and NHCOO in PU may be a bonus to improve the compatibility of the system. The strong tendency of PANI and PU to form hydrogen bonding has been verified by Rodrigues through various spectroscopic techniques, which was believed to be responsible for a certain degree of phase mixing in PANI/PU blend. Ho and coworkers also confirmed the hydrogen bonding between PANI and PU, and the stronger hydrogen bonding in the blend contributed to better miscibility, higher conductivity and tensile strength.

In the characterization of PANI filled PU/PMMA interpenetrating network system, Siddaramaiah mentioned that the hydrogen bonding formation between NH of PANI and NHCOO group of PU/PMMA polymer network had some effect on the physicomechanical, electrical as well as thermal properties of the conducting IPN. Yoshikawa *et al.* also suggested that the interaction between the carboxyl groups in PU and imine groups in PANI could induce miscibility of PANI/PU blends [16,19]. IPNs were prepared by sequential method. Functional groups, microstructure and mechanical properties of three PU/PANI ratios (90/10, 80/20, 70/30) are reported here.

2 Results and discussion

2.1 Fourier Transfer Infrared Spectroscopy

The IR spectra of three PU/PANI ratios are shown in figure 1. In all of the spectra, the strong peak around 3350 cm^{-1} comes from the stretching vibration of N–H bond in the urethane segments. The formation of PANI was revealed by the absorption bands at 3460, 1603, 1179, 1124 and 834 cm^{-1} , which were attributed to the vibrations of N–H, $\text{C}=\text{C}$ -, Ph–NH, Ph–NH–Ph, and C–N in the aniline unit [10]. Bands corresponding to urethane (CH_2 a 2926 – 2907 cm^{-1} , CH_3 a 2851 – 2841 cm^{-1} y C=O a 1725 – 1701 cm^{-1}) can be observed [20–22], and the peak at about 1600 cm^{-1} corresponds to C=C stretching peak in the benzene and quinoide rings [13,16]. Two peaks at 1510 and 1012 cm^{-1} arise from symmetric and asymmetric stretching vibration of N–C–N in the urethane-aniline, corresponding to the reactions of the –NCO groups with the NH_2 groups of the PANI [16].

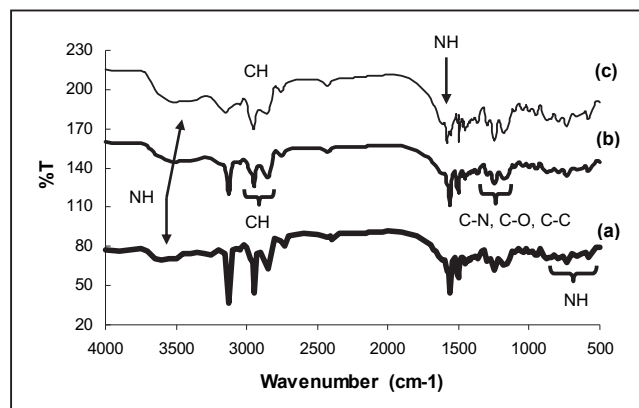


Fig. 1. IR spectra of three PU/PANI ratios, (a) 90/10, (b) 80/20 y (c) 70/30, respectively

In the region below 2000 cm^{-1} the spectrum exhibits two main bands, with maxima situated at 1574 and 1488 cm^{-1} , assigned to quinonoid and benzenoid ring stretching vibrations, respectively [13,23] while the bands at 1315 and 1244 cm^{-1} can be attributed to C–H stretching vibration with aromatic conjugation, and the absorption peak near 1160 cm^{-1} results from the $\text{N}=\text{Q}=\text{N}$ (Q denotes quinoid ring) stretching mode [23]. Two small peaks at 1034 and 1006 cm^{-1} are ascribed to the SO_3H groups after doped with ACS. The broader absorption around 1100 cm^{-1} accompanied by a shoulder at ca. 1080 cm^{-1} can be attributed to the C–O–C stretching vibrations. The absorption band at 1309 cm^{-1} corresponds to π -electron delocalization induced in the polymer by protonation [24–25]. A band characteristic of the conducting protonated form is observed at 1223 cm^{-1} and it is interpreted as a C–N⁺ stretching vibration in the polaron structure. The prominent 1149 cm^{-1} band has been assigned to a vibration of the $\text{–NH}^+=$ structure, which is formed during protonation [26–27]. A small band at 1167 cm^{-1} is observed in its place. The region of 1010–1170 cm^{-1} belongs to the aromatic C–H in-plane bending modes. Out-of-plane deformations of C–H on substituted aromatic rings are located in the region of 800–880 cm^{-1} . Combining the above results, it is concluded that the PU/PANI have been successfully prepared. Furthermore, the absorptions at 1734 and 1707 cm^{-1} are assigned to non-bonded and hydrogen-bonded urethane carbonyl C=O stretching, respectively. It is noteworthy from the spectra that the higher the PANI content is contained in the PU hybrid, the stronger the hydrogen-bonded carbonyl group is observed. Clearly, the incorporated PANI molecules in the hybrids have groups being able to induce hydrogen bonding and can alter the ratio of free vs. H-bonded urethane carbonyl groups of Pus [14, 16].

2.2 Dynamic Mechanic Analysis

DMA was used to study the dynamic mechanical behavior of IPNs. Figures 2 and 3 shows storage modulus for PU, PANI and PU/PANI (90/10, 80/20, 70/30) as function of tempera-

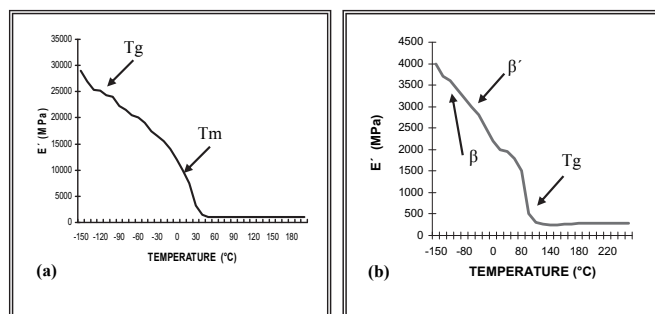


Fig. 2. DMA spectra of (a) PU and (b) PANI, respectively

ture respectively. For PU (figure 2a), a decrease in modulus occurred at the PU (around -90 °C) was attributed to the glass transition of the film containing residual NMP since an abrupt decrease in storage modulus occurred in this region. A secondary transition around 50 °C, related to the CH₂-motion of the HDI sequences of the PU segments. The DMA data indicate that the PUs based NMP can exhibit higher temperature resistance. The dynamical mechanical analysis (DMA) spectrum of the pure PANI is shown in Figure 2b. Three relaxation processes were detected: a peak at -95 °C (β); a shoulder (β') at -60 °C and the glass transition at 90 °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 location of Tg is in accordance with reported data for PANI plasticized with NMP [28-30].

The network spectra were recorded for PU/PANI ratios of 90/10, 80/20 and 70/10 (Figure 3). For the three networks, the PU glass transition shifted from -90 °C (pure PU, figure 2(a)) to -110 °C, and a peak at 48 °C was ascribed to the relaxation of an interphase formed between PU/PANI polymers, the shoulder at 95.7 °C was assigned to the glass transition of PANI, which was shifted to higher temperatures as compared with the free PANI, due to crosslinking [28].

Shifts of the carbonyl and -NH- absorption in the infrared, 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 PU and PANI phases and for the resulting good mechanical properties. Qi *et al.* (2008) used dynamic mechanical and dielectric thermal analyses together with infrared spectroscopy to identify molecular motions in PANI films cast from emeraldine base powder dissolved in the solvent NMP. These relaxations include a librational ring motion at around -80 °C and a glass transition (Tg) centred at 100 °C. They have also observed a permanent film hardening process at around 180 °C which is ascribed to polymer chain crosslinking, both physical (associated with chain entanglements) and more importantly chemical (chain-chain chemical bonding). Chemical crosslinking can be further identified with chain defects and residual impurities in the polymeric material. The

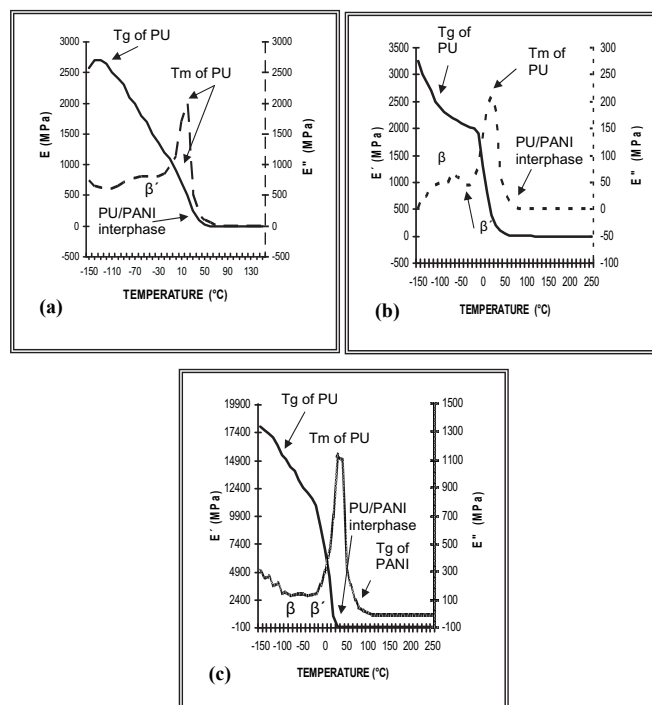


Fig. 3. DMA network spectra for PU/PANI ratios of (a) 90/10, (b) 80/20 and 70/30, respectively

importance of precise control of PANI synthesis and processing is therefore strongly emphasised. These results have clear implications for the thermal orientation process in PANI [31]. Melo *et al.* (2008) pointed out this β relaxation in the region of -80/-60 °C. By doing analysis on annealed samples, they have shown that β is linked to the residual content of water (from the film fabrication, moisture) in the films. So, the most probable hypothesis for Melo *et al.* would be the rotation of water molecules which are hydrogen bonded to the polymeric chain. Water molecules would act as side units of the polymer chain and become responsible for this relaxation. It could be linked to different phenomena especially to the presence of solvents containing a C=O bound (like NMP). Some authors have reported that the residual solvent (NMP) could exist in two forms in the polymeric material; free and hydrogen bonded NMP. Indeed, NMP can form hydrogen bond between the C=O present in its structure and the NH group present in PANI [32].

2.3 Scanning Electronic Microscopy

The morphologies of pure PU and PANI are shown in figure 4, respectively. The SEM micrograph of PU reveals a smooth continuous phase; some bumps appear on the micrograph, due to that the picture was taken from the fractured part of the polymer. Also, it can be seen the PANI form a homogeneous network, that which is a characteristic that causes the plastificant (NMP) during the synthesis, and it coincided

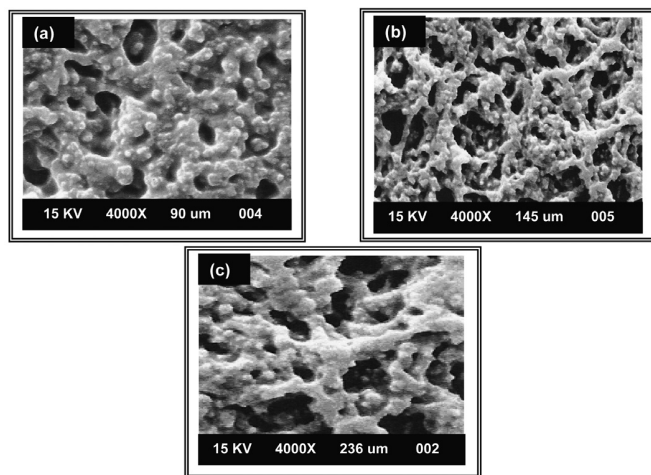


Fig. 4. SEM micrographs where (a) 90/10, (b) 80/20 and (c) 70/30 of PU/PANI, respectively

with that reported by Nabid et al [33] who also appreciated that the PANI surface presented a fibrial morphology with the extraction of NMP due to THF. Figure 4(c) displays the morphology of IPN with PANI contents of 30%. This micrograph indicates that the PANI primary particles disperse among the PU matrix, and coalesce to form aggregates. More aggregates are formed in the IPN as the PANI content increases from 10% to 30%. Furthermore, in the 90/10 ratio, the IPN structure is more compact that is to say, the cells are closed in comparison with the 80/20 and 70/30 ratios where the cells are open.

3 Conclusions

It was possible to prepare IPNs based in PU, PANI and PU/PANI ratio in 3 levels. The interconnection of PANI chains through PU segments has originated a series of new semi-conducting materials with good mechanical properties. By FTIR was possible to detect characteristic signals of PU, PANI, 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, along with the presence of a new relaxation in the DMA analysis two Tgs were detected for the samples, corresponding to PU and PANI networks, which suggest phase separation in a macroscopic level, characteristic of semi-IPN. Tg values shifted inward its respective polymer as PU/PANI ratio was changed. Trough SEM, the samples showed some characteristics of phase separation, which are proper of IPNs. Therefore when PU or PANI increased in the materials, these presented a heterogeneous surface, due to the control of one of the individual components.

4 Experimental

4.1 Materials

1,6-Hexanediol (Molecular weight 118.17 g/gmol, Fluka), N-methyl pyrrolidine (Molecular weight 85.15 g/gmol, Aldrich), HDI (Molecular weight 168.2 g/gmol, Fluka), Isopropanol (Molecular weight 60.10 g/gmol, Sigma-Aldrich), Aniline (Molecular weight 93.126 g/gmol, Sigma-Aldrich), Ammonium persulphate (Molecular weight 228.20 g/gmol, Fluka), Clorhidric acid (Molecular weight 36.46 g/gmol, Sigma-Aldrich), Sodium hydroxide (Molecular weight 35.10 g/gmol, Aldrich).

4.2 Methods

Synthesis of Polyurethane (PU), N-methyl pyrrolidine was dissolved in 1,6-hexanediol with an excess from HDI at 65 °C in nitrogen atmosphere during 3 h, finally, to carry out the reaction, the isopropyl alcohol was added.

The synthesis of Polyaniline (PANI) was prepared by oxidative polymerization of aniline. The solution of 0.2 M aniline ($\text{C}_6\text{H}_5\text{NH}_2$) and 0.1 M ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) mixed with 1 M HCl aqueous solution respectively, were individually kept in a refrigerator during 1.2 h with a controlled temperature (5 °C). Then the solution was filtered, the precipitate was washed with HCl, placed in NH_4OH and upset during 16 h. The solution was again filtered and the obtained polymer was dried during 2 h, finally, to the obtained pasta was added NH_4OH [34-35].

Synthesis of PU/PANI network was carried out through the reaction between the PU chains by means of the NCO groups and the PANI dissolved in NMP, where the concentrations (PANI) were 10, 20 and 30% m/m. The reaction time was 6 h. Later on, the materials were doped by means of camphor-sulfonic acid (CSA) (see figure 5). Finally, at the end of the reaction, the product obtained was poured in teflon badges and cured at 72 °C.

4.3 Characterization

The FTIR spectra of various samples in KBr pellets were obtained using a Perkin Elmer-FTIR instrument with a resolution of 4 cm^{-1} . The average of 16 scans was used to obtain each spectrum. All samples were vacuum-dried overnight prior to measurement [34].

Dynamic Mechanical Analysis (DMA) was performed on a TA Instrument 2980 dynamic mechanical analyzer under multifrequency mode at a temperature range of -1500 to 250 °C (heating rate 5°C/min), and a fixed frequency of 1 Hz using a dual cantilever clamp.

Scanning electron microscopy (SEM) was performed for sample micro-structural analysis on an electron microscope Joel JSV 5800 LV model. The voltage of acceleration was of 15 Kw [36].

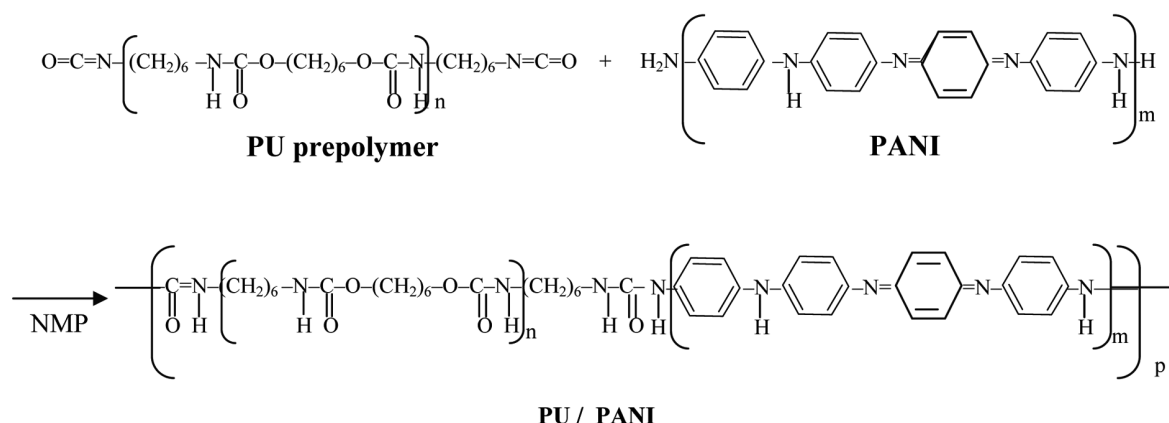


Fig. 5. Synthetic route for the preparation of PU/PANI

5 Acknowledgements

To DGEST for scholarship.

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