

Synthesis and characterization of composites of DBSA-doped polyaniline and polystyrene-based ionomers

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Abstract

The synthesis of composites of *n*-dodecylbenzene sulfonate-doped polyaniline (PANI-DBSA) and poly(styrene–metal acrylate) ionomers is presented. The ionomers of lithium, sodium and potassium were prepared by emulsion polymerization at different styrene-to-metal acrylate weight ratios. The composites made with the potassium ionomer exhibit the largest conductivity due to the higher content of acid groups that allows stronger interactions with the PANI chains compared to the Na and Li ionomers. IR spectroscopy suggests that hydrogen bonding interactions take place between PANI-DBSA chains and that amine salt groups form by chemical reactions between the amine groups of PANI and the acid groups of the ionomer. X-ray diffraction reveals that the ionomer affects the structural ordering of PANI-DBSA. All the PANI-DBSA–ionomer composites show higher thermal stability than the PANI-DBSA material. SEM shows a characteristic agglomerate morphology in all the composites. The composite showing the highest electrical conductivity was mixed with poly(*n*-butyl methacrylate) (PBMA) by extrusion and the films obtained have higher electrical conductivity than that of films of the same system without ionomer.

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1. Introduction

Polyaniline (PANI) is an electroconductive polymer that has considerable technological applications. Its use in electronic devices, chemical and biological sensors, selective membranes, etc., has been amply documented [1–8]. However, the insolubility, poor mechanical properties and low processability of PANI have hindered its industrial applications. To overcome these problems, numerous attempts have been made such as the use of long chain organic dopants [9–11], functionalization of aniline monomer ring [12,13] and preparations of PANI-thermoplastics composites [11,14]. In order to obtain composites with appropri-

ated electrical and mechanical properties, extensive efforts have been made to improve the compatibility between PANI and thermoplastic matrices [1,15,16]. The use of compatibilizers and the introduction of functional groups in the electroconductive polymer may increase the interactions between the blend components and therefore promote the interfacial adhesion between the phases. If the synthesis of PANI is performed in the presence of ionomers with the appropriate groups that are able to interact with the conducting polymer, then the enhancement of the thermal stability and its processability by extrusion may be possible [17,18].

In the present work, the synthesis of composites of *n*-dodecylbenzene sulfonate-doped polyaniline (PANI-DBSA) and polystyrene-based ionomers is presented. Three ionomers are used: poly(styrene–lithium acrylate) (PSALi),

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poly(styrene–sodium acrylate) (PSANa) and poly(styrene–potassium acrylate) (PSAK). The ionomers were prepared by emulsion polymerization at different weight ratios of styrene to metal acrylate. The electrical properties of the composites obtained are reported in this paper. The characterizations by infrared spectroscopy (IR), X-ray powder diffraction, thermogravimetry (TGA) and scanning electron microscopy (SEM) of the composites materials are also discussed. The mechanical processing of the composites was demonstrated by mixing them with a thermoplastic matrix (PBMA) in an extruder. The electrical properties of these films were measured and compared with films of PANI-DBSA and PBMA without ionomer, of which the electrical performance was reported elsewhere [8]. Results reveal that the presence of the ionomer enhanced the conductivity of the films.

2. Experimental

2.1. Materials

Aniline (99.5% from Aldrich) and styrene (reagent-grade from Resinas Guadalajara, Mexico) were distilled under vacuum before use. Ammonium persulfate (98.7% from Fermont), *n*-dodecylbenzene sulfonic acid (99.0% from Sicursa Industrial, Mexico), acetone (99.5% from Fermont), absolute ethanol (99.5% from Merck), sodium chloride (99.0% from Aldrich), acrylic acid (99% from Scientific Polymer Products), sodium dodecyl sulfate (99% from Tokyo Kasei), potassium persulfate (reagent-grade from Fermont), lithium hydroxide (99% from Spectrum), sodium hydroxide (98.4% from Fermont), potassium hydroxide (98.7% from Fermont) and poly(*n*-butyl methacrylate) (reagent-grade from Aldrich) were used as received. Lithium, sodium and potassium acrylates were prepared by the potentiometric titration of acrylic acid with the corresponding hydroxide.

2.2. Polymerization procedures

2.2.1. Polystyrene-based ionomers

Poly(styrene-co-potassium acrylate) (PSAK), poly(styrene-co-sodium acrylate) (PSANa) and poly(styrene-co-lithium acrylate) (PSALi) were synthesized at 60 °C by emulsion polymerization at 60 °C of styrene and the corresponding metal acrylate as described elsewhere [19]. The following weight ratios of styrene-to-metal acrylate were selected: 90/10 (PSAM-10), 80/20 (PSAM-20), 70/30 (PSAM-30) and 60/40 (PSAM-40), where M represents Li, Na or K.

2.2.2. PANI-DBSA–polystyrene ionomer composites

Aniline (0.013 mol) and ammonium persulfate (0.006 mol) were separately mixed with DBSA (0.04 mol) and NaCl (0.031 mol) in 30% v/v ethyl alcohol solution. Vigorous stirring was applied until homogeneous solutions were obtained. Next, 0.2 g of one of the ionomers was added to

the aniline solution while continuous stirring was maintained. All composite samples were made with the same weight ratio of PANI-DBSA to ionomer (80/20). The polymerization reaction was performed by adding the persulfate solution slowly to the aniline solution placed in an ice bath under N₂ atmosphere. The resulting solution was kept at 5 °C for 2 h with continuous stirring. The reaction product was precipitated using acetone, isolated by filtration, washed sequentially with ethyl alcohol and distilled water for several times, dried in vacuum at room temperature and finally powdered in a mortar.

2.3. Characterizations

The electrical conductivity of the composites compressed into pellets was measured by the standard two-point probe method. The measurements were done at room temperature with 6 mm diameter tungsten electrodes and a Proam multimeter. Proton nuclear magnetic resonance (¹H-NMR) spectra of the ionomers previously dissolved in CDCl₃ were obtained at room temperature on a Varian Unity Plus spectrometer. The peaks in the aromatic region (in the range of 6.2–7.2 ppm), assigned to the protons of the styrene ring, and the peaks in the region of 1–2.1 ppm, corresponding to the metallic acrylate protons, were used to calculate the composition of the ionomers. The IR characterizations were done with a Perkin–Elmer Spectrum GX FTIR spectrometer by the KBr pellet technique. X-ray powder diffraction patterns were obtained on a Rigaku Geigerflex diffractometer operated with CuKα ($\lambda = 1.542 \text{ \AA}$) radiation and a graphite monochromator. The thermal behavior was studied with a Perkin–Elmer TGA-7 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ with a nitrogen gas purge at a flow rate of 20 mL min⁻¹. The morphology of the composites was observed by means of a JEOL 5410LV scanning electron microscope. The samples were gold-sputtered prior to the SEM examination. To evaluate the processability and the thermal stability of PANI-DBSA/PSAK-40 composite, this material was mixed with PBMA in an extruder (model CS-194 AV) of Laboratory Maxwell. The rotational speed was 152 rpm and the temperatures were 100 and 120 °C for rotor and head, respectively. Both components were feed together to the extruder through the hopper at different weight ratios of PANI-DBSA/PSAK-40 to PBMA.

3. Results and discussion

Fig. 1 shows the electrical conductivity of the PANI-DBSA/PSALi, PANI-DBSA/PSANa and PANI-DBSA/PSAK composites as a function of the initial weight concentration of acrylate monomer used in the ionomer synthesis. The conductivity of the PANI-DBSA synthesized at the same conditions without ionomer was $0.032 \pm 0.001 \text{ S/cm}$. The PANI-DBSA/PSAK-40 composite showed the highest conductivity ($0.023 \pm 0.004 \text{ S/cm}$) of all the composites studied here.

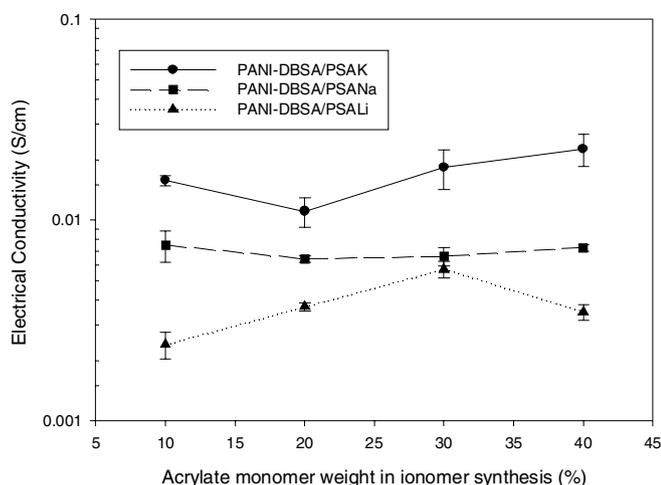


Fig. 1. Electrical conductivity of the PANI-DBSA/PSALi, PANI-DBSA/PSANa and PANI-DBSA/PSAK composites as a function of weight ratio of acrylate monomer used in ionomer synthesis.

The electrical conductivity of the individual composites did not significantly change with the variation of the acrylate content employed in the synthesis of the ionomers. Moreover, the conductivity decreased in the order: PANI-DBSA/PSAK > PANI-DBSA/PSANa > PANI-DBSA/PSALi. To understand these trends, the actual compositions of the ionomers were determined by $^1\text{H-NMR}$ spectroscopy. Table 1 depicts the compositions estimated from the spectra (not shown) of the different potassium ionomers. Clearly the amount of potassium acrylate incorporated in the copolymer increases as the concentration of the acrylate in the feed is raised; however, the amount incorporated in the ionomer is much smaller than the amount in the feed. With the sodium and lithium ionomers, the maximum amount of the acrylate incorporated does not exceed the 2%, even at the largest concentration of this ionomer (0.4 w/w_{styrene}) in the original emulsion recipe. In the batch emulsion copolymerization of a reactive water-insoluble monomer (such as styrene) with a less water-soluble monomer (such as acrylic acid), the amount of the acrylic monomer in the copolymer is much smaller than that loaded in the original emulsion due to differences in reactivity and concentration in the reacting loci, i.e., the micelles and the reacting polymer particles [20,21]. The rise in conductivity of the composites containing the potassium ionomer correlates with the increasing amount of the potassium species in the ionomer (Table 1). On the other hand, the insensitivity of the conductivity of the composites made with the Na and Li ionomers could be due to the quite small amounts of Na

Table 1
Molar compositions of PSAK evaluated by $^1\text{H-NMR}$ spectroscopy

Ionomer type	Styrene (mol%)	Potassium acrylate (mol%)
PSAK-10	97.9	2.1
PSAK-20	97.6	2.4
PSAK-30	96.9	3.1
PSAK-40	93.7	6.3

and Li acrylates in the ionomers. However, the conductivity of the composites made with K-based ionomer is consistently larger than those of the Na- and Li-based ionomers. Moreover, and because the hygroscopic characters of the components of the composite, water is detected in all the samples, as shown by TGA later. Inasmuch as Li has a higher hydration number, six molecules of water per molecule of Li ion, compared to 4 for the Na and K ions, which are minimum values measured by dielectric properties [22], together with smaller content of Li (and Na) in the ionomers compared with the K-based ionomers could explain the differences in conductivity of their respective composites (Fig. 1).

IR spectroscopy is a useful tool to elucidate possible interactions between DBSA-doped polyaniline and the ionomers, the composites were analyzed by IR. Fig. 2 depicts the FTIR spectra of PSAK-40 (spectrum A), PANI-DBSA (spectrum B) and the composite of PANI-DBSA/PSAK-40 (spectrum C). The composites of PANI-DBSA with PSANa and PSALi had similar spectra features than those observed for PANI-DBSA/PSAK and hence, they are not shown nor discussed.

The spectrum of the PSAK-40 shows spectral contributions of both the styrene and the potassium acrylate units. The typical bands of the styrene units detected in the spectrum A are: (i) a triplet at 3083, 3061 and 3027 cm^{-1} due to C–H aromatic stretching vibrations, (ii) overtones in the 2000–1650 cm^{-1} range, (iii) bands at 1602, 1493 and 1452 cm^{-1} due to the skeletal stretching modes of the semi-unsaturated carbon–carbon bonds and (iv) strong bands at 756 and 696 cm^{-1} produced by the out-of-plane C–H bending vibrations of the hydrogen atoms remaining

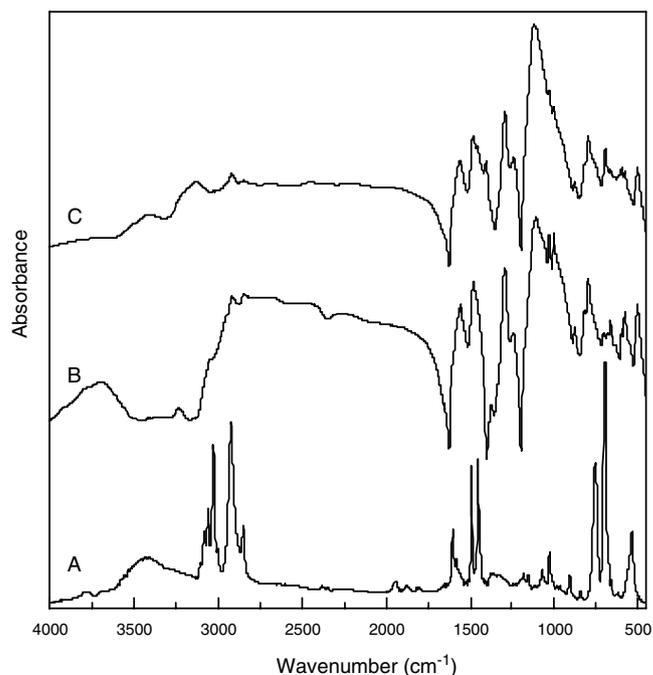


Fig. 2. Infrared spectra of (A) PSAK-40, (B) PANI-DBSA and (C) PANI-DBSA/PSAK-40.

on the aromatic ring. For the acrylate units, few bands are detected and they are semi-hidden by the strong styrene peaks. In this respect, the band at 1602 cm^{-1} is a superposition of a sharp peak due to $\text{C}=\text{C}$ stretching of the aromatic ring in the styrene units and a wide band due to symmetric and anti-symmetric resonance of the COO^- group [19]. Also a broad absorption band is seen at 3434 cm^{-1} due to the stretching of the inter-molecular associated OK (or OH) of the carboxylate group.

The spectrum of PANI-DBSA (spectrum B) shows peaks characteristics of the conducting form of PANI and of the DBSA dopant [23]. The band at 3229 cm^{-1} is the inter-chain hydrogen-bonded N–H band between amine and imine groups, while the weak band at 3414 cm^{-1} is due to free N–H vibration [24]. The bands at 1559 and 1480 cm^{-1} are due to stretching doped C–N of benzoid and quinoid functionalities, respectively. The sulfonic stretching absorption of the dopant is observed at 1185 and 1040 cm^{-1} and a peak due to C–H *p*-substituted aromatic out-of-plane bending of PANI appears at 797 cm^{-1} . In addition, this spectrum exhibits a broad absorption band at wavenumbers higher than 2000 cm^{-1} related to the metallic polaron energy absorption, which is characteristic of the conducting form of PANI [25]. The peaks observed around $2800\text{--}3000\text{ cm}^{-1}$ can be assigned to the hydrocarbon stretching of the DBSA dopant.

The spectrum of the PANI-DBSA/PSAK-40 composite (spectrum C) is dominated by the spectral contributions of PANI and DBSA. However, several peaks appear that can not be assigned to either PANI or DBSA: (i) a peak that is produced by out-of-plane C–H bending vibrations of the styrene units is resolved at 696 cm^{-1} (cf. spectrum A); (ii) a weak peak at 760 cm^{-1} due to vibration in styrene units of PSAK that appears as a shoulder of the peak at 795 cm^{-1} (characteristic of PANI-DBSA) and (iii) two bands produced by skeletal stretching modes of the semi-unsaturated carbon–carbon bonds of styrene in PSAK: one as a shoulder at 1452 cm^{-1} and another as a well

resolved band at 1403 cm^{-1} . On the other hand, a peak appears at 3407 cm^{-1} that can be assigned to the vibration modes of N–H free-bonds in PANI-DBSA and of O–K or O–H in PSAK. The characteristic absorption peaks of DBSA were observed in the composite spectra, which indicates that the presence of the ionomers did not affect the DBSA-doping of PANI. It is relevant the apparition of a new spectral contribution at 3123 cm^{-1} in the spectrum of the PANI-DBSA/PSAK-40 composite. This peak can be assigned to vibrations of NH_3^+ ion. It is well known that amine groups can react with acid groups to produce amide groups with the formation of one molecule of water per amide group formed [26]. This reaction can be carried out in two steps: (i) at ambient temperature or inclusive at lower temperatures, acid and amine groups can react to yield an amine-salt group, which is stable at ambient temperature; (ii) if this salt is heated at higher temperatures, say $185\text{ }^\circ\text{C}$ or slightly higher, amide groups can be produced [27]. The spectral band at 3123 cm^{-1} in PANI-DBSA/PSAK-40 suggests strongly that a chemical reaction was carried out between PSAK and PANI-DBSA. Due to the low temperature ($5\text{ }^\circ\text{C}$) in the PANI-DBSA/ionomer composite preparation, the only possible product with such spectral signature is the amine salt. A scheme of the reaction mentioned above is presented in Fig. 3. Rodríguez-Ríos et al. reported the complete transformation of amine salt groups to amide groups when blends of polyamide 6 and polystyrene were prepared in presence of PSAK at $250\text{ }^\circ\text{C}$ [26].

Fig. 4 shows the infrared spectra of PANI-DBSA (A), PANI-DBSA/PSAK-10 (B), PANI-DBSA/PSAK-20 (C), PANI-DBSA/PSAK-30 (D) and PANI-DBSA/PSAK-40 (E) in the $3300\text{--}3000\text{ cm}^{-1}$ spectral regions. The appearance of the new band at 3123 cm^{-1} is clearly noticeable in the composites with respect to PANI-DBSA. It is important to note that the intensity of the spectral contribution at 3123 cm^{-1} increases as the content of the potassium acrylate (Table 1) increases. Evidently, the intensity of

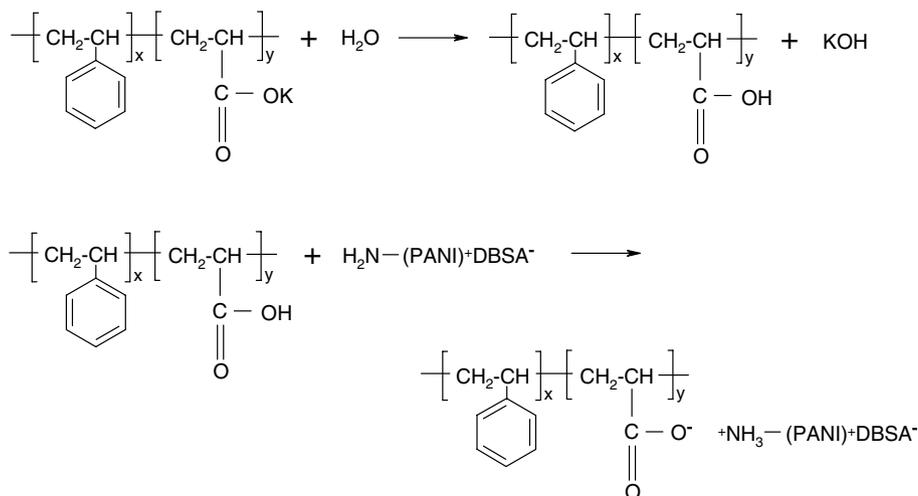


Fig. 3. Possible chemical reaction scheme between acrylate group of ionomers and the amino group of polyaniline.

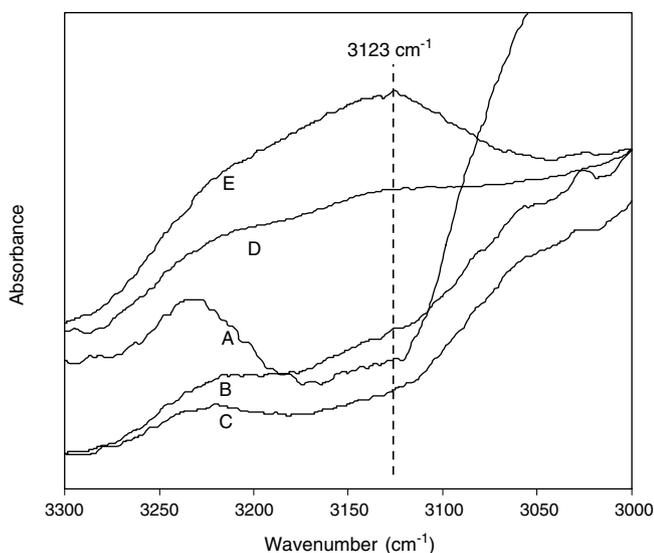


Fig. 4. Infrared spectra of (A) PANI-DBSA, (B) PANI-DBSA/PSAK-10, (C) PANI-DBSA/PSAK-20, (D) PANI-DBSA/PSAK-30, (E) PANI-DBSA/PSAK-40.

the spectral contribution detected at 3123 cm^{-1} correlates with the conductivity of the composites (Fig. 1). In fact, as this band is more intense there are more amine salt groups, which promote a larger conductivity. For composites prepared with PANI-DBSA and PSANa or PSALi the band in 3123 cm^{-1} is very weak. A poor content of metallic acrylic monomer determines that the formation of amine salt groups would be smaller and, in consequence, the conductivity of lithium and sodium composites is smaller than that of the potassium composite and almost does not increase with increasing Li or Na acrylate in the feed (Fig. 1).

X-ray diffractograms of PANI-DBSA (A), PSAK-40 (B) and PANI-DBSA/PSAK-40 (C) are compared in Fig. 5.

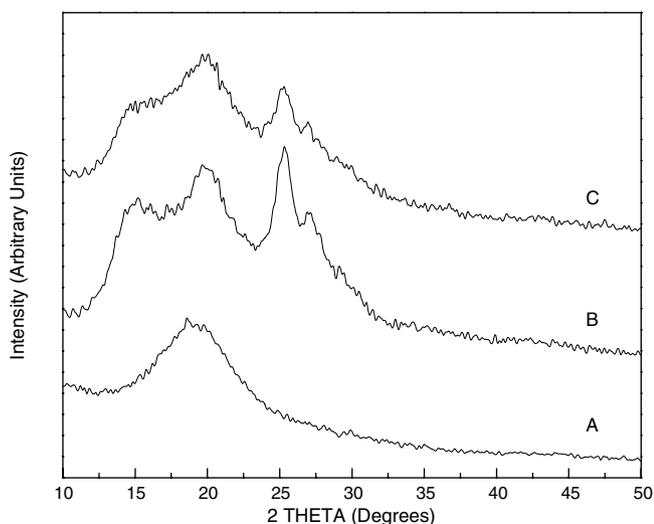


Fig. 5. X-ray powder diffraction patterns of (A) PSAK-40, (B) PANI-DBSA and (C) PANI-DBSA/PSAK-40 samples.

Again, the composite that exhibited the highest electrical conductivity was chosen to study the structural ordering of PANI. The PANI crystal cell is pseudo-orthorhombic with chains parallel to the c -axis where the dopant is placed in the centre of the cell [28]. The d -spacings obtained from the 2θ positions of the reflections are similar for PANI-DBSA and PANI-DBSA/PSAK-40, which indicates that the ionomer do not change the inter-chain separation of PANI and the contact distance between the dopant molecules and the PANI chains. However, the peak at $2\theta \sim 25^\circ$ is sharper in PANI-DBSA compared to that in PANI-DBSA/PSAK-40. This reflection is indexed to the (110) hkl -plane which implies that the ionomer decreases the order of the stacking formed by PANI chains and DBSA.

The thermal behavior of PANI-DBSA, PANI-DBSA/PSALi-40, PANI-DBSA/PSANa-40 and PANI-DBSA/PSAK-40 composites and PSALi-40, PSANa-40 and PSAK-40 ionomers are depicted in Fig. 6. The thermal behavior of the ionomers does not seem to depend on the particular cation included in its structure. For the three ionomers, it is evident a very similar evolution of the TG-curve. TGA detected only one step in the lose mass process for these three ionomers. This step began at ca. 270°C and ended near 380°C . This step is associated with the thermal degradation of the hydrocarbon backbone of the ionomers [19].

The PANI-DBSA and the composites began to lose mass at temperatures below 100°C ; however, the PANI-DBSA loses greater mass in this temperature range. The evaporation of residual moisture and oligomers is responsible for this initial mass loss. The second step of mass loss is observed at 215°C for PANI-DBSA and at 240°C for the composite samples. This second mass loss can be related to the decomposition of the DBSA dopant. For PANI-DBSA, a third and final mass loss is detected from 270°C

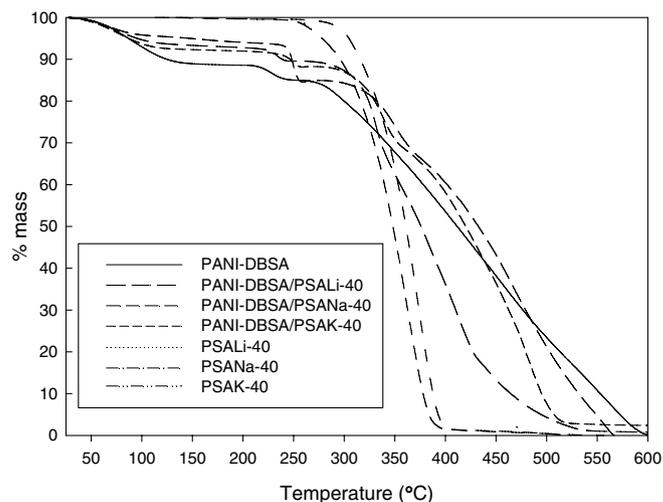


Fig. 6. TGA of PANI-DBSA, PANI-DBSA/PSALi-40, PANI-DBSA/PSANa-40 and PANI-DBSA/PSAK-40, PSALi-40, PSANa-40 and PSAK-40 samples.

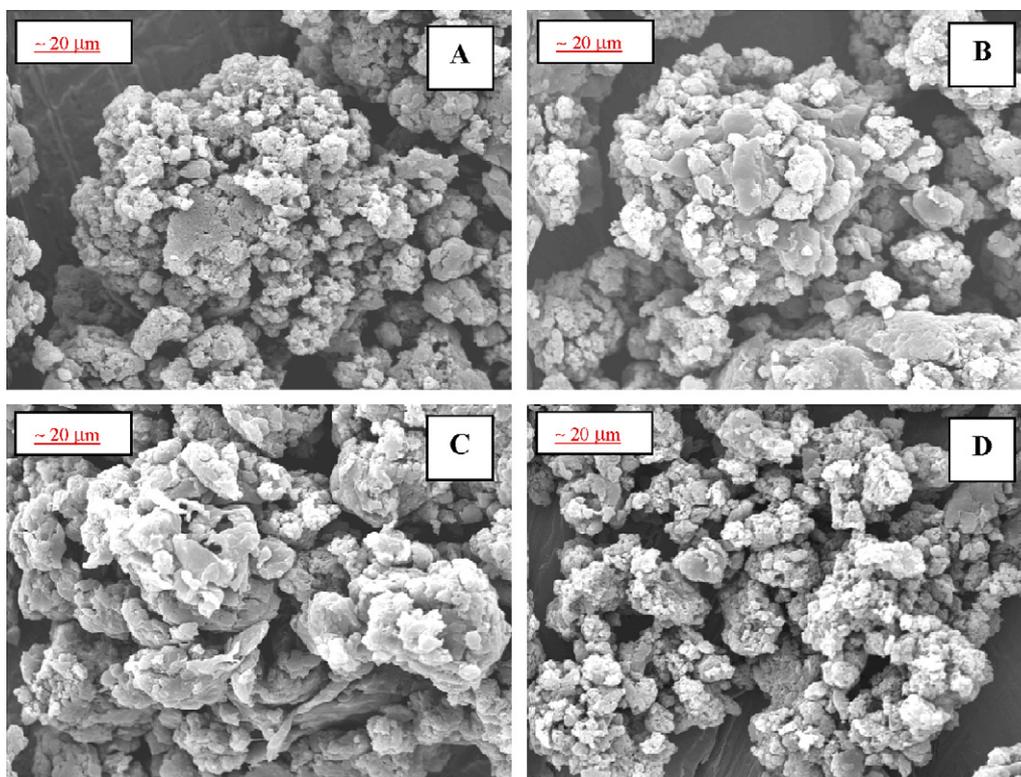


Fig. 7. SEM images of (A) PANI-DBSA, (B) PANI-DBSA/PSALi-40, (C) PANI-DBSA/PSANa-40 and (D) PANI-DBSA/PSAK-40.

to 600 °C. This process can be attributed to the degradation of the PANI backbones. The composites show a third step of mass loss at 300 °C, which is associated with the degradation of the ionomer in the samples. A fourth and final mass loss is seen around 365 °C, which may be attributed to the degradation of the electro-conducting polymer in the composites. The mass loss of the composite samples is less than that for PANI-DBSA below ~250 °C. The thermal process related to the dopant degradation in the composites occurs at slightly higher temperature than that for the PANI-DBSA. These results agree with the hypothesis that the ionomers establish chemical interactions with the electroconductive polymer in the composites. The physical interactions, such as hydrogen bonding, are more sensitive to temperature than the chemical interactions and practically disappear at temperatures below 120 °C. Clearly, TGA results indicate that the thermal stability of the composite samples is higher than that of PANI-DBSA. In fact, the PANI-DBSA composites are thermally more stable than the ionomers or the PANI-DBSA sample.

The morphologies of the powder samples of PANI-DBSA (A), PANI-DBSA/PSALi-40 (B), PANI-DBSA/PSANa-40 (C) and PANI-DBSA/PSAK-40 (D) are showed in Fig. 7. SEM study shows no significant morphology differences among the samples. The resulting powder was homogeneous and forms agglomerates, with a solid rock shape of different sizes. PANI salt synthesized in the absence of ionomers, formed smaller granules than those obtained in the other samples. This may be due to the com-

patibilizing action of the ionomer between PANI domains that increased the size of the PANI granules.

The mechanical–thermal processability of PANI-DBSA/PSAK-40 was demonstrated by making films of the composite with the thermoplastic PBMA at different weight ratios by extrusion. The blends were obtained as 1-mm thick homogeneous dark and tough tapes. Table 2 shows comparative electrical conductivity data of the blends of PANI-DBSA/PSAK-40/PBMA and PANI-DBSA/PBMA. The films of the electroconductive polymer PANI-DBSA mixed with PBMA at the same weight ratio exhibit lower conductivity than those containing the ionomer. These results confirm that the presence of the ionomer

Table 2
Electrical conductivity values of PANI-DBSA/PBMA and PANI-DBSA/PSAK-40/PBMA films obtained by extrusion as a function of electroconductive material to PBMA weight ratio

Weight ratio of polyaniline to thermoplastic ^a	Electrical conductivity (S/cm), ±10%	
	PANI-DBSA/PBMA	PANI-DBSA/PSAK-40/PBMA
70/30	2.3×10^{-4}	2.7×10^{-4}
60/40	4.1×10^{-5}	7.0×10^{-5}
50/50	6.4×10^{-6}	5.7×10^{-5}
40/60	$<10^{-9}$	3.2×10^{-5}
30/70	$<10^{-9}$	1.5×10^{-6}
20/80	$<10^{-9}$	$<10^{-9}$

^a In the case of the PANI-DBSA/PSAK-40/PBMA system, the values correspond to the weight ratio of PANI-DBSA/PSAK-40 to PBMA.

in the synthesis of PANI-DBSA enhances the thermal stability, allows the extrusion processing of electroconductive PANI and raises the conductivity of the extruded films.

4. Conclusions

DBSA-doped polyaniline composites were synthesized in the presence of poly(styrene-metallic acrylate) ionomers. The type and content of metal (Li, Na, K) in the acrylate group of the ionomer affects the electrical conductivity of the composites. The PANI-DBSA/PSAK composites exhibit the highest conductivities, which suggest that the higher content of the acid group in the ionomer allows stronger interactions with PANI chains compared to those made with the other ionomers. IR spectroscopy suggests that a chemical reaction takes place between the acid groups of the ionomer and the amine group of PANI to produce amine salt groups. This fact explains the higher thermal stability of the composites and the lower ordering of the composites compared to those of the DBSA-doped PANI. SEM revealed a similar agglomerated morphology in all samples, which is characteristic of DBSA-doped PANI. The PANI-DBSA/PSAK-40 composite can be mechanically mixed by extrusion with PBMA, showing significant higher electrical conductivity than the same system without ionomer.

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