

# Conducting SBS Block Copolymer–Polyaniline Blends Prepared by Mechanical Mixing

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**ABSTRACT:** Polyaniline was doped with dodecylbenzenesulfonic acid (Pani · DBSA) in an agate mortar and used as a conductive additive in melt blends with styrene–butadiene–styrene (SBS) block copolymer. These blends exhibit relatively high levels of electrical conductivity at low-weight fractions of the polyaniline complex. The melt blending process, performed in a two-roll mill or in a Haake internal mixer, increased the protonation degree of the Pani · DBSA, as indicated by X-ray photoelectron spectroscopy analysis. This result confirms the occurrence of a second doping process at high temperature. The mechanical performance decreases as the amount of Pani · DBSA in the blend increases, indicating a plasticizing effect of the DBSA. The higher temperature used in blending imparts better conductivity value but gives rise to a strong crosslinked material because of the presence of the sulfonic acid and the high extent of double bonds in the SBS compound. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 626–633, 2001

## INTRODUCTION

Electroconductive polymer–based materials with good processing and mechanical properties and tailored conductivity for a given application can be easily developed by mixing conductive polymers or fillers into conventional polymer matrices. Melt blends containing carbon black as a conductive filler have been extensively studied.<sup>1–7</sup> In contrast, the use of intrinsically conducting polymers in melt blends is not so common, prob-

ably because of the low stability of these polymers at temperatures normally required for a good melt-blend processing.

Among several conducting polymers, polyaniline is a very attractive material because of its environmental stability in the conducting form. In addition, it can be easily doped and transformed into a conductive form by protonating with strong acids.<sup>8</sup> Polyaniline doped with mineral acids such as chloridric acid or sulfuric acid is practically insoluble in most organic solvents and disperses inside an organic molten polymer matrix in a way similar to an inorganic filler. Conductivity values of the corresponding melt blends are not high because of their early thermal decomposition. The use of a special functional protonic acid as a protonating agent increases the processibility and improves solubility in common solvents and compatibility with bulk polymers

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that have a similar structure.<sup>9</sup> Examples of these systems can be found in literature, including polyaniline doped with dodecylbenzenesulfonic acid (Pani · DBSA) in melt blends with polyolefins,<sup>10–12</sup> polystyrene,<sup>13</sup> PVC,<sup>14</sup> and some thermoplastic elastomers.<sup>15</sup> Relatively high conductivity values have been achieved with these blends due to the relatively high thermal stability of this conductive form of polyaniline along with the temperature and processing conditions employed to prepare these blends not being so drastic as to promote significant thermal dedoping of the Pani · DBSA.

The use of styrene–butadiene–styrene block copolymers as matrices for conductive materials is very interesting because of its good processibility and mechanical properties. Davies et al. have reported some results on SBS block copolymers melt-blended with Pani · DBSA.<sup>15</sup> They found conductivity values on the same order as the pure conducting sample. However, the processing conditions and mechanical properties were not specified.

In this article we report on recent studies of melt blends of SBS block copolymer with Pani · DBSA. Its electrical conductivity and mechanical properties have been compared as a function of the blend composition and processing conditions. The doping degree of the conducting blend was also investigated using the X-ray photoelectronic spectroscopy (XPS) technique.

## EXPERIMENTAL

### Materials

Aniline (Ani; analytical grade, Merck (Darmstadt, Germany)) was distilled twice under vacuum and stored under nitrogen in a refrigerator. Ammonium peroxydisulfate (APS; analytical grade, Merck), chloridric acid (HCl; analytical grade, Merck), and dodecylbenzenesulfonic acid (DBSA; technical grade, Pro-Quimica do Brasil (Sao Paulo, Brazil)) were used without purification. Styrene–butadiene–styrene (SBS) block copolymer (TR-1061) was kindly supplied by Petroflex S.A. (Rio de Janeiro, Brasil). The SBS sample had the following characteristics: PBD content = 70 wt %;  $M_w = 120,000$ .

### Synthesis of Polyaniline Doped with DBSA

Polyaniline doped with HCl (Pani.HCl) was prepared by chemical oxidative polymerization of an-

iline in an aqueous acidic medium (1M HCl) with APS as an oxidant according to the procedure in the literature.<sup>16</sup> A 1:1 molar ratio of Ani:APS was employed, and the reaction was carried out at 0°C for 2 h. Deprotonation of the Pani.HCl samples was performed by stirring the Pani.HCl powder in a 0.1M aqueous solution of ammonium hydroxide for 24 h at room temperature, thus obtaining the polymer in the emeraldine base form (EB). The resulting polymer was then dried under vacuum for 48 h at room temperature. The redoping of the Pani emeraldine base with DBSA was performed by mixing the EB with DBSA in a proportion by weight of 1:3 in an agate mortar, as described in the literature.<sup>11</sup> The Pani · DBSA obtained by this method presented an electrical conductivity of  $0.92 \pm 0.2$  S/cm and a doping degree of 48 mol % related to the amount of nitrogen in the Pani chain. The doping degree was determined by gravimetry and X-ray photoelectron spectroscopy analysis (XPS).

### Blend Preparation

Blends of different compositions of SBS with Pani · DBSA were prepared in a Berstoff two-roll mill at 60°C for 10 min. The rolls were worked at two speeds: 15 and 20 rpm. SBS–Pani · DBSA blends were also prepared in a Haake internal mixer at 130°C and 60 rpm for 12 min. The blends were compression-molded at different times and temperatures under a pressure of 1.0 MPa.

### Characterization

Electrical conductivity was determined using the four-points standard method. A Keithley 614 electrometer and a Keithley 224A high-voltage supply were employed for analysis of low-resistivity samples. For high-resistivity samples a Keithley 617 electrometer was employed. The measurements were performed in compression-molded ( $4.0 \times 4.0 \times 0.5$  cm<sup>3</sup>) samples.

Stress–strain tests were performed on Instron 4204 equipment according to the ASTM 638 method at a crosshead speed of 100 mm/min.

The fracture morphology was studied by scanning electron microscopy (SEM) in a JEOL JSM-5300 microscope operating at 20 kV. The fracture surface of the sample was first microtomed in order to eliminate the signals related to the fracture phenomenon.

X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos Analytical Instru-

**Table I** Electrical Conductivity of SBS–Pani.DBSA Blends as Functions of Pani.DBSA Content and Molding Conditions

Pani.DBSA in Blend, (wt %)		Conductivity (S/cm)			
		Blend Compression-Molded at 100°C		Blend Compression-Molded at 150°C	
A <sup>a</sup>	B <sup>b</sup>	1 min	10 min	1 min	10 min
0	0	$7.3 \times 10^{-12}$	$7.3 \times 10^{-12}$	$7.3 \times 10^{-12}$	$7.3 \times 10^{-12}$
5	2.6	$0.8 \times 10^{-10}$	$2.2 \times 10^{-11}$	$0.6 \times 10^{-11}$	$1.6 \times 10^{-11}$
15	6.8	$3.5 \times 10^{-10}$	$3.7 \times 10^{-9}$	$2.3 \times 10^{-11}$	$3.9 \times 10^{-10}$
20	14.0	$2.3 \times 10^{-8}$	$7.3 \times 10^{-9}$	$4.2 \times 10^{-9}$	$1.7 \times 10^{-9}$
25	17.0	$2.4 \times 10^{-8}$	$2.2 \times 10^{-8}$	$8.9 \times 10^{-9}$	$1.9 \times 10^{-8}$
30	20.0	$2.4 \times 10^{-4}$	$1.9 \times 10^{-5}$	$1.3 \times 10^{-5}$	$0.7 \times 10^{-4}$
40	25.0	$1.9 \times 10^{-2}$	$2.7 \times 10^{-4}$	$8.5 \times 10^{-4}$	$1.4 \times 10^{-4}$
50	33.0	1.1	$7.9 \times 10^{-1}$	$4.2 \times 10^{-1}$	$6.7 \times 10^{-1}$

<sup>a</sup> Content of Pani.DBSA as a paste obtained after mixing Pani emeraldine base and DBSA in an agate mortar.

<sup>b</sup> Content of Pani.DBSA complex estimated from the doping degree corresponding to 48% of all nitrogen groups in the Pani chain, obtained from XPS measurements.

ment XSAM-800 dual-chamber spectrometer equipped with a hemispherical electron energy analyzer and a quad-anode X-ray source. The analyzer was operated in a fixed retardation ratio (FRR) mode. The energy scale calibration and the conditions of operation have been previously described.<sup>17</sup> To compensate for the surface charging effects, all binding energies were referenced to the C1s neutral carbon peak at 284.6eV. In peak synthesis the linewidth of the Gaussian peaks was maintained constant for all components in a particular spectrum.

## RESULTS AND DISCUSSION

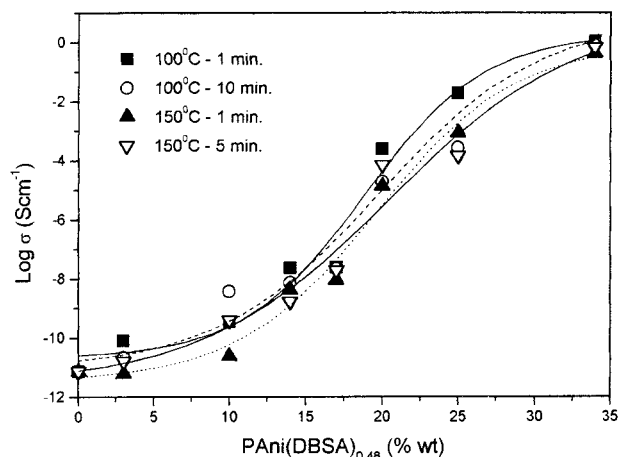
### Electrical Conductivity

The effect of the Pani · DBSA content on the electrical conductivity of SBS/Pani · DBSA blends has been studied by using compression-molded specimens obtained at different pressing conditions. For these studies, blends prepared in a two roll mill at 60°C were employed. Table I compares the electrical conductivity of blends with different compositions as a function of the molding time and temperature. As described in the Experimental section, the Pani · DBSA sample used in these blends is a mixture prepared in an agate mortar in a 1:3 proportion of Pani · DBSA by weight. According to a previous report,<sup>18</sup> this mixture is composed by Pani · DBSA complex with an excess

of DBSA, which does not participate in the doping process. The actual amount of the conducting filler, that is, the Pani · DBSA complex present in the blends, was then determined by taking into account the doping degree of Pani · DBSA, obtained by XPS measurements. This value corresponds to 48 mol % of the all nitrogen species in the Pani chain. Table I indicates the amount of Pani · DBSA sample put in the blend and the amount of the Pani · DBSA complex, which effectively acts as the conducting component.

The conductivity values of the blend containing around 33 wt % of this Pani · DBSA–conducting polymer are similar no matter what the conditions employed during the molding step. These values are close to the intrinsic conductivity of the pure Pani · DBSA used in these blends, indicating the method employed for blend preparation did not result in a thermal degradation or dedoping phenomenon of the polyaniline.

The dependence of the conductivity on the amount of Pani · DBSA is different that normally found in insulating polymer matrices loaded with conducting fillers. As observed in Figure 1, the insulator-conductor transition occurs lightly, whereas in carbon black–loaded composites, this transition is always very sharp.<sup>3</sup> As reported in the literature,<sup>19</sup> polyaniline is dispersed into an insulating matrix with a complex morphology constituted by oligomers of a very small size together with small particles and aggregates. The



**Figure 1** Electrical conductivity of SBS–Pani · DBSA blends as a function of the blend composition and compression-molding times and temperatures as indicated.

shorter chains of Pani are believed to partially dissolve in the melt, which on cooling form structures of a very fine continuous phase that acts as bridges, interconnecting the discretely dispersed Pani particles and aggregates and promoting the conductivity of the material. The authors believe this structural hierarchy composed by molecular, fibrillarlike, and discrete particle dispersions is responsible for the less sharp insulator–conductor transition in Pani-based blends.<sup>19</sup>

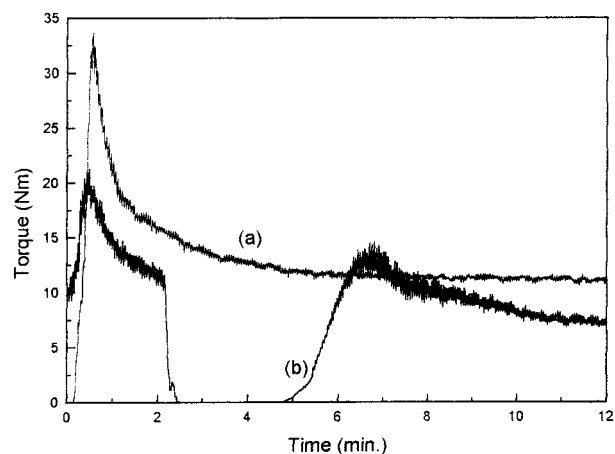
The estimated percolation threshold of Pani · DBSA concentration was found to be in the range of 7 wt %. The different times and temperatures used in the molding process did not affect the percolation threshold point but exerted a slight influence on the insulator–conductor transition. Indeed, blends compression-molded at 100°C display a more accentuated transition than those compression-molded at 150°C. This phenomenon may be related to the plasticizing effect of the DBSA, which is enhanced at higher temperatures. Therefore, small dispersed particles of Pani can be surrounded by the plasticized SBS matrix, contributing to an insulator–conductor transition in a way that's not as sharp.

An SBS–Pani · DBSA blend with a Pani · DBSA complex content corresponding to 14 wt % was also prepared in a Haake internal mixer at 130°C for 12 min in order to obtain a more uniform blend. After being compression-molded at 100°C for 1 min, this blend displayed a conductivity value in the range of  $10^{-2}$  S/cm, which is 6 orders of magnitude higher than the value observed for the same blend composition prepared in a two-roll

mill at 60°C. This result confirms the electrical stability of Pani · DBSA at 130°C under intensive mixing and suggests that a more effective melt blending operation results in a fracturing of the Pani aggregates into smaller particles and favors the formation of continuous conducting paths with a lesser amount of the conducting filler.

In spite of a very good electrical performance, the blend prepared under intensive mixing in a Haake internal mixer resulted in a powder material that could not be submitted to any mechanical testing. This feature characterizes a premature curing process during blending, which probably occurs because the butadiene component is a high proportion of the SBS block copolymer. The curing process can be observed from the torque development occurring during blending. Figure 2 illustrates the torque × time curves for SBS and its blend with 14 wt % of Pani · DBSA. The initial peak is related to the feeding torque of SBS. During the SBS processing the torque decreased with 2 min of blending and kept stable until the end of the experiment [Fig. 2, curve (a)]. The torque profile for SBS–Pani · DBSA blend [Fig. 2, curve (b)] displays a sharp decreasing at around 2 min with the addition of the Pani · DBSA component, confirming the plasticizing effect of DBSA. After around 4.8 min, the torque value started to increase sharply and reached a maximum at around 6.5 min and then started to decrease. This behavior indicates the curing process occurs with the formation of a strong network, which contributes to an increasing of the viscosity of the medium.

Evidence of the formation of a crosslinked material has been also provided by extraction exper-



**Figure 2** Torque versus time curves of (a) SBS block copolymer and (b) its blend with 14 wt % of Pani · DBSA complex, obtained by blending in a Haake internal mixer at 130°C for 12 min at 60 rpm.

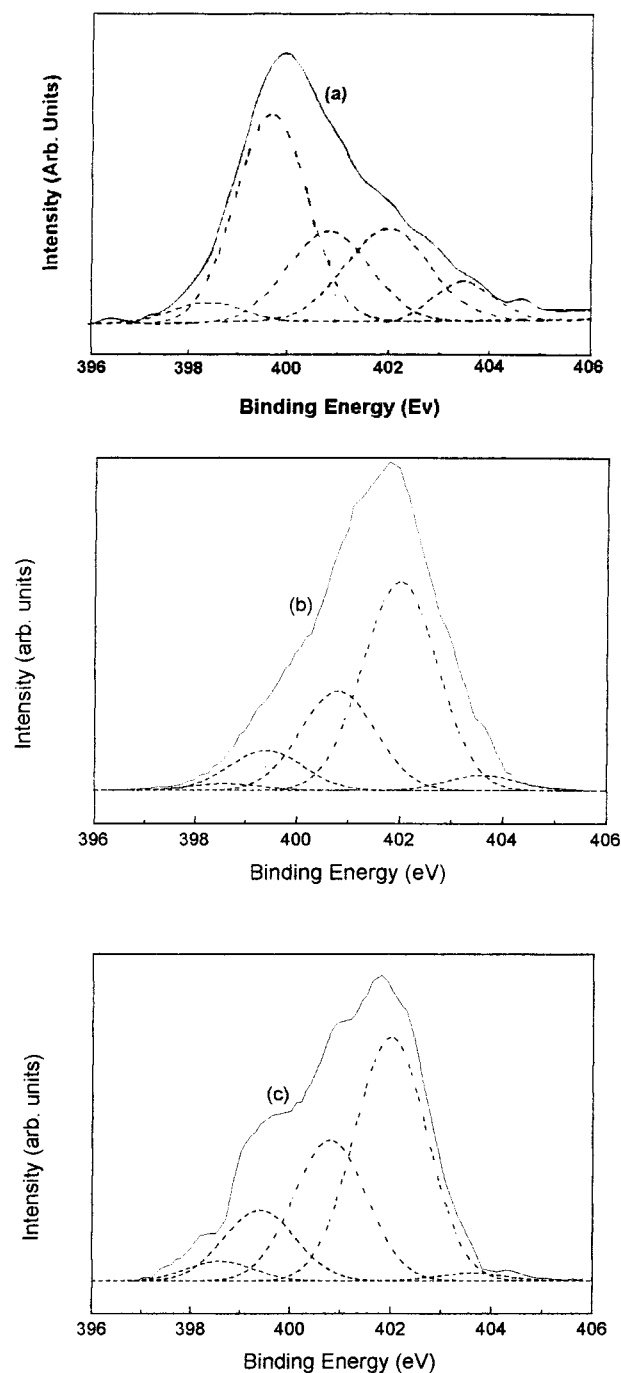
iments with toluene. Indeed, blends prepared in a two-roll mill at 60°C were almost completely dissolved in toluene, indicating no curing process during blending or molding. On the other hand, the powder material obtained from mixing SBS and Pani · DBSA in an internal mixer at 130°C was completely insoluble in toluene, confirming the presence of a vulcanized system composed of both SBS and Pani · DBSA.

### XPS Analysis

The high conductivity values observed for SBS–Pani · DBSA blends may be attributed to the occurrence of a “thermal doping” process. This process has been reported in the literature and results in an increasing of both conductivity and doping degree by mixing Pani and DBSA at high temperature without using auxiliary solvents.<sup>13,20</sup> In order to verify if a second doping process of the Pani component has been performed during the melt blending, we decided to utilize XPS analysis. This method constitutes a powerful tool for characterizing the doping degree of conducting polyaniline.<sup>21</sup> From the characteristic binding energies (BEs) of the photoelectron, the elements involved can be identified, and the peak intensity can be directly related to the atomic concentration in the sample surface. In addition, the various intrinsic redox states of Pani as well the different neutral and positive nitrogen species can be quantified from the properly curve-fitted N1s core-level spectrum.

The N1s core-level spectra corresponding to the Pani · DBSA used in the blends and to the SBS–Pani · DBSA blends prepared in a two-roll mill or in a Haake internal mixer are shown in Figure 3. The Pani · DBSA sample exhibits five peaks related to the nitrogen components [Fig. 3(a)]. The peaks with binding energies (BEs) at about 398.2 eV and 399.4 eV are related to the imine and amine groups, respectively. The three peaks with binding energies at 400.8, 402.0, and 403.5 eV can be attributed to the positively charged nitrogen, according to the literature.<sup>21</sup> The proportion of these peaks was found to be 0.48, which corresponds to the protonation degree. The proportion of each nitrogen component indicates that the protonation of imine groups is almost complete, as expected for an emeraldine salt with good conducting property.

The spectra of the blends reveal the presence of a higher amount of positively charged nitrogen as compared to that of pure Pani · DBSA. Almost all



**Figure 3** XPS N1s core-level spectra of (a) Pani · DBSA obtained by a redoping process in an agate mortar and their blends with SBS (14 wt % of Pani · DBSA) prepared, (b) in a two-roll mill at 60°C, and (c) in a Haake internal mixer at 130°C.

the imine groups have been protonated since the peak at 398.2 eV is very small. Table II summarizes the proportions of the various nitrogen species for the SBS–Pani · DBSA blends shown in Figure 3.

**Table II** Distribution of Nitrogen Species on Surface of SBS-Pani.DBSA Blends

	Proportion of		
	—NH—	=N—	N <sup>+</sup>
Pani.DBSA	0.47	0.07	0.48
SBS-Pani.DBSA blend in a two-roll mill at 60°C	0.11	0.02	0.87
SBS-Pani.DBSA blend in a Haake internal mixer at 130°C	0.15	0.04	0.82

The proportions of positively charged nitrogen for both blends were higher than that corresponding to the Pani · DBSA sample, indicating an additional protonation during the melt blending. The amine nitrogen decreased substantially below 0.5, suggesting that the amine units were also protonated. Similar results have been also reported by Kang et al. in their studies concerning the protonation degree of Pani doped with H<sub>2</sub>SO<sub>4</sub>.<sup>22</sup>

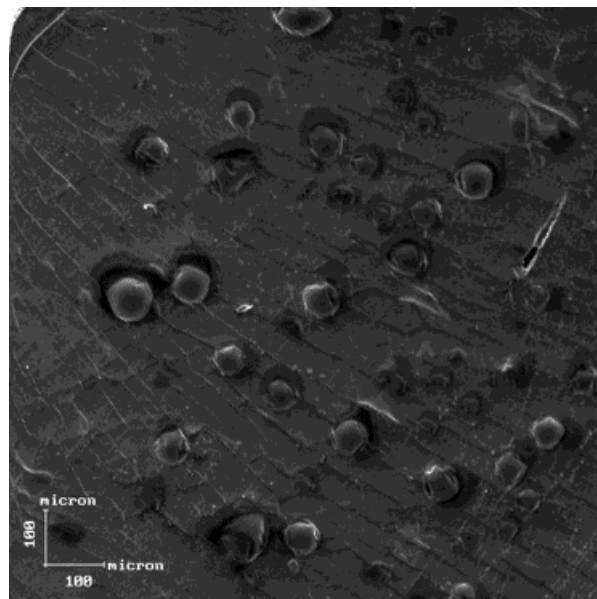
It is important to emphasize that the blend prepared in a two-roll mill displays a higher doping degree, as indicated by the higher amount of the positively charged nitrogen, in spite of its lower conductivity value as compared to the blend prepared in a Haake internal mixer. This behavior suggests that the higher conductivity of the blend obtained in the latter method must be associated with a better dispersion of the components and not with the protonation degree.

### Morphological Aspect

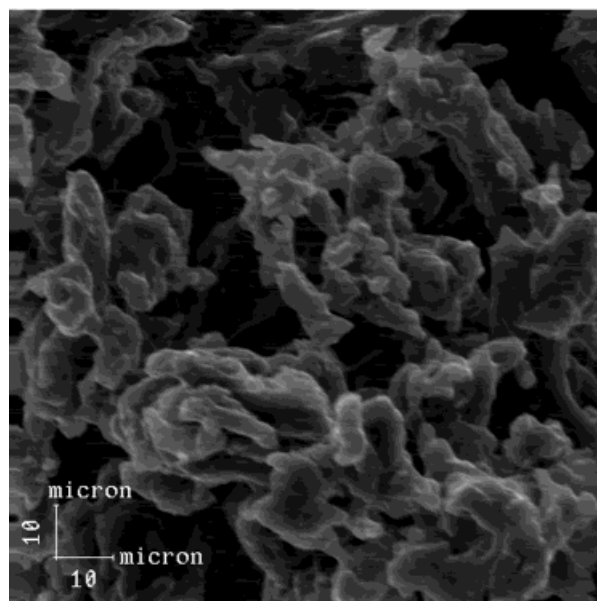
Figure 4 illustrates the micrographs of SBS-Pani · DBSA blends containing 14 wt % of the conducting component. The blend prepared in a two-roll mill [Fig. 4(a)] is characterized by a morphology constituted by large aggregates of Pani · DBSA dispersed into the SBS matrix. In spite of the chemical affinity of the hydrophobic chain of DBSA with the SBS matrix, the SBS and Pani · DBSA are incompatible and grossly phase separated. In addition, the mixing conditions in the two-roll mill (low temperature and low shear forces) could not break these aggregates into small particles.

The micrograph of the powder obtained by blending SBS and Pani · DBSA in a Haake internal mixer is shown in Figure 4(b). As discussed before, this powder is highly crosslinked. In this

case, the large domains of the Pani · DBSA aggregates are not present. A uniform and porous network can be observed, indicating this blend achieved a high level of dispersion. The higher level of molecular mixing and the formation of the crosslinked network, which both developed during this blend condition, restricts the conforma-



(a)



(b)

**Figure 4** SEM micrographs of SBS blends containing 14 wt % of Pani · DBSA complex and prepared (a) in a two-roll mill at 60°C and (b) in a Haake internal mixer at 130°C.

**Table III Mechanical Properties of SBS–Pani.DBSA Blends Prepared in a Two-Roll Mill at 60°C and Compression-Molded at 100°C for 1 Min, as a Function of Conductive Additive Content**

Pani.DBSA <sub>0,48</sub> (wt %)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)
0.0	21.0	5200
2.6	10.1	3900
6.8	10.1	4000
17.0	9.5	3900
25.0	2.0	900
33.0	0,5	60

tion mobility of the Pani chain and can explain the improved conductivity performance.

### Mechanical Properties

SBS–Pani · DBSA blends prepared at 60°C and compression-molded at 100°C for 1 min were submitted to stress–strain tests, and the results are presented in Table III. The presence of as low as 2.5 wt % of Pani · DBSA in the blend resulted in a significant decrease of both ultimate tensile strength and elongation at break as compared to the pure SBS sample. This behavior was more accentuated for blends containing a higher amount of Pani · DBSA. In spite of the good compatibility between the blend components promoted by the presence of the aliphatic chain of the DBSA, the mechanical performance was not very good, probably because of the plasticizing effect of the Pani · DBSA, which decreases the mechanical strength of the material.

### CONCLUSIONS

The results presented in this article demonstrate that melt blends of Pani · DBSA in SBS matrix present good electrical conductivity, reaching values as high as 1 S/cm with around 33 wt % of the conductive additive in the blend. The conductivity value is enhanced when the blend is performed at a higher temperature under intensive mixing in a Haake internal mixer. In this case, the higher shear forces increase the fracturing of the original aggregates and improve the level of dispersion of the Pani · DBSA particles within the SBS matrix. Unfortunately, this latter procedure also results

in a highly crosslinked material, probably because of the high concentration of the sulfonic acid and of the high extent of double bonds in the SBS matrix.

The melt processing of Pani · DBSA inside the SBS matrix promotes an additional protonation level of the Pani chains and consequently an improvement of the conductivity. Indeed, an increasing of the doping degree with the melt processing toward values corresponding to 82%–90% was observed from XPS analysis. These results indicate that the amine groups of the Pani chain have been also protonated by DBSA. This phenomenon, known as the “thermal doping” process, was also reported in the literature for the preparation of Pani · DBSA complex<sup>13</sup> and indicates a sufficient thermal stability of Pani · DBSA at temperatures as high as 60°C and 130°C.

The mechanical performance of the conductive blends was not so good when compared to pure SBS. Both tensile strength and elongation at break decreased with the addition of the conductive component, probably because of the presence of DBSA as the counteranion, which acted as both protonating and plasticizing agent. The plasticizing effect is known to decrease tensile strength.

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