

# Conductive Polyaniline–Polychloroprene Blends

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**ABSTRACT:** The electrical conductivity of polychloroprene (CR)/polyaniline (Pani) blends prepared by bulk and solution processes were investigated. Pani doped with HCl (Pani · HCl) and *p*-toluenesulfonic acid (Pani · TSA) were employed in vulcanized blends obtained by the bulk process. These blends showed an increase in the conductivity only for blend composition of CR/Pani = 50:50 wt %. At this composition, blends with Pani · HCl and Pani · pTSA presented conductivity values of  $10^{-9}$  and  $10^{-10}$  S · cm<sup>-1</sup>, respectively. CR/Pani · HCl blend films prepared by the solution process displayed surface conductivity values of  $10^{-4}$  S · cm<sup>-1</sup> with as low as 10–15 wt % of Pani · HCl. Surface analysis of these blends by X-ray photoelectron spectroscopy indicated no traces of the conductive additive. The surface composition was found to be exclusively constituted of CR. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1543–1549, 1998

**Key words:** polychloroprene; polyaniline; conductive blends

## INTRODUCTION

Electrically conductive rubber compounds have found important applications and are normally produced by blending conventional rubbers with conductive carbon black as a filler.<sup>1,2</sup> Nevertheless, the use of intrinsically conducting polymers, such as polypyrrole (PPy) and polyaniline (Pani), as a blend component may be somewhat attractive. Depending on the preparation procedure, these conducting polymers display higher electrical conductivity than carbon black in addition to electrochromic properties, which are important requirements for several technological applica-

tions in electronic, optical, biological, and other fields.<sup>3,4</sup> A few examples of conducting elastomer blends based on polyaniline have been reported in the literature.<sup>5–8</sup> High electrical conductivity has been achieved by melt blending Pani doped with dodecylbenzenesulfonic acid and SBS rubber<sup>5</sup> or its hydrogenated product.<sup>6</sup> Nitrilic rubber was also cold mixed with Pani doped with tetra-propylbenzenesulfonic acid in the presence of a vulcanization system.<sup>7</sup> After curing at 145°C, this blend has shown a bulk conductivity of about  $10^{-9}$  S · cm<sup>-1</sup> with 100 phr of the conducting polymer. EVA elastomers have also been mixed with *N*-alkylated Pani in a solution process followed by casting at room temperature.<sup>8</sup> The conductive blends were obtained by doping the blends in a methanesulfonic acid/propanol media.

The aim of this work is to investigate the electrical conductivity of polychloroprene (CR)/Pani blends prepared by mixing the components in solution or in bulk. The bulk process involves the

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cold mixing of Pani in a CR matrix containing the appropriated curatives for subsequent vulcanization by compression-molding at 150°C. It is well reported that the type of dopant strongly influences the thermal stability and conductivity of Pani.<sup>9,10</sup> Pani doped with low molecular weight dopants such as HCl shows a decreasing in the conductivity at high temperature ( $\approx 100^\circ\text{C}$ ) probably because of a dedoping process. In contrast, bulky dopants such as *p*-toluenesulfonic acid (TSA) and dodecylbenzenesulfonic acid (DBSA) provide more thermal stability in the conducting Pani. Therefore, for the solution process (at room temperature) we employed Pani doped with HCl (Pani · HCl), whereas for the bulk process, Pani doped with HCl (Pani · HCl) and with *p*-toluenesulfonic acid (Pani · TSA) were used to compare the results.

## EXPERIMENTAL

### Materials

Aniline (analytical grade Merck) was distilled twice under reduced pressure. CR [Neoprene W; density = 0.87 g/cm<sup>3</sup>;  $M_w = 460,000$ ] was generously supplied by DuPont do Brazil S.A. All reagents were of analytical grade and used without purification.

### Synthesis of Conductive Polyaniline

Pani hydrochloride (Pani · HCl) powder was synthesized by the oxidative polymerization of aniline in 1M aqueous HCl solution using ammonium persulfate as the oxidant, according to the literature.<sup>11</sup> A typical procedure involves a dropwise addition of 500-mL solution containing 0.33 mol of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in 1M HCl solution into a cooled ( $-5^\circ\text{C}$ ) 500-mL solution of aniline (0.22 mol) in 1M HCl solution, under stirring. The Pani · HCl thus prepared, presented a conversion of 60%.

The Pani · HCl powder was converted into Pani base (an emeraldine base—EB) by treatment with 0.1M aqueous NH<sub>4</sub>OH solution for 24 h under stirring, followed by drying under dynamic vacuum. The polymer exhibited number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of 15,000 and 58,000 g/mol, respectively, as determined by size exclusion chromatography (SEC) in 0.01M LiBr- *N*-methylpyrrolidone (NMP) with respect to polystyrene standards.

**Table I Basic Recipe for the CR/Pani Vulcanized Blends**

Polymer (CR/Pani)	100
MgO	4
ZnO	5
2-Mercaptoimidazoline (accelerator)	0.5
Phenyl- $\beta$ naphtylamine (PBN)	1
Tetramethylthiuram disulfide (TMTD)	0.5

The EB was purified by continuous extraction with tetrahydrofuran (THF), dried, and doped with the protonic acids, HCl and *p*-toluenesulfonic acid (TSA) by stirring the EB in a 1.0-M aqueous solution of the corresponding acids during 24 h at room temperature.

### Preparation of Conductive Composites with Polychloroprene

#### Bulk Process

CR was blended with Pani · HCl, Pani · TSA, or EB in various proportions on a two-roll mill at 50°C and a rotor speed of 15 rpm. The basic recipe, including the curatives, is given in Table I. The blends were compression molded for 30 min at 150°C and 6.7 MPa, obtaining vulcanized test specimens of 40 × 40 × 1 mm. The curing time was determined from a Monsanto Rheometer testing at 150°C, using the rubber formulation without Pani.

#### Solution Process

Appropriate amounts of Pani · HCl powder were mixed with a polychloroprene solution in CHCl<sub>3</sub> under stirring for a week to assure good dispersions. The polymers concentration was kept at 15 wt %. Then, films were cast by slow evaporation of the solvent at room temperature followed by drying at vacuum for 24 h.

Mixtures of the EB and CR were also obtained by stirring a 15 wt % solution of both components in NMP for a week at room temperature, followed by casting the solution at 100°C for 24 h. Films were also casted from CHCl<sub>3</sub> solution at room temperature. The films obtained by the solution process were 140–280  $\mu\text{m}$  in thickness.

#### Doping of the Blends

EB/CR blends were doped by dipping the film sample into a 1M HCl aqueous solution for 48 h or by exposing the film to HCl vapors for 8 h. The

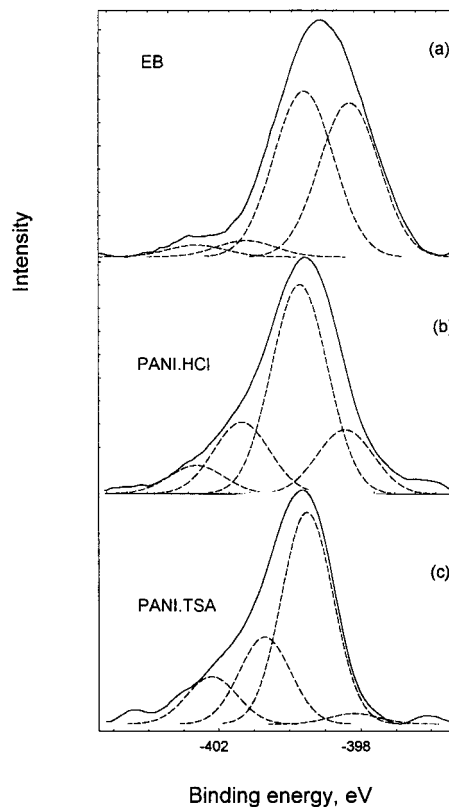
latter method consisted of putting a specimen (40 × 40 mm) into a glass flask containing a small beaker with NaCl and equipped with a dropping funnel containing concentrated H<sub>2</sub>SO<sub>4</sub>. The flask atmosphere was filled with HCl vapor by dropping H<sub>2</sub>SO<sub>4</sub> into NaCl located inside the flask. The doped films were washed several times with water and dried under vacuum.

### Characterization

The bulk electrical conductivity, used in vulcanized blends, was measured with a Keithley Electrometer 617 using contacts in sandwich configuration. The electrode area was 9 cm<sup>2</sup>. Silver paint was used between samples and electrodes so as to minimize the contact resistance. Surface electrical conductivity was measured by using a four-point probe technique.

Scanning electronic microscopy (SEM) was performed on a JEOL model JSM-5300. The sample surface was covered with gold before the analysis.

XPS spectra were taken on a Kratos Analytical Instruments 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 of the instrument was calibrated by setting Cu2p = 932.7, CuLMN = 918.7, Ag3d = 368.3, Au4f = 84., Ni(E<sub>Fermi</sub>) = 0 eV. The spectra were acquired using a MgK excitation. The X-ray gun was operated under mild conditions (75 W, 15 kV, 5mA), which did not produce perceptible radiation damage to the samples. The pressure in the analysis chamber was maintained at 10<sup>-9</sup> Torr. The samples were mounted onto a sample holder using a double-sided adhesive tape. Quantitative analysis of the sample surface was made based on the integral peak intensities as described elsewhere.<sup>12</sup> To make the measured binding energies comparable with earlier data,<sup>13-15</sup> all core-level spectra were referenced to the C1s neutral carbon peak set at 284.6 eV as in the earlier work.<sup>13,15</sup> The N1s and Cl2p signals were decomposed into individual components by a least-squares fitting procedure using, respectively, a Gaussian line shape and a natural Cl2p line profile as observed in poly(chloroprene). In fitting the N1s line, the positions of the components due to the amine and imine nitrogens were kept fixed at their positions found in EB.



**Figure 1** XPS profiles of (a) emeraldine base, (b) Pani · HCl, and (c) Pani · TSA.

## RESULTS AND DISCUSSION

### Characterization of Pani Samples Used in the Blends

The protonated Pani samples used in this study were obtained by treatment of the EB with the corresponding protonic acids. The conductivity of Pani · HCl remained around 10<sup>-2</sup> S · cm<sup>-1</sup>, whereas those doped with TSA displayed conductivity value in the range of 10<sup>-3</sup> S · cm<sup>-1</sup>. The efficiency of the EB protonation has been investigated by X-ray photoelectron spectroscopy (XPS). The XPS spectra of EB are typical of incompletely deprotonated polyemeraldine hydrochloride.<sup>13</sup> The N1s core-level of EB [Fig. 1(a)] comprises two major spectral features, at 399.3 and 398.1 eV, due to the amine (—NH—), and imine (=N—) nitrogen atoms, respectively. The presence of residual protonated units is evidenced by a high binding energy tail due to positively charged radical cationic nitrogen sites. The distribution of nitrogen atoms among the various chemical states can be appreciated from Table II, where the

**Table II** XPS Characterization Data for Undoped and Doped PANI

Samples	Surface Composition (%)								
	C	O	N	Components of N1s				Cl	S
				=N—	—NH—	N <sub>1</sub> <sup>+</sup>	N <sub>2</sub> <sup>+</sup>		
EB	85	3.5	11	41	51	6	0.2	0.4	
Pani · HCl	82	6.4	8.4	13	64	18	5.6	3.6	
Pani · TSA	77	13	5.6	1.0	58	30	10		4.2

high energy species are represented by a superposition of two Gaussians centered at 400.6 and 402.0 eV (components N<sub>1</sub><sup>+</sup> and N<sub>2</sub><sup>+</sup>, respectively). The proportion of the amine nitrogens is, as expected, close to 50%, while about one-fifth of the imine species remains in the protonated form. The incompleteness deprotonation is also evidenced by the presence of residual chlorine (see Table II). The atomic concentration of chlorine (0.4%) is perceptibly lower than that of cationic nitrogen (6%), which can be attributed to a low accuracy of quantifying trace amounts of these components.

The N1s spectrum of Pani · HCl [Fig. 1(b)] is composed of the same features as observed in EB, although their proportions change substantially due to protonation of imine structures. The content of the —N= feature falls to 13%, while that of the charged nitrogen atoms increases to 24% (see Table II). This latter value can well be used as a quantitative measure for the doping level. The reduced surface doping level of the Pani · HCl samples is most likely associated to the loss of chlorine under ultra high vacuum conditions of the XPS experiments.<sup>16</sup>

As in the case of EB, the spectral features associated to positive nitrogen species occupy an extended range, so that at least two Gaussians should be taken to fit the high binding energy wing of the N1s line. This is indicative of inhomogeneity in the environment of the positively charged nitrogen atoms, which may be due to steric effects.<sup>14</sup>

It can be seen from Table II that the protonation brings about an appreciable increase in the content of the amine nitrogens. That is, some of the initial imines of EB have been converted into the amine structure, probably through the 1,4-addition of HCl to the quinoid units.<sup>13</sup> The presence of covalent chlorine in the Pani · HCl samples is supported by the shape of the Cl2p line,

which contains, aside from the Cl<sup>-</sup> feature at 196.8 eV, an appreciable component at about 200 eV characteristic of the covalent Cl—C bond.<sup>13</sup> The peak synthesis of the Cl2p line reveals also a comparatively weak component at 198.2 eV whose chemical nature is unclear. A quantitative analysis gives 2.5% Cl<sup>-</sup>, which markedly exceeds the content of positively charged nitrogen sites. A likely reason is the presence of free HCl in the surface layers of the Pani · HC; samples.

The protonation of EB by TSA results in a substantially higher surface doping level compared to that observed with HCl [Fig. 1(c)]. This is not surprising, because TSA has much higher anion and should, therefore, be expected to possess a higher stability towards vacuum. As seen from Table II and Figure 1, the imine component of the N1s line practically disappears, whereas the proportion of the cationic nitrogen species increases to 35–40%. An unexpected result, which has not yet found a plausible explanation, is an appreciable increase in the content of the amine nitrogens relative to that in EB. It is not unlikely that the doping of Pani with TSA not only leads to the transfer of photoelectron emission intensity from the imine to cationic components, but also produces slight shifts of the imine and amine spectral features. Were the position of the —NH— and —N= features allowed to vary in fitting the N1s line profile, the quantification results would be different and would hopefully show a better stability of the proportion of the amine structure. Unfortunately, due to a low intensity of the N1s signal, the quality of the N1s line profile was not good enough to treat all the fitting parameters as freely adjustable. The low accuracy of quantification is also a likely reason of why the content of sulfur in the Pani · TSA complex appreciably exceeds the total content of the cationic nitrogen atoms. Another likely reason is the presence of

**Table III Electrical Conductivity of CR/Pani Vulcanized Blends**

CR/Pani Blend Composition (phr)	Volume Conductivity ( $S \cdot cm^{-1}$ )	
	Pani · HCl	Pani · TSA
100 : 0	$10^{-12}$	$10^{-12}$
90 : 10	$10^{-12}$	$10^{-12}$
80 : 20	$10^{-11}$	$10^{-11}$
70 : 30	$10^{-11}$	$10^{-11}$
60 : 40	$10^{-11}$	$10^{-11}$
50 : 50	$10^{-9}$	$10^{-10}$

unreacted free TSA in the surface layers of the doped Pani.

### Blends Prepared by Bulk Process

Table III presents the results concerning the bulk conductivity of CR/Pani · HCl and CR/Pani · TSA blends. An increase in the conductivity was only observed at high Pani content (CR/Pani = 50:50 wt %). In spite of the relatively high conductivity of the Pani · HCl or Pani · TSA samples, the bulk conductivity of the blends was very low ( $10^{-9}$  and  $10^{-10} S \cdot cm^{-1}$ , respectively). The surface conductivity values were similar to those observed for the bulk conductivity, indicating an homogeneous distribution of Pani in the samples. Similar values were reported in the literature for nitrilic rubber/Pani blends.<sup>7</sup> In spite of the higher thermal stability of Pani doped with sulfonic acids, the vulcanized blends containing this component presented a lower conductivity. These results may be attributed to the influence of the vulcanization system on the structure of the doped Pani.

Attempts have been made to increase the conductivity of vulcanized CR/Pani blends by using the EB in the blend formulation and subjecting the CR/EB blends to redoping with an HCl in solution or vapor. This procedure was chosen due to the higher thermal stability of EB compared to the protonated Pani.<sup>9</sup> Therefore, the problems related to the decomposition and dedoping of Pani · HCl, which could take place during the vulcanization process at  $150^{\circ}C$ , should be minimized. The compression-molded specimens were doped using the procedure described in the experimental part. Table IV shows the results concerning the bulk conductivity of the EB/CR = 50:50 wt % blends before doping and after the exposure to HCl in solution or in vapor phase. The doping by

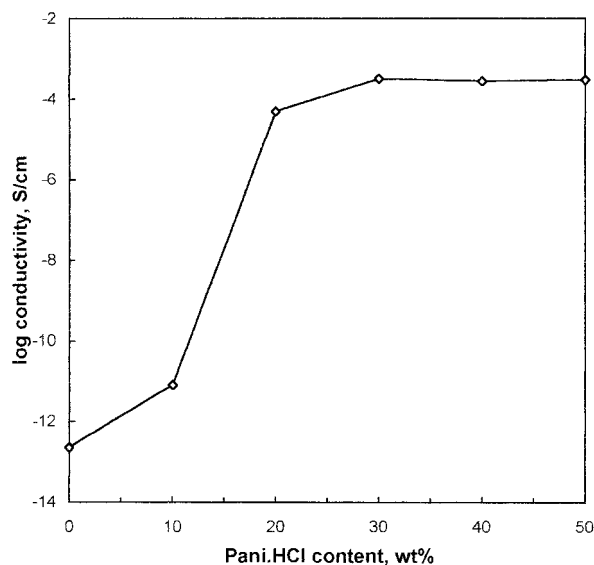
**Table IV Electrical Properties of Vulcanized CR/EB (50 : 50 wt %) Blends Submitted to a Postdoping Process**

Postdoping Conditions	Volumetric Conductivity, ( $S \cdot cm^{-1}$ )
Pure CR/EB blend	$10^{-12}$
CR/Pani · HCl blend	$10^{-9}$
Postdoped in HCl solution	$10^{-9}$
Postdoped in HCl vapor	$10^{-8}$

immersing the specimen into a 1.0M HCl aqueous solution for 48 h resulted in a conductivity value close to that reached in the CR/Pani · HCl blend of the same composition ( $10^{-9} S \cdot cm^{-1}$ ). The exposure to HCl vapor was more efficient. Indeed, a little higher conductivity ( $10^{-8} S \cdot cm^{-1}$ ) was achieved after an 8 h exposure. These values are, however, low.

### Blends Prepared by a Solution Process

CR/Pani · HCl film blends prepared by a solution process were submitted to surface conductivity analysis. Figure 2 illustrates the dependence of the conductivity with the Pani · HCl concentration. The Pani · HCl sample employed in these experiments was the same as that one used in the



**Figure 2** Effect of the Pani · HCl content on the surface electrical conductivity of CR/Pani · HCl blends prepared by a solution process.

**Table V** Electrical Conductivity of CR/EB (50 : 50 wt %) Film Blends, Prepared in a Solution Process and Submitted to a Postdoping Process

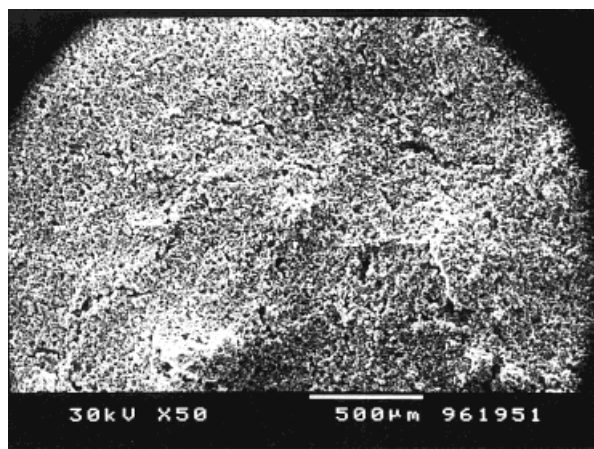
Postdoping Conditions	Surface Conductivity ( $S \cdot cm^{-1}$ )	
	Films from $CHCl_3$ Solution	Films from NMP Solution
Pure CR/EB blend	$6 \times 10^{-8}$	$2 \times 10^{-9}$
CR/Pani · HCl blend	$4 \times 10^{-4}$	—
CR/EB blend postdoped in HCl solution	$4 \times 10^{-4}$	$2 \times 10^{-5}$
CR/EB blend postdoped in HCl vapor	$2 \times 10^{-4}$	$2 \times 10^{-5}$

blends prepared by bulk process (roll milling), but the electrical conductivities were quite different. Indeed, the films obtained from solution process presented a defined insulator–conductor transition at a Pani · HCl concentration in the range of 10–15 wt % and limit values of conductivity as high as  $10^{-4} S \cdot cm^{-1}$ .

Conductive CR/Pani (50:50 wt %) blends were also obtained by exposing the EB/CR films to HCl vapor for 8 h. As indicated in Table V, the surface conductivity of the doped EB/CR film obtained from  $CHCl_3$  solution is similar to that one observed in the Pani · HCl/CR system. The film cast from the NMP solution displayed lower conductivity, probably due to the presence of a residual amount of NMP in the sample.

#### Surface Analysis of CR/ Pani · HCl Blends

The surface-scanning electronic microscopy of CR/Pani · HCl (50:50 wt %) film blend of Figure 3 presents a continuous layer of Pani · HCl with a



**Figure 3** SEM analysis of CR/Pani · HCl (50:50 wt %) film surface obtained by a solution process.

granular structure and high porosity, suggesting the presence of Pani · HCl at the surface.

The X-ray photoelectron spectroscopy (XPS) was used for the surface composition analysis of the blends prepared by both bulk and solution process. The surface of all Pani/CR blends studied in this work was composed of pure CR constituent, as evidenced by the complete absence of the N1s signal. An additional evidence was provided by the Cl2p core level, which had a single-component structure and a maximum at 200.4 eV characteristic of the covalent chlorine. No traces of anionic chlorine were observed. The lack of Pani · HCl in the surface layers of the blends is not unusual of polymer blends, and may well result from the surface segregation of CR.

#### CONCLUSIONS

Blends containing polychloroprene and conducting polyaniline have been prepared in bulk and in solution. For the bulk process, Pani doped with HCl or *p*-toluenesulfonic acid were employed. In spite of the lower thermal stability of Pani · HCl, the CR/Pani blends presented a little better electrical performance when this doped Pani was used as the conducting component.

Blends prepared from solution displayed better surface conductivity values at lower Pani concentration than those obtained from the bulk process. However, these values were lower than that found in the pure Pani · HCl sample. The surface observation by SEM indicated the presence of Pani · HCl close to the film surface.

In spite of a considerable difference in the surface conductivities of the blends prepared from solution or by rollmilling, the surface compositions of both blends, obtained by XPS analysis, constituted of CR rubber. A probable explanation

for the difference in the conductivity may be due to the process used for the blend preparation. In the bulk process (roll milling), the sample is submitted to shear forces that could break the Pani aggregates, giving rise to well-dispersed particles encapsulated by the CR matrix. Therefore, the conducting pathway is hardly formed. When the blend is prepared by casting, the Pani aggregates are not destroyed. The conducting particle size is larger, favoring the touching of each one and consequently the conducting phenomenon.

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