Conducting Elastomer Blends Based on Nitrile Rubber and Pani.DBSA

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Summary: Electrically conductive elastomer blends based on polyaniline-dodecylbenzene sulfonic acid (Pani.DBSA) and nitrile rubber (NBR) were prepared by polymerization of aniline in the presence of NBR, using a direct, one-step in situ emulsion polymerization method. At the same PAni content, the conductivity of the in situ emulsion-polymerized blends is higher than that of blends produced by mechanical mixing of both components. In addition, a morphology with the presence of PAni in the form of microtubules was achieved by the *in situ* process. Stronger interaction between the components were also confirmed by Rheological processing analysis (RPA). The vulcanization process decreases the conductivity of the blends prepared by both methods. The in situ polymerized blends also display higher tensile strength and also higher crosslink density

Keywords: conductive composite; electrical conductivity; emulsion polymerization; nitrile rubber; polyaniline; Raman spectroscopy; RPA

Introduction

Incorporation of conductive polymers into a hosting elastomer matrix constitutes a good approach for the development of special materials which combine electronic conductivity with elasticity and good mechanical properties imparted by the insulating rubber matrix.[1] Amongst several intrinsic conductive polymers, polyaniline (PAni) has been extensively studied because of its good conductivity, stability, easy synthesis and low-cost reagents.[2] Some examples of conducting elastomer blends based on polyaniline and unsaturated rubber have been reported in literature and involve polychloroprene,[3] ethylene-propylene-diene (EPDM),[4–9] styrene-butadiene (SBR) rubber,[7] and nitrile rubber (NBR).[7,10] Most of these blends have been prepared by mechanical mixing and displayed low values of conductivity, in the range of 10^{-6} to 10^{-9} $S \cdot cm^{-1}$.

The inverted emulsion polymerization of aniline (Ani) in organic medium in the presence of dodecylbenzene sulfonic acid (DBSA), reported by Osterholm et al,[11] opened new possibilities for the preparation of conducting composites in one step via in situ emulsion polymerization. This technique involves the previous dissolution of the hosting isolating polymer in an organic medium, together with aniline and the protonic acid. Normally DBSA is employed as the protonating agent because it can also act as emulsifier. The polymerization is carried out by adding dropwise the oxidant aqueous solution into the reaction medium. Several conducting polymer blends were prepared by this technique,[12–18] but none of them has employed vulcanizable unsaturated rubber as the hosting matrix. To our knowledge, the only composite involving unsaturated rubber was recently reported by Xie et al.[19] They have employed zinc sulfonated EPDM

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ionomer, which behaves as a thermoplastic elastomer and can be processed as plastic without vulcanization.

The aim of this paper is to compare the electrical, mechanical and rheological behaviors of blends constituted by NBR and polyaniline doped with DBSA (Pani.DBSA), prepared by different methods: mechanical mixing and in situ emulsion polymerization method. The effect of the vulcanization process on the electrical conductivity of both systems was also investigated.

Experimental

Materials

Aniline (Merck, p.a.), DBSA (Pro-Quimil, commercial grade) and ammonium persulfate (APS) (Merck, p.a.) were used without purification. Toluene (Vetec, commercial grade) was distilled. NBR (acrylonitrile content = 33%; average number molecular weight = 50,000) was kindly supplied by Petroflex Ind. Com. (Brazil).

Preparation of PAni.DBSA

PAni.DBSA was synthesized by emulsion polymerization of aniline, according to the method developed by Osterholm et al.[11] In a typical procedure, 0.1 mol of aniline and 0.15 mol of DBSA were dissolved in 1000 mL toluene and cooled in an ice bath. Then, a solution containing 0.04 mol of APS in 40 mL of distilled water was added dropwise. The total polymerization time was 24h. The polymerization was terminated by pouring the resulting emulsion into methanol. The dark green powder of PAni.DBSA was recovered, filtered, washed several times with methanol and dried under vacuum for 48 h at room temperature.

Blend Preparation

The physical blends were prepared by blending different amounts of NBR and PAni.DBSA in a two roll mill at 80 °C for 5 min. After homogenization, part of the non vulcanized blends was compression-molded at 160 °C for 10 min. The other part was compounded with the curing agents in the following order: zinc oxide (5.0 phr), stearic acid (0.5 phr), , sulfur (S) (0.3 phr) and CBS (2.0 phr).

The preparation of NBR/PAni.DBSA blends by the in situ emulsion polymerization followed the same procedure as that used for the synthesis of PAni.DBSA, by using the NBR previously dissolved in toluene. Different NBR/Ani ratios were used to obtain blends with different amounts of PAni.DBSA. After the polymerization, the emulsion of NBR/PAni.DBSA was precipitated by pouring into methanol. The dark green sediment was filtered, washed with methanol and vacuum dried for 48 h. The conversion was determined gravimetrically. From the amount of the Pani.DBSA determined gravimetrically, it was possible to calculate the proportion of polyaniline in the blend.

Part of the blend was compression-molded at 160 °C for 10 min and the other part was compounded with the curing agents as previously indicated.

Rheometric Measurements and Testing

The curing characteristics of the different mixtures were determined by using an oscillating disk rheometer (ODR) (Tecnologia Industrial), operating at 160 °C and 1° arc, following the ASTM D 2084-81 method. The specimens for mechanical testing were vulcanized at 160 °C and 6.7 MPa in a hydraulic press up to the optimum curing time (the time corresponding to 90% of the maximum torque,t_{90}). Then, dumbbell shaped tensile test specimens (ASTM 638- testing number 5) were punched out of the compression molded sheets. Tensile testing was performed on an Instron 4204 Universal Testing Machine, at a crosshead speed of 100 mm.min^{-1}.

Characterization

The surface electrical conductivity was measured in a Keithley 6517A electrometer, using the conventional four points method using a home made four probes

Table 1.
Electrical properties of non vulcanized NBR/PAni.DBSA blends

Blend composition (wt%)		surface conductivity (S/cm)	
NBR	PAni.DBSA	emulsion polymerization	mechanical mixing
100	0	1.4×10^{-9}	1.4×10^{-9}
94	6	0.8×10^{-7}	0.3×10^{-8}
85	15	0.7×10^{-4}	0.1×10^{-7}
73	27	3.0×10^{-3}	2.5×10^{-7}
52	48	2.0×10^{-2}	5.0×10^{-4}
38	62	2.0×10^{-1}	7.0×10^{-3}
0	100	0.6	0.6

device with a medium distance between the probes of 0.171 ± 0.03 cm.

The morphology of the samples was determined by scanning electron microscopy (SEM) on a JEOL equipment model JSM-5300 with 10kV of voltage acceleration. The micrographs were taken from the fracture surface of the compressed material, which was previously coated with a thin gold layer.

Raman spectra for 632.8 nm exciting radiation (He-Ne laser, Spectra Physics, mod 127) were recorded on a Renishaw Raman Imaging Microscope (system 3000) containing an Olympus metallurgical microscope and a CCD detector. The laser was focused using a 50× objective lens with a spatial resolution of 1 μm.

The rheological characteristics of non-vulcanized compounds were monitored with the help of rubber processing analyzer (RPA 2000). The rheometer was operated in a frequency sweep mode with an arc oscillation of 0.5° at 100 °C. The dynamic properties of the compounds vulcanized in the RPA cavity at 160 °C with an arc oscillation of 0.5° for 12 minutes were also carried out in a frequency sweep mode with an arc oscillation of 0.5 ° at 60 ° C.

Results and Discussion

Non Vulcanized Blends

The conductivity values of non vulcanized blends prepared by both in situ emulsion polymerization and mechanical mixing are compared in Table 1. In all compositions studied, the emulsion-polymerized systems presented significantly higher conductivity values than the corresponding physical blends. These results suggest a more homogeneous distribution of PAni.DBSA in the NBR matrix.

The morphologies of NBR/PAni.DBSA (85:15 wt%) blends obtained by both processes are illustrated in Figure 1. Blends prepared by mechanical mixing are characterized by the presence of large agglomerates of PAni.DBSA heterogeneously

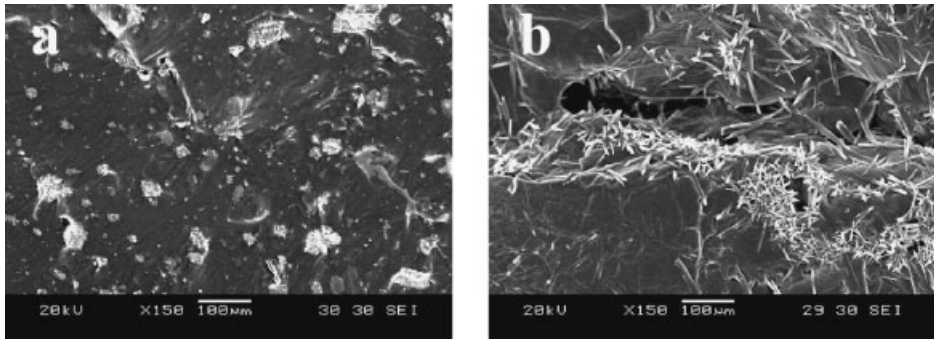


Figure 1.
SEM micrographs of NBR/PAni.DBSA (85:15 wt%) non vulcanized blends prepared by (a) mechanical mixing and (b) by in situ emulsion polymerization.

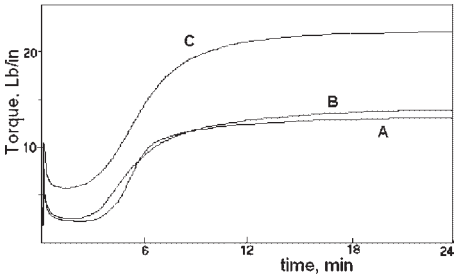


Figure 2.
Rheograms of (A) pure NBR and the NBR/Pani.DBSA (85:15 wt%) blends prepared by (B) physical mixing and (C) in situ polymerization.

dispersed and without great evidence of conducting pathways between them. The emulsion process resulted on the formation of PAni.DBSA as microtubules with relatively high aspect ratio and connected each other, producing conducting pathways. This morphological characteristic may be responsible for the higher conductivity values in emulsion-polymerized blends.

Vulcanized Blends

Blends prepared by both physical and chemical procedures were vulcanized in order to prepare samples for mechanical testing. Figure 2 compares the rheograms of NBR/Pani.DBSA (85:15 wt%) blends with that of pure NBR. Blend prepared by physical mixing displayed similar behavior as that of pure NBR. However, blend prepared by in situ polymerization presented substantial increase on minimum torque, indicating a viscosity increase of the system probably because of strong interaction between the phases. The maximum torque also increases, suggesting an increase of crosslink density. The presence of Pani.DBSA polymerized together with the NBR matrix also acts as accelerator for the curing process, as indicated by the decreasing on scorch time.

The tensile curves of blends containing 15% and 27% of Pani.DBSA are compared in Figure 3. In spite of the poor mechanical properties of Pani.DBSA itself, the presence of 15% and 27% of this component in blends prepared by physical mixing resulted in an increase of both ultimate tensile strength and elongation at break, as compared to pure NBR. These results suggest some compatibility between the components caused by some physical interactions, through hydrogen bond between the amine and nitrile functional groups. Blends prepared by in situ polymerization resulted in a substantial increase on tensile strength and a decrease on elongation at break, suggesting a reinforcing action of polyaniline, imparted by stronger interactions with the NBR matrix, probably of chemical nature.

The electrical conductivity of vulcanized blends is compared to non vulcanized blends in Table 2. The vulcanization process decreases the electrical conductivity of the blends prepared by both mechanical mixing or in situ polymerization. Another unexpected result was observed with the in situ polymerized blend with high amount of Pani.DBSA. For non vulcanized blends, the conductivity increases as the amount of Pani.DBSA increases, due to the possible formation of a conducting

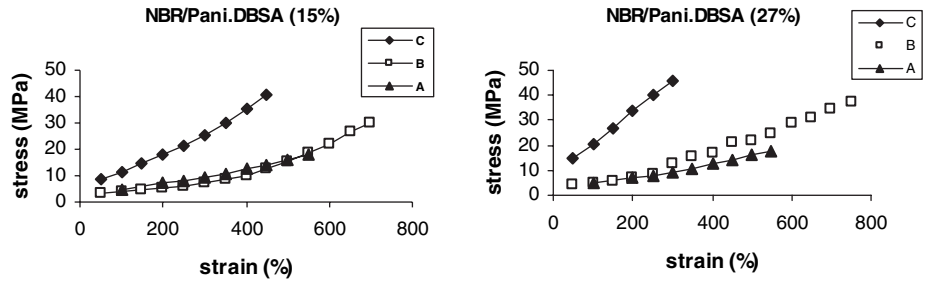


Figure 3.
Stress vs strain curves of (A) NBR and their blend with Pani.DBSA; (B) physical blend; (C) in situ polymerization.

Table 2.
Electrical conductivity of non vulcanized and vulcanized NBR/Pani.DBSA blends as a function of the preparation procedure.

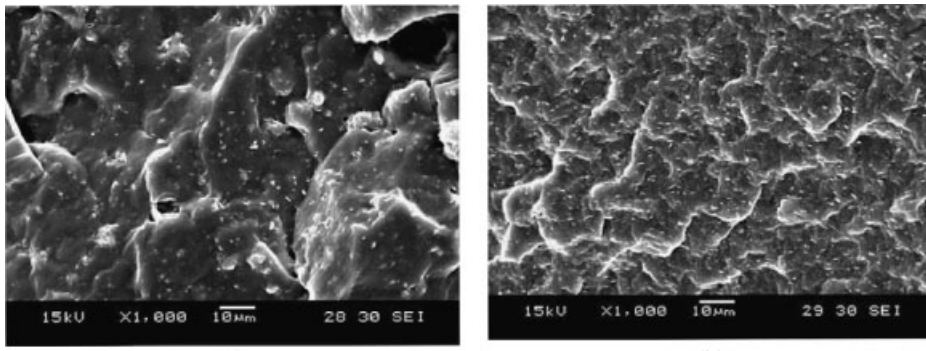
Blend components		electrical conductivity (S/cm)			
NBR(%)	Pani.DBSA(%)	non vulcanized		vulcanized	
		physical blend	in situ blend	physical blend	in situ blend
100	0	1.0×10^{-11}	1.0×10^{-11}	1.0×10^{-11}	1.0×10^{-11}
85	15	1.4×10^{-9}	6.6×10^{-5}	3.3×10^{-9}	3.3×10^{-8}
75	25	2.0×10^{-7}	1.0×10^{-3}	1.4×10^{-9}	2.0×10^{-6}
52	48	5.0×10^{-4}	2.0×10^{-2}	3.3×10^{-9}	3.3×10^{-9}

pathway. However, for vulcanized blend, a substantial decrease on conductivity is observed when higher amount of Pani.DBSA was employed (48%). The changes of electrical behavior with the vulcanization process may be related to the higher degree of dispersion of polyaniline inside the NBR matrix, caused by the shear forces during the processing of the blends in a two roll mill, while incorporating the curing agents.

Figure 4 presents the morphology of vulcanized NBR/Pani.DBSA (85:15 wt%) blends as a function of the preparation procedure. In both cases, the Pani.DBSA is well dispersed inside the NBR matrix. By comparing the morphologies of vulcanized blends to those obtained for non vulcanized blends (Figure 1), one can observe that the shear forces applied during the compounding of the curing agents improve the dispersion of the polyaniline and destroy the conducting pathway. This phenomenon is more accentuated for in situ polymerized blend because of the increasing of viscosity of this blend and consequently the shear forces necessary to process, as it will be discussed later. This behavior may also explain the lower conductivity observed in in situ polymerized blend with higher amount of Pani.DBSA.

Rheological Properties

Rheological processing analysis (RPA) can provide additional informations regarding polymer-polymer interactions in heterogeneous blends and composites. Figure 5 compares the elastic shear modulus as a function of oscillating frequency, for NBR/Pani.DBSA (85:15 wt%) blends prepared by different procedures. The presence of Pani.DBSA increases the modulus of both non vulcanized and vulcanized blends prepared by physical mixing, suggesting some interaction between the components. However, substantial increase on modulus was observed in blends prepared by in situ polymerization, vulcanized and non vulcanized, indicating a reduction of chain



(a) (b)

Figure 4.
SEM micrographs of NBR/PAni.DBSA (85:15 wt%) non vulcanized blends prepared by (a) mechanical mixing and (b) by in situ emulsion polymerization.

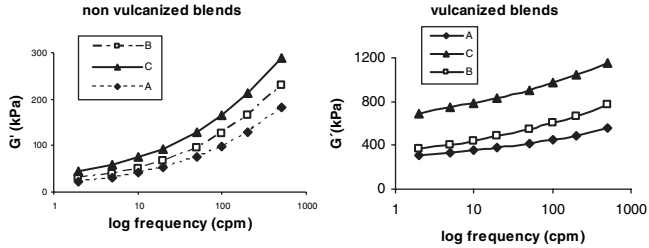


Figure 5.
Variation of shear modulus with the oscillating frequency in logarithmic form for (A) pure NBR, and NBR/Pani.DBSA (85:15 wt%) blends prepared by (B) mechanical mixing and (C) in situ polymerization.

mobility as a consequence of the high entanglement between the Pani chains and also good interactions. These interactions should be of chemical nature, since the cation radicals formed during the first step of the aniline polymerization should react with the double bond of the unsaturated rubber, initiating the grafting process. The attack of the aniline cation radical on the double bond should create a new free radical on the other carbon, which may either react with another aniline cation radical or initiate a crosslink process. The strong modulus increase of vulcanized blend containing Pani.DBSA in situ polymerized is characteristic of filler-loaded rubber vulcanizates. This result is in agreement with tensile properties and suggests a reinforcing effect of Pani.DBSA, mainly in in situ polymerized blend.

Raman Spectroscopy

Raman spectroscopy used in the microscope mode is very efficient for the characterization of interactions between the components in a polymer blends.[20] Figures 6(a) and (b) compare the resonance Raman spectra of non vulcanized NBR/PAni.DBSA (85:15 wt%) blends obtained by mechanical mixing and by in situ emulsion polymerization. In both cases, it is possible to observe intense overlapping bands at 1320 and 1337 cm^{-1}, corresponding to C-$N^{+\bullet}$, stretching modes of delocalized polaronic charge carriers, which is characteristic of the protonated imine form of polyaniline. These results indicate that in both cases, PAni.DBSA component is in the doped (protonated) form. Therefore, the lower conductivity values achieved in blends obtained by mechanical mixing can not be only attributed to a deprotonation process which could be take place during blending in the two roll mill. It is suggested that a peculiar morphology, constituted by agglomerated domains of PAni.DBSA without the formation of efficient conducting pathways may be the main reason for the decreased conductivity values in physical blends.

Figure 7 illustrates the Raman spectra of the corresponding vulcanized blends.

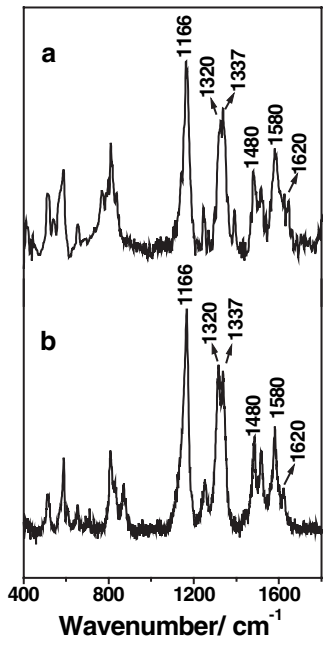


Figure 6.
Resonance Raman spectra of non vulcanized NBR/PAni.DBSA (85:15 wt%) blends prepared by (a) mechanical mixing and (b) by in situ emulsion polymerization.

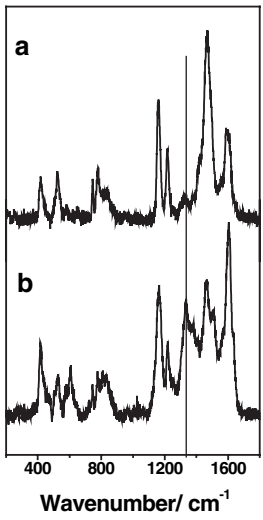


Figure 7.
Resonance Raman spectra of vulcanized NBR/PAni.DBSA (85:15 wt%) blends prepared by (a) mechanical mixing and (b) by in situ emulsion polymerization

The in situ polymerized blend still presented intense overlapping bands at 1320 and 1337 cm^{-1}, after vulcanization, indicating that the vulcanization process did not result in deprotonation of Pani.DBSA. However, for blend prepared by mechanical mixing (Figure 7a), these absorptions have been drastically reduced with the vulcanization, suggesting a deprotonation process.

Conclusion

NBR/Pani.DBSA blends prepared by in situ polymerization resulted in conducting elastomer material with higher conductivity and a morphology characterized by the presence of fibers. The higher minimum torque in the ODR measurements and higher shear modulus of the in situ polymerized blends also indicate a strong interaction between the blend components in in situ polymerized blends.

The in situ polymerized blends exhibit a substantial increase of the tensile strength, suggesting that Pani.DBSA in these blends acts as a reinforcing agent for NBR matrix.

The vulcanization process did not influence significantly the protonation of Pani.DBSA in in situ polymerized blends, as indicated by Raman spectroscopy. Therefore, the decrease of the conductivity with the vulcanization for these blends may by due to the break of the conducting pathway, due to shear forces applied during blend compounding. In the case of physical blend, the vulcanization process contributes for the deprotonation of Pani.DBSA. This phenomenon associated to the dispersion of the Pani.DBSA agglomerates during mixing may be responsible for the significant decrease in conductivity.

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[1] Anand J, Palanapian S, Sathyanarayana DN, Prog Polym Sci 1998; 23: 993.
[2] Heeger AJ, Synth Met 1993; 57: 3471.
[3] Pinho MS, Gorelova MM, Dezzotti M, Soares BG, Pertsin AJ, J Appl Polym Sci 1998; 70: 1543.
[4] Faez R, De Paoli MA, J Appl Polym Sci 2001; 82: 1768.
[5] Faez R, De Paoli MA, Eur Polym J 2001; 37: 1139.
[6] Faez R, Gazotti WA, De Paoli MA, Polymer 1999; 40: 5497.
[7] Tsanov T, Ditcheva-Kortchakova M, Terlmezyan L, Polym & Polym Comp 2000; 8: 115.
[8] Faez R, Schuster RH, De Paoli MA, Eur Polym J 2002; 38: 2459.
[9] Schmidt V, Domenech SC, Soldi MS, Pinheiro EA, Soldi V, Polym Degrad Stab 2004; 83: 519.
[10] Vallim MR, Felisberti MI, De Paoli MA, J Appl Polym Sci 2000; 75: 677.
[11] Osterholm JE, Cao Y, Klavetter F, Smith P, Polymer 1994;35: 2904.
[12] Ruckenstein E, Sun Y, Synth Met 1995;74: 107.
[13] Jeon BH, Kim S, Choi MH, Chung IJ, Synth Met 1999;104: 95.
[14] Xie HQ, Ma YM, J Appl Polym Sci 2000;76: 845.
[15] Paul RK, Pillai CKS, J Appl Polym Sci 2002;84: 1438.
[16] Xie HQ, Ma YM, Guo JS, Synth Met 2001;123: 47.
[17] Xie HQ, Ma YM, Guo JS, Polymer 1998; 40: 261.
[18] Oh SY, Koh HC, Choi JW, Rhee HW, Kim HS, Polym J 1997;29: 404.
[19] Xie HQ, Pu QL, Xie D, J Appl Polym Sci 2004; 93: 2211.
[20] Pereira da Silva JE, Faria DLA, Torresi SIC, Temperini MLA, Macromolecules 2000; 33: 3077.

