In Situ Polymerization of Aniline in the Presence of Carbon Black

Fernando G. Souza, Jr.,[1] Lys Sirelli,[1] Ricardo C. Michel,[1] Bluma G. Soares[1], Marcelo H. Herbst[2]

[1]*Institute of Macromolecules, Federal University of Rio de Janeiro, Centro de Tecnologia, Ilha do Fundão, Rio de Janeiro 21945–970, Brazil*
[2]*Institute of Physics, Federal University of Rio de Janeiro, Centro de Tecnologia, Ilha do Fundão, Rio de Janeiro 21945–970, Brazil*

Received 14 September 2005; accepted 5 February 2006
DOI 10.1002/app.24280
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A hybrid material of polyaniline doped with dodecylbenzenesulfonic acid and conductive carbon black (PaniDBSA/CB) was prepared by *in situ* polymerization. The presence of low amount of CB (up to 25 wt %) resulted in a decrease in resistivity as compared to pure PaniDBSA. Composite with 25 wt % of CB presented the lowest resistivity and a tubular morphology characterized by microtubules with high aspect ratio evidenced by SEM examination. Higher amount of CB give rise to materials with higher resistivity values and a granular morphology, similar to pure carbon black. Ultraviolet–visible and electron paramagnetic resonance analyses were employed to evaluate the polaron concentration. X-ray diffraction was used to characterize the molecular structure of these composites. It was observed a decrease in the crystallinity degree and a shift of the polaron band transition toward lower wavelength as the amount of CB in the composite increases. From the EPR measurements, one can suggest that the higher chain order and polaron mobility is observed in hybrid with 25% of CB. This behavior is in agreement to the electrical resistivity values and SEM microscopy. The effect of CB on thermal stability of the composites was also investigated. The effect of the PaniDBSA/CB hybrid material on the processability and resistivity of the composites based on styrene-butadiene-styrene (SBS) block copolymer as the insulating matrix have been also evaluated. J Appl Polym Sci 102: 535–541, 2006

Key words: carbon black; polyaniline; hybrid material; conductivity; SBS

INTRODUCTION

Polyaniline has attracted much attention in the last two decades due to their potential applications in various hitech aspects, such as active electrodes in batteries,[1] in microelectronics,[2] as electrochromic material for displays,[3,4] sensors[5–7] as well as electromagnetic shielding.[8] The advantages of Pani compared to other conducting polymers are its easy chemical synthesis, its high stability toward environmental exposition, and special electronic properties, which can be reversibly controlled by both charge transfer doping and protonation.[9]

The development of composites constituted by conducting polymers with other conducting materials is also very important to combine the specific properties of each component. Several papers in literature report different ways to prepare these composites and the good properties that can be achieved with them. For example, Pani has been combined with platinum particles to provide materials with high catalytic activity for the oxidation of methanol and other reactions, and more resistant to contamination with by-products, compared to the pure metal.[10] Polyaniline–graphite composites have also been prepared by dispersing Pani doped with 2-acrylamide-2-methyl-1-propanonesulfonic acid and graphite powder to develop monolithic electrochemical actuators.[11] Additionally Pani/graphite nanocomposite was synthesized via *in situ* polymerization of aniline in the presence of exfoliated graphite nanosheets.[12] Pani–carbon black composites have also been prepared by potentiodynamic method in acid electrolyte containing aniline and a suspension of carbon black.[13] The chemical polymerization of aniline in the presence of carbon black has also been reported, giving rise to a polymeric conducting composite denoted as Eonomer®.[14,15] According to the authors, these materials are more stable than pure Pani and result in easier processable blends with thermoplastics.

This work investigates the effect of conductive carbon black on the electrical and morphological properties of polyaniline protonated with dodecyl benzene sulfonic acid (DBSA). The hybrid conducting materi-

Correspondence to: B. G. Soares (bluma@ima.ufrj.br).
Contract grant sponsors: Conselho Nacional de Desenvolvimento Científico e Tecnológico-CNPq, Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro-FAPERJ, and Light Serviços de Eletricidade S.A.

als were prepared by the *in situ* polymerization of aniline in the presence of Printex XE2B carbon black using DBSA as the protonating agent and ammonium peroxydisulfate as the oxidant agent. The use of DBSA is very interesting because of the better processability and compatibility that can be achieved when these materials are used in blends with insulating polymers. The obtained products were characterized by ultraviolet–visible (UV–vis) spectrometry, scanning electron microscopy, X-ray diffraction, electron paramagnetic resonance (EPR), and resistivity measurements.

Some preliminary studies involving the effect of this hybrid material on the processability and resistivity of the composites based on styrene-butadiene-styrene (SBS) block copolymer as the insulating matrix have also been performed.

EXPERIMENTAL

Materials

SBS (TR-1061; PBD content = 70 wt %; $<M_w>$ = 120,000; density = 0.98 g/cm^3) was kindly supplied by Petroflex S.A. (Rio de Janeiro, Brazil). Carbon black [CB; printex XE-2, DBP = 370 mL/100 g, BET = 1000 m^2/g, density = 2.04–2.11 g/cm^3] was kindly supplied by Degussa (Frankfurt, Germany). Aniline (analytical grade from Vetec, Brazil), ammonium peroxydisulfate (APS) (analytical grade from Vetec, Brazil), and DBSA (commercial grade from Solquim LTDA, Brazil) were used without further purification.

Synthesis of PaniDBSA and the hybrid materials

Polyaniline doped with DBSA (PaniDBSA) and their composites with carbon black (CB) were synthesized by one step route in toluene medium. In a typical procedure, 4.7 mL (0.051 mol) of aniline and 16.7 g (0.051 mol) of DBSA were dissolved into 250 mL of toluene under constant stirring. The medium was kept at 0°C and an aqueous solution containing 11.36 g (0.051 mol) of APS in 40 mL of water was slowly added over a period of 20 min. After 6 h, the reaction medium was poured into methanol, filtered, washed several times with methanol, and dried. In the case of PaniDBSA–CB composites (PaniDBSA/CB), different amounts of CB were first dispersed into the toluene. Then, aniline and the other reagents were added, following similar procedure described earlier. The conversion of aniline into polymer was determined gravimetrically from the difference between the total weight of sample obtained in the experiment and the weight of CB initially present in the medium and assuming that the formed polyaniline contains 50% of the nitrogen in the imine form and all imine groups were protonated by the DBSA.

Preparation of the composites with SBS

The SBS copolymer was first introduced in a Haake internal mixer operating with rotor Cam, at 100°C and 60 rpm. After 2 min, the conductive filler was added and the mixture was performed for 8 min. The blends were then laminated into a two-roll mill and compression-molded at 100°C for 3 min, and 1.0 MPa pressure.

Characterization

The electrical resistivity measurements of Pani, DBSA, CB and the hybrid materials PaniDBSA/CB were performed by the conventional four-point method, according to the literature,[16,17] on pressed pellets of composites particles prepared at room temperature. The equipment used for this measurements is composed by an electrometer Keithley 6517A, a multimeter Minipa ET2907 and a home made four probes device with a medium distance between the probes of 0.171 $\pm$ 0.03 cm.

The volume resistivity of the SBS-based composites were performed using two-plaques technique, according to the literature[16,17] and a Keithley 6517A electrometer. The results involve the media of five measurements. The measurements were performed in compression-molded samples, as disks of 38 mm diameter and about 1 mm thickness, for 5 min.

The morphology of the samples was determined by scanning electron microscopy (SEM) on a JEOL equipment model JSM-5300 with 10 kV of voltage acceleration. The micrographs of PaniDBSA and the hybrids PaniDBSA/CB were taken from the surface of the film obtained after evaporation of a small aliquot withdrawn from the reaction medium. The micrograph of CB was taken from the powder. All samples were coated with a thin layer of gold.

The ultraviolet–visible spectrometry measurements were performed on a Varian UV–vis Spectrometer Model CARY 100. The samples were dissolved in toluene in a concentration of 5.5×10^{-5} g/mL. The absorption effect generated by the CB particles dispersed in the solution was eliminated using normalized curves, which was obtained by subtracting the value of the smallest absorbance of each solution in the corresponding UV–vis spectrum.

pH measurements of a DBSA aqueous solution were performed in a pHmeter ANALYSER model 300*M*. The solution was prepared by dissolving 2.0122 g of DBSA into 200 mL of distilled/deionized water. 50 mL of this solution was then stirred with 0.4999 g of CB for 3 h.

Wide-angle X-ray scattering (WAXS) measurements were performed on a Miniflex Rigaku diffractometer with copper X-ray tube (CuKα, wavelength λ = 1.5418 Å) and a graphite monocromator. The data were collected in the step-by-step mode of 0.05° from 5 to 40° in 2θ.

TABLE I
Resistivity and Composition of PaniDBSA/CB Hybrid Materials

Components weight (g)		Conversion of PaniDBSA (wt %)	Composition of the composite		Resistivity (Ω cm)	Standard deviation of the resistivity
Aniline	CB		PaniDBSA (wt %)	CB (wt %)		
4.76	0.00	49	100	0	8.70×10^{0}	3.97×10^{0}
4.78	0.30	43	94	6	5.25×10^{0}	1.25×10^{0}
4.79	1.60	46	75	25	1.11×10^{0}	3.51×10^{-2}
4.65	1.63	46	74	26	1.18×10^{0}	1.37×10^{-1}
4.87	2.86	58	63	37	1.20×10^{1}	4.26×10^{-1}
4.83	4.46	72	52	48	2.94×10^{2}	2.96×10^{1}
0.0	5.40	–	0	100	1.28×10^{0}	1.73×10^{-1}

Thermogravimetric analyses of PaniDBSA and the hybrids were performed on a SDT2960 analyzer from TA Instruments, operating under nitrogen flow, in the temperature range of 100–700°C and at a heating rate of 10°C/min.

The EPR measurements were performed on a Bruker ESP-380 FT-CW spectrometer operating in X-band (~9.5 GHz) and frequency modulation of 100 MHz. The spectra were measured at room temperature in a cylindrical resonating cavity. The *g*-factors were determined against diphenylpicrylhydrazyl standard (DPPH) ($g = 2.0023$). To avoid saturation of the EPR signal, all spectra were measured in low power (0.5 mW), using modulation amplitude of 0.3 mT. The EPR susceptibilities were estimated by double-integrating the EPR signal, using the Bruker WinEPR® software.

RESULTS AND DISCUSSION

Electrical resistivity of the hybrid materials

The effect of the CB content on the conversion of aniline into PaniDBSA and electrical resistivity of the hybrid composites is summarized in Table I. With low amount of CB, the conversion of PaniDBSA presents a slight decrease. Higher amount of CB resulted in a substantial increase of the conversion. This may be due to the presence of excess of DBSA molecules adsorbed in CB, which were not complete eliminated in spite of the repeated washing process.

The electrical resistivity of PaniDBSA/CB composites also depends upon the amount of CB in the composite. At lower CB loads (up to 25%), the resistivity decreases, suggesting that CB particles act as electrically conductive bridges. The lowest value of resistivity was obtained in a composite containing 25 wt % of CB. Similar behavior has been also reported for composite constituted by Pani and graphite.[12] After this point, there is an increase of resistivity, whose values are somewhat higher than the pure components.

UV–vis and EPR spectroscopy

The decrease of conductivity with higher amount of CB may be attributed to changes in the oxidation state and/or protonation degree of the polymer. UV–vis spectroscopy is considered as an important tool for the investigation of the electronic structure of Pani and more specifically the charge carrier delocalization in this polymer. Figure 1 compares the normalized UV–vis absorption spectra of PaniDBSA and their corresponding composites with CB. PaniDBSA exhibits two absorption peaks at 400 and 830 nm, which can be assigned to the π–π^* transition on the polymer chain and to the polaron band transition, respectively.[18] The polaron band at 830 nm (in pure PaniDBSA) presented a blue shift and a substantial decrease in intensity as the CB concentration in the hybrid increases. For the hybrid material containing 48% of CB, this polaron band appeared at around 730 nm with a significant decrease of the intensity. This behavior suggests that the degree of charge delocalization becomes lower as the amount of CB increases.

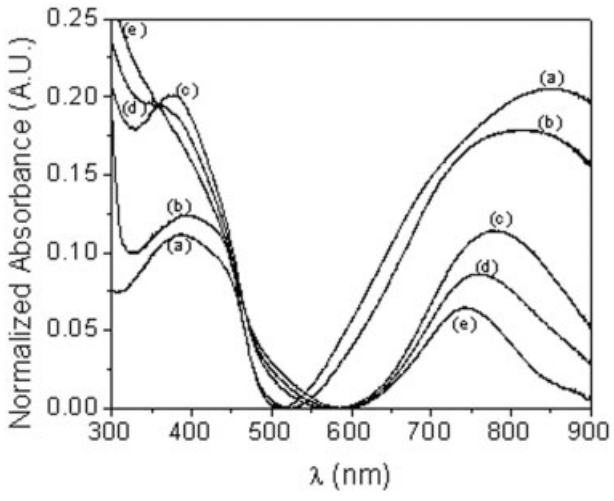

Figure 1 Normalized UV–vis Spectra of (a) PaniDBSA and the PaniDBSA/CB hybrid composites with (b) 6%, (c) 25%, (d) 37%, and (e) 48% of carbon black.

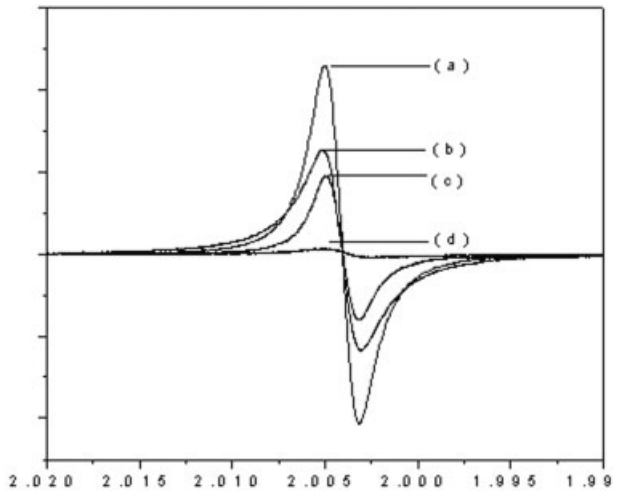

Figure 2 EPR spectra of (a) PaniDBSA and the PaniDBSA/CB hybrid composites with (b) 6%, (c) 25%, (d) 37%, and (e) 48% of carbon black.

Figure 2 illustrates the EPR spectra of the hybrid materials as a function of the CB content. Increasing the amount of CB in the hybrid composites resulted in a decreasing of the EPR signal intensity at $g = 2.0041(2)$. The relative polaron concentration was estimated by double integration of the EPR signal. This estimative afforded similar polaron concentration for the hybrid prepared with 6 and 25% of CB, whereas for that containing 48% of CB, the polaron concentration is roughly one order of magnitude smaller. When comparing the EPR spectra of PaniDBSA with those of the hybrid composites, one can observe a substantial decrease of the line width (ΔH_{pp}) for the hybrid containing 25% of CB. For conducting polymer systems, the line width is related to the structural order, that is, the conjugation length: the smaller the line width, the greater the polaron mobility is.[19] From the EPR measurements, one can suggest that the higher chain order and polaron mobility is observed in hybrid with 25% of CB. This behavior is in agreement to the electrical resistivity values and SEM microscopy.

The metallic character of these composites can be also estimated from EPR spectra, by measuring the asymmetric parameter A/B values of the low-field maximum and high-field minimum amplitudes.[20] This parameter was found to be 1.0 for 6% CB sample, 1.2 for 25% CB, and 1.7 in the case of 48% CB sample, indicating an increase of the metallic character as the CB concentration increases. These results are in accordance with the resistivity measurements for the 6% and 25% CB composites. The higher metallic character found for the 48% CB hybrid is not understandable on these grounds, and should be related to the appearance of distinct, not polaronic, paramagnetic species in this composite.

The protonation degree and also the conductivity of polyaniline depend on the pH of the medium. At higher amount of CB, the resistivity of the composite is higher probably because of the increase of the pH of the medium caused by the adsorption of part of DBSA by CB particles. The effect of CB on the pH of the medium was evaluated by measuring the pH of a DBSA aqueous solution without and with CB. These values are listed in Table II. In fact, the presence of CB resulted in a small increase of the pH value, which corresponds to ~31.5% of all H^+ available cations adsorbed by CB. This phenomenon may be contributing for the increasing of the conversion of PaniDBSA at higher amount of CB and also for the decreasing in conductivity and a blue shift of the polaron band transition.[21]

The increase of resistivity with the presence of large amount of CB may be also attributed to a reduction process that takes place during the polymerization of aniline imparted by CB. It was reported in the literature that, among several types of carbonaceous materials, carbon black displays the highest ability toward chemical oxidation.[22] The reduction process of the Pani chain by the CB may also be responsible for the significant blue shift of the polaron band, according to the results reported by Albuquerque et al.[23,24]

SEM morphology of hybrid composites

The peculiar electrical behavior of PaniDBSA/CB composites, especially with low amount of CB, may be also related to the morphology. Figure 3 presents the SEM micrographs of the hybrid composites as a function of the CB content. The morphology of PaniDBSA is characterized by the presence of tubules and plates, as also reported by other authors.[25–27] The PaniDBSA/CB composite containing 25 wt % of CB displays more defined microtubules with higher aspect ratio. Beyond this concentration, these microtubules are not formed and the morphology looks similar to that of pure CB, characterized by the presence of grains, whose diameter varies from 3 to around 10 μm [see Figs. 3(b)–3(d)]. From these results, on can assume that the lowest resistivity found in PaniDBSA/CB composite with 25 wt % of CB is better related to the orienta-

TABLE II
pH of DBSA Aqueous Solution Without and With CB

	Average	99% CI
DBSA		
pH	1.98	0.18
$[H^+]$	1.06×10^{-2}	9.35×10^{-4}
DBSA/CB		
pH	2.14	0.82
$[H^+]$	7.19×10^{-3}	2.76×10^{-3}

CI, confidence interval.

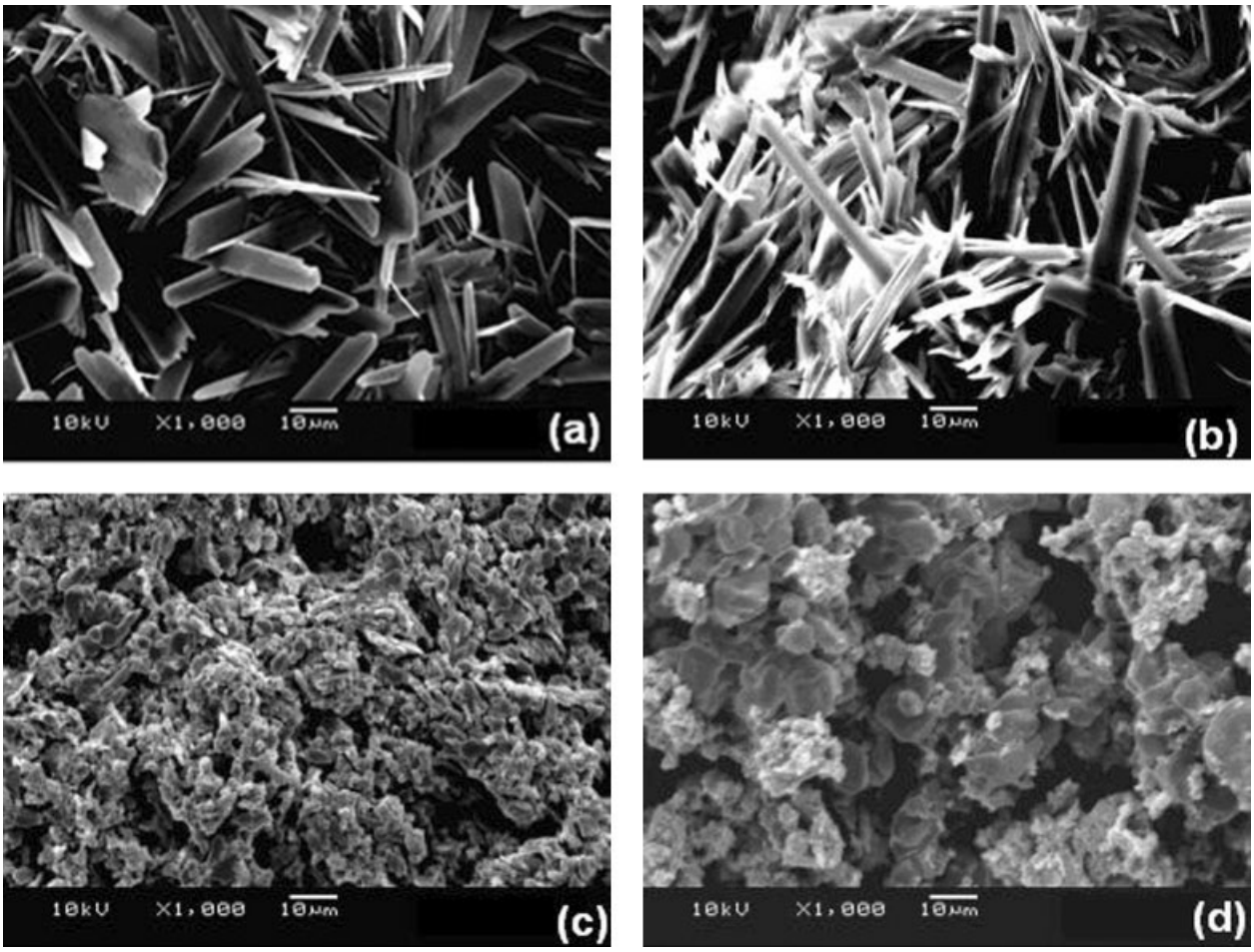

Figure 3 Micrographs of (a) PaniDBSA and the PaniDBSA/CB hybrid composites with (b) 25%, (c) 37%, and (d) 48% of carbon black.

tion of the polymer chain, favoring the polaron mobility as confirmed by EPR spectra. The different behavior observed from UV–vis spectroscopy of the 25% CB hybrid can be attributed to the fact that the UV–vis spectra were taken from the solution and do not reflect the chain orientation observed in the solid state.

X-ray diffraction scattering

Figure 4 shows the X-ray diffraction patterns of the PaniDBSA and PaniDBSA/CB composites. PaniDBSA exhibits six main reflections at $2\theta = 17°$, 23°, 26°, 30°, 35°, and 36°. The structure of the crystalline phases of PaniDBSA is orthorhombic.[28–32] These results agree with those of Fischer et al.,[28] Lux[29] and Zilberman et al.[32] who observed reflections at the same angles for Pani powder prepared from solutions of concentrated sulfuric acid. The presence of 6% of CB in the composite resulted in different X-ray diffraction patterns with peaks of lower intensity, indicating a decreasing of crystallinity and also the formation of different crystallites. Those sharp peaks become weak and

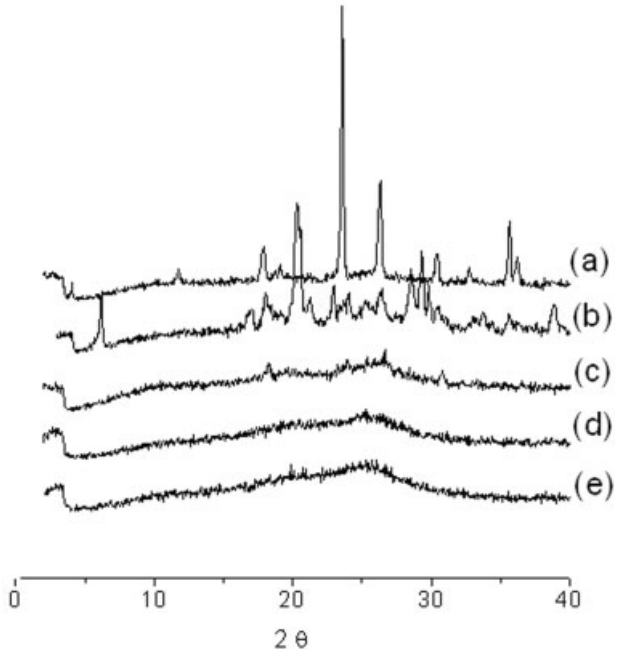

Figure 4 XRD patterns of (a) PaniDBSA and the PaniDBSA/CB hybrid composites with (b) 6%, (c) 25%, (d) 37%, and (e) 48% of carbon black.

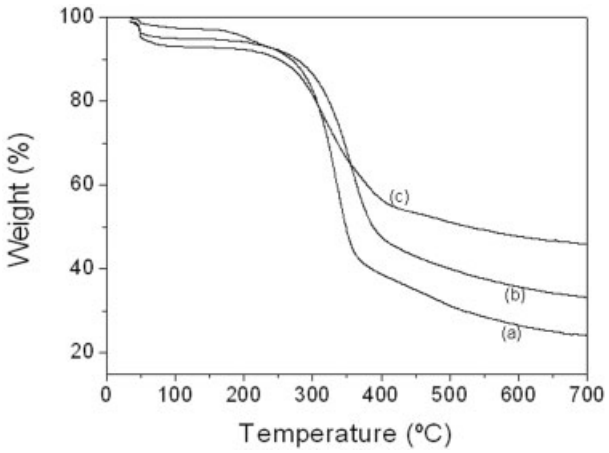

Figure 5 Thermogravimetric analysis of (a) PaniDBSA and the PaniDBSA/CB hybrid materials with (b) 6% and (c) 25% of carbon black.

broad as the concentration of CB in the composite increases. This indicates that the presence of CB in a high proportion disturbs the crystallization of the Pani chains. The PaniDBSA/CB composites with 37 and 48 wt % of CB exhibit similar amorphous pattern as found in CB sample. This result is possibly because the high CB concentration has acted as thread "impurities" to the growth of the Pani crystallites and more and more amorphous Pani was formed.

It is interesting to point out that the composite with 25 wt % of CB, which presents the lowest resistivity and also a tubular morphology, does not give sharper peaks in X-ray diffraction. These results suggest that the higher conductivity (lower resistivity) achieved in this sample is mainly due to the higher chain order and polaron mobility as observed in the EPR spectra, indicating a better contribution of intrachain conductivity.

Thermogravimetric analysis

The decomposition thermograms of the PaniDBSA and its hybrids are shown in Figure 5. The presence of CB improves the thermal stability of the hybrids. This stability is reflected by the displacement of the decomposition curve toward a little higher temperature, mainly in system containing 6% of CB. According to Avlyanov,[14] the improved thermal stability of doped, conjugated polymers on the carbon black can be explained by multiple π–π interactions between the unsaturated backbone of the intrinsically conductive polymer (ICP), the aromatic rings of the CB substrate, and the planar aromatic dopant ions. These interactions should limit the rotational freedom of the conjugated polymer segments and therefore enhance the thermal stability of the polymer.

The higher amount of nondegradable residue in hybrid containing 25% of CB (around 46%) is related to the amount of CB and the residue coming from the PaniDBSA, since pure PaniDBSA normally gives rise to around 24% of nondegradable residue.

Effect of hybrid materials on processability and resistivity of SBS-based composites

Figure 6 compares the torque-time curves of the SBS-based composites as a function of the conducting filler nature. All these composites were prepared with 15 wt % of conducting filler. The initial increase in torque results from the addition of the SBS into the mixer. The second increase of torque after 2 min corresponds to the load insertion of the filler into the internal mixer. After this, the torque drops as the polymeric material soften until a value characteristic of the blend.

The presence of CB resulted in a substantial increase of final torque, indicating a decrease of processability. On the other hand, the presence of PaniDBSA resulted in a decrease of final torque as a consequence of the plasticizer effect imparted by DBSA. The final torque of SBS loaded with 15 wt % of the hybrid material (containing 25% of CB) was similar to that of pure SBS, indicating no influence of this filler on the processability of SBS.

The effect of the hybrid material on the resistivity of SBS-based composites is summarized in Table III. SBS loaded with CB presents a percolation threshold lower than 15% of CB. With 15% of CB, the resistivity is several orders lower than the SBS loaded with the same amount of PaniDBSA or PaniDBSA/CB hybrid material. It is important to emphasize the significant lower resistivity of the SBS loaded with PaniDBSA/CB hybrid compared to pure PaniDBSA. It is believed that during the blend preparation in the internal mixer, the relatively high temperature and

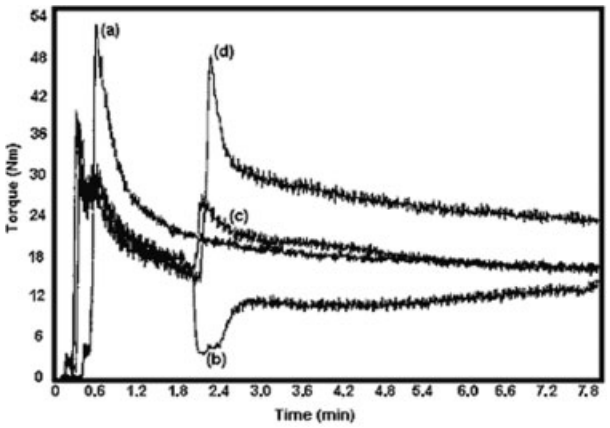

Figure 6 Torque-time curves of (a) pure SBS and the SBS-based conducting composites containing (b) 15% of PaniDBSA, (c) 15% of PaniDBSA/CB, and (d) 15% of CB.

TABLE III
Resistivity Values of SBS Conducting Composites as a Function of the Composition and Conducting Filler Nature

Filler content (%)	SBS/PaniDBSA		SBS/PaniDBSA/CB		SBS/CB	
	VR (Ω cm)	99% CI	VR (Ω cm)	99% CI	VR (Ω cm)	99% CI
0	2.8×10^{12}	8.4×10^{11}	2.8×10^{12}	8.4×10^{11}	2.8×10^{12}	8.4×10^{11}
15	6.3×10^{12}	3.2×10^{11}	6.3×10^{10}	2.0×10^{9}	1.6×10^{3}	1.3×10^{1}
30	2.9×10^{6}	6.4×10^{4}	5.8×10^{2}	6.1×10^{1}	2.0×10^{2}	1.9×10^{0}
45	8.3×10^{4}	4.0×10^{2}	4.8×10^{1}	3.1×10^{0}	–	–

VR, volume resistivity; CI, confidence limit.

shearing forces contribute for the dedoping of the PaniDBSA. The presence of CB in the hybrid material avoids the degradation of PaniDBSA, thus resulting in lower resistivity. These results are very important for technological purpose, since relatively high conductivity values can be reached without affecting the processability of the matrix.

CONCLUSIONS

PaniDBSA/CB hybrid materials were synthesized by *in situ* polymerization. The presence of low amount of CB (up to 25 wt %) resulted in a decrease in resistivity as compared to pure PaniDBSA. The composite containing 25 wt % CB also displayed a tubular morphology characterized by microtubules with high aspect ratio. Higher amount of CB give rise to materials with higher resistivity values and a granular morphology, similar to pure carbon black. The higher resistivity values achieved in composites with higher amount of CB are in agreement with the blue shift of the polaron band transition observed in UV–vis spectroscopy and also with the decrease in crystallinity observed in X-ray diffraction patterns. These phenomena were attributed to an increase of the pH of the medium caused by the adsorption of part of DBSA by the CB particles and also to an oxidation process of the Pani chain.

Surprisingly, the composite containing 25% of CB, which displayed the lowest resistivity value, also presented a decrease in crystallinity and a blue shift of the polaron band transition. However, the EPR data confirm the increased polaron mobility in this sample. These results indicate that the lower value of resistivity is better associated to the tubular morphology, which makes easier the polaron mobility. At this CB concentration, the decrease in crystallinity does not exert substantial influence on resistivity.

Regarding SBS-based conducting composites, those containing CB presented the lowest percolation threshold. However, the PaniDBSA/CB hybrid filler presents the better combination of conductivity and processability.

Souza Jr. also thanks FAPERJ for the scholarship. The authors are grateful to Núcleo de catálise da COPPE/UFRJ for XRD analysis.

References

1. Kancko, M.; Nakamura, H. J Chem Soc Chem Commun 1985, 346.
2. Chen, S. A.; Fang, Y. Synth Met 1993, 60, 215.
3. Jelle, B. J.; Hagen, G. J Electrochem Soc 1993, 140, 3560.
4. Jelle, B. J.; Hagen, G.; Sunde, S. Synth Met 1993, 54, 315.
5. Grant, L.; Guernion, N.; Ratcliffe, N. M.; Teare, C. In Materials Chemistry Conference, Bangor, Australia, 2001. Abstracts, P62.
6. Lee, J. K.; Yoo, D. S.; Handy, E. S.; Rubner, M. F. Appl Phys Lett 1996, 69, 1686.
7. Osada, Y. E.; de Rossi, D. E., Eds. Polymer Sensors and Actuators; Springer Verlag: Germany, 2000.
8. Malinauskas, A. Polymer 2001, 42, 3959.
9. MacDiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. Mol Cryst Liq Cryst 1985, 121, 173.
10. Ocong, P.; Leger, J. M.; Lamy, C.; Genies, E. M. J Appl Electrochem 1996, 19, 462.
11. Li, L. W.; Johnson, C. L.; Wang, H. L. Polymer 2004, 45, 4769.
12. Du, X. S.; Xiao, M.; Meng, Y. Z. Eur Polym J 2004, 40, 1489.
13. Del Rio, R.; Zagal, J. H.; Andrade, G. D. J Appl Electrochem 1999, 29, 759.
14. Avlyanov, J. K. Synth Met 1999, 102, 1272.
15. Omastová, M.; Podhradská, S.; Prokes, J.; Janigová, I.; Stejskal, J. Polym Degrad Stab 2003, 82, 251.
16. Girotto, E. M.; Santos, I. A. Quim Nova 2002, 25, 639.
17. Valdes, L. B. Proc IRE 1954, 42, 420.
18. Cao, Y.; Smith, P.; Heeger, A. J. Synth Met 1989, 32, 263.
19. Han, M. G.; Cho, S. K.; Oh, S. G.; Im, S. S. Synth Met 2002, 126, 53.
20. Coulon, C.; Clérac, R. Chem Rev 2004, 104, 5655.
21. Kuramoto, N.; Genies, E. M. Synth Met 1995, 68, 191.
22. Wampler, W. A.; Barak, S.; Rajeshwar, K. Carbon 1996, 34, 747.
23. Albuquerque, J. E.; Mattoso, L. H. C.; Balog, D. T.; Faria, R. M.; Masters, J. G.; MacDiarmid, A. G. Synth Met 2000, 113, 19.
24. Albuquerque, J. E.; Mattoso, L. H. C.; Faria, R. M.; Masters, J. G.; MacDiarmid, A. G. Synth Met 2004, 146, 1.
25. Huang, J.; Wan, M. J Polym Sci Part A: Polym Chem 1999, 37, 151.
26. Long, Y.; Chen, Z.; Wang, N.; Zhang, Z.; Wan, M. Phys B: Condens Matter 2003, 325, 208.
27. Habaa, Y.; Segal, E.; Narkis, M.; Titelman, G. I.; Siegmann, B. A. Synth Met 1999, 106, 59.
28. Fischer, J. E.; Tan, X.; Scher, E. M.; Cajipe, V. B.; MacDiarmid, A. G. Synth Met 1991, 41, 661.
29. Lux, F. Polymer 1994, 35, 2915.
30. Josefowicz, M. E.; Epstein, A. J.; Pouget, J. P.; Masters, J. G.; Ray, A.; Sun, Y.; Tan, X.; MacDiarmid, A. G. Synth Met 1991, 41, 723.
31. Pouget, J. P.; Josefowicz, M. E.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. Macromolecules 1991, 24, 779.
32. Zilberman, M.; Titelman, G.; Siegmann, A. J Appl Polym Sci 1997, 66, 243.