Electroconducting Composites Based on Polyaniline and Monomer-Swollen Polychloroprene

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ABSTRACT: Electroconductive polychloroprene (CR)–polyaniline (Pani) composites were prepared by swelling the vulcanized rubber material in aniline followed by immersing the specimen in an aqueous solution of HCl containing ammonium persulfate as the oxidant. The results obtained from surface and volume conductivity, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) analysis suggest that the Pani component is preferentially located in the surface layer. These composites display better electrical and mechanical performance than those obtained by mixing both polymer components in the bulk state. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2329–2334, 1999

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INTRODUCTION

Polyaniline has been found to have several interesting applications in electronic, optical, and biological areas because of its conducting and electrochromic properties.[1] Unfortunately, it is extremely difficult to process and normally displays poor mechanical performance. One approach to reaching good physical and electrical properties is to develop composite systems by blending a common polymer with polyaniline either in solution[2] or by a melt process.[3,4] When the conventional polymer is an elastomer, the corresponding composite prepared by a melting process presents a low electrical conductivity.[5] This behavior may be attributed to the presence of a vulcanizing system, required to impart good mechanical proper-

ties to the rubber materials. Indeed, in the preceding article concerning the electrical conductivity of polychloroprene (CR)/polyaniline (Pani) blends, we found an electrical conductivity as low as 10^{-9} S cm^{-1}, with the addition of Pani in a concentration as high as 50 wt %, when the composite was prepared by a bulk process.[6]

Several articles have dealt with the development of conducting polymer blends by preparing the intrinsically conducting polymer in the presence of an insulating polymer matrix.[7–12] One classical example consists of an vapor-phase polymerization of pyrrole on polymer films impregnated with the oxidant.[8–10] The same approach was also applied for the development of Pani-based electroconducting composites.[11–13] For this purpose, thermoplastic films were swollen in an aniline monomer and then immersed in a cooled solution of the oxidant. This procedure normally results in better values of electrical conductivities.

Based on this idea, we decided to study a similar polymerization system involving the *in situ* polymerization of aniline swollen in vulcanized

CR specimens. In this communication, we discuss the electrical and mechanical properties of the CR/Pani composites prepared by this method. The surface composition by X-ray photoelectron spectroscopy (XPS) was also analyzed.

EXPERIMENTAL

Materials

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

Preparation of CR/Pani Composites

Vulcanized CR samples were obtained as described in the previous report.[6] The specimens with a dimension of 40 × 40 × 1 mm were allowed to swell in aniline for different times and then wiped with a cloth. The content of the absorbed aniline in the rubber samples was estimated by comparing the weight of the initial specimens with those of the swollen ones. The polymerization was carried out by immersing the swollen CR in the cooled aqueous solution of ammonium persulfate (0.3M) in a 1M aqueous solution of HCl for 1 week at −10°C. After the polymerization, the specimens were washed with a 1M solution of HCl, then with water, and dried under a vacuum at 50°C. The Pani content in the composites was determined by submitting the samples to extraction with methanol in an Soxhlet apparatus for 24 h. This procedure is able to extract all nonreacted aniline inside the specimen.

Characterization

Surface electrical conductivity was measured with the help of a Keithley 617 electrometer using the conventional four-point probe method. Volume conductivity was obtained in the same electrometer by using contacts in a sandwich configuration. The electrode area was 9 cm^2. All measurements were performed at room temperature and at an air relative humidity of 70%.

Tensile properties were obtained on an Instron 4204 testing machine at room temperature with a draw speed of 100 mm/min. For these measurements, specimens of 2-mm thickness were prepared according to ASTM D638.

Scanning electron micrographs were taken on a JEOL Model JSM-5300. Both the sample surface and the cryofracture surface were covered with gold before the analysis.

XPS measurements were carried out on a Kratos XSAM-800 dual-chamber spectrometer, under conditions described elsewhere.[6,14] Quantitative analysis of the sample surface was made based on the integral peak intensities. All spectra were referenced to the C1s neutral carbon peak set at 284.6 eV as in the earlier work.[1] 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 CR. 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 the emeraldine base (EB).

RESULTS AND DISCUSSION

Table I shows the electrical conductivity of CR/Pani composites as a function of the swelling time of the CR-vulcanized samples in the aniline medium. As expected, the amount of absorbed aniline in these CR specimens increased with the time. These samples containing different amounts of aniline were then treated with an ammonium persulfate/HCl aqueous solution for 1 week. The surface conductivity increased substantially (from 10^{-12} to 10^{-7} S cm^{-1}) when only 16 wt % of aniline was present inside the specimen (1 h swelling) and continuously increased with the amount of the absorbed aniline until about 25 wt %. After this point, the aniline content increased with the time, as expected, but the conductivity was not affected.

This behavior is better illustrated in Figure 1. The volume conductivity values were similar to the pure CR sample whatever was the content of the absorbed aniline or the Pani content formed during the *in situ* polymerization. The conducting CR/Pani composites were submitted to extraction with methanol for 24 h in a Soxhlet apparatus. After the extraction, the rubber surface retained the characteristic green color of the protonated Pani while the interior was completely decolored. These results indicate that the *in situ* polymerization takes place at the surface of the material. Since aniline can diffuse inside the rubber specimen, the low volume conductivity can be attributed to the difficulty of diffusion of the oxidizing

Table I   Electrical Conductivity of CR/Pani Composites as a Function of the Swelling Time of the Vulcanized Rubber in Aniline

Swelling Time (h)	Content of Absorbed Aniline (%)	Content of Pani (%)	Surface Conductivity (S cm^{-1})	Volume Conductivity (S cm^{-1})
1	16	14	7×10^{-7}	2×10^{-12}
2	25	20	2×10^{-5}	7×10^{-11}
3	28	23	3×10^{-5}	7×10^{-11}
4	39	30	3×10^{-5}	8×10^{-11}
5	41	33	2×10^{-5}	8×10^{-11}
6	43	34	2×10^{-5}	8×10^{-11}
7	46	36	3×10^{-5}	6×10^{-11}
72	51	38	4×10^{-5}	7×10^{-11}

agent into the polymer bulk. The surface conductivities of these composites are lower than those of pure Pani, which was found to be equal to 10^{-2} S cm^{-1}.[6]

The formation of conductive Pani at the CR surface can be observed by scanning electron microscopy (SEM). Figure 2 illustrates the SEM micrographs of the CR/Pani composite taken from the surface [Fig. 2(a)] and the cryofracture [Fig. 2(b)]. The surface of the compound presents a homogeneous distribution of Pani with a granular structure. The micrograph of the cryofracture presents two distinct regions consisting of the pure CR phase inside the sample and the surface layer containing the Pani was well adhered to the matrix.

XPS was employed to determine the surface composition of these samples. Figure 3 illustrates the N1*s* and Cl2*p* core-level spectra surfaces of the CR-vulcanized sample and of the CR/Pani composite. The spectrum of a vulcanized CR sample [Fig. 3(b)] displays the Cl2*p* line at 200.0 eV,

Figure 2   SEM of the CR/Pani composite prepared by *in situ* polymerization of aniline in the presence of vulcanized CR: (a) surface analysis; (b) cryofracture of the sample.

Figure 1   Surface conductivity of CR/Pani composites prepared by the *in situ* polymerization of aniline.

Figure 3   XPS core-level spectra of (a) N1*s* and (b) Cl2*p* of the CR-vulcanized sample and (c) N1*s* and (d) Cl2*p* of the CR/Pani composite.

which is characteristic of the covalent Cl—C bond. No traces of nitrogen were observed, as expected [see Fig. 3(a)]. The N1*s* spectrum [Fig. 3(c)] of the CR/Pani composite shows the typical signals due to the protonated Pani, that is, amine groups (—NH—) at 399.4 eV, imine groups (=N—) at 398.2 eV, and the positively charged nitrogen groups at 400.7 and 402.2 eV (components N_1^+ and N_2^+, respectively).[15,16] The Cl2*p* spectrum of the composite [Fig. 3(d)] presents a signal at 196.8 eV, characteristic of chloride ions in the protonated Pani. In addition to this peak, another one with lower intensity can be observed at 200.0 eV. This peak appears in the same region as the Cl2*p* peak related to the CR sample.

The distribution of nitrogen and chloride atoms with various chemical states can be found from the quantitative analysis of the spectra (Table II). The positively charged components N_1^+ and N_2^+ (32 and 5%, respectively) predominate over the imine groups (8.8%) in the CR/Pani sample, as expected. The quantitative analysis of the CR/Pani surface also revealed a doping degree of Pani corresponding to 0.37. This value was obtained by relating the amount of positively charged nitrogen with the noncharged nitrogen groups (amine and imine). It is curious to see in Table II that, despite the higher doping degree of Pani in the composite related to the pure Pani · HCl, the surface conductivity of the composite is three or-

Table II   XPS Characterization Data for the CR-Vulcanized Sample, Pure Pani · HCl, and the CR/Pani Composite

	Surface Composition (%)										
					Components of N1*s*				Components of Cl2*p*		Surface Conductivity
Sample	C	O	N	Cl	=N—	—NH—	N_1^+	N_2^+	Cl⁻	Cl—C	(S cm⁻¹)
CR	78	3.2	0	19.0	—	—	—	—	0	100	—
CR/Pani · HCl	80	7.1	8.4	4.8	8.8	54	32	5	78	22	4×10^{-5}
Pani · HCl[a]	82	6.4	8.4	3.6	13	64	18	5.6	98	—	2×10^{-2}

[a] Data taken from ref. 6.

Table III Mechanical and Electrical Properties of CR/Pani Composites Prepared by Bulk Process and by *In Situ* Polymerization

Sample	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Surface Conductivity (S cm^{-1})
Pure CR	23	5000	—
CR/Pani = 50 : 50 by bulk process	3	900	10^{-9}
CR/Pani by *in situ* polymerization	10	3300	10^{-5}

ders lower. Two factors may be responsible for these results: The first concerns the possibility of chlorine elimination under ultrahigh vacuum conditions of the XPS experiments, as reported in the literature.[17] This elimination should be minimized when the rubber is present in the sample. In addition, a small amount of CR was also detected at the composite surface (about 5%), as indicated by the Cl2p peak at 200.0 eV. The presence of the rubber at the surface may also be contributing to the lower conductivity values.

The tensile properties of the CR/Pani composites prepared by *in situ* polymerization and a bulk process are compared in Table III. CR/Pani prepared by a bulk process was previously discussed and involves the blending of both polymer components together with the curative system followed by vulcanization.[6] Both ultimate tensile strength and elongation at break decrease when Pani is incorporated into the vulcanized rubber material. Nevertheless, it is interesting to note the higher mechanical performance associated to the higher surface conductivity of the composite prepared by *in situ* polymerization. When Pani was blended with CR in the bulk process, a very high amount of Pani (about 50%) was required to achieve better conductivity. This so-high proportion of the brittle Pani strongly affects the tensile properties.

CONCLUSIONS

From the results presented in this communication, we can conclude that electroconductive polymer composites based on the CR vulcanized matrix swollen in aniline can be prepared. In such materials, Pani is preferentially located in the surface layers. This behavior was suggested from the differences found in the surface and volume conductivity values and SEM analysis. In addition, XPS analysis also revealed that Pani · HCl is the main constituent of the surface although some amount of CR can be found. The Pani component

in the composite presented a higher doping degree but lower surface conductivity when compared with the pure Pani · HCl sample. This result may be associated to the presence of the rubber component at the surface, as indicated by the XPS analysis. In addition, the vulcanization system may be affecting the conducting process. The influence of the curing components on the electrical conductivity of these materials will be studied in forthcoming articles. Finally, the composites prepared by the *in situ* polymerization technique present better electrical and mechanical performance than those obtained by mixing Pani · HCl with CR in a bulk process.

REFERENCES

1. Frommer, J. E.; Chance, R. R. In Encyclopedia of Polymer Science and Technology; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1986; Vol. 5.
2. Minto, C. D. G., Vaughan, A. S. Synth Met 1996, 81, 81.
3. Zilberman, M.; Titelman, G. I.; Siegmann, A.; Haba, Y.; Narkis, M.; Alperstein, D. J Appl Polym Sci 1997, 66, 243.
4. Ikkala, O. T.; Laaksob, J.; Väkipartack, K.; Virtaneb, E.; Ruohonenc, H.; Järvinenb, H.; Takab, T.; Passiniemi, P.; Österholmb, J. E. Synth Met 1995, 69, 97.
5. Vallim, M. R.; Felisberti, M. I.; De Paoli, M.-A. In Proceedings 2nd Simposio Iberoamericano de Polimeros, 4th Simposio Latinoamericano de Polimeros, 6th International Macromolecular Colloquium, Gramado, 1994; pp 215–217.
6. Pinho, M. S.; Golerova, M. M.; Dezotti, M.; Soares, B. G.; Pertsin, A. J. J Appl Polym Sci 1998, 70, 1543.

7. De Paoli, M.-A. In Handbook of Organic Conductive Molecules and Polymers; Nalwa, H. S., Ed.; Wiley: New York, 1997; Vol. 2, Chapter 18.

8. Zoppi, R. A.; Felisberti, M. I.; De Paoli, M.-A. J Polym Sci Polym Chem Ed 1994, 32, 1001.

9. Kurachi, K.; Kise, H. Macromol Chem Phys 1995, 196, 929.

10. Mano, V.; Felisberti, M. I.; Matencio, T.; De Paoli, M.-A. Polymer 1996, 37, 5165.

11. Ermusheva, S. Yu.;Yarysheva, L. M.; Volynskii, A. L.; Bakeev, N. F. Polym Sci Ser A 1996, 38, 761.

12. Byun, J. W.; Im, S. S. Synth Met 1993, 55–57, 3501.

13. Byun, S. W.; Im, S. S. Polymer 1998, 39, 485.

14. Pertsin, J.; Gorelova, M. M.; Levin, V. Yu.; Makarova, L. I. J Appl Polym Sci 1992, 45, 1195.

15. Kang, E. T.; Neoh, K. G.; Khor, S. H.;Tan, K. L.; Tan, B. T. G. J Chem Soc Chem Commun 1989, 696.

16. Kang, E. T.; Neoh, K. G., Tan, T. C., Khor, S. H., Tan, B. T. G., Macromolecules 1990, 23, 2918.

17. Yue, J., Epstein, A. J. Macromolecules 1991, 24, 4441.