An electroactive elastomer: polyaniline/nitrile rubber

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(Received 6 February 1991; revised 17 June 1991; accepted 1 August 1991)

An electroactive elastomeric material was prepared by the electrochemical graft copolymerization of aniline with nitrile rubber. The synthesis has been carried out potentiostatically, potentiodynamically or galvanostatically in a non-aqueous medium using a nitrile-rubber-coated working electrode. Infra-red spectra of the products resemble a superposition of nitrile rubber and polyaniline spectra. However, thermogravimetry, differential scanning calorimetry and solubility experiments indicate that the polyaniline chains grow as grafted branches of the nitrile rubber chains. Scanning electron microscopy indicates no phase segregation in accordance with this assumption. Cyclic voltammetry experiments indicate that the new material has the same electroactivity as pure polyaniline.

(Keywords: conducting graft copolymer; electroactive elastomer; polyaniline; nitrile rubber)

INTRODUCTION

Different approaches have been used in order to improve the mechanical properties of conductive polymers. The use of surfactants as counterions in the electrochemical polymerization of polypyrrole was proven to produce films with polystyrene-like mechanical properties[1]. Flexible polyaniline with 41% elongation at break has been prepared by the electrochemical reduction of the polymer in organic solvents[2]. Preparation of composites of insulating and conductive polymers has also proven to produce materials that retain the properties of both components of the composite. By using this last approach, we prepared previously the following materials: polypyrrole/poly(vinyl chloride)[3], polyaniline/cellulose acetate[4], poly(3-methylthiophene)/nitrile rubber[5] and, more recently, polyaniline/nitrile rubber[6].

The electrochemical synthesis of polyaniline (PAn) was first described in 1862[7] and its electrochromic properties were reported for the first time in 1876[8]. After the discovery of the remarkable conductive properties of polyacetylene, much research work has been directed towards studying the properties of PAn. This interest stems from its conductivity associated with its high stability. However, PAn is normally obtained as a powdery material, either by electrochemical or by chemical synthesis in aqueous solutions. This powder can be pressed into pellets, but cannot be transformed into self-supporting films by common processing methods.

In the literature we find several reports on the electrochemical preparation of PAn composites with poly(methyl methacrylate)[9], Nafion[10,11], nylon-6[12], and poly(ethylene imine)[13]. The technique used generally consists of combining a polymer that can be swollen in the electrolyte solvent and the necessary polymerization conditions. Also, graft copolymers of PAn and poly(*p*-aminostyrene) have been chemically prepared by the usual oxidative polymerization method using an aqueous acid solution of aniline, the oxidizing agent and the supporting polymer[14].

Nitrile rubber (NBR) is a copolymer of butadiene and acrylonitrile produced on a large scale with different comonomer proportions. Its advantages over other rubbers are its resistance to acid attack and its ease of vulcanization. Thus it was a good candidate to combine properties with PAn. On the other hand, PAn can be prepared in conductive form in non-aqueous media using trifluoroacetic acid and an appropriate electrolyte[15].

The aim of this work was the synthesis of an elastomeric material with the electrochemical properties of PAn associated with good mechanical properties and chemical inertness. This material was obtained as a graft copolymer of polyaniline and nitrile rubber.

EXPERIMENTAL

Potentiodynamic synthesis was performed using a solution of aniline (freshly distilled, 0.1 M), $(C_4H_9)_4NBF_4$ (Aldrich, used as received, 0.1 M) and CF_3COOH (Aldrich, used as received, 1.0 M) in dry acetonitrile. The working platinum electrode (1.0 cm^2) was coated with a film of nitrile rubber (NBR) by casting a toluene solution (40 $g\,l^{-1}$). A platinum foil was used as counter-electrode. All potentials described in this work are related to an Ag/AgCl electrode. The potential was cycled from 0 to 2.0 V at a scanning rate of 20 $mV\,s^{-1}$ up to a constant peak current. The potential scans were performed using a FAC 200 potentiostat interfaced to an IBM-PC compatible computer.

Potentiostatic synthesis was performed at different potentials, namely 1.5, 1.3, 1.0, 0.8, 0.7 and 0.6 V. For these experiments, we used the same concentrations as above.

The films obtained were characterized by infra-red

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0032-3861/92/112427-04

spectra using a Jasco model A-202 spectrophotometer. Thermogravimetric analysis (t.g.a.) and differential scanning calorimetry (d.s.c.) were carried out in a Du Pont Thermal Analyzer model 1090B at a heating rate of 10°C min^{-1} under a N_2 atmosphere. Scanning electron microscopy was done using a Cambridge Instruments Stereoscan 100 with an acceleration voltage of 25 kV and 70 Å resolution.

The nitrile rubber (NBR), poly(butadiene-*co*-acrylonitrile), used in this work was produced and supplied by Nitriflex, and has a 71:29 butadiene:acrylonitrile content. The rubber was purified by dissolution in chloroform and coagulation in methanol.

RESULTS AND DISCUSSION

Synthesis of the material was initially performed potentiodynamically[6]. As reported previously, NBR samples with different acrylonitrile contents (29, 32, 39 and 45%) were tested. The 29% NBR furnished the most homogeneous product. Galvanostatic synthesis also provided uniform and homogeneous samples. In *Figure 1* we compare the cyclic voltammetric curves for pure PAn and for PAn/NBR obtained galvanostatically at 0.5 mA cm^{-2}. For PAn/NBR we observe a broadening of the redox peaks and a peak potential shift. However, the aspects of the curves indicate that the electrochemical processes observed and the electroactivity of PAn/NBR are very similar to those of pure PAn.

The infra-red spectra of pure NBR, pure PAn and PAn/NBR (potentiostatically prepared at 0.7 V) are shown in *Figure 2*. The NBR spectrum shows characteristic absorptions at 2250 cm^{-1} (C≡N stretching), 1665 and 1640 cm^{-1} (C=C stretching) and 1440 cm^{-1} (out-of-plane C–H wagging). The PAn spectrum also has characteristic absorptions at 1555 and 1485 cm^{-1} assigned to C=N stretching, at 1298, 1238 and 1140 cm^{-1} assigned to aromatic amines and the BF_4^- absorptions at 503, 796 and 1082 cm^{-1}. The PAn/NBR spectrum resembles a superposition of the spectra of both components with predominance of NBR absorption bands. In particular, we have absorptions at 1140 cm^{-1} assigned to amine C–N stretching, 1490 cm^{-1} assigned to C=C stretching of the aromatic rings and 1585 cm^{-1} assigned to C=N stretching.

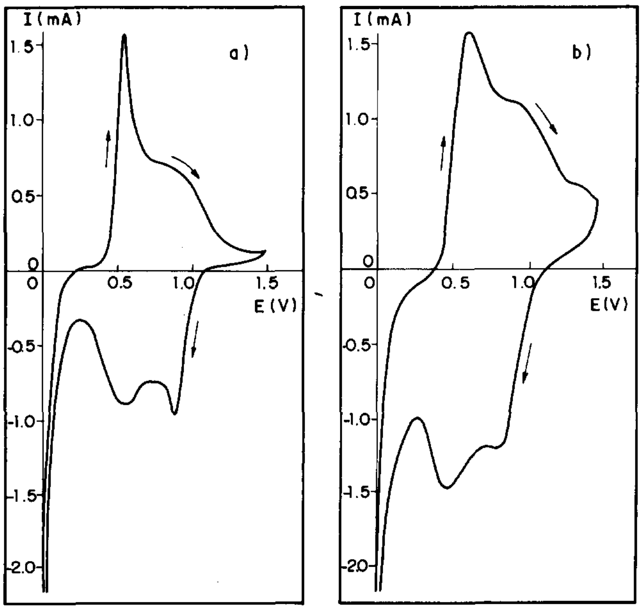

Figure 1 Cyclic voltammetry of galvanostatically (0.5 mA cm^{-2}, 0.5 C cm^{-2}) prepared PAn (a) and PAn/NBR (b) samples. Measurements were made at 20 mV s^{-1} in 1 M CF_3COOH and 0.1 M $(C_4H_9)_4NBF_4$ acetonitrile solution

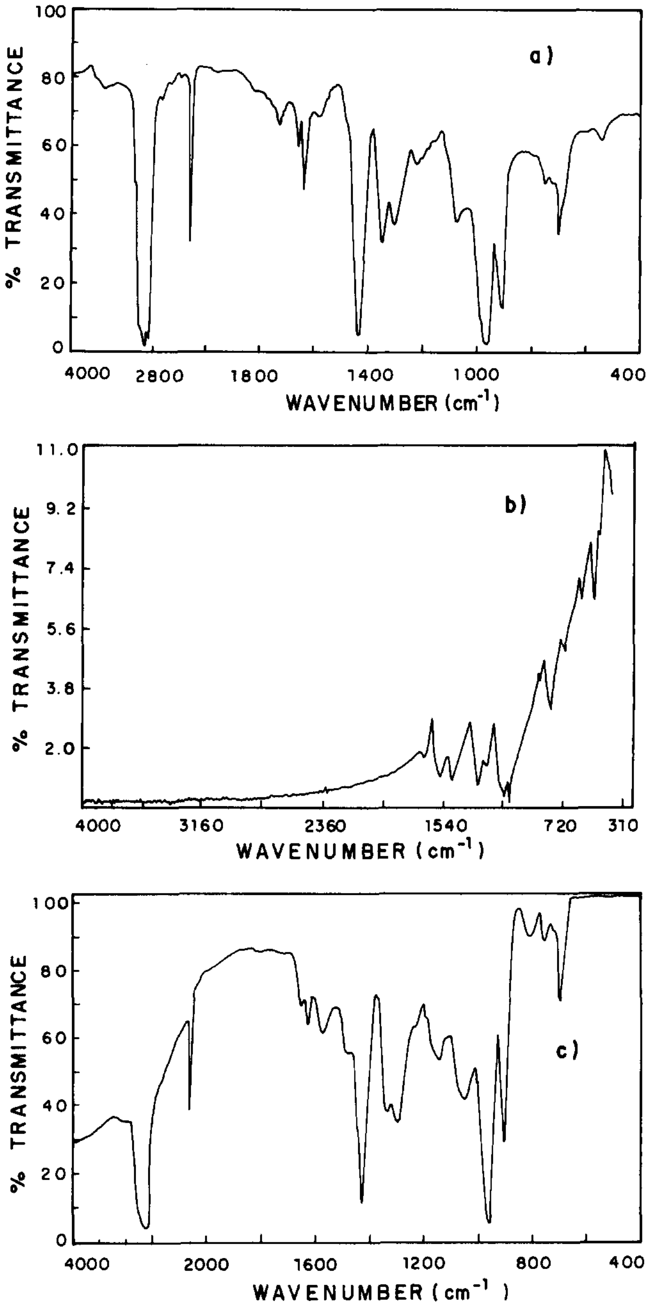

Figure 2 Infra-red spectra of (a) film of pure nitrile rubber, (b) KBr pellet of pure polyaniline (*FTi.r.*) and (c) film of PAn/NBR

The t.g.a. curve for PAn/NBR under a nitrogen atmosphere is shown in *Figure 3*. The overall appearance of this curve is similar to the t.g.a. curve obtained for pure NBR. However, a careful analysis reveals distinct features. For PAn/NBR a slow mass loss is observed after 100°C, reaching 6% at 360°C. This could be assigned to low-molecular-weight oligomers adsorbed in the rubber. However, in previous t.g.a. measurements with aqueous HCl-prepared PAn, the weight loss at

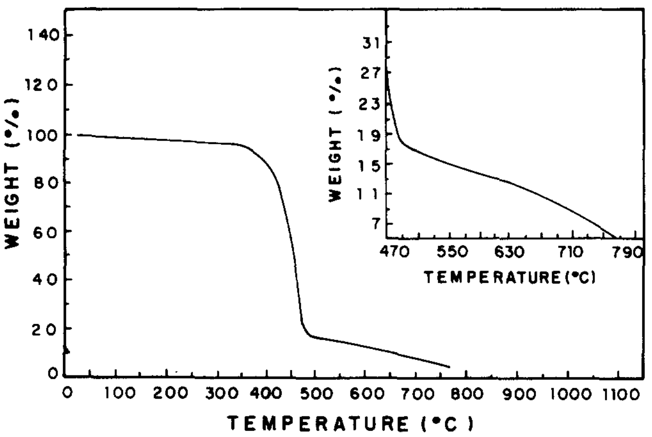

Figure 3 Thermogravimetric curve for PAn/NBR at 10°C min^{-1} under a nitrogen atmosphere. The insert shows an expansion of the 470–790°C range of the same thermogram

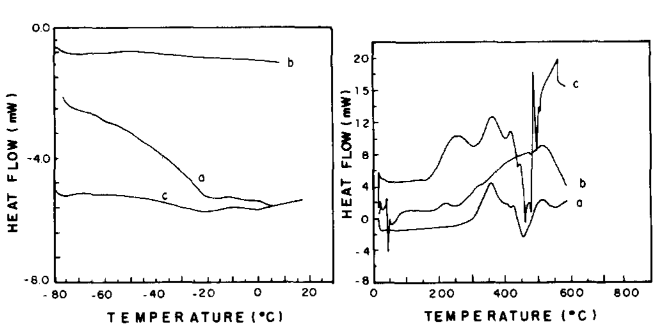

Figure 4 Differential scanning calorimetry curves for (a) pure NBR, (b) pure polyaniline and (c) PAn/NBR. Heating rate = 10°C min^{-1}

100°C was assigned to entrapped solvent volatilization[16]. Above this temperature there is a loss of mass up to 500°C (82%). This loss is smaller than the mass loss observed for pure NBR in this temperature range (96%). The lower slope of the mass loss curve in this temperature range could indicate a superposition of PAn and NBR degradation or the degradation of a third material. A subsequent slow mass loss of 12% occurs up to 650°C.

The d.s.c. analysis was performed in two temperature ranges, from −80 to 20°C and from 20 to 600°C (*Figure 4*). By careful analysis of the pure NBR low-temperature curve, we observe an endothermic transition at −60°C assigned to its T_g and an exothermic transition at −20°C. Pure PAn shows no transitions in this temperature range. The PAn/NBR curve does not show the T_g transition observed for the pure rubber, but an endothermic transition observed at −45°C could be assigned to its T_g. The exothermic transition at −20°C is also observed. By analysing the high-temperature d.s.c. we observe that PAn/NBR shows thermal processes that coincide with pure PAn and pure NBR. However, in addition, it also shows heat variations at 260, 425, 440, 505 and 570°C. These results, associated with the t.g.a. results, strongly suggest that the material obtained is not a composite or a blend but a grafted copolymer. This part of the thermogram is shown in detail in the insert of *Figure 3*.

In order to test this conclusion, we performed solubility tests with the material obtained. In a previous work with a polypyrrole/NBR composite, it was shown that the rubber could be completely washed away, producing partially oriented pure polypyrrole[17]. We have also tested our previously obtained polypyrrole/poly(vinyl chloride) composites in the same way and observed ~100% mass recovery of PVC from the material[3]. This unquestionably showed that these materials were composites. In the case of PAn/NBR, a weighed film was immersed in toluene or chloroform for several hours with stirring. A swelling with 10% loss of dry weight was observed, but no rubber dissolution could be detected. On the other hand, in another work we observed that PAn becomes soluble after deprotonation in a basic solution[18]. However, upon immersion of the material in a 1.0 M NH_4OH solution in acetonitrile, we observed a slight colour change but, also in this case, no dissolution could be detected.

The scanning electron micrographs of the cross-sections of a pure NBR film and of a PAn/NBR film are shown in *Figure 5*. Although the PAn/NBR surface is rough, if we compare its cross-section with that of the pure rubber we observe no phase separation or segregation. Roughness of the surface is probably produced during evaporation of the swollen solvent or peeling from the electrode. These results indicate that we have either a blend with very compatible components or copolymer formation. Samples prepared at different current densities

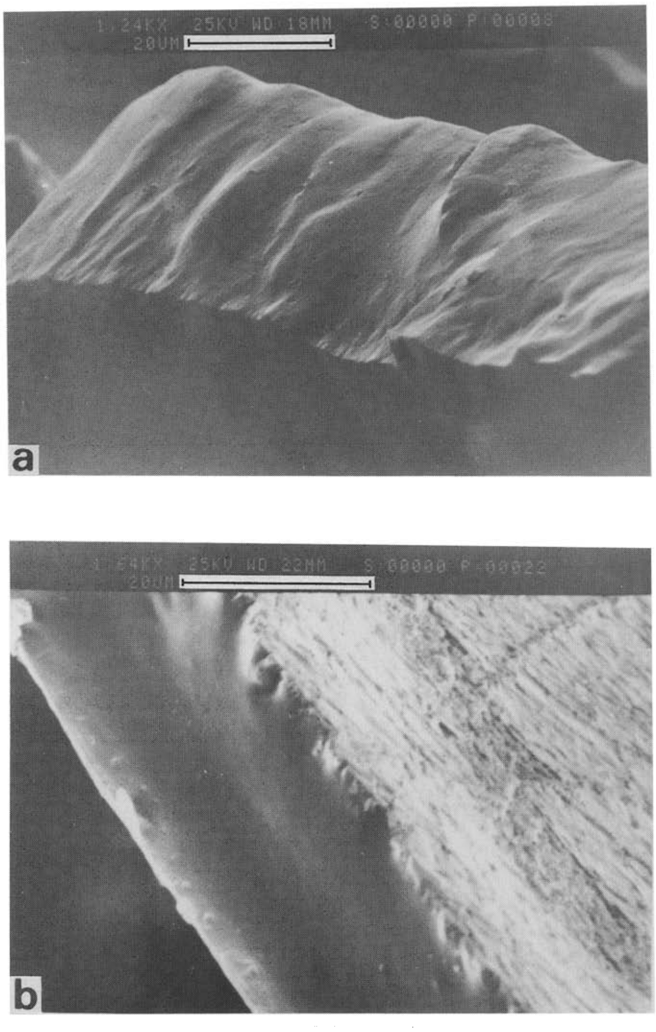

Figure 5 Scanning electron micrographs of the cross-sections of (a) pure NBR film and (b) PAn/NBR film. The bars at the top represent 20 μm

have been investigated by the same technique, with similar results.

CONCLUSIONS

From our results we conclude that, in contrast with the previously obtained composites, the characterization of the material prepared in this work points towards a graft copolymer of polyaniline and 71:29 nitrile rubber.

The electropolymerization mechanism of aniline is assumed to occur by the initial formation of a cation radical and subsequent reaction of this radical with neutral aniline with loss of protons[10]. Although much controversy still persists as to the nature of the propagation reaction, the first step is undoubtedly cation radical formation. Unsaturated polymers are very sensitive to free-radical attack, and indeed graft copolymerizations with these polymers are routinely performed using free-radical initiators. The local concentration of NBR carbon–carbon double bonds around the aniline cation radicals formed in the rubbery matrix is probably high enough to compete with aniline polymerization. Thus, it would be rather expected that aniline cation radicals would react with these bonds, initiating the grafting process (in fact, the lower intensity of the 1640 cm^{-1} band in the spectrum in *Figure 2c* in relation to that in *Figure 2a* indicates C=C bond consumption). The aniline cation radical attack on the C=C bond will attach it to the rubber chain and simultaneously create a new free radical on the other carbon. This new free radical may either react with another aniline cation radical or initiate crosslinking. This may also be the reason for the insolubility of PAn/NBR.

We conclude that free-standing films of the graft copolymer of PAn and NBR were obtained and that this material is electroactive. Work is in progress to characterize the electrochemical and electrochromic properties of the copolymer, as well as to study its vulcanization.

ACKNOWLEDGEMENTS

Partial support from Nitriflex and financial support from the CNPq/RHAE programme under grant number 208/88-N.M. are gratefully acknowledged. E.L.T. also thanks FAPESP for a fellowship (Proc.N.90/0011-9-QI). We also thank Dr Panero for profitable suggestions.

REFERENCES

1 Peres, R. C. D., Pernaut, J. M. and De Paoli, M.-A. *J. Polym. Sci., Polym. Chem. Edn.* 1991, **29**, 225

2 Kitani, A., Kaya, M., Yano, J., Tsujioka, S.-I. and Sasaki, K. *J. Polym. Sci., Polym. Chem. Edn.* 1988, **26**, 1531

3 De Paoli, M.-A., Waltman, R. J., Diaz, A. F. and Bargon, J. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 1687

4 Rodriguez, M. A., Rezende Duek, E. A. and De Paoli, M.-A. Int. Conf. on Science and Technology of Synthetic Metals, Tübingen, 1990

5 Zoppi, R. A. and De Paoli, M.-A. *J. Electroanal. Chem.* 1990, **290**, 275

6 Tassi, E. L. and De Paoli, M.-A. *J. Chem. Soc., Chem. Commun.* 1990, 155

7 Letheby, M. *J. Chem. Soc.* 1862, **224**, 161

8 Goppelsröder, M. F. *Comptes Rendus* 1876, **82**, 331

9 Lacroix, J.-C. and Diaz, A. F. *Makromol. Chem., Macromol. Symp.* 1987, **8**, 17

10 Orata, D. and Buttry, D. A. *J. Electroanal. Chem.* 1988, **257**, 71

11 Bidan, G. and Ehui, B. *J. Chem. Soc., Chem. Commun.* 1989, 1568

12 Gregory, R. V., Kimbrell, W. C. and Kuhn, H. H. *Synth. Met.* 1989, **28**, C-823

13 Akhtar, M., Weakliem, H. A., Paiste, R. M. and Gaugham, G. *Synth. Met.* 1988. **26**, 203

14 Li, S., Cao, Y. and Xue, Z. *Synth. Met.* 1987, **20**, 141

15 Osaka, T., Nakajima, T., Naoi, K. and Owens, B. B. *J. Electrochem. Soc.* 1990, **137**, 2139

16 Wei, Y. and Hsueh, K. F. *J. Polym. Sci., Polym. Chem. Edn.* 1989, **27**, 4351

17 Naoi, K. and Osaka, T. *J. Electrochem. Soc.* 1987, **134**, 2479

18 Rodrigues, M. A. and De Paoli, M.-A. Int. Conf. on Science and Technology of Synthetic Metals, Tübingen, 1990

19 Genies, E. M., Boyle, A., Lapkowski, M. and Tsintavis, C. *Synth. Met.* 1990, **36**, 139