Electrochemical, electrochromic and mechanical properties of the graft copolymer of poly(aniline) and nitrilic rubber

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The electroactivity and electrochromism of the graft copolymer of poly(aniline) and nitrilic rubber were studied by cyclic voltammetry, frequency response analysis and spectroelectrochemistry in the visible range. The mechanical properties were determined by stress–strain measurements. Results indicate that the graft copolymer exhibits mechanical properties similar to a crosslinked elastomer with the electrochromic and electrochemical properties typical of oxidized poly(aniline).

(Keywords: electroactivity; electrochromism; graft copolymer)

INTRODUCTION

Different strategies have been used to improve the mechanical properties and the processability of conductive polymers. By using surfactants as counterions it is possible to prepare electrochemically poly(pyrrole) films with poly(styrene)-like mechanical properties[1]. Solution processable conductive polymers may also be electrochemically prepared[2]. Also, blending a conductive and an insulating polymer produces materials which combine the properties of both components. This may be achieved electrochemically, as in the case of the electropolymerization of pyrrole on a poly(vinyl chloride) support[3], poly(aniline) on cellulose acetate[4], poly(3-methylthiophene) on nitrilic rubber[5] and, more recently, poly(aniline) on nitrilic rubber[6].

The interest in poly(aniline) stems from its stability in the oxidized conductive form[7,8]. Poly(aniline) obtained by chemical or electrochemical synthesis in HCl solution is a powdery material in the conductive oxidized form, however, precluding most of its potential technological applications. In its base form it is soluble in organic solvents and the films prepared by casting become conductive after solvent evaporation in an acidic atmosphere[9]. When prepared in high-molecular-weight acid its conductive form is soluble in organic solvents, permitting film preparation by casting[10].

Electrochemical preparation of poly(aniline) blends with different insulating polymers has been reported using poly(acrylic ester)s[11], Nafion[12,13], nylon-6[14] and poly(ethyleneimine)[15]. Graft copolymers of poly(aniline) and poly(aminostyrene) have also been electrochemically prepared using an organic acid as the electrolyte[16].

A successful electrochemical preparation of such a blend or graft copolymer requires the choice of a compatible polymer which can be swollen in the electrolyte solvent under the polymerization conditions. In this respect, nitrilic rubber (NBR), a copolymer of butadiene and acrylonitrile, appears as an ideal combination for poly(aniline) for its compatibility and resistance to chemical attack by strong acids. As proposed in a previous paper, the poly(aniline) chains grow as grafted branches of the NBR chains, following the aniline cation radical reaction with the C=C bond in the rubber backbone[17].

Considering the implications that this improvement may have for the applications of the material, it appeared of interest to us to carry out a detailed investigation of its electrochemical, electrochromic and mechanical properties. In this paper, we report the results obtained by cyclic voltammetry, frequency response analysis, spectroelectrochemistry and stress–strain measurements. Furthermore, scanning electron microscopy (SEM) was used to correlate the morphology with the electrochemical response of the films under various experimental conditions.

EXPERIMENTAL

Poly(aniline)–nitrilic rubber graft copolymer (PANI–NBR) films were prepared using previously described electrochemical methods[17]. The electrolyte was a 0.1 M solution of freshly distilled aniline in dry acetonitrile containing CF_3COOH (1.0 M) and $(C_4H_9)_4NBF_4$ (0.1 M), or, in some cases, $HClO_4$ (1.0 M) and $(C_4H_9)_4NClO_4$ (0.1 M). The working electrode was a platinum foil coated with films of NBR (71% butadiene and 29% acrylonitrile). Films having different thicknesses were obtained by

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evaporation of different volumes of a toluene solution of NBR ($40\,g\,l^{-1}$). All reagents were Fluka p.a. grade. After the galvanostatic synthesis ($0.5\,mA\,cm^{-2}$ and $0.5\,C\,cm^{-2}$), the PANI–NBR films were washed with pure acetonitrile, dried and stored for characterization. For the spectroelectrochemical measurements we used a transparent, conductive working electrode (ITO glass) coated with $10\,\mu l\,cm^{-2}$ of NBR solution, giving a film thickness of $6\,\mu m$. The graft copolymer film thicknesses were measured by scanning electron microscopy (SEM) in the dry state after peeling from the electrode. The pure poly(aniline) film thicknesses were measured on the electrode using an Alpha-step profilometer. For the mechanical properties measurements the films were also peeled from the electrodes.

The electrochemical and electrochromic properties of the PANI–NBR films were studied using a three-electrode cell with an Ag–AgCl electrode with an acetonitrile salt solution bridge as the reference electrode and a platinum foil as the counter electrode. Cyclic voltammetry was performed using an Amel 551 potentiostat coupled to an Amel 567 ramp generator and an X/Y recorder. A frequency response analyser (Solartron 1250) coupled to a Solartron 1286 potentiostat and interfaced with a Vectra HP computer was used for the impedance measurements. The sinusoidal perturbation was 10 mV and the frequency range was 10 mHz to 65 kHz.

The optical system for the spectroelectrochemical measurements consisted of a polychromatic light source, a collimating lens, a monochromator (Applied Physics), an electrochemical cell with two optical windows and a detector connected to a signal amplifier. The ramp generator and potentiostat signals were analysed by an IBM PC/XT computer simultaneously with the amplifier signal.

The mechanical properties were measured using an EMIC MEM 500 equipment interfaced with a PC/XT compatible computer. The strain rate used was $100\,mm\,min^{-1}$. The samples were galvanostatically obtained films of 10 × 40 × 0.05 mm. The results represent an average of five specimens.

RESULTS AND DISCUSSION

Cyclic voltammetry studies

The responses of pure poly(aniline) and PANI–NBR were compared in organic acid solutions under different potential ranges. *Figure 1* shows the first cyclic voltammograms of pure poly(aniline) prepared in solutions containing BF_4^- or ClO_4^-. With BF_4^- we observe a higher charge while the redox peaks are broad and poorly defined. After prolonged cycling the poly(aniline) (BF_4) film loses electroactivity. Similar results are reported by Goto *et al.*[18] for poly(aniline) studied in propylene carbonate–ethylene carbonate solutions. The cyclic voltammogram of pure poly(aniline) in ClO_4^--containing solution shows well defined peaks and a smaller separation between the anodic and cathodic peaks (ΔE_p). This indicates that films of poly(aniline) (ClO_4) are characterized by an electrochemical process with faster kinetics than poly(aniline) (BF_4). Similar differences in terms of peak responses are also observed for the parent PANI–NBR(BF_4) and PANI–NBR(ClO_4) films (*Figure 2*). Cyclic voltammograms of poly(aniline) in organic solvents reveal slower and less reversible systems with broader oxidation and reduction peaks in comparison to voltammograms of poly(aniline) in aqueous HCl solutions. These differences can be assigned to the production of shorter chain segments in the organic medium synthesis.

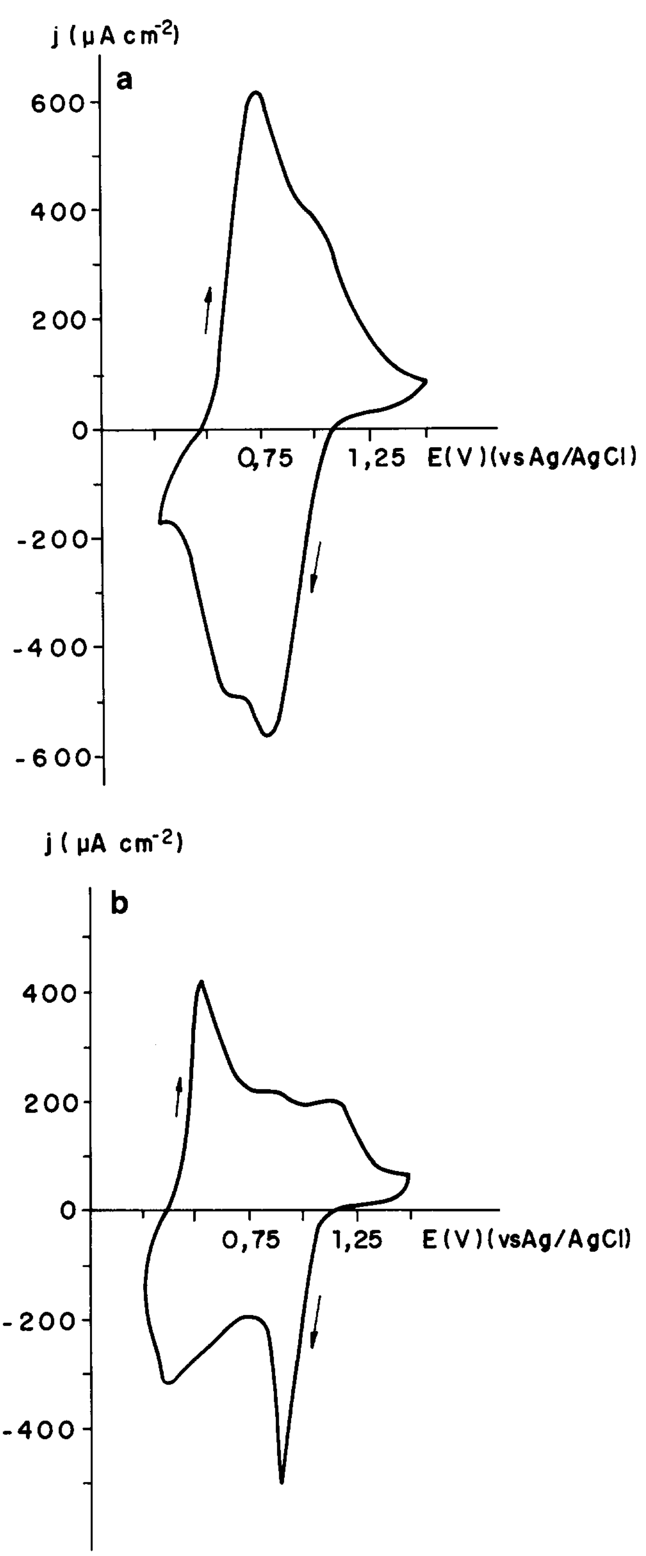

Figure 1 Cyclic voltammograms for poly(aniline) films ($0.2\,\mu m$ thick) on a Pt electrode at $20\,mV\,s^{-1}$ in (a) $(C_4H_9)_4NBF_4$, CF_3COOH acetonitrile solution and (b) $(C_4H_9)_4NClO_4$, CF_3COOH acetonitrile solution

The above-mentioned results confirm that the PANI–NBR films generally retain the electrochemical properties of pure poly(aniline). They also indicate that the behaviour of both types of film electrode is largely

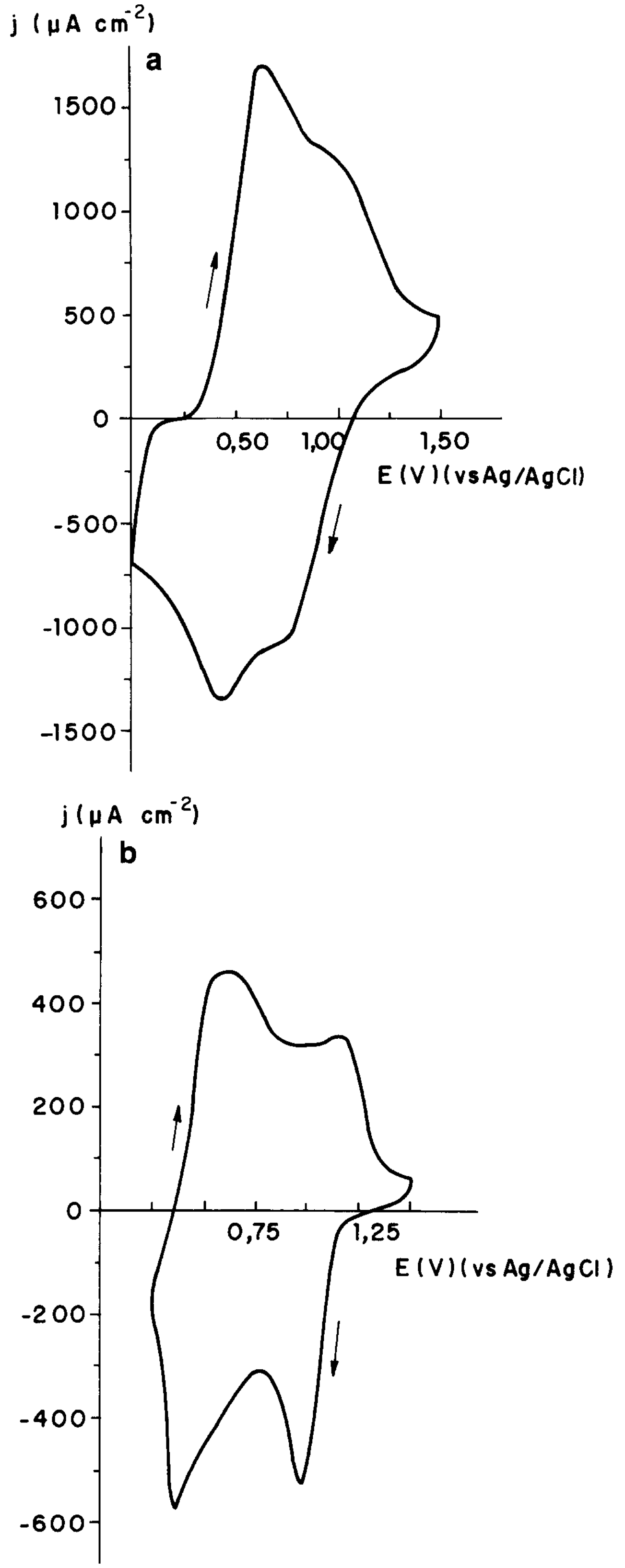

Figure 2 Cyclic voltammograms for PANI–NBR films (24 μm thick) on a Pt electrode at 20 mV s^{-1} in (a) $(C_4H_9)_4NBF_4$, CF_3COOH acetonitrile solution and (b) $(C_4H_9)_4NClO_4$, CF_3COOH acetonitrile solution

affected by the nature of the counterion. Since the differences appear to be mainly of a kinetic nature (*Figures 1* and *2*), it is reasonable to ascribe them to differences in electrode morphology induced by the acid–electrolyte couple in the synthesis. This is confirmed by the SEM analysis reported in *Figure 3*. The surface of the poly(aniline) (BF_4) film has a granular structure of high porosity (*Figure 3a*), while that of the poly(aniline) (ClO_4) film is rather compact with superposed bundles of fibres (*Figure 3b*).

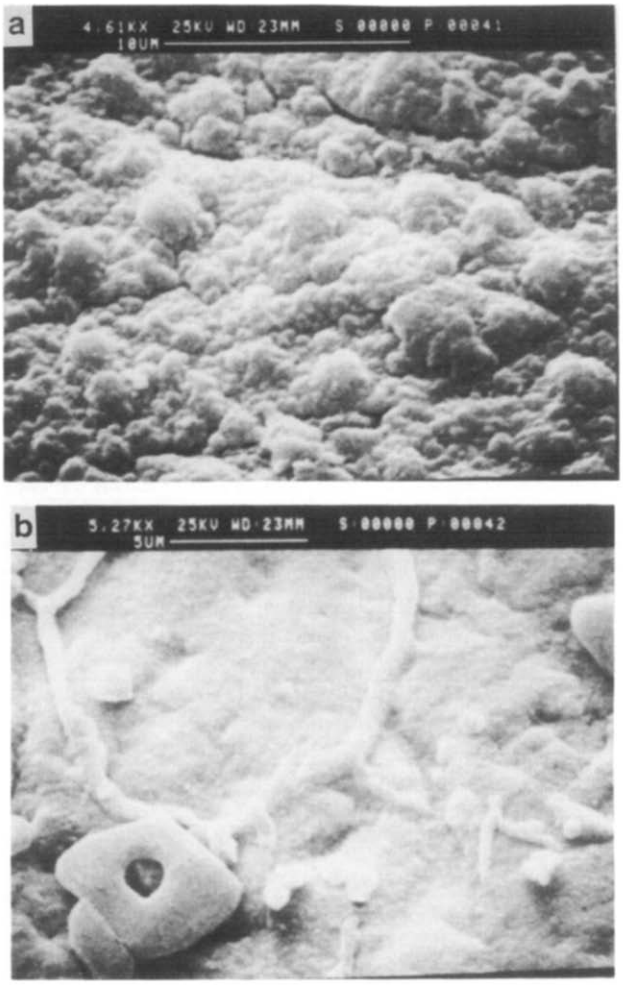

Figure 3 SEM micrographs of film surfaces: (a) poly(aniline) (BF_4); (b) poly(aniline) (ClO_4)

Table 1 Voltammetric data for PANI–NBR films prepared with different NBR thicknesses in 0.1 M $(C_4H_9)_4NBF_4$, 1.0 M CF_3COOH acetonitrile solution (scan rate 20 mV s^{-1}, voltage range 0–0.8 V *versus* Ag–AgCl)

Volume[a] (μl cm^{-2})	Q_{synth}[b] (C cm^{-2})	Q_{cat}[c] (C cm^{-2})	I_{pa}[d] (mA cm^{-2})	I_{pc}[e] (mA cm^{-2})
0	0.5	0.024	1.23	0.75
10	0.5	0.022	0.63	0.67
20	0.5	0.022	0.59	0.80
40	0.5	0.020	0.85	0.95
50	0.5	0.030	1.13	0.98

[a] Solution volume used for NBR film casting
[b] Synthesis charge density
[c] Cathodic charge density
[d] Anodic peak current density
[e] Cathodic peak current density

In order to investigate the correlation between the electrochemical response and the preparation method of the PANI–NBR films we prepared and tested films with NBR substrata of different thicknesses (*Table 1*). The synthesis charge density reported was calculated as a function of reaction time at 0.5 mA cm^{-2} and is not the effective synthesis charge because there are side reactions producing soluble products. Also, the redox potential E° values of the PANI–NBR films are not affected by the NBR film thickness (*Figure 4*). Therefore, we may conclude that the electrochemical properties of the poly(aniline)-containing graft copolymer are not affected by the rubber component.

A comparative analysis of the dependence of the anodic peak current values on the scan rate for pure poly(aniline) and graft copolymer films with various thicknesses indicates a linear behaviour for scanning rates below 20 mV s^{-1} (*Figure 5*), as observed by other authors[19,20]. At higher rates the behaviour deviates from linearity, suggesting that the mechanism passes from kinetic control to mass transfer control. Again, the response of the PANI–NBR film does not substantially differ from that of pure poly(aniline).

Another characteristic of the two materials is their cycling stability to potentials lower than 1.0 V (*versus* Ag–AgCl). If the cycling range is extended to 1.5 V (*versus* Ag–AgCl) the oxidation of the films becomes irreversible and the charge density is reduced.

Impedance studies

Impedance is a valuable tool for evaluating the properties of electrochemically active polymers such as poly(pyrrole)[21] and poly(aniline)[22]. The data obtained from Nyquist plots are the charge transfer resistance R_{ct}, the limiting resistance R_L, the double layer capacitance C_{dl} and the limiting capacitance C_L[23].

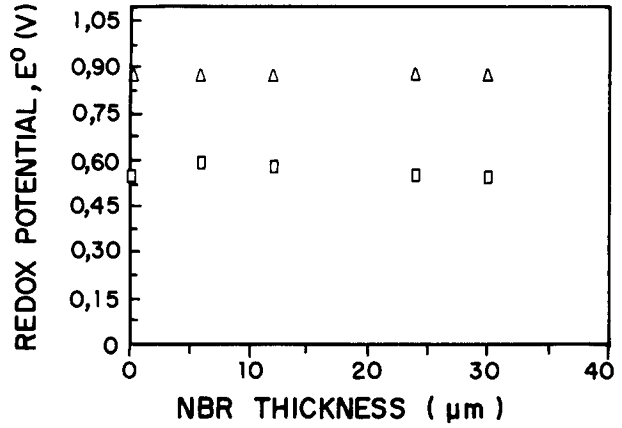

Figure 4 Variations in the potentials related to the first (E_1°, □) and the second (E_2°, △) redox processes of poly(aniline) as a function of NBR film thickness. The measurements were made in 0.1 M $(C_4H_9)_4NBF_4$, 1.0 M CF_3COOH acetonitrile solution

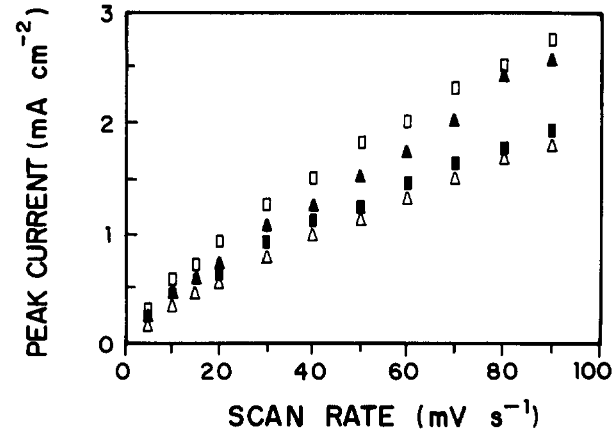

Figure 5 Anodic peak current (I_{pa}) *versus* scan rate in 0.1 M $(C_4H_9)_4NBF_4$, 1.0 M CF_3COOH acetonitrile solution for: (□) pure poly(aniline); (▲) PANI–NBR (10 μl cm^{-2}); (■) PANI–NBR (20 μl cm^{-2}); (△) PANI–NBR (60 μl cm^{-2})

Impedance data on pure poly(aniline) have been previously reported[22,24,25]. However, data and their interpretation for its blends with insulating materials are not available. The impedance parameters of poly(aniline) and PANI–NBR films were measured in order to compare the characteristics of the two materials and to gain further information on the mechanisms of their respective electrochemical processes.

In *Figure 6* are shown the overall impedance responses of a poly(aniline) film (0.2 μm thick) in 0.1 M $(C_4H_9)_4NClO_4$, 1.0 M CF_3COOH acetonitrile solution under positive and negative polarizations (*versus* Ag–AgCl). *Table 2* summarizes the relevant parameters obtained from these curves analysed by a modified Randles circuit and using a computer-based fitting program.

At a polarization of ca. 0.25 V (*Figure 6a*), a very large value of film resistance is revealed by a large, high frequency semicircle, confirming the insulating nature of the polymer in its reduced state. Under a more anodic polarization, i.e. 0.5 V (*Figure 6b*), the complex impedance Z''–Z' plot develops a defined, single semicircle followed by an impure capacitive behaviour.

We noticed that the charge transfer resistance, associated with the width of the semicircle at high frequencies, is potential dependent. Accordingly, when the polarization is extended to the second redox process, i.e. 1.15 V, the semicircle is very wide (*Figure 6c*). This reflects the other conductor–insulator transition. When the poly(aniline) film is extensively oxidized, i.e. at 1.5 V, the impedance response (*Figure 6d*) reflects a poor electrode behaviour, possibly associated with degradation phenomena[26]. At a moderate cathodic polarization (*Figure 6e*), the electrode assumes again the Randles-type behaviour, returning to a highly resistive and electrochemically inactive condition in the reduced state (*Figure 6f*).

Figure 7 illustrates the alternating current (a.c.) impedance response and *Table 3* lists the parameters for

Table 2 Impedance parameters for a poly(aniline) film (0.2 μm thick) in 0.1 M $(C_4H_9)_4NClO_4$, 1.0 M CF_3COOH acetonitrile solution

E (V)	R_{ct} (Ω)	C_{a1} (μF cm^{-2})	C_L (mF cm^{-2})	R_L (Ω)
0.25	5 000	40	–	–
0.50	60	21	10	180
1.15	9 000	40	–	–
1.50	18 400	17	–	–
0.90	210	38	5.9	296
0.35	8 000	40	–	–

Table 3 Impedance parameters for a PANI–NBR film (24 μm thick) in 0.1 M $(C_4H_9)_4NClO_4$, 1.0 M CF_3COOH acetonitrile solution

E (V)	R_{ct} (Ω)	C_{a1} (μF cm^{-2})	C_L (mF cm^{-2})	R_L (Ω)
0.25	5000	47	–	–
0.53	–	–	11.6	170
1.15	12 000	51	–	–
1.50	20 000	47	–	–
0.95	200	29	6.4	185
0.33	5700	41	–	–

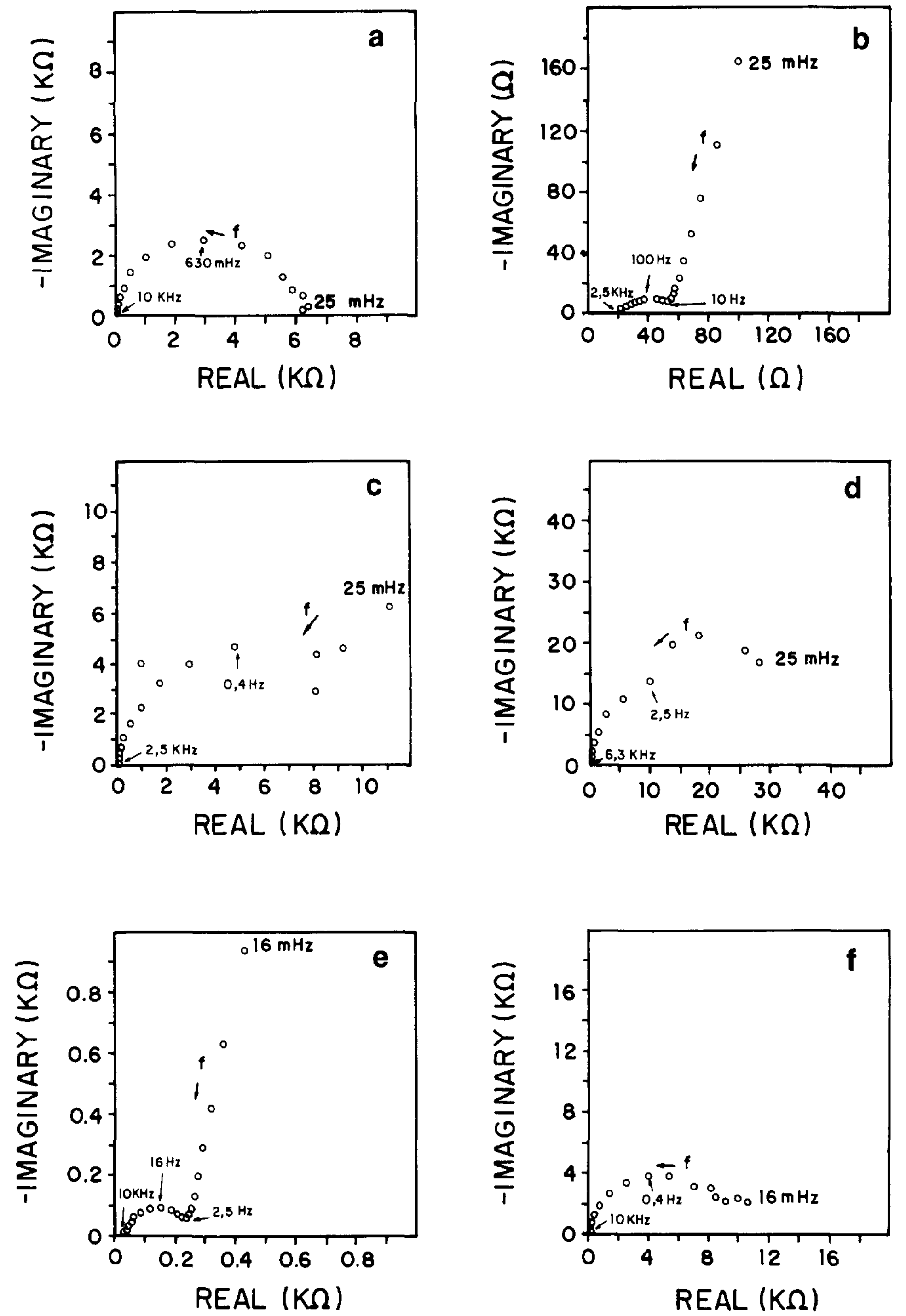

Figure 6 Impedance response of a poly(aniline) film (0.2 μm thick) in $(C_4H_9)_4NClO_4$, CF_3COOH acetonitrile solution under various polarizations (*versus* Ag–AgCl): (a) 0.25 V; (b) 0.50 V; (c) 1.15 V; (d) 1.50 V; (e) 0.90 V; (f) 0.35 V

a PANI–NBR(ClO_4) film (24 μm thick) in the same electrolyte as above. Comparison with *Figure 6* reveals similarities and differences between both films. The responses are almost identical in the insulating, reduced state (compare *Figure 7a* with *6a*) and in the high anodic degradation state (compare *Figure 7d* with *6d*). At moderate anodic polarizations (at ca. 0.5 V) the responses are different; the PANI–NBR film develops a 45° Warburg line and a capacitive line (*Figure 7b*), suggesting that the kinetics of the electrode process are predominantly diffusion controlled.

A similar behaviour is observed with a 12 μm thick PANI–NBR(ClO_4) film. The impedance parameters reported in *Tables 3* and *4* show that the values of R_{ct}, related to the interfacial electrochemical charge transfer process of the PANI–NBR film electrode, do not depend on the film thickness. It must be pointed out that the films used in this work (24 and 12 μm thick) show a capacitor-like behaviour for potentials at which the conducting state is present. In both cases a 45° Warburg line is observed, while for pure poly(aniline) it is absent (see *Figure 6b*).

Based on our early work[17] and on the above-reported electrochemical studies we propose that the polymeric electrode configuration consists of poly(aniline) nuclei growing from the electrode surface. The NBR matrix

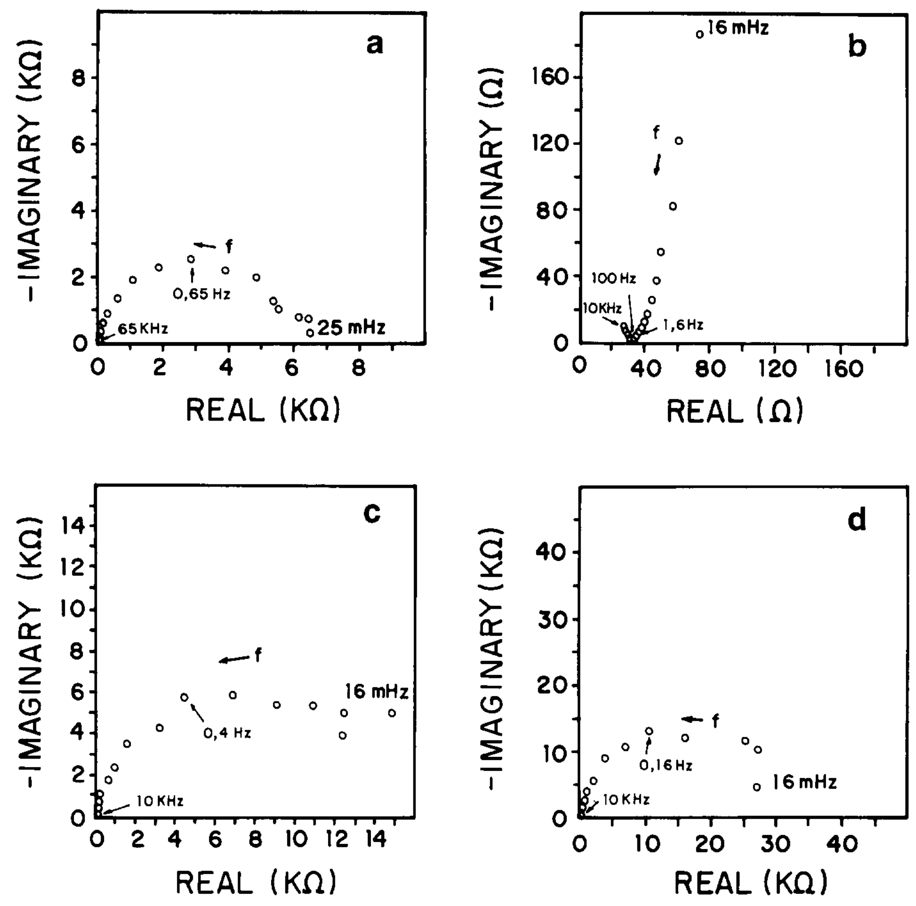

Figure 7 Impedance response of a PANI-NBR(ClO_4) film (24 μm thick) in $(C_4H_9)_4NClO_4$, CF_3COOH acetonitrile solution under various polarizations (*versus* Ag-AgCl): (a) 0.25 V; (b) 0.53 V; (c) 1.15 V; (d) 1.50 V

is swollen by the solvent and poly(aniline) chains are homogeneously distributed within a porous NBR framework as grafted branches. The electron transfer occurs from the electrode and is limited by the rubber film. This assumption would account for the fact that poly(aniline) preserves its specific electrochemical properties also in the PANI-NBR graft copolymer electrodes. The difference would remain in the mass transport kinetics, since in the blend electrode the electrolyte counterions have to penetrate the rubber to reach the poly(aniline) branches, as is evidenced by the electrochemical results described in this work.

Optical measurements

In theory the electronic absorption of the reduced form of poly(aniline) should be assigned to the aromatic amine chromophore. This absorption should be observed in the ultra-violet region. The absorption spectrum of reduced (−0.2 V *versus* Ag-AgCl) PANI-NBR(ClO_4), however, shows two absorptions at 440 and 900 nm (*Figure 8a*). These absorptions are also observed for pure poly(aniline) and have been assigned by several researchers to polarons or localized cation radicals[27–30]. These absorptions produce a yellowing of the film and indicate the presence of irreversibly oxidized electroactive sites. By oxidizing the graft copolymer from −0.2 to 0.9 V these absorption bands shift from 900 to 750 nm and from 440 to 420 nm (*Figure 8b*). This latter absorption is related to the presence of quinone-type structures produced by the oxidation process. A further oxidation to 1.2 V shifts only the low energy band to 670 nm and partially bleaches the film. In all cases, an absorption tail extends into the near infra-red range. The colour changes from yellow to green and bluish-green. This also corresponds to the first anodic peak in the cyclic voltammogram (*Figure 2b*), and

Table 4 Impedance parameters for a PANI-NBR film (12 μm thick) in 0.1 M $(C_4H_9)_4NClO_4$, 1.0 M CF_3COOH acetonitrile solution

E (V)	R_{ct} (Ω)	C_{al} (μF cm^{-2})	C_L (mF cm^{-2})	R_L (Ω)
0.25	4000	57	–	–
0.50	–	–	11.8	90
1.10	11 000	33	–	–
1.50	12 000	78	–	–
0.90	110	54	6.6	190
0.35	850	43	6.2	335

Table 5 Stress-strain parameters for crude NBR and for two PANI-NBR(BF_4) films obtained at different current densities

Sample	Stress at yield (MPa)	Stress at break (MPa)	Strain (%)
NBR	0.27±0.05	0.10±0.02	680±64
PANI-NBR[a]	0.23±0.02	0.12±0.02	1120±300
PANI-NBR[b]	0.35±0.01	0.28±0.08	2430±650

[a] Obtained at 0.1 mA cm^{-2}
[b] Obtained at 0.5 mA cm^{-2}

to the first insulator–conductor transition with decrease of R_{ct} (*Figure 7b*).

A similar behaviour was observed with films of PANI–NBR(BF_4) and poly(aniline) (ClO_4) synthesized in the same conditions. This confirms that the nitrilic rubber does not interfere with the electrochromic properties of the poly(aniline) in the graft copolymer.

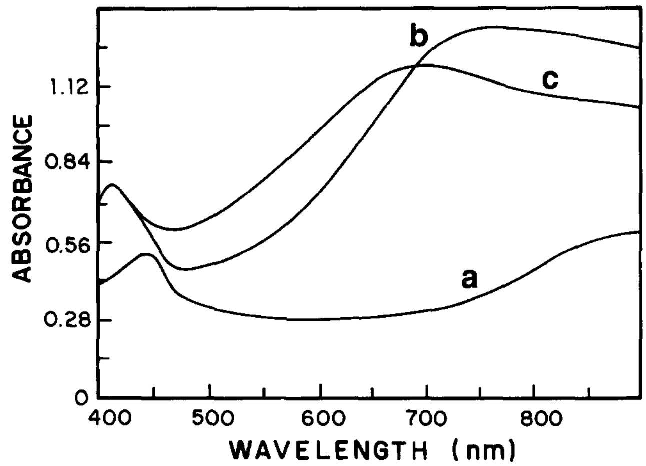

Figure 8 Absorption spectra for a PANI–NBR$(ClO)_4$ film (6 μm thick) polarized at (a) −0.2, (b) 0.9 and (c) 1.2 V *versus* Ag–AgCl

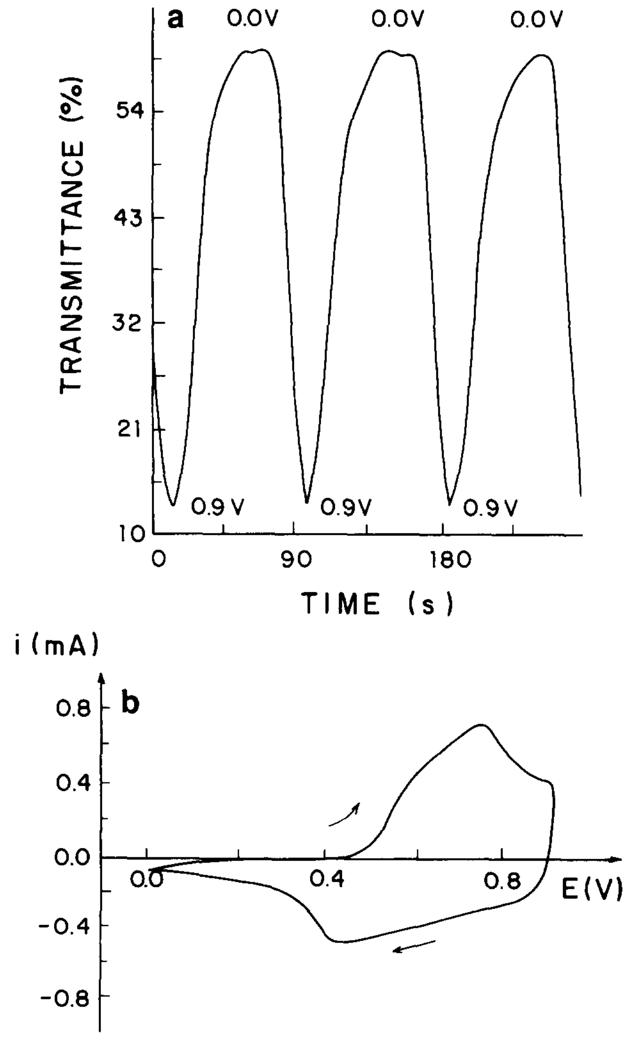

Figure 9 Variation in the transmittance at 670 nm for a PANI–NBR$(ClO)_4$ film (6 μm thick) during cyclic voltammetry (0–0.9 V at 20 mV s^{-1})

This experiment also showed that the higher chromatic contrast for PANI–NBR(ClO_4) is observed at 670 nm. A transmittance variation of 47% between the reduced (bleached) and oxidized (coloured) states is observed at this wavelength during successive cyclic voltammetries (*Figure 9*). This contrast is two times higher than for PANI–NBR(BF_4). There is also a pronounced difference in the transmittance at 670 nm in the reduced (bleached) state (0 V *versus* Ag–AgCl) for both films: 59% for PANI–NBR(ClO_4) and 37% for PANI–NBR(BF_4). These data corroborate the hypothesis of higher overoxidation of the conductive polymer when using the BF_4^- anion.

Optical memory experiments with PANI–NBR(ClO_4), under open circuit and ambient atmosphere, indicated a higher stability for the oxidized than for the reduced form. After 24 h there is a 10% decrease of the maximum absorbance and the open circuit potential shifts from 0.9 to 0.75 V for the oxidized form. For the reduced form the maximum absorbance increases by 80% and the potential shifts from −0.2 to 0.75 V after 24 h.

Stress–strain measurements

In *Figure 10* are shown the stress–strain curves for crude NBR and two PANI–NBR(BF_4) films synthesized at different current densities. Crude NBR shows the behaviour of a very soft and weak material. Both PANI–NBR(BF_4) samples show typical elastomeric behaviour with a stress at yield higher than the stress at break and a high elongation at break. However, curves of the films obtained at higher current density resemble much more the stress–strain curves for vulcanized rubbers. The numerical results are reported in *Table 5*.

These results contrast with those obtained by Niwa *et al.*[31,32] who observed a toughening of poly(vinyl chloride) and poly(ethylene acetate-*co*-vinyl chloride) upon electrochemical blending with poly(pyrrole). In another work, no modification was observed for the poly(vinyl chloride) mechanical properties upon blending with poly(pyrrole)[3]. However, the transformation of crude NBR from a soft and weak material to an elastomer upon electrochemical polymerization of aniline is also an indication of the grafting of poly(aniline) onto the rubber backbone. It also suggests that some of these poly(aniline) branches may be acting as crosslinks to the rubber chains.

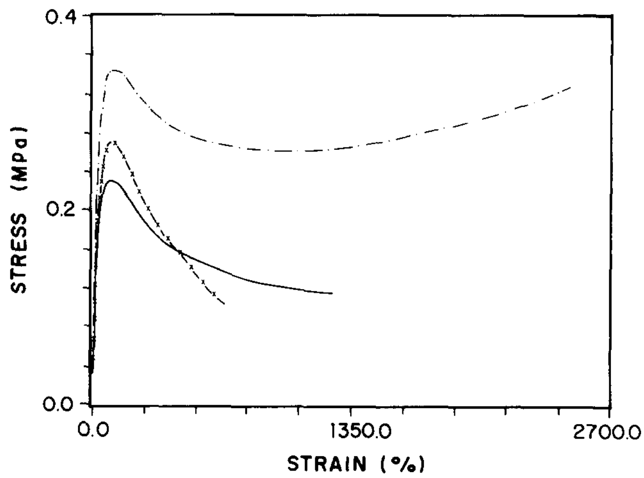

Figure 10 Stress–strain curves at a strain rate of 100 mm min^{-1} for crude NBR (– × – × –), PANI–NBR(BF_4) synthesized at 0.1 mA cm^{-2} (——) and PANI–NBR(BF_4) synthesized at 0.5 mA cm^{-2} (–·–·–)

CONCLUSIONS

We have shown in this work that the electrochemical polymerization of aniline in a nitrilic rubber matrix produces an elastomeric material with electrochemical and electrochromic properties resembling those of pure poly(aniline), as confirmed by cyclic voltammetry, impedance and optical measurements. These properties are largely affected by the acid–electrolyte couple used in the synthesis, with better results observed for films doped with ClO_4^-. In addition, the material has the mechanical properties of a crosslinked elastomer.

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