Synthesis and characterization of a composite containing poly(3-methylthiophene) and nitrilic rubber

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The electrochemical synthesis of a composite of poly(3-methylthiophene) and poly(acrylonitrile-*co*-butadiene), nitrilic rubber, is described. The effect of the synthesis conditions on the electrochemical properties of the material was studied by cyclic voltammetry and chronoamperometry. I. r. spectroscopy thermogravimetry, d.s.c., elemental analysis and scanning electron microscopy were used to characterize the inclusion of the conductive polymer in the rubber matrix. The data indicated a low miscibility between the composite components. Stress–strain measurements indicated a toughening of the composite material in relation to the pure rubber. The electrical conductivity of the composite is one order of magnitude lower than that of the pure polymer.

(Keywords: synthesis; characterization; composites)

INTRODUCTION

Until 20 years ago polymers were used in many technological applications as insulating materials. However, in the last 10 years a large number of publications and patents have indicated that polymers made up of a conjugated hydrocarbon backbone show not only metallic conductivity but can also have semi-conducting properties[1]. These materials are known as intrinsically conductive polymers and have many potential technological applications. For most of these applications, good processability and suitable mechanical properties are highly desirable.

The most popular approach to solve this problem has been the preparation of blends and composites. In this case, the conductive polymer contributes to improve the electrical characteristics and the insulating host provides the mechanical properties of the material[2–4]. According to Bidan[5], there has been a lot of progress in the synthesis of composites involving conducting polymers and matrices, such as, Nafion, clays, polyelectrolytes, thermoforming polymers and latexes.

We have developed the electrochemical synthesis of a composite of poly(3-methylthiophene) (P3MeT) and nitrilic rubber (NR). NR was chosen for its high resistance to acids and thermal stability. We have previously observed that this rubber could be swollen by the solution used in the electrochemical synthesis of P3MeT and that the product is electroactive[6]. In this study, we report on the electrochemical, thermal and mechanical properties of the composite, as well as on the different synthetic routes involved.

EXPERIMENTAL

A single compartment electrochemical cell equipped with a Ag/AgCl double junction reference electrode and a platinum sheet counter electrode was used. The working electrode was another platinum sheet with both faces coated with a film (100 μm thick) of NR (N726, from Nitriflex) cast from toluene solution (40 g l^{-1}). For the synthesis, a 0.1 M tetrabutylammonium tetrafluoroborate plus 0.5 M freshly distilled 3-methylthiophene dry acetonitrile solution was used. An Omnimetra PG 05 potentiostat was used for the potentiostatic synthesis at 1.70, 1.85 and 1.95 V during 5 min and at 1.70 V for 15 and 30 min. In the galvanostatic mode, a current density of 4 mA cm^{-2} with different charge densities (4.8, 7.2 and 9.6 C cm^{-2}) and a charge density of 4.8 C cm^{-2} with different current densities (2.0, 4.0 and 8.0 mA cm^{-2}) were applied. Potentiodynamic syntheses were performed by scanning the potential from 0 to 1.8 V at 50 mV s^{-1}. For comparative purposes pure P3MeT was prepared under the same conditions. Elemental analyses were performed using a Perkin Elmer 2400 CHN analyser. The electrochemical properties of the products were analysed by cyclic voltammetry and chronoamperometry using a 0.1 M tetrabutylammonium tetrafluoroborate–acetonitrile solution.

T.g.a. (20–950°C at 10°C min^{-1}) were performed using a DuPont model 1090 B and 9900 thermal analysis system, using purified nitrogen as the purging gas. D.s.c. was performed under the same conditions in two temperature ranges (−160 to 0°C and 20 to 600°C).

The conductivities of the films were measured using four-point probe equipment coupled to a Keithley 530 system. For pure P3MeT powder pellets were prepared

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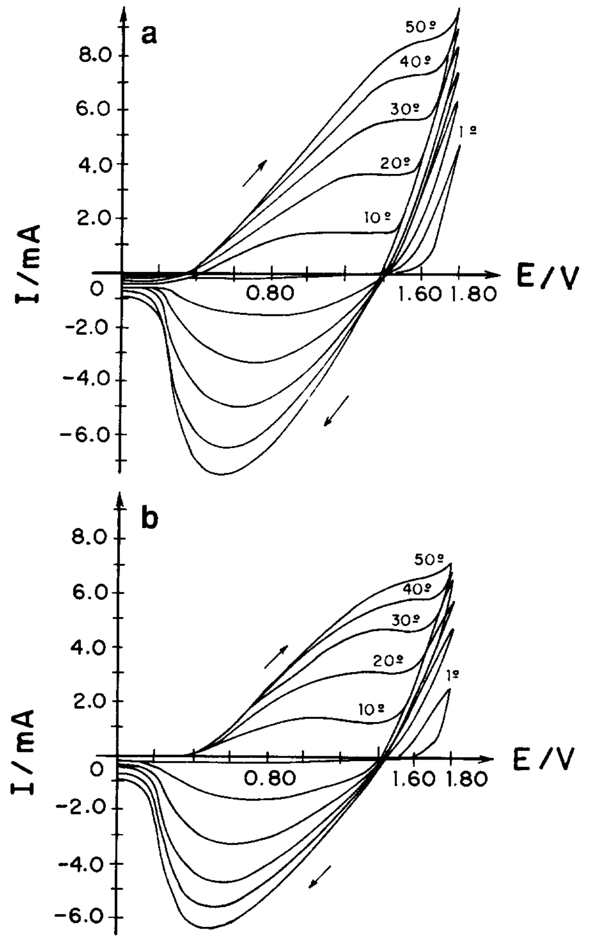

Figure 1 Cyclic voltammetric curves for the potentiodynamic synthesis of: (a) P3MeT; (b) composite

by pressing under 2.5×10^8 Pa. Scanning electron microscopy (SEM) of gold metallized samples was carried out using a Jeol JS-T300 microscope with a 20 kV potential. For the stress–strain measurements films (10 × 40 mm) were used in EMIC MEM 200 equipment interfaced to a PC/XT compatible computer. A 20 N cell and a crosshead speed of 50 mm $\min^{-1}$ were used. The results given are an average of five replicate measurements.

RESULTS AND DISCUSSION

Irrespective of the electrochemical synthesis method used, the pure P3MeT films obtained were not self-supporting and could not be peeled from the platinum electrode. By using a NR-coated working electrode, dark, self-supported flexible films were obtained. Depending on the synthesis conditions the films were homogeneous.

Electrochemical synthesis and characterization

By observing the first cyclic voltammograms presented in *Figure 1*, it can be noted that monomer oxidation occurs at 1.80 V. The subsequent curves show a broad anodic wave at low potential corresponding to the polymer redox process. The increases in the anodic and cathodic charge indicate the formation of P3MeT in the rubber-coated electrode. The charge increase and the redox potential shift agrees with previously published data for the polymerization of 3-methylthiophene on bare platinum electrodes[7,8]. This indicated that the NR does not impede the electrochemical behaviour of the conductive component of the composite, P3MeT, opening up new possibilities of producing a conductive elastomeric material.

In order to improve the composite homogeneity with retention of the elastomer mechanical properties, potentiostatic and galvanostatic synthesis was performed under different conditions. Initially the redox behaviour was evaluated by cyclic voltammetry. The diffusion coefficient of the counter anion was estimated by chronoamperometry as suggested by Genies *et al.*[9]. These authors estimated the diffusion coefficient of the perchlorate ion in polypyrrole by the charge variation as a function of time in a double potential step experiment. Under these conditions, the redox process is controlled by a linear semi-infinite diffusion in the time interval where the charge changes as a function of the square root of time, $t^{1/2}$. In this range, the slope of the curve is equal to $(2nFAC^*D^{1/2})/\pi^{1/2}$, where D is the diffusion coefficient and C^* is the active site concentration. The diffusion coefficient was calculated to be $10^{-10}\,\mathrm{cm^2\,s^{-1}}$. This number was estimated considering the active site concentration to be 4 M. This was obtained using the material density ($1.51\,\mathrm{g\,cm^{-3}}$), the molecular weight of the repeating unit and the degree of doping.

Chronoamperometric studies with composites of poly(vinyl chloride) and P3MeT indicated that an increase in the insulating polymer thickness induces a decrease in the counterion diffusion coefficient[10]. The apparent diffusion coefficient was measured from the slope of the linear part of the current (I) *versus* $t^{1/2}$ curve. Since the concentration of active sites cannot be precisely measured, the authors expressed the chronoamperometric results as a function of $C^*D^{1/2}$, obtaining $10^{-7}\,\mathrm{mol\,cm^{-2}\,s^{-1/2}}$ for pure P3MeT and for the composite. A lower $C^*D^{1/2}$ value was reported for thicker PVC films, indicating a lower diffusion coefficient.

Figure 2 shows the chronoamperometric results for a

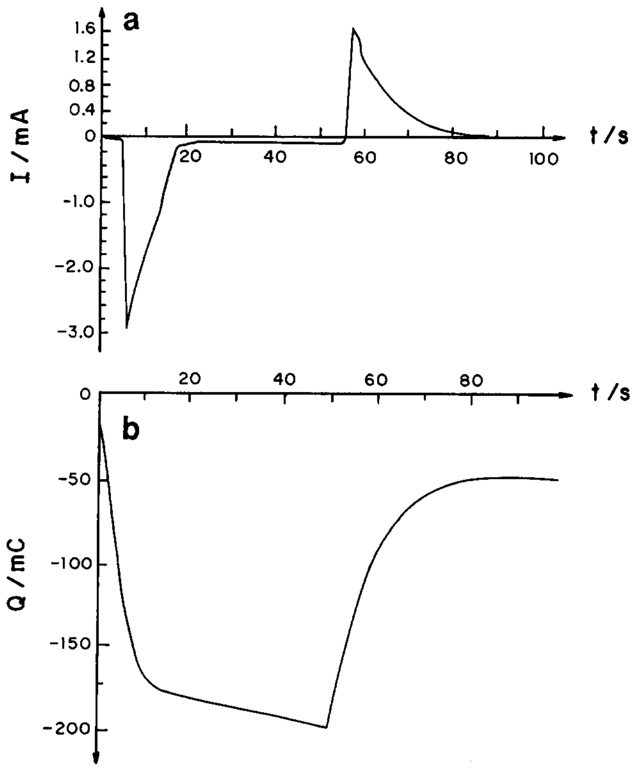

Figure 2 Chronoamperometric curves for a composite obtained at 1.70 V for 5 min: (a) I *versus* t; (b) Q *versus* t

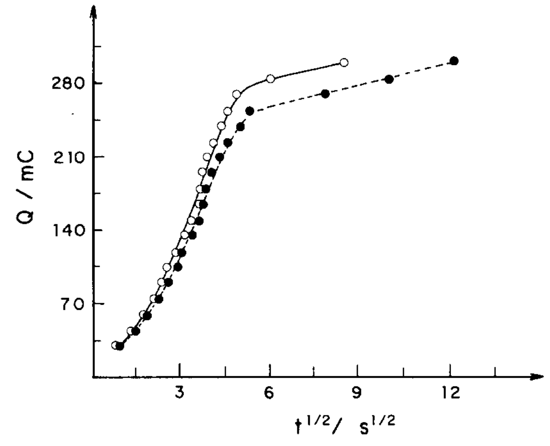

Figure 3 Plot of the charge, Q, as a function of $t^{1/2}$: (○) pure P3MeT; (●) composite (both obtained at 1.70 V for 5 min)

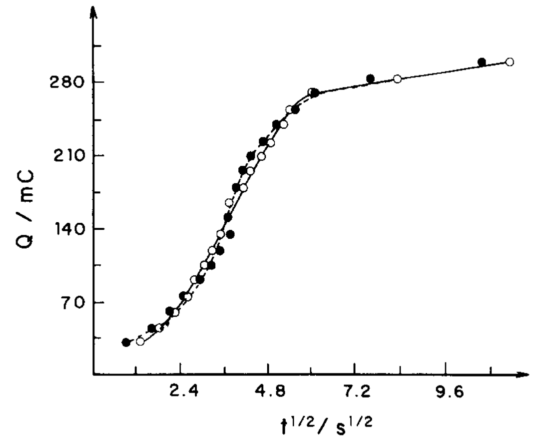

Figure 4 Plot of the charge, Q, as a function of $t^{1/2}$: (○) pure P3MeT; (●) composite (both obtained at 4.0 mA cm^{-2} and 4.8 C cm^{-2})

composite synthesized at 1.70 V for 5.0 min. Exactly the same results were obtained with a pure P3MeT film. The charge (Q) *versus* $t^{1/2}$ curves shown in *Figure 3* were drawn from these experiments. Within experimental error, the curve for pure P3MeT and for the composite are superimposed. The slope of the linear part of the curve (3–5 s$^{1/2}$) is 0.08 C s$^{-1/2}$ for pure P3MeT. If this is equated to $(2nFAC^*D^{1/2})/\pi^{1/2}$ it is possible to estimate the diffusion coefficient, provided the other parameters are known.

The same experiment and calculations for the composite and for pure P3MeT obtained galvanostatically gave results similar to those shown in *Figure 2*. By analysing the variation of Q as a function of $t^{1/2}$, a more pronounced superposition of the curves is observed (*Figure 4*). The slope in the 2.5–5 s$^{1/2}$ range is 0.06 C s$^{-1/2}$. The results are summarized in *Table 1*. Assuming a linear semi-infinite diffusion control during the experimental time interval and by adopting the reasoning proposed by Roncali and Garnier[10], the relative diffusion coefficients were estimated. First, the slope of the curves was related to $(2nFAC^*D^{1/2})/\pi^{1/2}$. In order to calculate the diffusion coefficients shown in *Table 1*, the number of electrons involved was considered to be one[11] and the geometrical area of the working electrode was taken to be 1.0 cm^2.

These data indicate that the transport process in the composites prepared galvanostatically and potentiostatically are similar since the $C^*D^{1/2}$ values are of the same order of magnitude. Also, it indicates that the composite has the same redox behaviour as pure P3MeT.

Characterization by non-electrochemical methods

Optical microscopy of composites prepared by the different methods has shown that the galvanostatically prepared composites had the most homogeneous distribution of P3MeT in the NR matrix. As a consequence, films prepared at 4.0 mA cm^{-2} and 4.8 C cm^{-2} were characterized by other techniques.

By elemental analysis, the acrylonitrile content of the pure rubber was confirmed to be 29.7%. The concentration of tetrafluoroborate (degree of doping) of pure P3MeT was also confirmed to be 30%. For the composite, the N to S ratio indicated a 9:1 NR to P3MeT ratio.

Toluene extraction of the composite indicated a 70% soluble fraction in the composite. The i.r. spectrum of the dry residue of the extract indicated the presence of NR. This shows that most of the rubber present has no chemical interaction with the conductive polymer, thereby indicating its composite nature.

Composite films with an area of 1.0 cm^2 and a thickness in the range of 0.07–0.10 mm showed a conductivity of 0.2 S cm^{-1} on the face which originally adhered to the working electrode (the other face had no detectable conductivity). Pure P3MeT pellets showed a conductivity of 1.2 S cm^{-1}. The conductive/insulating behaviour of composites has been described by others for polypyrrole/NR composites[12]. These authors used three models to explain this behaviour for NR films with a thickness of: (a) $<2\,\mu$m; (b) $2\,\mu$m; and (c) $>2\,\mu$m. In case (a), the conductive polymer grows perpendicularly to the electrode surface, reaches the other surface and coats this surface with the conductive polymer. In this case both faces are conductive. In case (b) the conductive film just reaches the other surface of the insulating matrix. In case (c) the conductive film does not reach the other face of the insulating matrix to show this conductive/insulating behaviour.

These assumptions were confirmed by SEM measurements. *Figure 5* shows that the surface of the NR is smooth and compact, while pure P3MeT has a granular morphology with grains a few micrometres in diameter forming randomly oriented fibres.

The scanning electron micrograph of the composite surface which originally adhered to the surface of the working electrode is shown in *Figure 6a*. This face is smooth and compact. The presence of crazes indicates that the film is fragile and tough. The other surface (*Figure 6b*), in contrast, is smooth with spherical particle

Table 1 Slope of the Q *versus* $t^{1/2}$ curves and calculated diffusion coefficients

Material	$Qt^{-1/2}\times10^2$ (C s$^{-1/2}$)	$C^*D^{1/2}\times10^6$ (mol cm^{-2} s$^{-1/2}$)
P3MeT[a]	8	1.5
P3MeT/NR[a]	7	1.3
P3MeT[b]	6	1.1
P3MeT/NR[b]	9	1.7

[a] Obtained at 1.70 V for 5 min
[b] Obtained at 4.0 mA cm^{-2} for 20 min

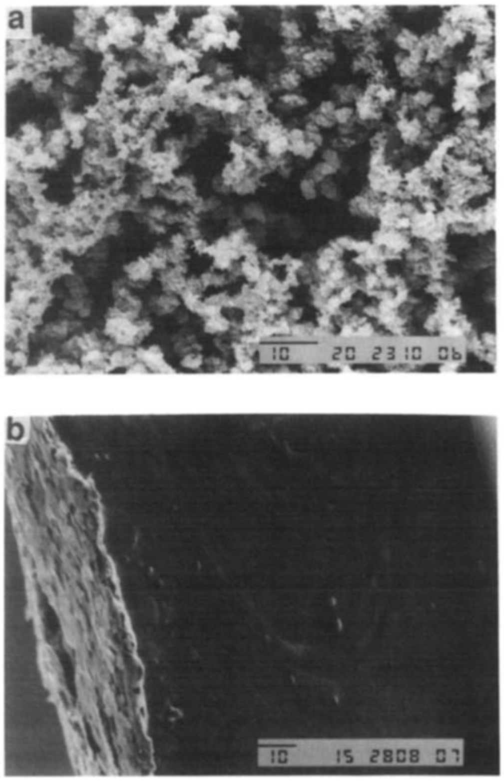

Figure 5 Scanning electron micrographs of: (a) pure P3MeT; (b) pure NR. The scale bars are in μm

agglomerates, similar to those observed in pure P3MeT. The cross-section micrograph, *Figure 6c*, shows clearly that the surface originally adhering to the working electrode has a pattern similar to pure P3MeT. Going in the direction of the other face, a dispersion of particles and finally a homogeneous and smooth surface, probably pure NR, is observed. These results corroborate the conductivity measurements.

The t.g.a. of the NR (*Figure 7*) shows two plateaux of weight loss: the first finishing at 350°C, assigned to polybutadiene block degradation, and the other starting at 500°C, assigned to the degradation of the polyacrylonitrile blocks[13]. D.s.c. indicated two exothermic transitions at 350 and 510°C, corroborating this assignment.

For pure P3MeT the t.g.a. curve presents three plateaux (*Figure 7*): the first finishing at 175°C assigned to solvent loss, the second between 175°C and 340°C assigned to the loss of the dopant anion and the third above 340°C assigned to polymer degradation[14]. The thermal stability of poly(3-alkylthiophene) has been studied in detail by Wang and Rubner[15]. They related the thermal loss of the dopant anion to conformational changes of the polymer chains and assigned the endothermic peak to this process. The d.s.c. measurements above room temperature showed an endothermic process in the 90–180°C range, assigned to the loss of the dopant, and an exotherm centred at 360°C, assigned to the degradation of the remaining 'neutral' (dedoped) P3MeT.

The thermogram of the composite (*Figure 7*) is similar to a superposition of the other two curves in *Figure 7*. Considering the above arguments, the inflections in this curve can be assigned from 25 to 340°C, to loss of acetonitrile with simultaneous loss of tetrafluoroborate; from 340 to 480°C, to the degradation of the polybutadiene blocks and of the dedoped P3MeT; and from 480 to 950°C to the further degradation of the dedoped P3MeT and of the polyacrylonitrile blocks.

The thermal transitions observed in the composite d.s.c. curve also resemble a superposition of the pure P3MeT and NR curves, with the exception of an exotherm at ~250°C, which seems to be an intrinsic composite thermal transition. In the low temperature range (-160 to 0°C), the pure P3MeT/tetrafluoroborate ion shows a transition at ~-85°C (*Figure 8*). For the NR two transitions are observed at -25 and -75°C, the first being assigned to the glass transition temperature (T_g) of the pure rubber with a 29% acrylonitrile content[16]. For the composite two transitions are observed at -20 and at -40°C. The first can be assigned to the T_g of the rubber matrix indicating a very low miscibility with the conductive polymer. The second transition seems to be a shift of the -75°C rubber transition, but a superposition of peaks cannot be disregarded.

In the stress–strain tests the crude pure NR showed an average stress at break of 0.18 MPa and a strain at

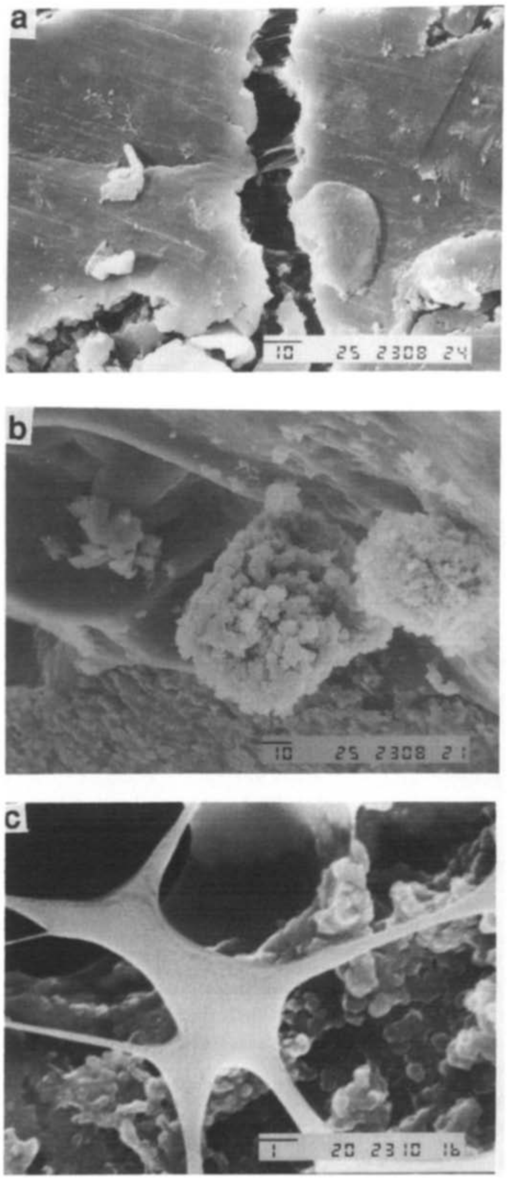

Figure 6 Scanning electron micrographs of the composite: (a) face originally adhered to the working electrode; (b) face originally in contact with solution; (c) cross-section. The scale bars are in μm

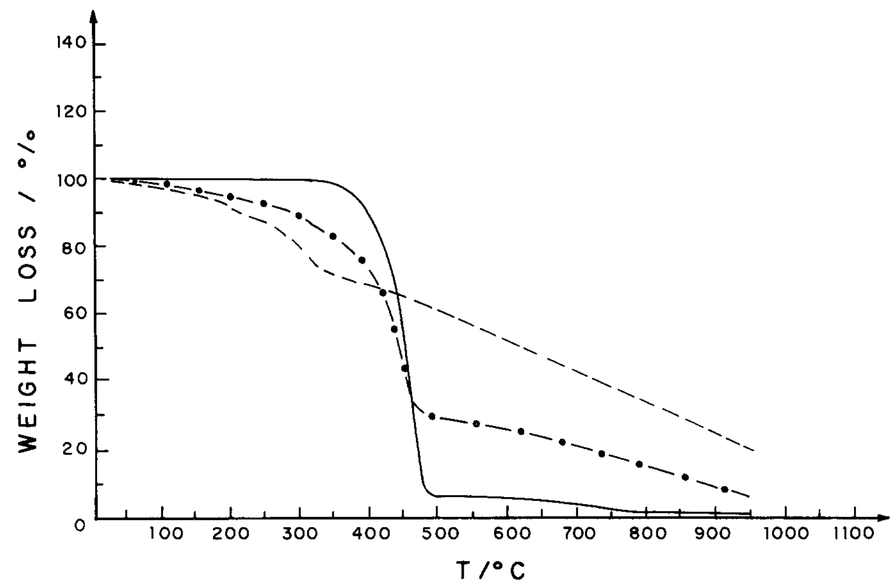

Figure 7 Thermogravimetric curves for: (——) Nr; (– – –) P3MeT; (—·—) composite. Heating rate: 10°C min^{-1}

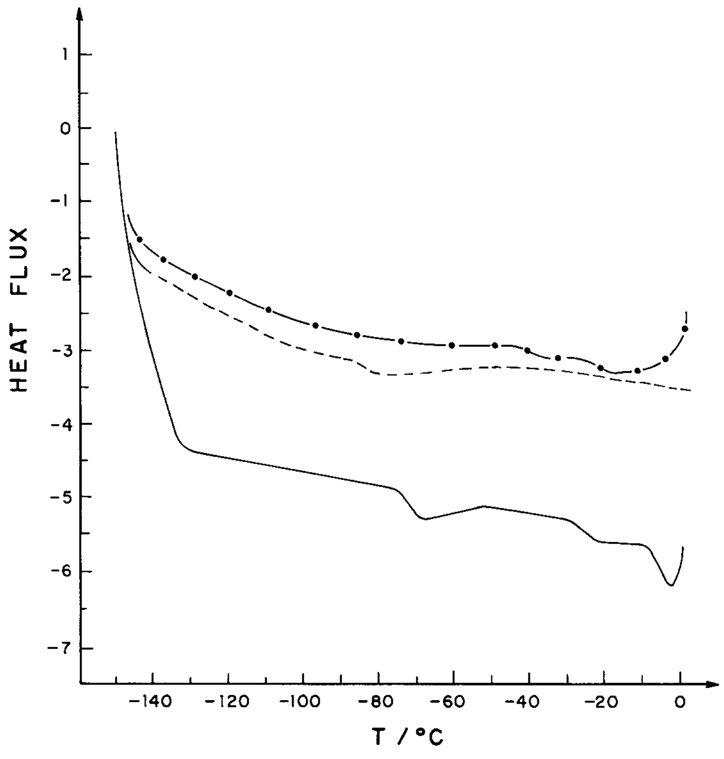

Figure 8 D.s.c. curves for (——) NR; (– – –) P3MeT; (—·—) composite. Heating rate: 10°C min^{-1}

break of 580%. For the composite the average values were 0.43 MPa and 74%. *Figure 9* shows the stress–strain results. The pure crude rubber shows a curve characteristic for a soft elastomer and the composite shows a curve characteristic for a hard, tough material.

A comparison of the mechanical properties of composites with those of the insulating polymer host has been reported for composites of poly(vinyl chloride) and polypyrrole[17]. In this case, the properties of the composite resemble those of the insulating component with a decrease in the stress and maintenance of the elongation at break. This behaviour has been assigned by others to restraint of the chain mobility of the polymer matrix due to the presence of the conducting polymer[18,19]. In the case of the P3MeT and NR composite, we assigned the hardening of the rubber to the same effect: P3MeT acting as a reinforcing filler for the elastomer.

CONCLUSIONS

It has been shown that it is possible to obtain a new elastomeric composite by including P3MeT in a matrix of NR. It can be prepared electrochemically at constant potential or current density. However, electrochemical

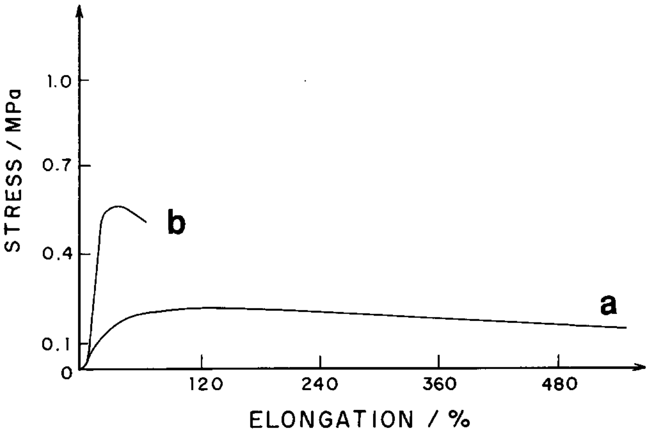

Figure 9 Stress–strain curves for: (a) NR; (b) composite

characterization showed that films prepared at a current density of $4.0\,\mathrm{mA\,cm^{-2}}$ ($4.8\,\mathrm{C\,cm^{-2}}$) show a higher cyclability and a redox behaviour comparable to pure P3MeT. These films are easily detached from the electrode and show good mechanical properties. A low miscibility between the composite components was observed.

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