

Polypyrrole–Poly(epichlorohydrin-co-Ethylene Oxide) Blend: An Electroactive, Electrochromic and Elastomeric Material

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We report on the preparation of an elastomeric blend with electrochemical and spectroelectrochemical properties similar to those of pure polypyrrole. The title elastomer used is an ionic conductor. Cyclic voltammetry and chronoamperometry experiments show the electroactivity of the blend. A transmittance contrast of 50% at 700 nm between the reduced and the oxidized forms of the blend is evidence of the pronounced electrochromism of the blend. Differential scanning calorimetry suggests an association of the guest conductive polymer with the ethylene oxide blocks of the rubber copolymer host. Stress–strain measurements show that the conductive polymer guest increases the rigidity and toughness of the elastomer host.

Mixtures of polymers range from homogeneous to heterogeneous and are classified by plastic technologists as blends or composites. Perfectly homogeneous mixtures, however, are not thermodynamically stable.¹ Thus, a certain degree of immiscibility often occurs. Polymeric blends of two or more polymers are obtained by mechanical mixing, solution casting or polymerization of one component in a polymeric matrix. There is a vast amount of literature on the field and the production of blends became very important in the last decade for obtaining new materials by combining well known polymers.² The aim of making these mixtures is to achieve a synergistic combination of the properties of the components of the blend. With blends of conductive and insulating polymers, the objective is the preparation of polymeric materials with good mechanical properties and the processability associated with electronic conductivity or electrochromism.

Conductive blends can be prepared by mechanical mixing, casting of a solution containing the components of the blend or polymerization of one polymer into another. The last method can be achieved either chemically or electrochemically producing blends or interpenetrating networks. Besides the methods used to characterize polymeric materials, these blends can also be studied by electrochemical methods, owing to the redox characteristics of the doping process of the conductive polymer. However, for technological applications it is also important to explain the ionic diffusion and structural changes occurring during the redox process. Several researchers also use electrochemical methods alongside spectroscopic techniques, such as Raman, IR, UV–VIS, EPR and ellipsometry.

Polypyrrole has been widely studied although its conductivity is not as high as that of polyacetylene. Its stability to exposure to the environment and to repeated redox cycles, however, make it very attractive for technological applications.³ Its colour ranges from a light yellow in the reduced form to a deep brown in the oxidized state. When polypyrrole is oxidized, *i.e.* when the pyrrole chain is positively charged, the anions of the electrolyte are drawn into the material to neutralize the charge. Electrogravimetry using a quartz crystal microbalance has shown that, depending on the hydration radius of the dopant anion, there can be diffusion of the cation or of the anion of the electrolyte into the polymer bulk.⁴ If the polymer is doped with inorganic low molecular weight anions, for example ClO_4^- , during reduction this anion diffuses into the electrolyte and during oxidation it is reinserted into the polymer. On the other hand, if one uses anionic surfactant dopants (dodecyl sulfate or *p*-toluene sulfonate), there is no removal of the dopant during the reduction process, but insertion of a cation. During the reoxidation this

cation may diffuse back into the electrolyte, or insertion of a further anion may take place, depending on the potential range used. These changes are followed by intense spectral changes.

Conductive polymeric blends were first prepared by the electrochemical deposition of polypyrrole onto an electrode coated with a film of poly(vinyl chloride), PVC.⁵ In this method the insulating material is swollen by the electrolyte solution containing the monomer; the monomer begins to polymerize at the electrode/polymer interface, and the polymerization then advances across the polymer phase to the polymer/electrolyte interface. The combination of the electronic properties of the conducting phase and the mechanical properties of the insulating phase produced a unique material with conductivities in the range $10\text{--}100\text{ S cm}^{-1}$ and thermo-plastic-like mechanical properties.

Following the electrode-coating method, blends were prepared with polypyrrole and PVC and with polypyrrole and brominated poly(vinylcarbazole); the electrochromism of these samples was studied.⁶ An electrical conductivity of 2 S cm^{-1} coupled with 60% transmittance of light at 633 nm was achieved for this blend prepared by potentiostatic pyrrole polymerization onto an ITO electrode covered with a film of the insulating host polymer. According to the authors, the bleached reduced blend is more stable than pure polypyrrole prepared under the same conditions.

Using different heterocycles, such as dithieno[2,3-*b*:2',3'-*d*]pyrrole, 5,10,10-trimethyl-5,10-dihydrodibenzo[*b,e*]azasiline and *N*-vinylcarbazole, blends with PVC were electrochemically prepared by the electrode-coating method.⁷ Blending with PVC was reported to ameliorate the stability of the polyheterocycles. The blends showed strong electrochromic contrast in the visible region giving rise to potential applications in electrochromic devices.

Chemical polymerization was also used for the preparation of polypyrrole–PVC blends by the interphase polymerization of pyrrole between aqueous solutions of iron(III) salts and organic solutions of pyrrole separated by PVC films.⁸ By this method, the structure of the blend could be altered by changing the organic solvent or the oxidant. The reported conductivities of the films were in the range $0.1\text{--}10\text{ S cm}^{-1}$.

Blends of polypyrrole with the elastomeric terpolymer of ethene, propene and 5-vinylnorborn-2-ene, EPDM, were obtained by incorporation of the oxidant into the rubber as filler, followed by exposure to pyrrole vapour.⁹ The host rubber film was prepared by calendaring and this provides a method for large-scale production of blends of a rubber with a conductive polymer. Conductivities, however, were reported to be near 10^{-7} S cm^{-1} .

The electrode-coating method was used by Naoi and Osaka to prepare a blend of nitrilic rubber with polypyrrole.¹⁰ After rinsing the nitrilic rubber with an appropriate solvent the authors studied the remaining polypyrrole and observed no differences from a directly grown polypyrrole, suggesting no chemical interaction between the host and the guest polymers. The method, however, proved useful for obtaining polypyrrole with a controlled morphology.

To use a conductive polymer in a battery or in an electrochemical device, several conditions must be fulfilled, such as stability to several redox cycles, high chromatic contrast and high chemical stability. These parameters will be influenced by the electrode/electrolyte interface. In a solid-state device, where an ionically conductive polymer is used as electrolyte, the properties of this solid/solid interface are critical and could be optimized by increasing the compatibility between the polymeric electrode and electrolyte. The vulcanizable elastomeric copolymer of epichlorohydrin(1-chloro-2,3-epoxypropane) and ethylene oxide, commercially produced under the trade name of Hydrin-C, has been used previously as a solid electrolyte in a solid-state electrochromic device, indicating its good ionic conductivity.¹¹ In this paper we describe the preparation of a blend of polypyrrole with this ionic conductor as a first step to obtain an electrode material compatible with the polymeric electrolyte material.

Experimental

The copolymer of epichlorohydrin and ethylene oxide used in this work (Hydrin C) was from Zeon Chemicals Inc. The blend was prepared by the working-electrode coating method; 100 μl of a 4% solution of Hydrin-C in chloroform was deposited over a 2.0 cm^2 area of the working electrode and evaporated producing a transparent 10 μm thick film. For spectroelectrochemistry measurements, a glass slide coated with tin oxide (ITO, from Nippon Sheet Glass, 100 Ω) was used as working electrode, in all other experiments a Pt sheet was used. Pyrrole (Aldrich, freshly distilled) was galvanostatically (0.5 mA cm^{-2} , 45 s) polymerized in a two-electrode one-compartment cell using a 0.05 mol l^{-1} aqueous solution containing 0.025 mol l^{-1} sodium dodecyl sulfate (Aldrich). The electrochemical properties were studied by cyclic voltammetry and chronoamperometry using a 0.5 mol l^{-1} aqueous KCl solution as electrolyte. Spectroelectrochemical experiments were performed by placing the three-electrode cell with optical windows in the sample compartment of a Hewlett-Packard HP8452 diode array spectrophotometer.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed using a DuPont 9900 thermal analysis system at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ and under N_2 atmosphere. Scanning electron microscopy (SEM) was carried out using a JEOL JS-T300 instrument under 20 kV potential, using samples metallized with gold. An EMIC MEM-500 instrument interfaced to a PC was used for the stress-strain experiments, using a cross-head speed of 50 mm min^{-1} , a cell of 2 $\text{kgf}\dagger$ and five specimens per sample.

Results and Discussion

The Hydrin-C rubber film coated onto the working electrode is swollen by the aqueous monomer-electrolyte solution allowing polymerization to occur in its bulk, starting from the electrode/rubber interface and moving towards the rubber/electrolyte interface, as observed in previous works.¹⁰ The first evidence for the formation of the blend is the darkening of the rubber film on the working-electrode surface. Following

the polymerization of pure polypyrrole, the conducting polymer is obtained in the oxidized/doped state. Gravimetric determination by rinsing the blend with chloroform indicated that the blend contained 10% of polypyrrole. After preparation it was characterized by electrochemical, spectroelectrochemical and non-electrochemical methods.

Characterization by Electrochemical and Spectroelectrochemical Methods

In Fig. 1(a) and (b) we compare the cyclic voltammetry curves for the polypyrrole-Hydrin-C blend and pure polypyrrole prepared under the same experimental conditions. The curve for the blend shows very broad anodic and cathodic waves in contrast to that of pure polypyrrole. Two anodic and two cathodic waves can, however, be identified in both curves indicating two reversible redox processes. The differences in the current response can be assigned to the dependence on cation and anion diffusion rates from the electrolyte solution into the films, despite the ionic conductivity of the Hydrin-C rubber. The shifts in the anodic and cathodic peak potentials for the blends compared with those in pure polypyrrole are caused by the ohmic resistance of the rubber, as previously observed in other rubber-conductive polymer blends.^{12,13} The amount of charge consumed by the blend during redox processes is much lower compared with that in pure polypyrrole, as would be expected from the low concentration of conductive polymer in the blend.

Repeated double-potential-step chronoamperometric experiments were performed with the blend to study its stability to a large number of redox cycles. Pure polypyrrole doped with dodecyl sulfate was reported to retain its electrochemical and electrochromic properties for 2×10^4 double

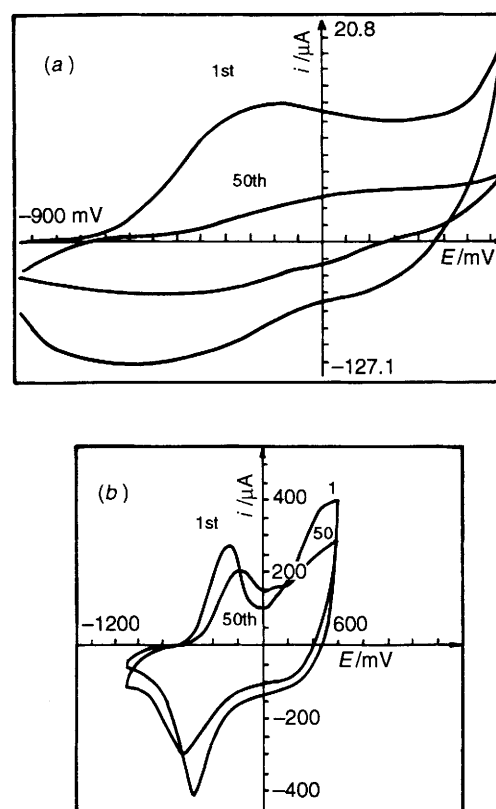


Fig. 1 Comparison of the cyclic voltammetry of (a) the blend polypyrrole-Hydrin-C and (b) polypyrrole-dodecyl sulfate, measured in an aqueous 0.5 mol l^{-1} KCl solution at 50 mV s^{-1} in the -0.900 – 0.600V vs. SCE range

\dagger 1 $\text{kgf} = 9.80665 \text{ N}$.

potential steps.¹⁴ The variation of the charge density of the blend during the first and 1400th double potential steps is shown in Fig. 2. There is a variation of the coulombic efficiency (expressed as the ratio between the oxidation and reduction charge densities) after 1400×10^3 steps, revealing a small degree of irreversibility in the charge/discharge process. Also, the time necessary for the stabilization of the current in the reduction step increases as a function of the number of steps.

The variation of the spectra of polypyrrole-dodecyl sulfate as a function of potential during cyclic voltammetry (2 mV s^{-1} , 0.5 mol l^{-1} aqueous KCl) is compared with that of a blend in Fig. 3. The spectral changes are qualitatively similar; however, a shift of the absorption maximum to lower energy in the oxidized state is observed upon comparing pure polypyrrole and the blend. This suggests that blending slightly affects the energy of the bipolaronic levels formed during the doping process. For the reduced, bleached state of the blend a higher absorptivity is observed in the visible/near-IR region in comparison to pure polypyrrole; this can be assigned to the absorption of the rubber component of the blend. A transmittance variation of 50% at 700 nm was measured during a cyclic voltammetry experiment with a scan rate of 2 mV s^{-1} .

Characterization by Non-electrochemical Methods

In Fig. 4 we compare TG curves for the sodium salt of dodecyl sulfate, pure polypyrrole-dodecyl sulfate, pure Hydrin-C and the blend. The steepest weight loss, observed in the curve for pure polypyrrole at *ca.* 180°C , is coincident with the pure dopant weight loss temperature, showing that the predominant process is the thermal decomposition of dodecyl sulfate with the production of volatiles. The curve for Hydrin-C shows a pronounced weight loss at 300°C , corresponding to dehydrochlorination and polyether-chain scission, followed by a slower weight loss with complete volatilization of all the residues at 800°C . The blend contains predominantly Hydrin-C and its TG curve shows a first weight loss at 300°C with a lower slope, followed by a much slower loss assigned to the polypyrrole phase. The thermal degradation behaviour is mostly dominated by the more concentrated phase.

The DSC curves compared in Fig. 5 show two phase transitions for pure crude Hydrin-C and for the blend, both associated with glass-transition temperatures. For pure Hydrin-C, the transition at -36°C is associated with the epichlorohydrin blocks, owing to the lower mobility of these blocks induced by the polarity of the chlorine atom. The other transition at -72°C is associated with the blocks with higher mobility (ethylene oxide). In the case of the blend, the transition assigned to the ethylene oxide blocks of the copolymer is shifted to -62°C , suggesting an increase in rigidity

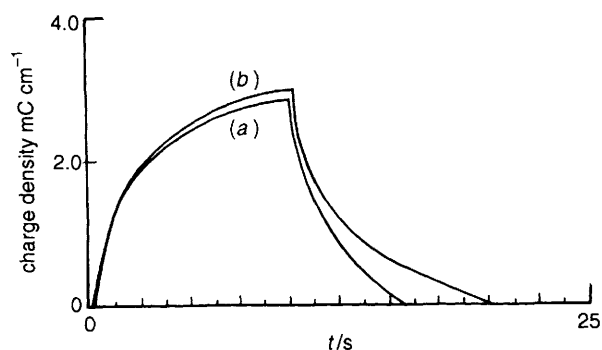


Fig. 2 Variation of the charge density as a function of time during a double potential step applied to the polypyrrole-Hydrin-C blend: (a) first step, (b) 1400th step

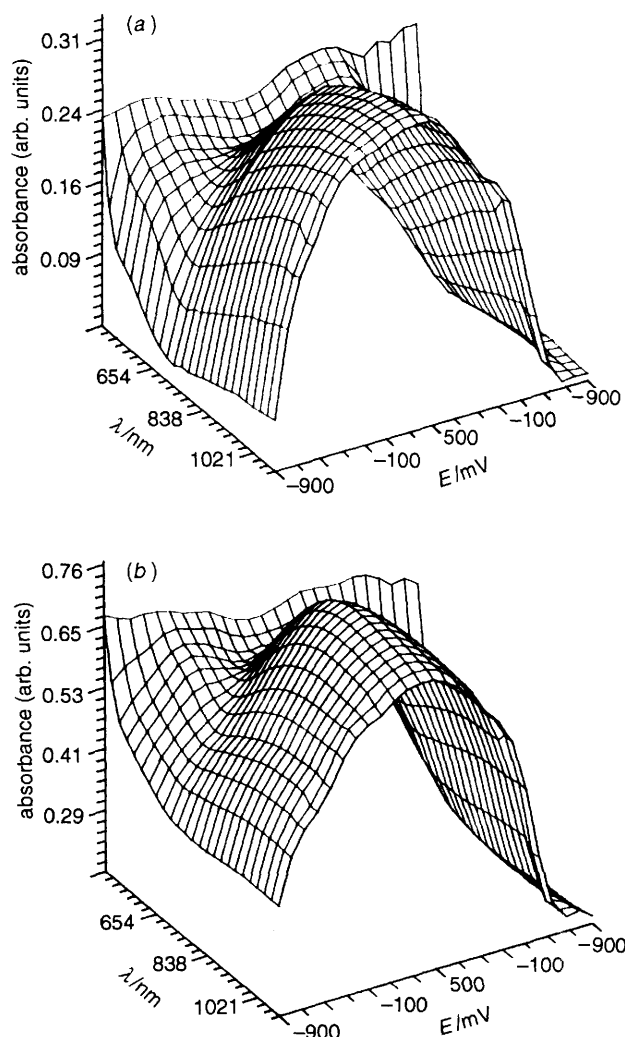


Fig. 3 Variation of the spectra as a function of potential in a cyclic voltammetry experiment in an aqueous 0.5 mol l^{-1} KCl solution at 2 mV s^{-1} for (a) polypyrrole-dodecyl sulfate and (b) its blend with Hydrin-C

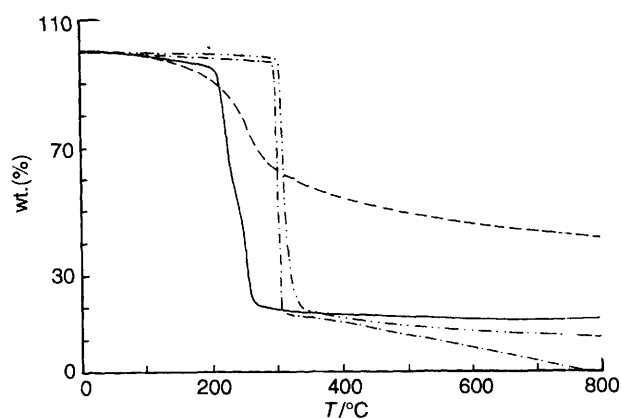


Fig. 4 Thermogravimetry ($10^\circ\text{C min}^{-1}$), comparing: (—) sodium dodecyl sulfate, (---) polypyrrole-dodecyl sulfate, (-·-·-) Hydrin-C and the (—) blend

caused by its association with the polypyrrole chains. The transition assigned to the epichlorohydrin blocks is not shifted.

The stress-strain curve for crude Hydrin-C shows the typical soft and weak behaviour of a crude elastomer, as indicated by the low modulus and high strain, Fig. 6. Despite the low concentration (10%) of polypyrrole in the blend, a

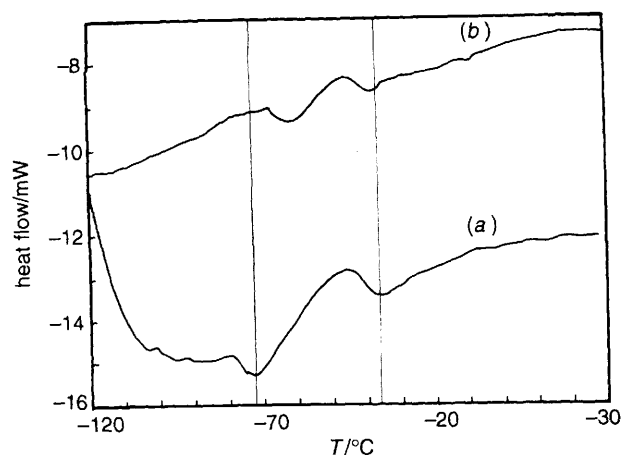


Fig. 5 Comparison of the differential scanning calorimetry curves ($10^{\circ}\text{C min}^{-1}$) for: (a) pure Hydrin-C and (b) blend. Increasing negative values of heat flow indicates an endothermic process.

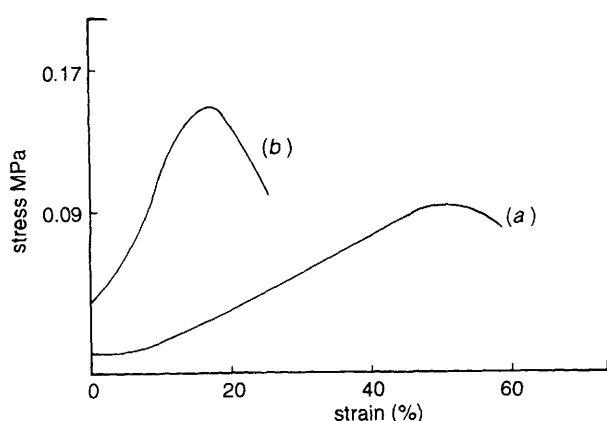


Fig. 6 Comparison of the stress-strain curves (50 mm min^{-1}) for: (a) pure Hydrin-C (crude) and (b) blend

pronounced change in the stress-strain curve is observed with a pronounced increase in the modulus and decrease of the strain, showing a hardening and toughening of the material. This is assigned to the localization of the conductive polymer within the ethylene oxide blocks of the copolymer, reducing the mobility of the rubber chains.

A previous study on the morphology of conductive polymer blends showed that the electrochemically polymerized chains grow perpendicularly to the working electrode surface.¹⁰ According to these authors and to our previous results with other blends, the conductive polymer grows from the working electrode surface towards the rubber/electrolyte interface. This effect can be observed in the scanning electron micrographs shown in Fig. 7. Comparing the surface of pure Hydrin-C [Fig. 7(a)], with the surface of a blend where the polymerization of pyrrole was performed for a time sufficiently short to have no polypyrrole on the rubber/electrolyte surface [Fig. 7(b)], we observe that a small concentration of the conductive polymer is already sufficient to produce a detectable change in the morphology of the surface of the material. When the polymerization time is extended, the morphology of the surface is similar to that of pure polypyrrole with the formation of globules, Fig. 7(c).

Conclusions

Our results show that a partially miscible blend of polypyrrole and the copolymer of ethylene oxide and epichlorohydrin

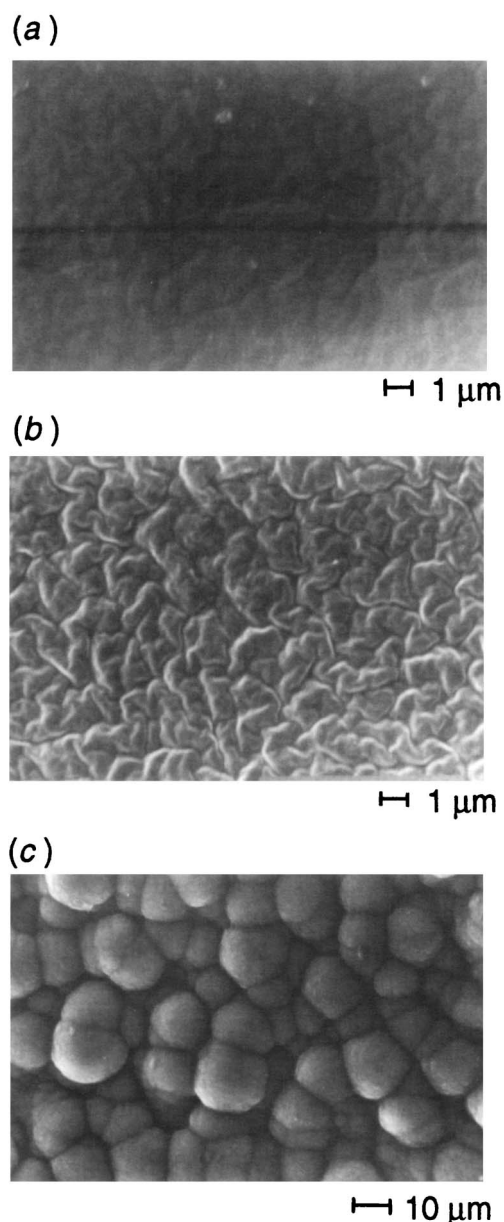


Fig. 7 Scanning electron micrographs of: (a) pure Hydrin-C, (b) blend with low polypyrrole content and (c) blend with high polypyrrole content

(Hydrin-C) can be prepared by an electrochemical method. This material retains the electrochemical and electrochromic properties of polypyrrole with a 10% loss of electrochromic contrast and lower stability to repeated redox cycles caused by the ohmic resistance of the rubber component of the blend. The mechanical properties, however, are very similar to those of a vulcanized rubber.

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