Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Selampinar, F. , Akbulut, U. and Toppare, L.(1996) 'Conducting Polymer Composites of Polypyrrole and Polyimide', Journal of Macromolecular Science, Part A, 33: 1, 309 — 318

To link to this Article: DOI: 10.1080/10601329608020387

URL: http://dx.doi.org/10.1080/10601329608020387

MACROMOLECULAR REPORTS, A33(SUPPLS. 5&6), 309-318 (1996)

CONDUCTING POLYMER COMPOSITES OF POLYPYRROLE AND POLYIMIDE

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ABSTRACT

Polymeric composites with conductivities ranging from 1 to 10 S/cm were prepared by electrochemically polymerizing pyrrole in a matrix of polyimide. The polyimide/polypyrrole (PI/PPy) composites were characterized by SEM, TGA, FT-IR and electrical conductivity measurements. The cyclic voltammetry technique was used to determine the electroactivity and the electrochemical properties of PPy and PI/PPy.

INTRODUCTION

Electronically conductive polymers are an extremely interesting class of materials that have gained popularity in the last decade. Most studies have focused on the synthesis of conducting polymers, such as polyacetylene, polypyrrole and their derivatives. Since Diaz [1] polypyrrole is the one that is studied most extensively because of its high electrical conductivity and good environmental stability. However it is hard and brittle, because of these poor

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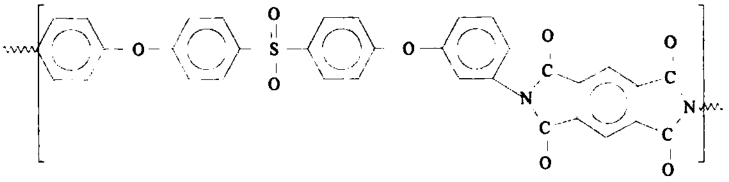
*To whom correspondence should be addressed mechanical properties its potential application is greatly restricted. In order to improve these mechanical properties, the preparation of the composites from a conductive polymer and an insulating polymer has been proposed [2 - 5]. The most successful method to form the composites was found to be electrochemical preparation of conducting polymer on an electrode coated with an insulating polymer. As the host polymers, polyvinyl chloride [2, 3] polycarbonate [5], polyvinylalcohol [6] were used. In these cases, the host polymers were required to swell in the solvent used for the polymerization of pyrrole. Such composite films are of great importance not only because they possess improved mechanical properties but also because they might extend the applications of conducting polymers in the fields of energy storage, solar energy conversion, electrode active materials.

Here we report and electrochemical method for preparing composite conducting films from polypyrrole (PPy) and polyimide (PI). Since the 1960s lightweight improved performance polymeric materials have been replacing metals in environmentally harsh applications that require prolonged high temperature stability, resistance to moisture and humid environments. Aromatic polyimides are most widely studied polymeric materials for applications subjected to harsh environment exposure. The aromatic polyimides which contain heteroatoms show excellent thermal stability and mechanical properties. Because of these properties they have been widely used in a variety of applications such as aviation materials or aviation coatings, electronics/microelectronics.

The composite films from PI and PPy were obtained by electro-oxidizing pyrrole into a PI substrate coated on a platinum electrode surface in an electrolyte solution of acetonitrile. The characterizations were done via TGA, SEM, FTIR analyses.

MATERIALS

Pyrrole (Merck) was distilled before use. PI was synthesized in Gebze Research Center of Turkish National Scientific Research Council. The structure of PI is:



Acetonitrile (Merck) and dimethylformamide (DMF) was used without further purification. Tetrabutylammonium tetrafluoroborate (TBAFB) was supplied from Aldrich.

PREPARATION OF COMPOSITE PI/PPY FILMS

A PI coated electrode was obtained by depositing 2.5 wt% solution of PI in DMF onto a platinum (Pt) foil electrode and allowing the solvent to evaporate. With PI/PPy electrode (1.5 cm^2) as the working electrode, a platinum foil counter electrode and Ag/Ag^+ reference electrode, pyrrole was electro-oxidatively polymerized onto the PI film coated Pt electrode in a three compartment cell containing acetonitrile solution of pyrrole and TBAFB at a constant potential of +1.3 V. After polymerizations, the composite films were rinsed with acetonitrile, dried at room temperature and removed from the electrode. A PPy content in the composite was estimated from the increase of the weight after the polymerization of pyrrole.

As a control experiment, we repeated the above experiments with no pyrrole monomer in the cell. In these runs we observed that the insulating polymer PI do not undergo oxidation under the conditions of the polymerization of pyrrole.

Conductivities of samples were measured via four probe technique. The composites were characterized by FT-IR (Matson 1000) and SEM (Cambridge Stereoscan, S4-10). The thermal gravimetric analysis was recorded on a DuPont 2100 instrument.

TABLE 1

% PPy	Electrode side (S/cm)	Solution side (S/cm)
23	1	1.5
55	2.2	4.1
67	3.9	4.9
70	3.9	5.2
100	10	10

RESULTS AND DISCUSSION

As pyrrole was being polymerized onto a PI/Pt electrode, the transparent PI film on Pt turned black which could be peeled off from electrode. The PI film on the Pt electrode is swollen by an electrolyte solution, pyrrole and dopant penetrate through the PI layer to the Pt surface. The pyrrole polymerized on the Pt surface and doped by BF_4^- at the same time. The conducting polymer then diffuses back towards solution, producing a homogeneous composite of the two polymers.

The composites obtained with different weight percentage of PPy show rather small differences in conductivities. The conductivity of the films surface that was in contact with Pt was the same that of the other side. The films exhibit a fairly high conductivity even at low PPy content (Table 1).

The FTIR spectra in Figure 1 represent that of pure PPy, PI, PI/PPy. The spectrum of PPy yields an intense peak at 1083 cm^{-1} due to the dopant ion (BF_4^-). The characteristic bands for PI are 1780 cm^{-1} carbonyl asymmetric stretching, 1720 cm^{-1} carbonyl symmetric stretching, 1380 cm^{-1} C-N symmetric stretching and 725 cm^{-1} carbonyl out of plane bending. The electrolytic film contains these bands revealing that the PI is maintained in the blend.

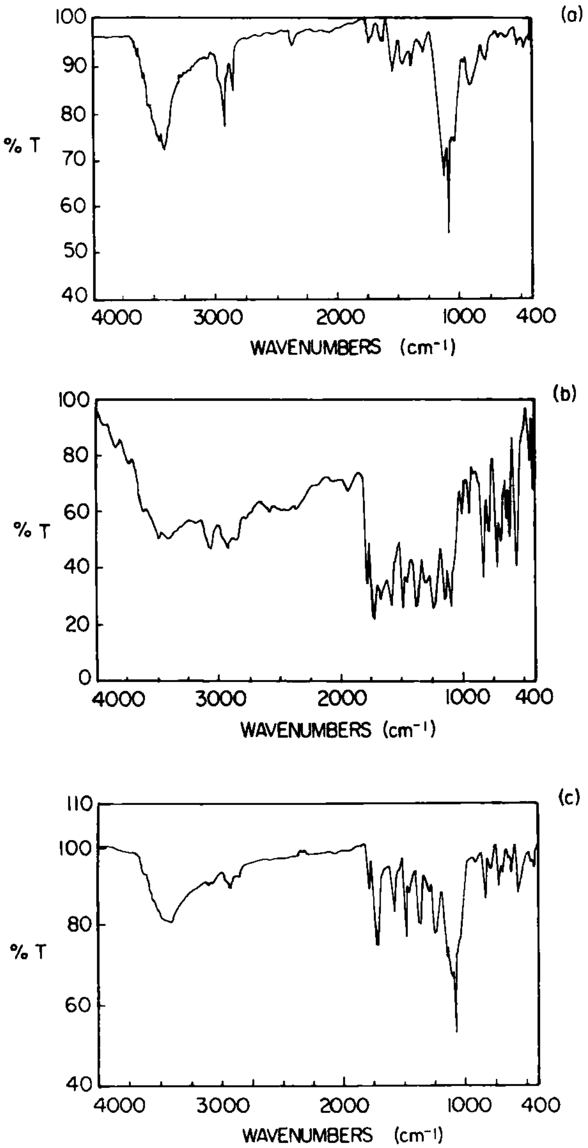


Figure 1: FTIR spectra of: a) PPy b) PI c) PI/PPy electrolytic film

The morphology of the composite films was studied by scanning electron microscopy. In Figure 2 scanning electron micrographs of both sides are shown. The electrode side of the composite films is rather smooth. On the solution side of the composite films cauliflower-like projections are observed.

Thermal gravimetry analyses of the composite film reveals a 20% weight loss at around 620 °C (Fig 3a) whereas the pure polyimide has two major weight loss patterns at the lower temperatures. Thus, thermal stability of the PI has been further improved by blending with PPy.

The electrochemical behaviors of PPy and PI/PPy films were determined in acetonitrile-TBAFB system which is totally electro-inert in the range of ±3.00 V. All measurements in this work were done versus Ag/Ag^+ reference electrode and at room temperature. Figure 4a shows the cyclic voltammogram of PPy at bare Pt from -0.2V to +1.2 V. The plot shows a peak for oxidation of the film around 0.55 V on the anodic sweep and the corresponding reduction peak at around +0.2 V in cathodic sweep. Multi-sweep cyclic voltammograms of PI/PPy composite electrodes are given in Figure 4b. The oxidation peak is at 0.5 V and the corresponding reduction peak is at 0.2 V. As the runs were continued the oxidation peak switches to 0.75 V and reduction peak to 0.1 V (Fig 4c). It is well known that thin films of PPy (less than 0.1 μm thick) are electroactive and can be switched between the neutral and oxidized state at about 0.1 V versus SCE [7]. In aprotic solvents and in the absence of oxygen the reaction is coulombically reversible and the film can be switched between the two oxidation states repeatedly without the decay of the electroactivity. The electrochromic behavior of PPy are clearly demonstrated showing that PPy is actually reduced and oxidized. These properties also were observed for PI/PPy electrode. This means that the PI is sufficiently porous to allow pyrrole and the electrolyte to diffuse across the film and react at the Pt electrode.

CONCLUSION

By electrochemically polymerizing pyrrole into a PI insulating polymer, we obtained composite materials from PI and PPy with high

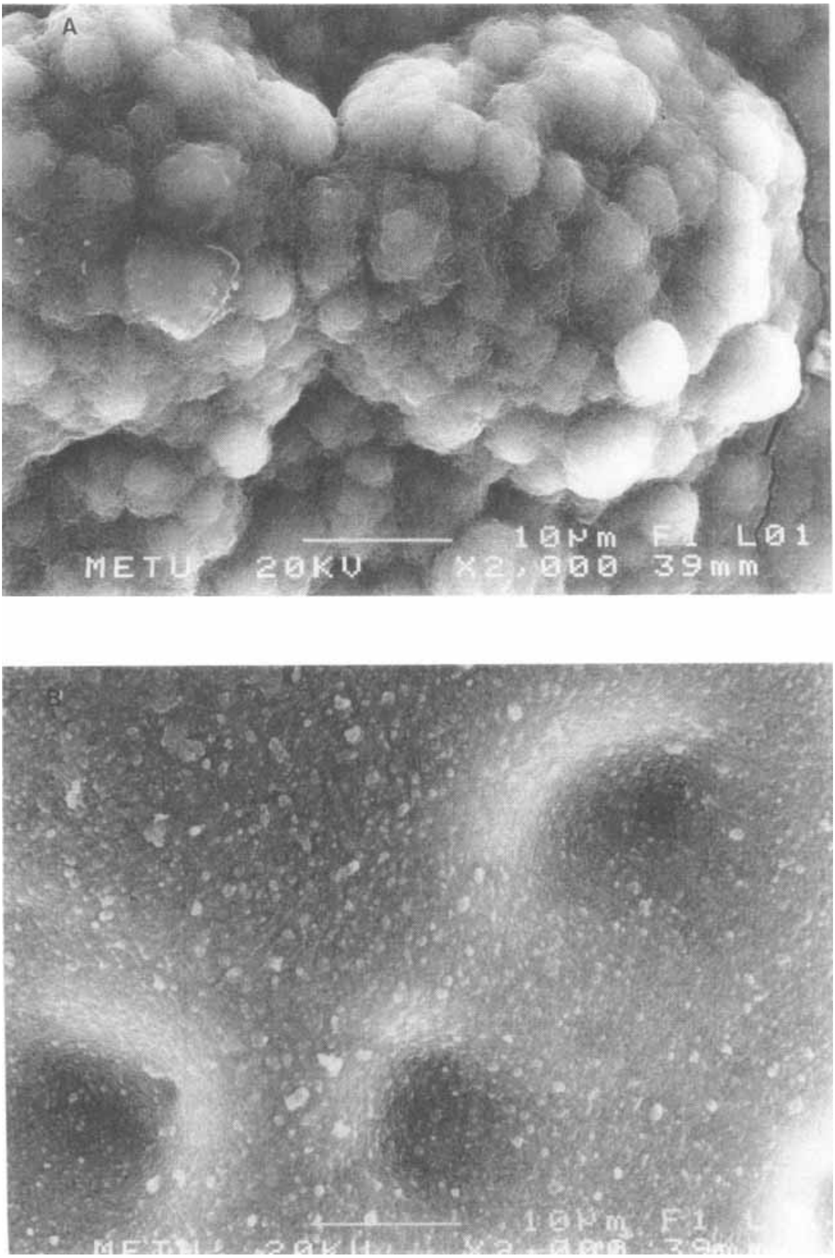


Figure 2: SEM PI/PPy films: a) Solution side b) Electrode side

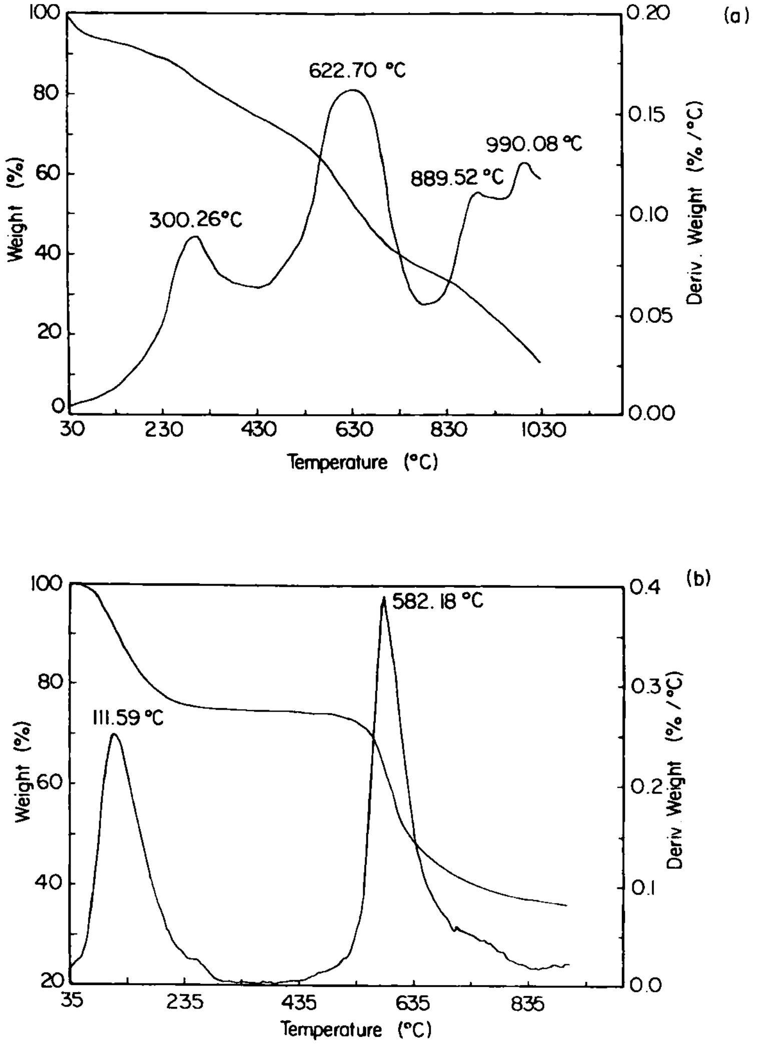


Figure 3: Thermal Gravimetry analysis of: a) PI/PPy film b) PI

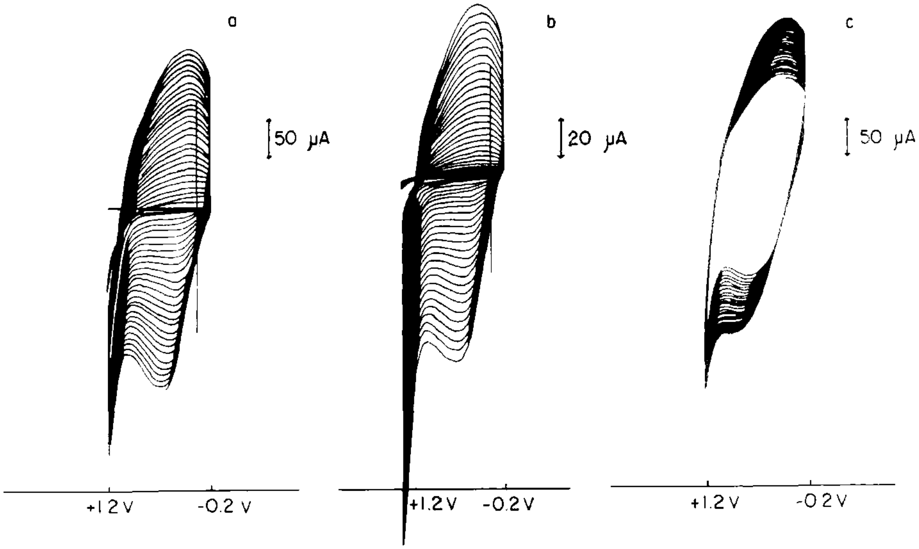


Figure 4: Cyclic voltammogram of Pyrrole in acetonitrile on: a) bare platinum b) PI coated electrode (first 20 cycles) c) PI coated (last 20 cycles)

conductivity, good stability to harsh environmental conditions. The conductivity of PPy is combined with the good thermal stability of PI and this improvement may find applications in various areas.

ACKNOWLEDGMENTS: This work was supported by TBAG-1422 and DPT95K120498 Grants. We also thank Dr. A. Güngör for the preparation of PI.

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