

Synthesis and Structural Investigation of Conductive Composites from Cellophane and Polypyrrole

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SYNOPSIS

A versatile method for preparing conducting composites from cellophane and pyrrole by an interface technique has been attempted. Polymerization of pyrrole into the porous matrix of cellophane produces black, flexible composite film with conductivity comparable to that of polypyrrole and mechanical properties very similar to cellophane. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The utilization of electrically conductive polymers in many technological applications is limited owing to the fact that they have poor atmospheric stability and processibility. Most of the work in the area of conducting polymers has been concentrated in two main classes of polymers: polyacetylene and its derivatives¹ and polyheterocyclic cations.² Though polyacetylene has good mechanical properties with high electrical conductivity when doped with iodine ($\sigma = 100 \Omega^{-1} \text{ cm}^{-1}$), its poor stability to ambient conditions restricts its utilization. On the other hand, a polyheterocyclic cation such as polypyrrole exhibits high electrical conductivity and stability to ambient conditions, but its mechanical properties are poor, i.e., low elongation at break and brittleness.⁴

Hence, one of the ways to produce such polymers in a tough, processable, stable form is to make composites with stable passive polymers. Composites have been prepared by introducing a polymer film at the interface between aqueous ferric chloride (FeCl_3) and pyrrole (diluted in toluene).^{5,6} This method allows the preparation of polypyrrole-impregnated composites of cloth and paper as well as other polymers, including ionomeric membranes.⁷

In the present work, we applied the interface

technique for the preparation of conducting polymeric composites from cellophane and polypyrrole. Cellophane films are semipermeable and porous, which make them an ideal matrix for polymerization of pyrrole. Besides cellophane having good mechanical properties, it imparts flexibility and strength to the composite, whereas polypyrrole, being electrically conducting and stable, makes the composite highly conducting and stable to ambient conditions.

EXPERIMENTAL

A cellophane + polypyrrole (cello + PPy) composite was prepared according to the previously published procedure.⁵ Cellophane sheet in the form of thin films of commercial variety was obtained from Kesoram Rayon Ltd., Calcutta. The film was about 35 μ thick and transparent and contained an amount of glycerol, which makes it flexible. The percentage (%) crystallinity of this film as received was 59.09%. Pyrrole was obtained from Sisco Research Laboratories in the pure form. It was further purified by distillation under vacuum. The molecular weight of pyrrole was 76.09. Of the different methods of preparation of composites such as vapor-phase deposition,⁸ electrochemical deposition,⁹ plasma¹⁰ (C.V.D.) deposition, and growth of thin films at the interface,¹¹ it was found that the last method is convenient for the preparation of cello + PPy composite. It was essential to remove glycerol from the film before doping with pyrrole. The film was, therefore, dipped in distilled water for 24 h and then dried.

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The ferric chloride (FeCl_3) solution (10% w/v) was kept in a Petri dish of diameter 10 cm. A cellophane sheet of size 7×7 cm was supported on a stand as shown in Figure 1 such that the lower surface of the film is in contact with the FeCl_3 solution. A diluted solution of pyrrole in toluene (10% w/v) was spread uniformly on the top surface of the cellophane film. It was observed that the diffusion of pyrrole across the film allows it to come into contact with FeCl_3 , which acts as a catalyst for the polymerization of pyrrole in the host film. It was observed that for the diffusion of pyrrole and the polymerization to be complete a time period of about 6 h was adequate. However, to ensure complete polymerization, the reaction was allowed to proceed up to 24 h.

To prepare composites having different contents of PPy, the amount of pyrrole solution spread on the film was varied between 0.2 and 2 mL. At the end of the reaction, the film was removed from the Petri dish, washed with distilled water, and then kept in a desiccator for drying. The films were weighed before and after the composite formation, which allowed us to find the percentage content of PPy in the composite.

Cello + PPy composites having different PPy contents were synthesized so that a composite of cello + PPy having an optimum content of PPy with

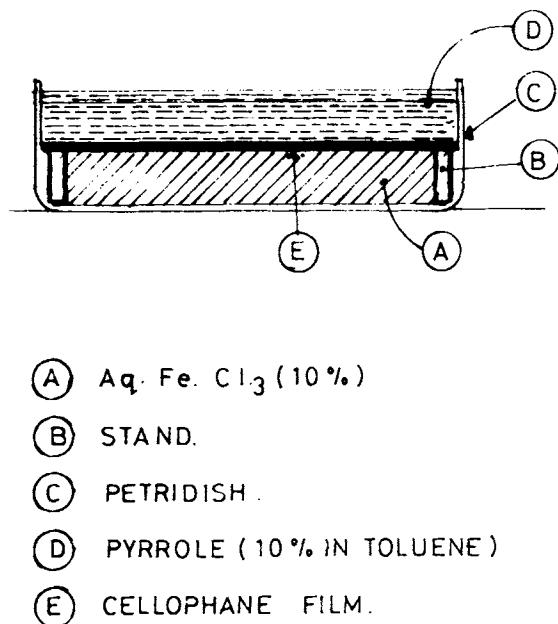


Figure 1 Experimental setup for the preparation of cello + PPy composite.

Table I Values of % PPy and Thickness for Cello + PPy Composites

Sample	% PPy	Thickness ($\times 10^{-6}$) m
Cellophane (controlled)	0	35
Cello + PPy (0.1 mL)	2.62	44
Cello + PPy (0.2 mL)	5.4	46
Cello + PPy (0.5 mL)	13.09	47
Cello + PPy (1.0 mL)	17.4	52
Cello + PPy (1.25 mL)	33.0	53
Cello + PPy (1.5 mL)	35.1	54
Cello + PPy (2 mL)	42.8	55

good mechanical and electrical properties could be achieved. Mechanical properties like tensile strength, % elongation, load at break, and Young's modulus of the composite films having different percentage content were evaluated using an Instron tester. Crystallinity and other parameters regarding the structure of the composites were studied using the wide-angle X-ray scattering technique.

RESULTS AND DISCUSSION

Weight uptake measurements were done to calculate the percentage uptake of PPy with cellophane as the amount of pyrrole polymerizing onto cellophane was varied. It is observed that as the amount of pyrrole solution spread on the cellophane film during the synthesis increased, the percentage content of PPy in the composite correspondingly increased. Besides weight gain, thickness measurements were also carried out for the composite films. It is observed that as the percentage content of PPy in cellophane increased, there was a corresponding increase in the thickness of the film, as shown in Table I.

The tensile strength, percentage elongation, load at break, and Young's modulus for the composite films having different contents of PPy changed as the PPy content increased. Also, the tensile strength increased and the percentage elongation decreased, leading to increase in the Young's modulus as the percentage content of PPy increased (Fig. 2).

A typical X-ray diffractogram for cellophane is illustrated in Figure 3(a), which shows mainly three peaks corresponding to (101), (10 $\bar{1}$), and (002) planes. The X-ray diffractogram of the composite [Fig. 3(b)] shows the changes in the intensities of

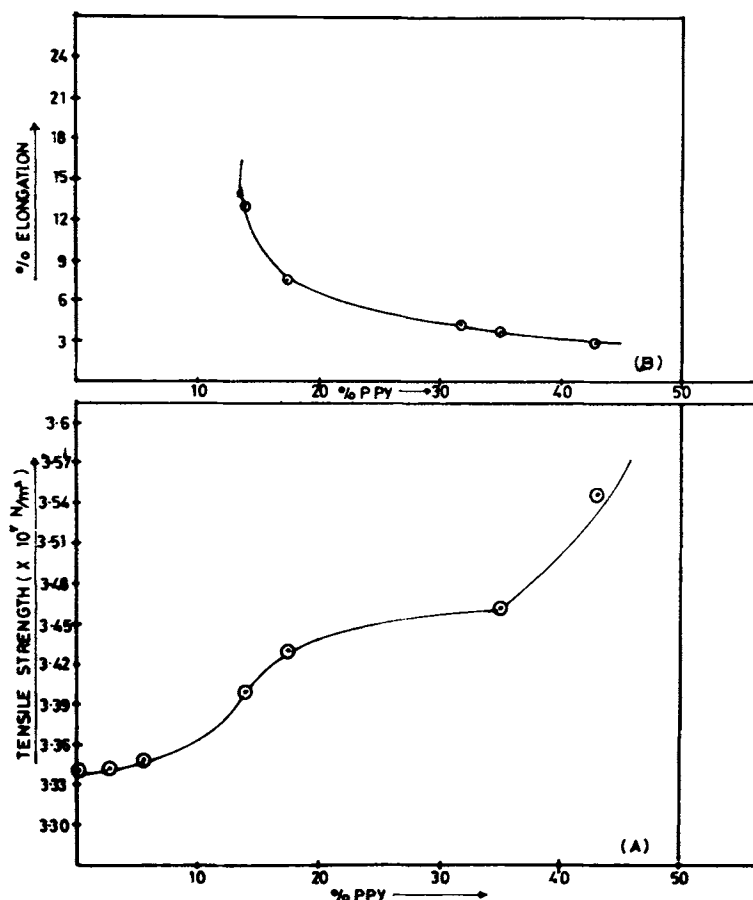


Figure 2 (A) Plot of tensile strength vs. % PPy. (B) Plot of % elongation vs. % PPy for cello + PPy composites.

the peaks corresponding to cellulose II as well as the appearance of a new peak at $2\theta = 26^\circ$. This peak is probably due to PPy. For the sake of comparison, a diffractogram corresponding to pure PPy is also depicted in Figure 3(c).

In the present work, XRD analysis was used to determine the crystallinity of the composite film. The crystallinity was calculated using Manjunath's formula. The variation in crystallinity as the percentage content of PPy varies is shown in Figure 4. It is seen that as the percentage content of PPy increases the crystallinity of the composite decreases.

From Figure 2, it can be seen that there is a sudden increase in the tensile strength when the percentage of PPy is about 10–12%. Similarly, a drastic decrease in the percentage crystallinity was noted when the PPy content was about 10–12%.

In a separate set of experiments, we verified that the electrical conduction of controlled cellophane is of the order of 10^{-12} S/cm. When doped with various

amounts of PPy, it was observed that the electrical conductivity increases by eight orders of magnitude. The increase in electrical conduction as a function of PPy content is depicted in Figure 5, from which it can be seen that there is a sharp increase in conductivity when the PPy content is about 10–12%. This indicates that the percolation threshold exists at about 10–12% of PPy content. This result indicates that the electrical conductivity of cellophane can be increased by proper doping. Though the increase does not reach metallic conduction, the level achieved is from insulating to semiconducting.

The percolation threshold observed for electrical conduction is in accord with the observation of a similar sudden change in percentage crystallinity and tensile-strength measurements. This behavior is similar to the one reported for PMMA/graphite¹² and polyacetylene/LDPE systems.¹³

Thus, these studies have revealed that a stable and flexible cello + PPy composite film can be pre-

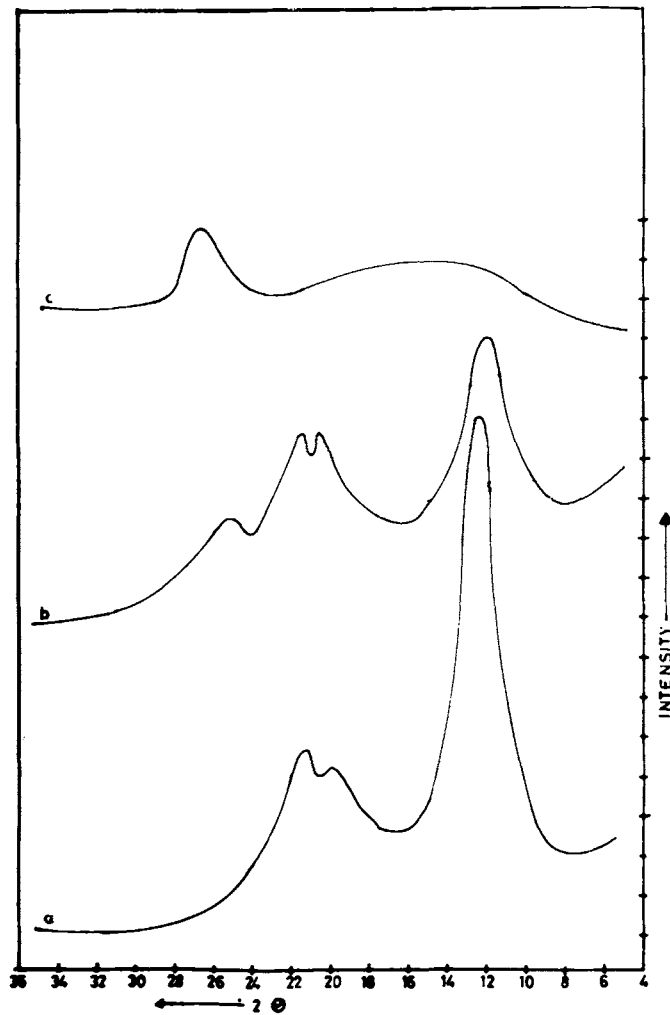


Figure 3 (a) A typical X-ray diffractogram of cellophane. (b) A typical X-ray diffractogram of cello + PPy composite. (c) A typical X-ray diffractogram of pyrrole.

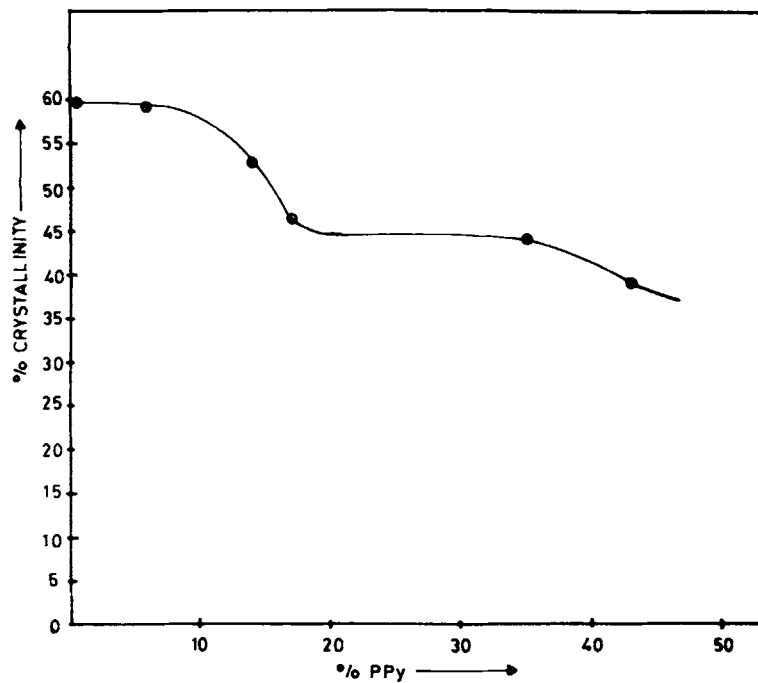


Figure 4 Plot of % crystallinity vs. % PPy for cello + PPy composites.

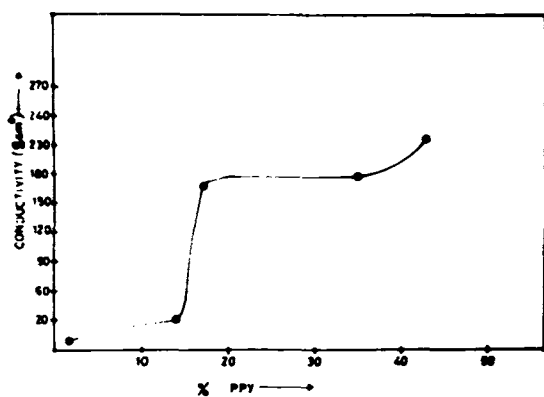


Figure 5 Plot of conductivity vs. % PPy for cello/PPy composites.

pared having good mechanical properties and electrical conduction. Attempts are being made to use such composites for humidity sensors and polymeric battery, the details of which are being given in a separate communication.

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