Structural, Mechanical, and Electrical Properties of Electropolymerized Polypyrrole Composite Films

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ABSTRACT: Electrochemical polymerization of pyrrole in a solution containing dissolved poly(vinyl alcohol) (PVA) produces a homogeneous, free-standing, flexible, and conductive polymer film. The films were characterized using infrared spectroscopy, wide-angle X-ray diffraction analysis, and scanning electron microscopy. The appearance of standard and some new absorption bands for polypyrrole (PPy) and PVA confirms the composite formation. The mechanical properties of conducting PVA + PPy films were studied and found to be improved with respect to the control PPy films. The electrical conductivity of the PVA + PPy films was measured by using standard four- and two-probe methods. The conductivity of the films was found to depend on the pyrrole content. These conducting composites were further used as gas sensors by observing the change in current with respect to ammonia gas. It was observed that the current decreases when these composites were exposed to ammonia gas. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2511–2517, 2001

Key words: IR spectroscopy; X-ray diffraction; SEM; elemental analysis; mechanical properties; gas sensors

INTRODUCTION

Electrochemically conducting polymers have been the subject of great interest to chemists and physicists over the past 30 years. Polypyrrole (PPy) is one of the most important conducting polymers which belongs to the heterocyclic conjugated polymeric system.[1] To improve the structural and electrical properties, the preparation of composite materials containing a conducting polymer alloyed with a nonconducting polymer was proposed. This idea was successfully applied to polyacetylene[2] and, more recently, composite materials, containing an electropolymerizable conducting polymer like PPy and nonconducting polymers like poly(vinyl chloride) (PVC)[3] or poly(vinyl alcohol) (PVA),[4] were syn-

thesized. In recent publications,[5] it was also reported that conductive polymer composites can be prepared by electrochemically polymerizing pyrrole on a working electrode precoated with polymer such as PVC. Among several approaches used to circumvent processing difficulties,[6–8] the electrochemical route is especially attractive. Wang et al. reported conductive composites prepared by electrochemically polymerizing pyrrole in PVC blended with an electrolyte.[9] Apart from chemical polymerization, PPy can be successfully prepared by an electrochemical method.

In the present investigation, therefore, an attempt was made to prepare composite materials containing a conducting polymer (PPy) alloyed with a classical nonconducting polymer (PVA) and to investigate its structural, mechanical, and electrical properties. In this communication, we show, for the first time, that a conducting polymer like pyrrole can be electropolymerized in a solu-

tion containing dissolved PVA and that the resulting composite film has interesting structural and mechanical properties together with high electrical conductivity.

EXPERIMENTAL

Pyrrole (99%) was obtained from the Aldrich Chemical Co. (Milwaukee, WI) and was distilled before use. PVA was obtained from LOBA Chemicals (Bombay, India) having a degree of polymerization of 1700–1800 and viscosity of 25–32 CP. Toluene-4-sulfonic acid, used as a supporting electrolyte, was obtained from Fluka Chemicals (Buchs, Switzerland).

The PPy + PVA films were prepared in potentiostatic conditions on a stainless-steel electrode in a single-compartment cell containing 0.1M PPy, 0.1M PTS (toluene-4-sulfonic acid), and 5% w/v PVA in distilled water. The counterelectrode was a graphite rod and a saturated calomel electrode was used as a reference electrode. The electropolymerization was carried out using a PARC 273A potentiostat/galvanostat having the run-270 software system. After electropolymerization, the working electrode was dried at room temperature and rinsed with distilled water. The resulting flexible composite film was then easily removed from the electrode for structural and electrical conductivity measurements.

The thickness of the films was determined by a thickness gauge (Model Backer-Mercer type C-17). The PPy content of the films was determined by doing simple calculations based on elemental analysis. SEM studies of the films, coated with gold, were performed using a Philips scanning electron microscope (Model 515).

FTIR spectra of the samples were recorded on a Perkin-Elmer spectrophotometer. The conductivities of the free-standing PVA + PPy films were measured using a standard two-probe method. The dependence of the electrical conductivity of PVA + PPy films was measured over a temperature range from 303 to 353 K. The sample was placed in a chamber with a heating rate of 2–3°C/min, and the conductivity of the sample was recorded at each temperature.

RESULTS AND DISCUSSION

IR Spectral Analysis

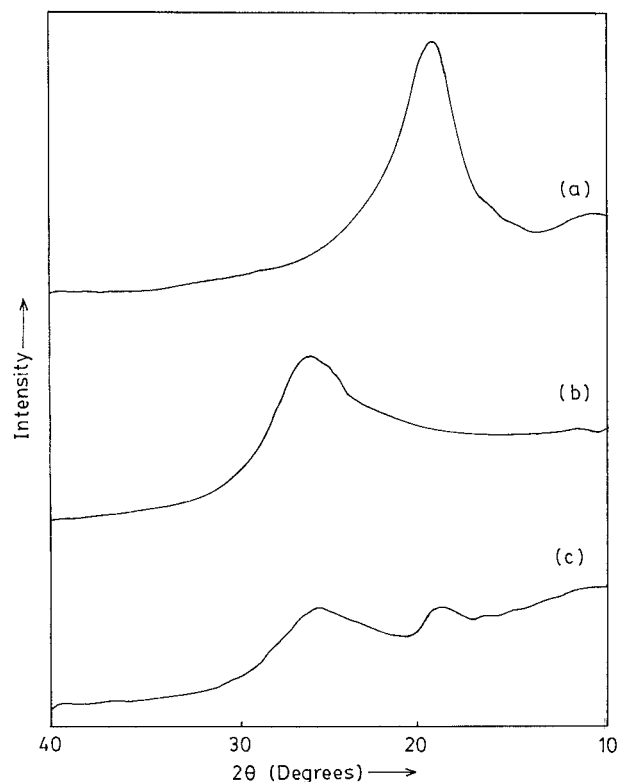IR spectra of pure PPy, pure PVA, and a conducting PVA + PPy composite are shown in Figure 1.
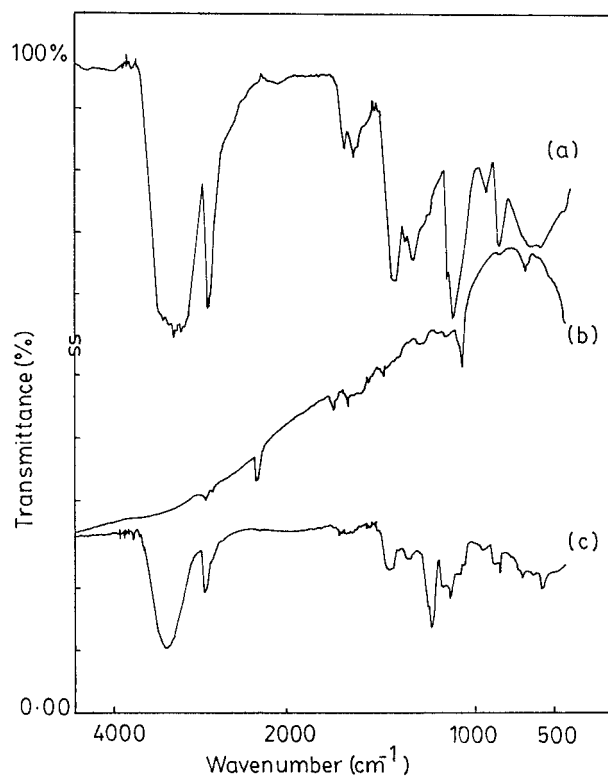
Figure 1 Infrared spectra of (a) pure PVA, (b) pure PPy, and (c) PVA + PPy composite films.

The IR spectrum of pure PPy [1(a)] shows absorption bands near 1550 cm^{-1} (C=C stretching of pyrrole ring), 1200 cm^{-1} (—CH bending vibration), 1050 cm^{-1} (—NH bending deformation), and 950 cm^{-1} (—CH out-of-plane bending). The IR spectrum of PPy is similar to that reported in the literature.[10] The IR spectrum of pure PVA is shown Figure 1(b). The absorption band at 1141 cm^{-1}, sensitive to crystallization, is present and reported to be due to C—C and C—O stretching. The absorption band appearing at 1326 cm^{-1} is reported to be due to C—H and O—H bending. Absorption due to CH$_2$ bonding at 1430 cm^{-1} appears with a strong intensity. The absorption band at 2942 cm^{-1} (C—H stretching) also appears with a very strong intensity. The IR spectrum of PVA is similar to that reported in the literature.[11] Curve (c) of Figure 1 shows the IR spectrum of conducting PVA + PPy, which is somewhat similar to that of conducting PPy with a diminished peak intensity. The conspicuous absence of absorption bands around 1550, 2942, and 2910 cm^{-1} confirms the interaction between PPy and PVA.

Wide-angle X-ray Diffraction Analysis

Wide-angle X-ray diffraction scans (WAXD) of pure PPy, pure PVA, and conducting PVA + PPy

Figure 2 Wide angle X-ray diffraction spectra of (a) pure PVA, (b) pure PPy, and (c) PVA + PPy composite films.

composite films are shown in Figure 2(a–c), respectively. The XRD scan of pure PVA [Fig. 2(a)] shows an amorphous halo at $2\theta = 19.7°$. Figure 2(b) shows an XRD scan of pure PPy which shows an intense peak around $2\theta = 26.0°$. The XRD scans of pure PPy and pure PVA are similar to those reported in the literature.[12,13] Curve (c) of Figure 2 shows an XRD scan of conducting PVA + PPy, which is somewhat similar to that of conducting PPy. From Figure 2(c), it can be observed that the presence of an amorphous halo at $2\theta = 25.8°$ and a peak with diminished intensity at $2\theta = 19.4°$ confirms the presence of PVA and PPy. However, changes in the relative intensity and a slight shift to lower angles indicates an interaction between PVA and PPy.

Elemental Analysis

An analysis of all samples was carried out for C, H, and N content. From the elemental analysis of the samples, it was observed that the values of the carbon and hydrogen content of the PVA + PPy composite are different from those for the

pure PVA and PPy samples. We carried out hypothetical calculations by taking values of the mol ratios of PVA and PPy and it was found that the theoretical value agrees with the experimentally observed one when it is assumed that two molecules of PVA become attached with one molecule of PPy during polymerization. On the basis of molecular weights, it means that 20% of PVA may be present in the actual composite film.

Morphological Studies: SEM

Morphological studies of the PVA + PPy composites were carried out using SEM (Phillips SEM 515). Figure 3(a,b) shows the electron micrographs of the PVA + PPy composite for 5 and 20 min, respectively. The films prepared under different conditions show typical small globules together with some needlelike structures. It was seen during the course of the studies that for samples grown for 5 min [Fig. 3(a)] many globules

Figure 3 Scanning electron micrograph of PVA + PPy composite films: (a) PVA + PPy composite film for 5-min growth; (b) PVA + PPy composite film for 20-min growth.
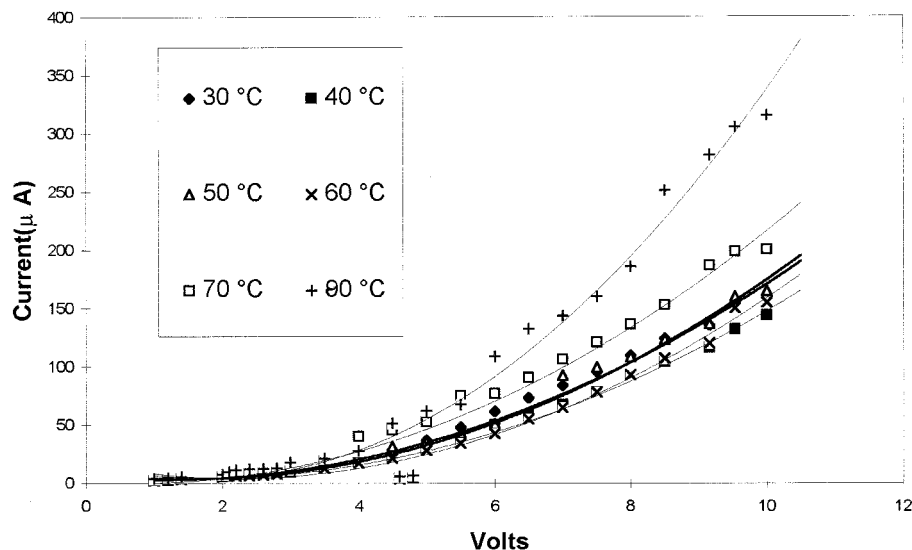
Figure 4   Current (I)–voltage (V) characteristics of PVA + PPy composite films.

with a tiny needlelike structure are present. However, as time of preparation increases to 20 min, the development of needles was far better, although globulelike features still exist. The average length of the needles was found to be 12 μm.

Electrical Conductivity Measurements

The current–voltage characteristics of PVA + PPy films at various temperatures (30–80°C) was studied. It was seen that I–V characteristics of these films are nonlinear, indicating nonohmic behavior of the samples (Fig. 4). Assuming that the normal energy band picture can be applied to an insulating thin film, there would appear to be six possible separate conduction mechanisms. Testing of the observed data for various mechanisms was carried out by assuming certain basic relations during the analysis. The data were plotted as log I versus log V, log I versus $1/T^4$, and log σ versus $1/T$. Analysis of such plots revealed that the mechanism of ionic conduction, Schottky and Poole–Franklel emission, hopping, and impurity conduction can be ruled out. Therefore, it is most likely that the current is limited due to the space charge (Fig. 5). This mechanism was indeed found to be true as our plot of log I versus log V shows a slope equal to unity for low fields and equal to 2 for high fields. To study the variation of conductivity (σ) with temperature, the plots of log (σ) versus the reciprocal of absolute temperature were obtained for conducting PVA + PPy film and is shown in Figure 6. The calculation of σ was made on the basis of the I–V plot shown in Figure

4. Since this plot is nonlinear, it is evident that region from 0 to 4 V can be considered as a "low field," and from 4 to 10 V, as a "high field" region. Values of σ were calculated for these two different regions and used to plot two graphs for log σ versus $1/T$ for low- and high-field regions. An illustrative graph for the high field is shown in Figure 6. It may be seen that there is a sharp increase in conductivity when temperature was increased from 30 to 40°C. However, at higher temperature, the increase seems to be gradual. Therefore, the average slope of a straight line was obtained for a best possible fit by considering points at higher temperature. The activation energy calculated on the basis of this slope was found to be 0.02 eV. Similarly, the activation energy calculated for the low-field region was found to be 0.01 eV, which is much lower. Such low values of activation energies indicate that the mode of conduction is electronic.

Mechanical Properties

The tensile strength for pure PVA film and pure PPy was found to be 40.46 and 32.4 MPa, respectively. This compares well with the values reported in the literature.[13,14] It was observed that the tensile strength of the conducting composite film of PVA + PPy is 65.33 MPa. This value is higher than that for pure PPy films. Thus, the mechanical properties of PPy films were found to have been improved by the formation of composites with PVA.
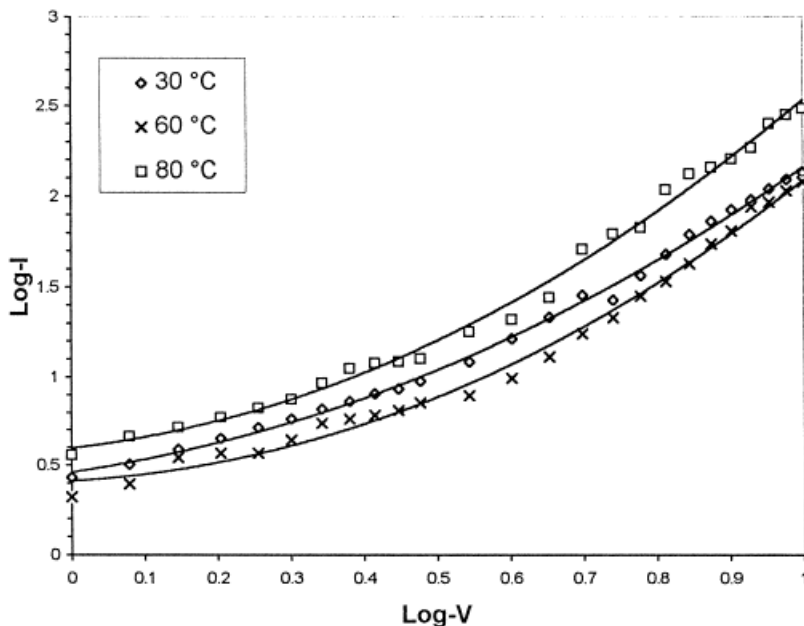
Figure 5 Log(I)–log(V) characteristics of PVA + PPy composite films.

Response to NH$_3$ Gas

The development of gas sensors is important at present as environmental pollution has become a great problem. A large number of gas sensors based on SNO$_2$, ZnO and other semiconductors have been used. They suffer from some shortcomings and, therefore, developing newer materials for gas sensing and for improving the sensitivity is a major task.

With the development of conducting polymers, it was realized that such materials should be of potential use for application in gas sensors, mainly because their conductivities can be controlled and changed easily. Polyacetylene, PPy, and polyaniline display interesting electrical properties and can be doped after or during the polymerization. The conductivity of such materials is found to change when exposed to certain gases such as chlorine and ammonia. The type and amount of doping, the thickness of the film, and the synthesizing conditions allow us to increase the conductivity manifold. Use of such materials for the detection of gases was reported.[15] Since pure PPy is mechanically not stable, it was reported from this laboratory that their composites with other polymers like cellophane, PVDF, and PVC can be synthesized electrochemically and used for gas sensors.[16] In the present investigation, we synthesized the composite of PVA + PPy and, therefore, it was thought to be interesting to test this material for gas sensors.

When the composite film was exposed to ammonia gas, it was noticed that there was a sudden decrease in the current. The graphical presentation of the response with respect to time is shown in Figure 7(a). It can be seen that the decrease in current is about 0.5 mA and the change was brought about in less than 50 s. When the gas was desorbed, the current again started increasing and reached its steady value of 0.9 mA in about another 50 s [Fig. 7(b)]. Figure 8 also shows the cyclic behavior when the gas is in (absorption) and when the gas is out. This behavior was found when the test chamber was evacuated and ammo-
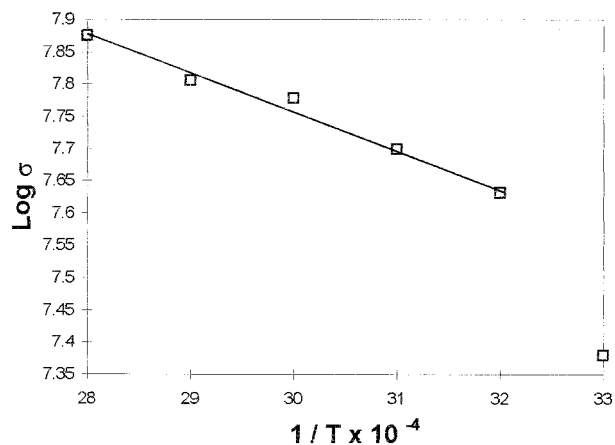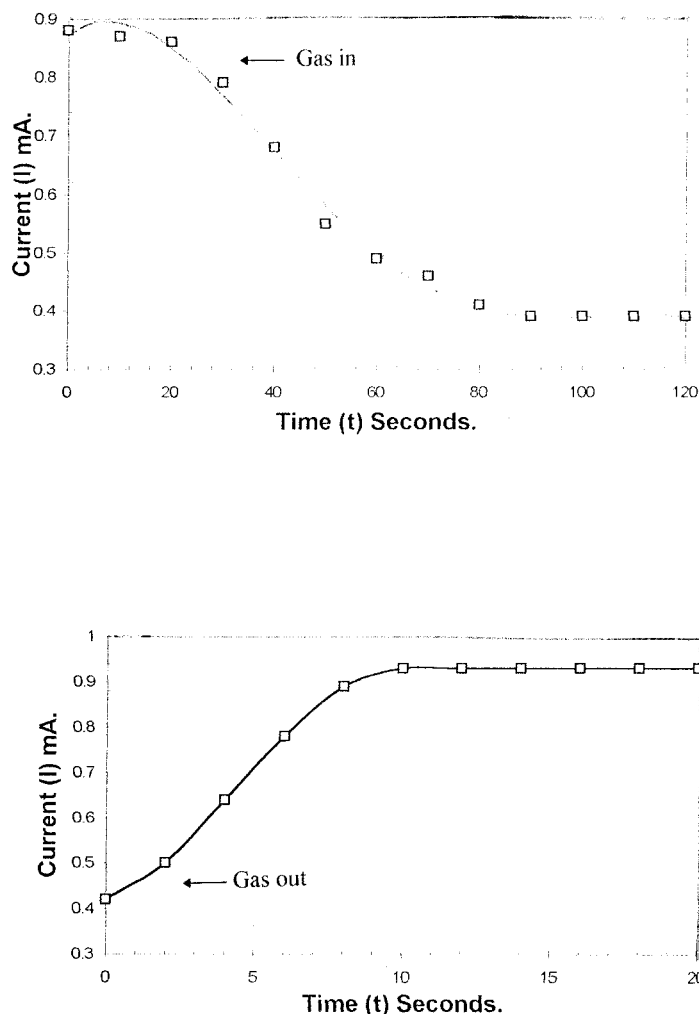

Figure 6 Log(σ) versus 1/T characteristics of PVA + PPy composite films.

Figure 7 (a) PVA + PPy films when exposed to ammonia gas (gas in). (b) PVA + PPy films when exposed to air (gas out).

nia (100%) was allowed to flow in. It was decided in the next set of experiments to determine the sensitivity of the material and, therefore, the percentage of ammonia flowing in the test chamber was decreased to 2% (w.r.t. N_2 in the mixture). Even in this case, the response was quite fast but the total change in the current was slightly less than 0.5 mA. In the next few experiments, we decreased the content to 0.1% of NH_3 w.r.t. N_2 and it was found that the sensitivity is still good, but the total decrease in the current is reduced and is about 0.35 mA.

The decrease in the current on exposure to ammonia gas can be understood from the fact that nitrogen contains a lone pair of electrons which can be donated to the initially oxidized PPy. This will neutralize the PPy cation (+ charge) and,

therefore, the number of carriers will decrease, resulting in a decrease of the current. The reaction can be represented by
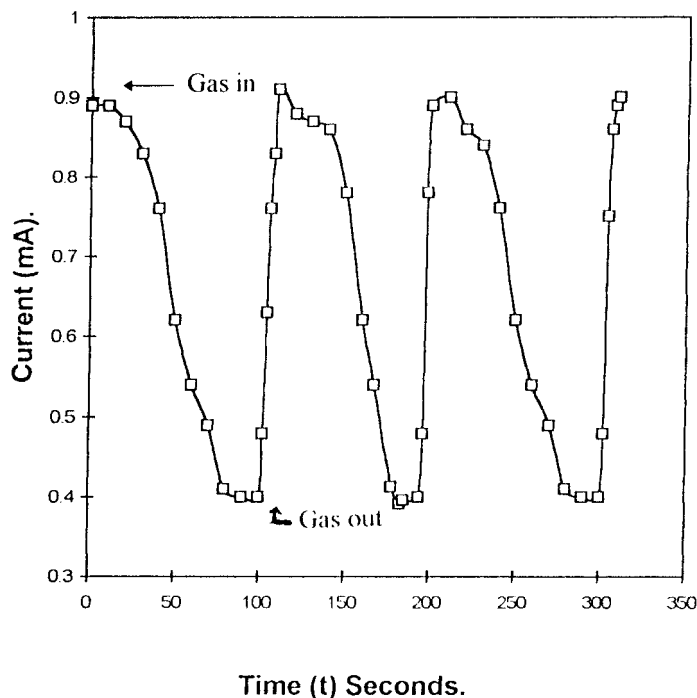
$$PPy^+ + \ddot{N} H_3 \rightarrow PPy^0 + N H_3^+$$
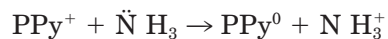
absorption reaction

$$PPy^0 + N H_3 \rightarrow PPy^+ + N H_3 \uparrow$$
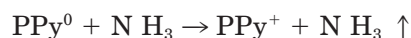
desorption reaction

The desorption of gas by a vacuum or by bringing the test chamber to the normal air results in the reformation of PPy^+ and, therefore, the current increased to the steady-state

Time (t) Seconds.

Figure 8   Cyclic behavior of PVA + PPy films treated with ammonia gas.

level. In previous experiments in this laboratory, it was reported that the neutralized films show a much better response. On the basis of those results, it was concluded that vacant sites and porosity in the film are necessary for increased sensitivity.

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