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Blends of Polypyrrole and Poly(vinyl alcohol)

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ABSTRACT: Blends of the conducting polymer polypyrrole (PPy) and poly(vinyl alcohol) (PVA) were prepared electrochemically and characterized by Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry, and scanning electron microscopy (SEM). The two polymers are intimately mixed at the molecular level as evidenced by (a) the loss of crystallinity of PVA in blends containing at least 20% PPy and (b) new infrared absorption bands in the blends that are not found in the spectra of the pure homopolymers. The blends are produced as thin, conducting layers on the electrode as shown in SEM micrographs.

Introduction

Electrochemical synthesis of conducting polymers has become an important research area in polymer science. Among these polymers, polypyrrole (PPy) has received a great deal of attention because of its high electrical conductivity and its environmental stability. However, its intractibility limits the practical application of PPy as a conducting polymer. One approach to improving the physical properties of conducting polymers is to use them as blends with insulating polymers that possess good mechanical properties, thus combining the desirable properties of both polymers. It is also desirable to maintain the percentage of conducting polymer in the blend at a minimum to take advantage of the properties of the host polymer.

We have previously reported conducting polymer blends of polypyrrole and various insulating polymers with the goal of improving miscibility and homogeneity of the blends.[1,2] Conductivity and physical properties are directly related to compatibility. We have recently shown that hydrogen-bonding between PPy and poly(bisphenol A carbonate) (PCR) can greatly enhance the miscibility of the blend. With that blend we have achieved threshold conductivities as low as 7%.[1]

In this paper we have chosen poly(vinyl alcohol) (PVA) as the host polymer. PVA offers tempting possibilities because it is transparent and commercially available. PVA exhibits inter- and intramolecular hydrogen-bonding, which causes the polymer chains to have a somewhat regular crystalline morphology.[3] The crystal structure of atactic PVA was first proposed by Bunn[4] in 1948. Also, no essential differences are observed in the X-ray diffraction patterns of PVA samples with different tacticities. With the host polymer coated on the electrode surface, it is very difficult for pyrrole molecules to penetrate the PVA film to reach the electrode surface and initiate polymerization. Attempts to make conducting polymer blends by heating the PVA to induce cross-linking and then immersing it in water to allow swelling have yielded polymerized product in the PVA matrix.[5,6] This process has certain difficulties, especially that the PVA film on the electrode should be sufficiently water-insoluble but still water-swellable. Miyata et al. prepared PVA polymer blends chemically using gas-phase polymerization in which the PVA film contained iron(III) chloride.[7] Our modification involves dip coating the electrode with a DMSO solution of PVA and air drying. We then place the dip-coated electrode into the electrolysis cell before it completely dries. This procedure circumvents the need to cross-link the PVA and allows the use of a nonaqueous solvent without changing the electrolyte. As we show herein, X-ray diffraction analysis allows, in the case of PVA, the study of blend homogeneity.

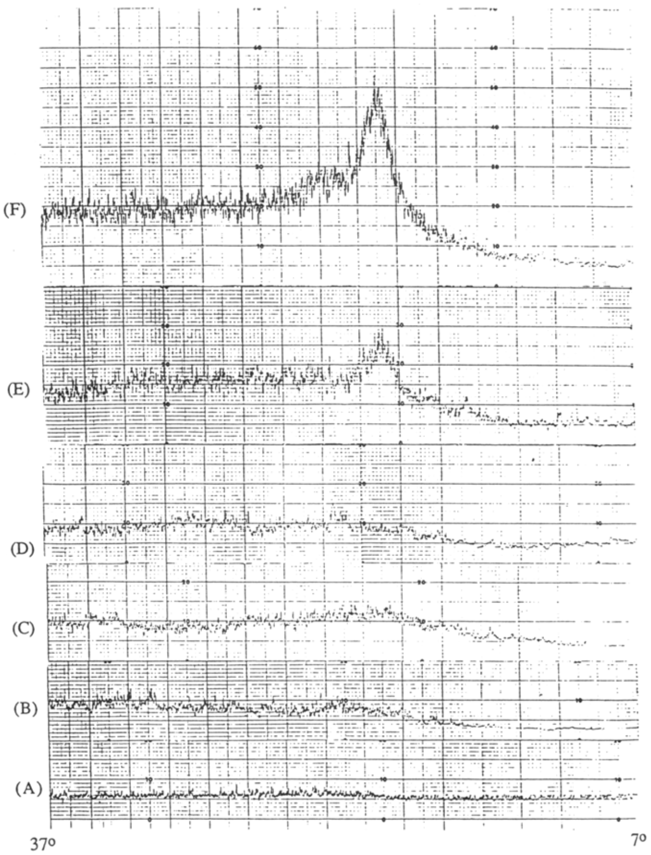

Figure 1. X-ray diffraction of PVA gel exposed to the air: (A) 0 days, (B) 1 day, (C) 2 days, (D) 4 days, (E) 10 days, (F) PVA gel immersed in CH_3CN for 10 min.

Experimental Section

Materials. Poly(vinyl alcohol) (PVA), 100% hydrolyzed, nominal MW 86 000 (Aldrich), was used as received in powder form. T_g and T_m were measured to be 65 and 220 °C, respectively. This polymer is about 25% syndiotactic as estimated from the IR band intensity ratio D_{916}/D_{850}.[13] The X-ray diffraction spectrum indicates extensive crystallinity.

Electrochemical Polymerization. PVA was dip-coated on the electrode surface from a 5% (w/w) DMSO solution and air dried for 24 h before inserting the electrode into the electrolysis cell. At that time the DMSO had not completely dried out, and PVA was in a stable gel state. Once the PVA gel is placed in the CH_3CN solvent, DMSO diffuses out of the PVA matrix. Oxidation was carried out at a potential of 1.1 V vs Ag/Ag$^+$ as reference

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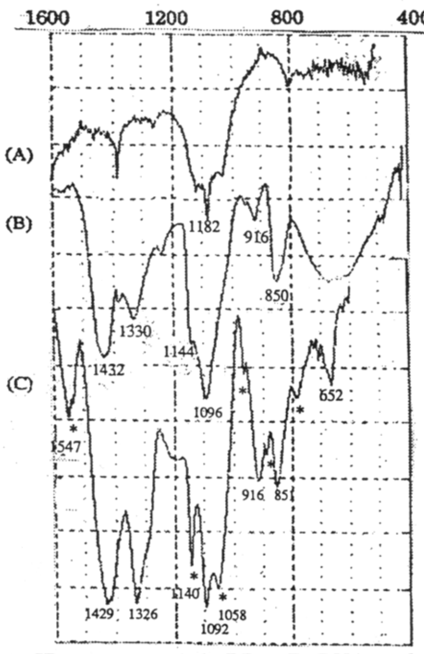

Figure 2. IR spectrum of (A) PPy, (B) PVA, and (C) PPy/PVA.

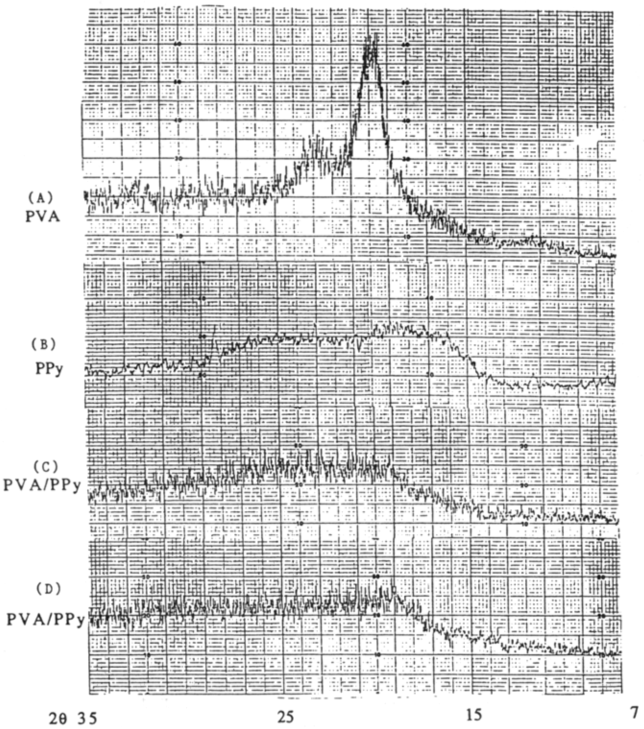

Figure 3. X-ray diffraction spectrum of polymers and their blends: (A) PVA, (B) PPy, (C) 20% PPy in the blend, (D) 80% PPy in the blend.

electrode. We found that pyrrole starts to polymerize on the electrode surface and grows into the PVA matrix in a manner similar to that of other insulating polymers that we have studied.[1,2] Electrolysis was stopped after predetermined times to obtain a range of PPy concentrations. We note that this method always results in a concentration gradient throughout the blend. The conducting polymer blends were peeled off the electrode surface and dried under vacuum for 24 h before any spectra or conductivity measurements were made. These films had thicknesses in the range 5×10^{-3}–1×10^{-2} cm. The IR spectra show these blends to be free of DMSO. Details of electrolysis conditions and other solvent and electrolytes used are described elsewhere.[1] PPy concentrations were determined by elemental analyses for nitrogen (M-H-W Labs, Tuscon, AZ).

Apparatus. Infrared studies were carried out on a Beckman FT1100 FTIR spectrometer. Scanning electron micrographs were obtained with a Zeiss Novascan 30 instrument. X-ray diffraction scans were carried out on a Philips X-ray diffraction instrument. Thermogravimetric analy (TGA) measurements were made with a Dupont 2100 instrument at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) studies were performed on a Perkin-Elmer 7 thermal analysis system at a heating rate of 10 °C/min. Weight percents of conducting polymer blends were determined by elemental analysis.

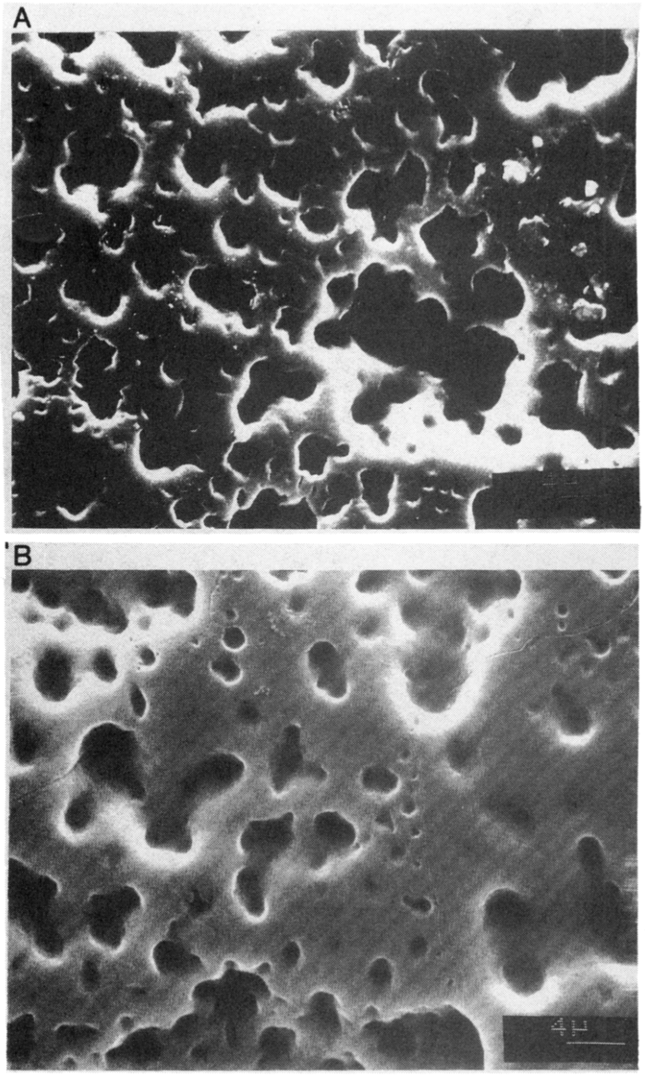

Figure 4. (A) SEM micrograph of the PVA/PPy blend on the electrode side (before washing). (B) SEM micrograph of the PVA/PPy blend on the electrode side (after washing).

Results and Discussion

The threshold conductivity of conducting polymer blends depends, among other factors, on the degree of homogeneity of the blend.[1,2] Previous efforts to enhance blend homogeneity by selecting polymer combinations that permit intermolecular hydrogen-bonding have been effective.[1]

DMSO swells the PVA polymer matrix by disrupting the hydrogen-bonding present in the pure polymer. The X-ray diffraction analyses of Figure 1 demonstrate this as a loss of crystallinity. Exposing the PVA–DMSO gel to the atmosphere for several days allows the DMSO to evaporate, and crystallinity returns as shown by the X-ray diffraction pattern. Immersing the PVA gel in acetonitrile for 10 min and then air drying results in an almost complete recovery of crystallinity. This evidence suggests that PVA gel is a promising host polymer for conducting polymer blends.

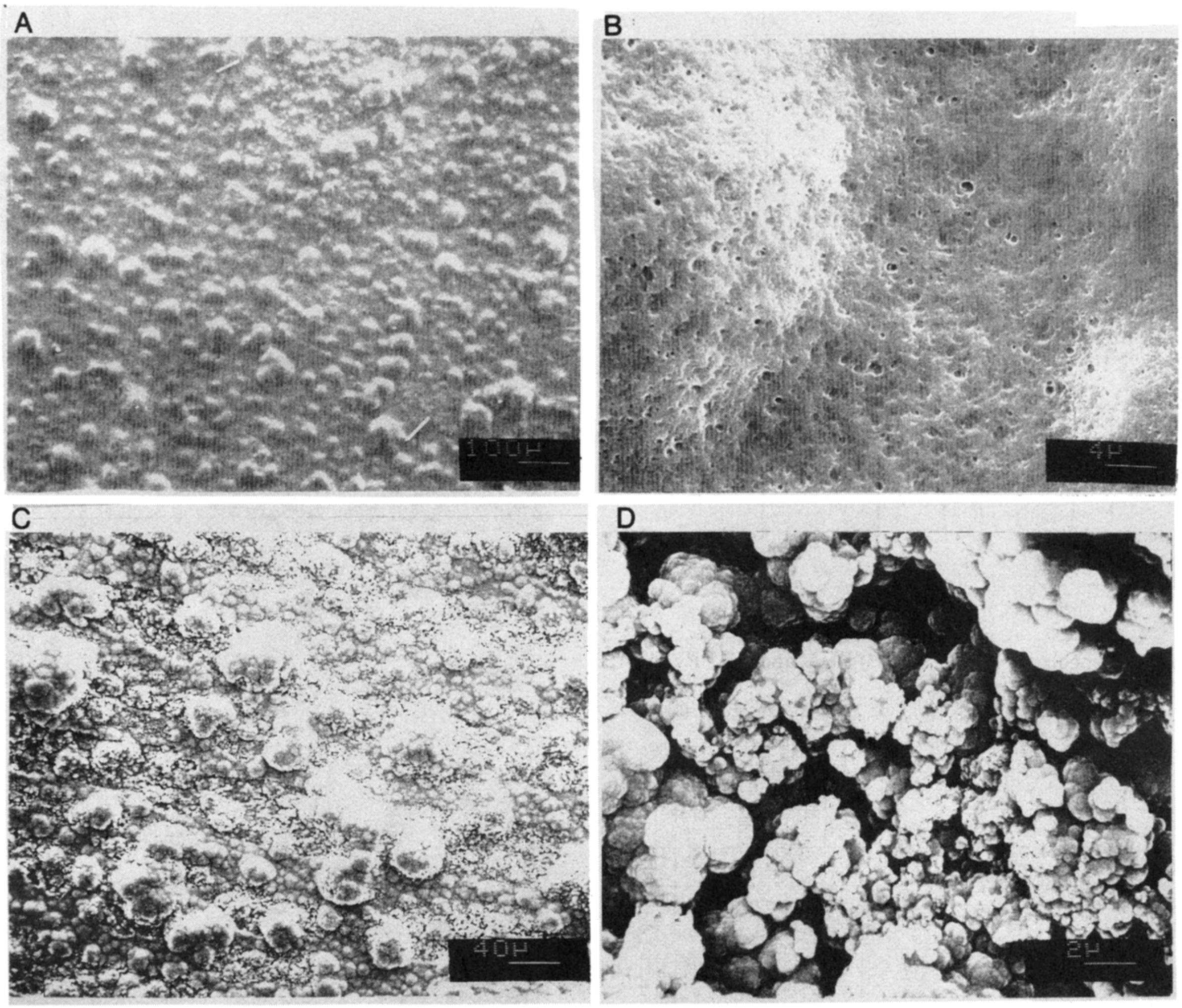

Figure 5. (A) SEM micrograph of the PVA/PPy blend on the solution side (before washing). (B) Magnification of (A). SEM micrograph of the PVA/PPy blend on the solution side (after washing). Magnification of (C).

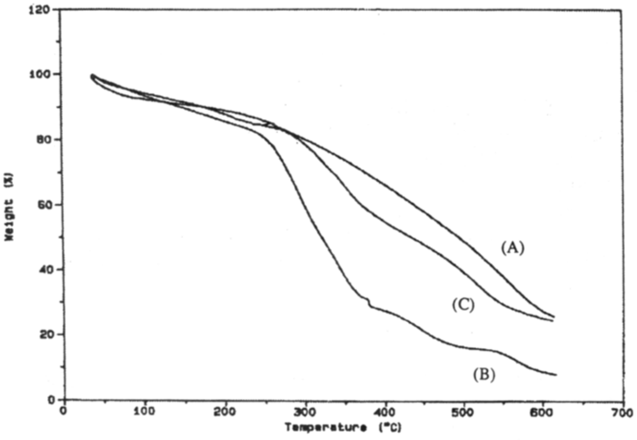

Figure 6. TGA curves of (A) PPy, (B) PVA, and (C) PPy/PVA.

Solvent exchange between DMSO and acetonitrile takes place when PVA gel is placed in the cell; meanwhile, pyrrole diffuses through the PVA film and polymerizes on the electrode. The degree of homogeneity of these PPy/PVA blends can be characterized by their IR and X-ray diffraction spectra.

Figure 2 shows the IR spectra of PPy, PVA, and PPy/PVA blend. The broad band at 600–700 cm^{-1}, assigned to OH twisting, has diminished in the blend to a sharp peak at 652 cm^{-1}. There is also a dramatic change of relative intensity of peaks at 916 and 850 cm^{-1} (skeletal vibrations). The band at 1140 cm^{-1}, which is assigned to C–O stretching, is sensitive to crystallization.[8,9] This band becomes sharper in the blend due to the removal of crystallites in PVA. The band at 1547 cm^{-1} is assigned to ring vibrations of PPy. These changes in absorption bands suggest that hydrogen-bonding of PVA in the blend has diminished. The most notable change is the band at 1140 cm^{-1}, which becomes sharper in the blend due to the removal of PVA crystallites.

The degree of homogeneity is also suggested by the X-ray diffraction spectra (Figure 3). The high degree of crystallinity of PVA is known to arise from strong inter- and intramolecular hydrogen-bonding.[4] When PPy chains intrude into the crystalline lattice, the hydrogen-bonding between PVA chains is lost. X-ray diffraction spectra show no signs of crystallinity when the PPy content in the blend reaches 20%. The lack of evidence of new crystallite formation lends support to the assertion that polymer blending occurs at the molecular level.

Scanning electron microscopy (SEM) micrographs indicate that the electrode side of the film blend is essentially pure PPy; i.e., the SEM micrographs taken before and after washing with hot water are indistinguishable (Figure 4). SEM micrographs of the solution side of the film, however, are quite different after washing (Figure 5), indicating that PVA has been removed.

The documented[11,12] decomposition of PVA is not clear in the blend. Instead, the blend exhibits a higher decomposition temperature than pure PVA, and the expected two-stage weight loss starting at 260 °C[11,12] is

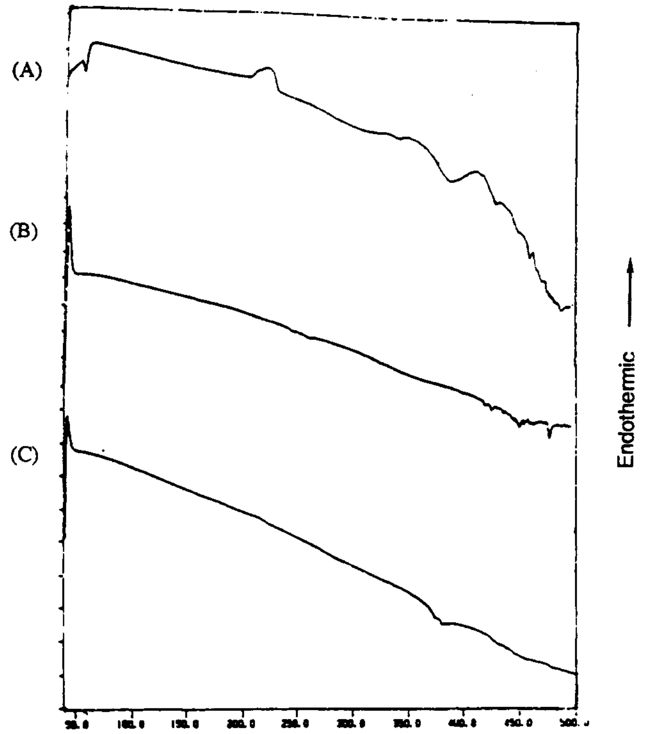

Figure 7. DSC scans of (A) PVA, (B) PPy, and (C) 15% PPy in the blend.

not evident (Figure 6). PPy does not have a discrete decomposition temperature. Instead, it exhibits a gradual weight loss. At 600 °C the blend and PPy have almost the same weight percent remaining. These TGA curves do not show the significant improvement in thermal stability that we found in previous studies with PPy/PCR[1] and with PPy/PVMK[2] (PVMK = poly(vinyl methyl ketone)).

While a single T_g was observed in the DSC scans of PPy/PVMK and PPY/PCR,[1,2] the DSC scan of 15% PPy/PVA (Figure 7) shows no T_g or T_m for PVA. This is additional confirmation of the complete loss of crystallinity of PVA in the blends that contain as little as 15% PPy. The lack of a new T_g does not support the strong PPy–PVA interaction that we suggest, nor does it deny it.

Conductivity data of PPy/PVA composites have been determined previously,[10] so we do not report these data.

Conclusions

Conducting polymer blends of PPy in PVA are prepared electrochemically by dip coating PVA in DMSO solution onto the electrode and electrolyzing the pyrrole before the DMSO has completely diffused away. The crystallinity of the PVA and the hydrogen-bonding that prevails are broken down when PPy grows into the PVA network. The blends appear to be homogeneous. These assertions are confirmed by IR, SEM, TGA, DSC, and X-ray data. No T_g is observed in the blends. DSC and X-ray data indicate that the blends lose crystallinity when less than 15-20% PPy is present.

References and Notes

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