Solid State Science and Technology, Vol. 12, No. 1 (2004) 29-35

COMPOSITES OF CONDUCTING POLYMER: PREPARATION AND CHARACTERIZATION

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ABSTRACT

The preparation of conducting polymer composite films in aqueous medium using pyrrole monomer, *p*-toluene sulfonate electrolyte and an insulating polymer over indium-tin oxide electrode has been studied. The free standing, flexible and conductive polymer composite films were prepared by potentiostatic method. Poly(vinyl alcohol) and carboxymethylcellulose were used as insulating polymers to make composite films with polypyrrole conducting polymer. The prepared composite films were characterized by Fourier Transform infrared spectroscopy (FT-IR), UV-spectroscopy, scanning electron microscopy (SEM) and measuring the conductivity. It was found that the conductivity increased with the increase in insulating polymer concentration. The morphology of the polymer composites were found different with the different process conditions. The FT-IR results suggest the successful formation of the composite of polypyrrole and the insulating material.

INTRODUCTION

Of late, the research interest in conducting polymers is still going on because of their versatile promising applications in the field of energy storage [1] sensors [2], electronic and optical devices [3] and so on. Conducting polymers such as polyaniline, polypyrrole, polythiophene and polyphenylene etc. can be prepared by chemical or electrochemical polymerization. The advantage of chemical synthesis is that it offers mass production at a reasonable cost. On the other hand, electrochemical method involves the direct formation of conducting polymers with better control of polymer film thickness and morphology, which are suitable for use in electronic devices.

Among all the conducting polymers, polypyrrole has received much attention since the monomer pyrrole is easily oxidized, water soluble and commercially available. Although pyrrole is capable of producing conducting polymers with high electrical conductivity, environmental stability and good redox properties [4], still, it offers some drawbacks such as poor processability and lacks essential mechanical properties. Efforts to overcome these drawbacks have led to numerous researches on the synthesis of polypyrrole by both electrochemical and chemical routes. Among them, a significant strategy to approach both

high electrical conductivity and desirable mechanical properties is through preparing composites of polypyrrole polymer with other insulating polymers having desirable mechanical properties [5-6]. The polymer composites can be prepared either by electrochemical or chemical polymerization. In this technique, a number of insulating polymers, namely, poly(styrenesulphonate) [6], polycarbonate [7], poly(vinyl chloride) [8], rubber [9], poly(vinyl alcohol) [10], etc. have been combined with polypyrrole in aqueous or organic medium to produce polypyrrole polymer composites which will have the conducting properties of polypyrrole with some of the superior mechanical properties of the insulating polymer. In this present study, we have chosen two insulating materials namely, carboxymethylcellulose, a natural biodegradable polymer, and polyvinyl alcohol for the preparation of polypyrrole-carboxymethylcellulose and polypyrrole-polyvinyl alcohol conducting polymer composites by electrochemical method in aqueous medium.

EXPERIMENTAL

The composite films of polypyrrole-carboxymethylcelllulose (PPY-CMC) and polypyrrole-polyvinyl alcohol (PPY-PVA) were electrochemically prepared by the oxidation of pre-distilled pyrrole (Fluka) monomer with p-toluene sulfonate dopant in the presence of carboxymethylcellulose, and polyvinyl alcohol, respectively, in aqueous medium. The electrochemical synthesis was carried out in a one-compartment cell using a potentiostat. An indium-tin-oxide (ITO) glass was used as the working electrode (anode) while a carbon rod was used as the counter electrode (cathode). The anodic potential of the working electrode was measured as 1.2 volt against a saturated calomel reference electrode. The aqueous solution containing 0.3 M pyrrole and 0.1 M p-toluene sulfonate dopant was electrochemically polymerized using various concentration of carboxymethylcellulose (ranging from 0.01 M to 0.04 M) and polyvinyl alcohol (ranging from $2x10^{-4}$ mmol to $13x10^{-4}$ mmol) at room temperature for 5 hours to form PPY-CMC and PPY-PVA polymer composite films, respectively, of 50-70 μm thickness. The composite films thus produced on the ITO glass surface as an insoluble film were rinsed thoroughly with distilled water and then peeled off from the electrode. It was then dried in the oven at 60 °C for 24 hours before measuring the conductivity by four-probe method. The electromagnetic shielding effectiveness measurement was carried out on PPY-CMC films in the microwave band of 8-12 GHz.

RESULTS AND DISCUSSION

PPY-CMC polymer composite films

The conductivity of the PPY-CMC composite films measured at room temperature was found to increase from 0.70 S/cm to 26.73 S/cm with the increase of carboxymethylcellulose concentration from 0.01 M to 0.04 M (Figure 1).

Figure 2 shows the FT-IR spectra of PPY-CMC composite film in the wave number ranges between 4000 and 400cm^{-1}. The characteristic absorption bands of PPY at 1546 cm^{-1}, 1170 cm^{-1} and 966 cm^{-1} were clearly observed in PPY-CMC composite film.

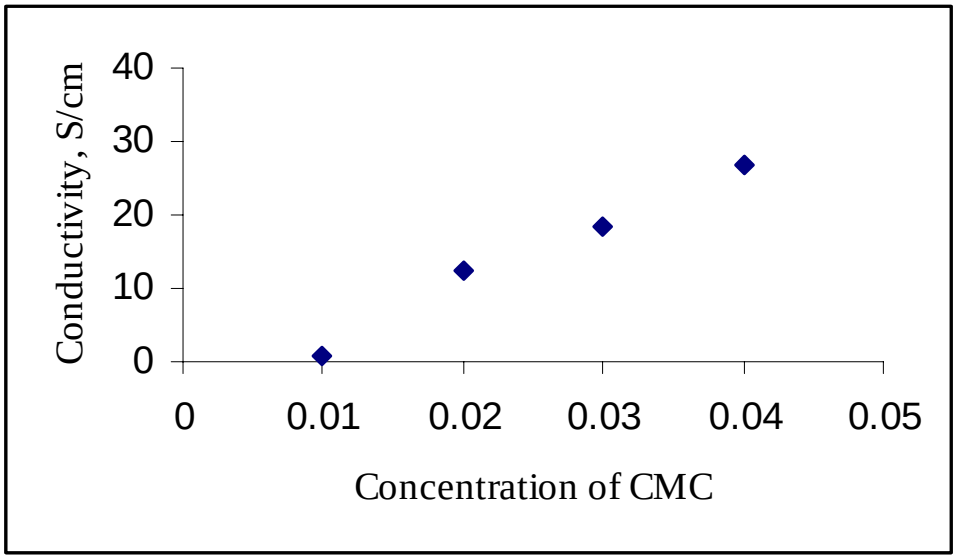

Figure 1. Conductivity of PPY-CMC vs. concentration of CMC.

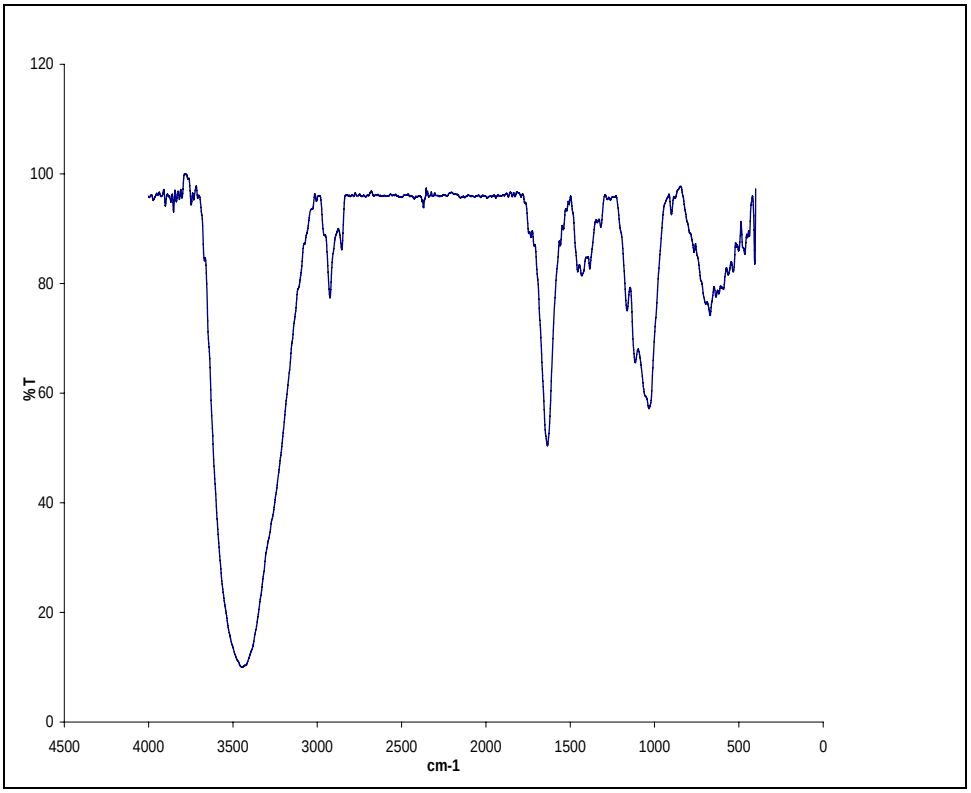

Figure 2. The FT-IR spectra of PPY-CMC composite film.

The TGA result (Figure 3) shows that the major decomposition of the composite film of PPY-CMC occurred between 318°C to 680°C with a residue of about 64.8% while the major

decomposition of polypyrrole film occurred between 380°C to 695°C and it left a residue of about 62% at695 °C.

In order to find the possible application of the prepared PPY-CMC composite films in electromagnetic shielding application, the prepared film was tested using 8-12 GHz range. The prepared PPY-CMC polymer composite film was capable of exhibiting a high shielding effectiveness (SE) around 40 dB (Figure 4).

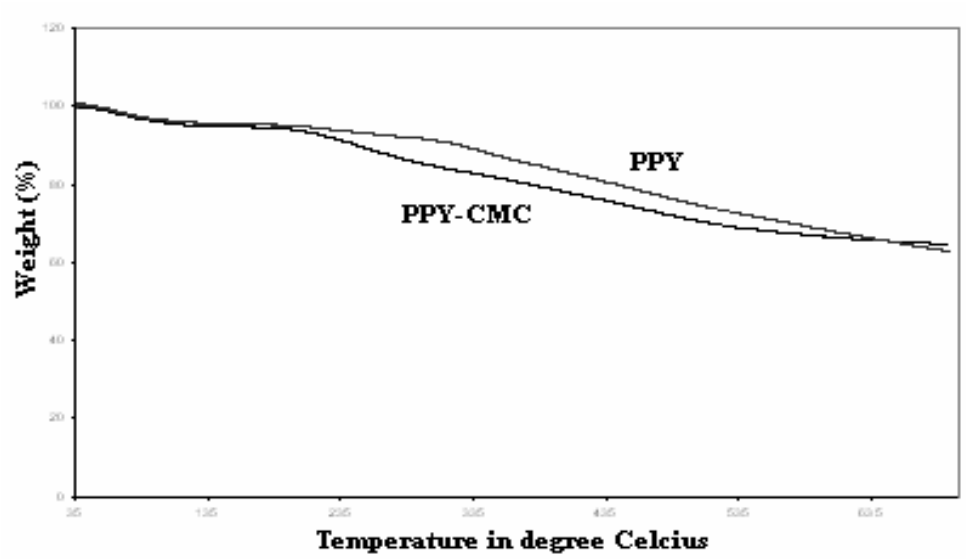

Figure 3. Thermogravimetric analysis of PPY-CMC film.

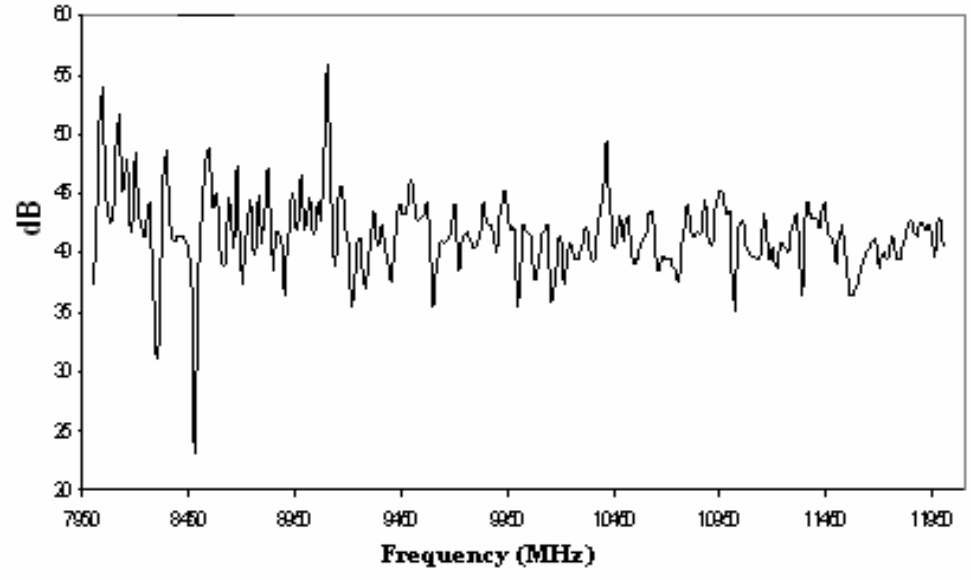

Figure 4. The electromagnetic shieldeffectiveness of PPY-CMC in the frequency range of 8-12 GHz.

PPY-PVA composite films

Figure 5 shows the conductivity of PPY-PVA films prepared at various concentration of PVA. It shows that the conductivity increased with the increase of PVA concentration. The conductivity was measured at room temperature by four-probe technique.

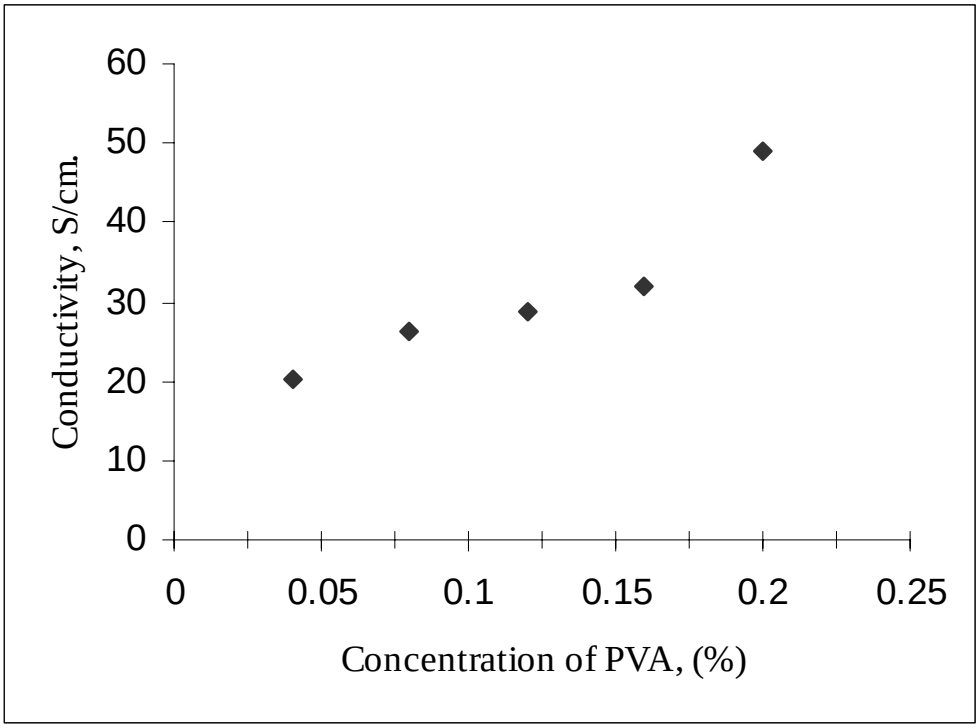

Figure 5. Conductivity of PPY-PVA Films versus PVA Concentrations.

The infrared absorption spectrum of the polypyrrole-polyvinyl alcohol (PPY-PVA) polymer composite film, PVA and PPY are shown in Figure 6. The spectra for PPY-PVA films show a strong absorption band in the region of 3454-34336 cm^{-1} due to N-H stretching vibration of polypyrrole. The C=C ring stretching vibration of PPY occurred at 1542 cm^{-1}. The peak at 1172 corresponds to the S-O stretching vibrations of sulfonate. Bands between 1100 and 1000 cm^{-1} are all due to C-H vibrations. Bands near 2900 are due to -CH_2- group. The band at 1172 cm^{-1}, which is assigned to C-O stretching and sensitive to PVA crystallization [11], appears much sharper and little broad in the PPY-PVA spectra than in the PVA spectra. This indicates the removal of PVA crystallites in the PPY-PVA composite film. Thus, the FT-IR-spectra of PPY-PVA film shows the characteristic polypyrrole absorption bands between 1650-1000 cm^{-1} and the characteristic peak due to sulfonate group and the loss of PVA crystallites at 1172 cm^{-1}, which confirms the formation of PPY-PVA composite film.

The thermogravimetric analysis (TGA) result of PPY-PVA film produced from using 0.2% PVA shows that the initial weight loss of 5.41 % occurred at 162.5 °C while the major decomposition started at from 277 °C. Finally, a residue of 65.37 wt% remained at 698 °C. The heating was carried out from 35 °C to 700 °C with a heating rate of 10.0 °C / minute.

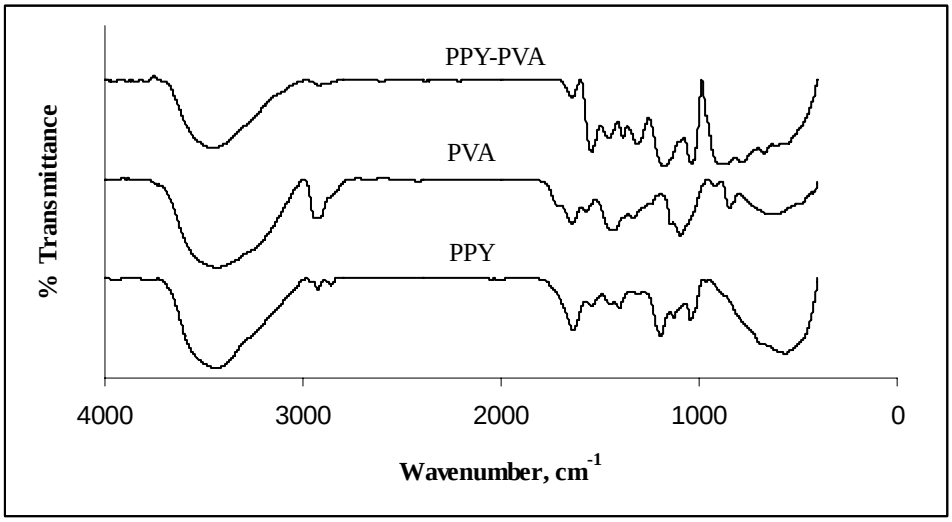

Figure 6. FT-IR spectrum of PPY-PVA, PVA and PPY.

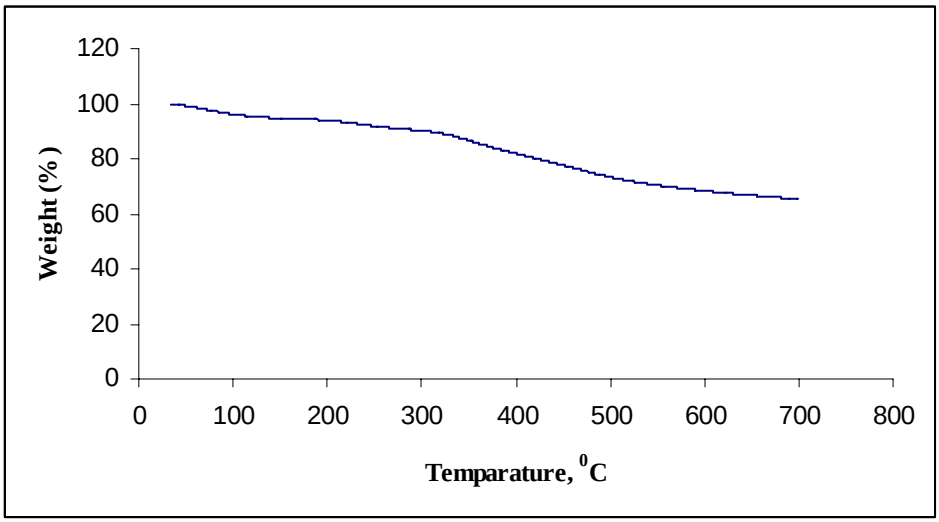

Figure 7. Thermogravimetric analysis of PPY-PVA film.

CONCLUSIONS

We wish to report the successful electrochemical deposition of polypyrrole-carboxymethylcellulose and polypyrrole-polyvinyl alcohol composite films by potentiostatic method in aqueous medium. The FT-IR results show that polypyrrole was incorporated in both carboxymethylcellulose and polyvinyl alcohol to form the conducting composite polymer films. The FT-IR result of PPY-PVA films shows the complete loss of crystallite of PVA in the PPY-PVA composite and also confirms the incorporation of p-toluene sulfonate in the polypyrrole structure. The conductivity of both the PPY-CMC and PPY-PVA composite films increased with the increase of CMC and PVA, respectively. The TGA results show the different decomposition pattern for polypyrrole, polypyrrole-carboxymethylcellulose and polypyrrole-polyvinyl alcohol composite polymer films. It has

been observed that the prepared polyrrole-carboxymethylcellulose composite films are capable of offering a high shielding effectiveness above 40 db, which proves that these materials can be used in electromagnetic shielding applications.

ACKNOWLEDGMENT

The authors wish to acknowledge the financial support for this work under IRPA-8 grant No. 09-02-04-0261-EA001 from the Ministry of Science and Technology, Malaysia.

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