PREPARATION AND CHARACTERIZATION OF CONDUCTING POLYMER COMPOSITE FILMS: POLYPYRROLE AND POLYETHYLENE GLYCOL

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Abstract

Polypyrrole-polyethylene glycol (Ppy-PEG) composites were synthesized by electrochemical method using *r*-toluene sulfonate as a dopant in aqueous medium. Polyethylene glycol was used as the insulating material in order to impart enhanced mechanical properties to the conducting polymer composite films. The composite films were synthesized with various percentages of PEG, and were characterized by FT-IR spectroscopy, conductivity measurement, optical microscopy (OP), X-ray diffraction (XRD) and dynamic mechanical analysis (DMA). The FT-IR result reveals the successful incorporation of PEG into the polypyrrole structure forming Ppy-PEG composite films. The conductivity of the composite films prepared from using 0.20% PEG was found to exhibit the highest conductivity (61.28 Scm^{-1}) among all the prepared composite films measured at room temperature. The optical microscopy of Ppy-PEG shows the globular surface morphology. The XRD analysis of Ppy-PEG composite films shows that the composite films are amorphous. The enhanced mechanical properties of the Ppy-PEG composite films are the direct consequence of incorporating PEG in the polypyrrole structure.

Abstrak

Polipirol-polietilena glikol (Ppy-PEG) komposit telah disintesiskan secara elektrokimia memggunakan *r*-toluena sulfonat sebagai dopan dalam perantara akueus. Polietilena glikol digunakan sebagai bahan penebat untuk menguatkan sifat mekanik terhadap filem polimer pengalir. Filem polimer pengalir telah disediakan dengan pelbagai peratus PEG dan dicirikan dengan menggunakan spektroskopi FT-IR, pengukuran konduktiviti, mikroskopi optik (OP), pengimbasan analisis sinar-X dan analisis mekanikal dinamik (DMA). Kajian FT-IR ke atas filem komposit PPy-PEG nyata menunjukkan kemasukan PEG ke dalam struktur polipirol berkaitan dengan pembentukan filem komposit Ppy-PEG. Filem komposit Ppy-PEG dengan menggunakan 0.20% PEG telah memberi nilai konduktiviti tertinggi iaitu 61.28 Scm^{-1} berbanding dengan yang lain pada suhu bilik. Mikroskopi optik Ppy-PEG menunjukkan sifat morfologi permukaannya yang berbentuk sfera. Keputusan XRD menunjukkan bahawa filem komposit Ppy-PEG adalah bersifat amorfus. Peningkatan sifat mekanik untuk Ppy-PEG filem komposit adalah akibat daripada kemasukan PEG dalam struktur polipirol.

Introduction

Conducting polymers, as their name suggests, are a group of conjugated polymers that exhibit excellent electrical conductivity. Conducting polymers belong to a novel class of materials that are being evaluated for application in charge storage devices (batteries, capacitors), electromagnetic screens, sensors, membranes, corrosion protective coatings [1]. Conducting polymers from five-member heterocyclic compounds are very interesting. Among conducting polymers, polypyrrole has been one of the most studied polymers because of its physical and electrical properties that have led to several applications such as solid state devices and electronics [2].

However, the typical polypyrrole, which is insoluble and infusible, exhibits poor processability and lacks essential mechanical properties. Efforts to overcome these drawbacks have led to numerous researches on the synthesis of polypyrrole. Among them a significant strategy to approach both high electrical conductivity and desirable mechanical properties is through the use of bulky organic sulfonate dopants [3-9] or preparing composites of polypyrrole with other insulating polymers having desirable mechanical properties [10-12]. In other words, a combination of a conventional polymer with conductive polymer allows the creation of new polymeric materials with specific electrical properties.

Conducting polymers can be prepared by using either chemical or electrochemical polymerization [13]. 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.

In our present study, the polypyrrole-polyethylene glycol (Ppy-PEG) composite films were prepared by electrochemical method in which pyrrole was used as the monomer, polyethylene glycol was used as an insulting polymer while sodium salt of *r*-toluene sulfonic acid was used as an electrolyte together with a suitable solvent. The main purpose of this study is to investigate the effects of various percentages of PEG in the pyrrole solution on the structure, conductivity, molecular order, mechanical properties and morphology of the Ppy-PEG composite films.

Materials and methods

Electrochemical Method

This is a widely used method for the preparation of composite films. Generally, a coating of an insulating polymer is grown on the electrode followed by the electrodeposition of conducting polymer on the pre-coated electrode. Electrochemically prepared composite films Ppy-PEG composite films were carried out in potentiostatic conditions (Model: PS 605, USA) in a one step polymerization technique where PEG, pyrrole and a suitable dopant were mixed in the solution.

Electrodes

The standard electrochemical technique, which employs a divided cell containing a working electrode, a counter electrode and a reference electrode, was used to produce the composite films. Electrodes should be chosen carefully so that they are not oxidized during the electrochemical oxidation process [14]. An indium-tin-oxide (ITO) glass was used as the working electrode (anode) and a carbon rod was used as the counter electrode (cathode). The commonly used reference electrode was the saturated calomel electrode (SCE).

Monomer, Insulting Polymer and Electrolyte

Ppy-PEG composite films were prepared from the aqueous solution containing pyrrole (supplied by Fluka) as the monomer; polyethylene glycol as the insulting polymer and sodium salt of *r*-toluene sulfonic acid (supplied by Fluka) as the electrolyte. Pyrrole was distilled and kept at 4 ^{o}C before use.

Preparation of Ppy-PEG Composite Films

Electrochemical deposition of Ppy-PEG composite films was carried out at room temperature (25 ^{o}C) with a constant voltage of 1.2 volt (versus SCE) for 2 hours. The composite films were synthesized with various percentages of PEG ranging from 0.00 % to 1.80 % in the pyrrole solution containing 0.2 M pyrrole and 0.1 M *r*-toluene sulfonate. The thickness of the prepared films was about 40 µm. After deposition, the films were peeled from the electrode, washed thoroughly with distilled water and dried in vacuum for 24 h.

Characterization of the Composite Films

The infrared spectra of the samples were recorded in the wavenumber range from 400-4000 cm^{-1} using a Perkin Elmer FTIR model 1725X spectrophotometer. The electrical conductivity was measured at room temperature using a standard Four Point Probe technique. The probes were placed on surface of the film. The calculation of the conductivity is stated as below:

$$(s) = I \ln 2 / p Vt$$

Where s = conductivity, I = current in ampere (A), V = voltage (V), and t = thickness of the films in centimeter (cm)

X-ray diffraction measurements were performed using a XRD Philip PW-1390 model. The optical microscopy (Invested Trinocular Microscope VBT-2T) was used to get the micrographs of the samples. The dynamic storage modulus of sample was obtained from a Perkin Elmer Pyris Diamond DMA with a heating rate of 2 °C per minute and at a frequency of 1 Hz.

Results and Discussion

Molecular Structure of Ppy-PEG Composite Films

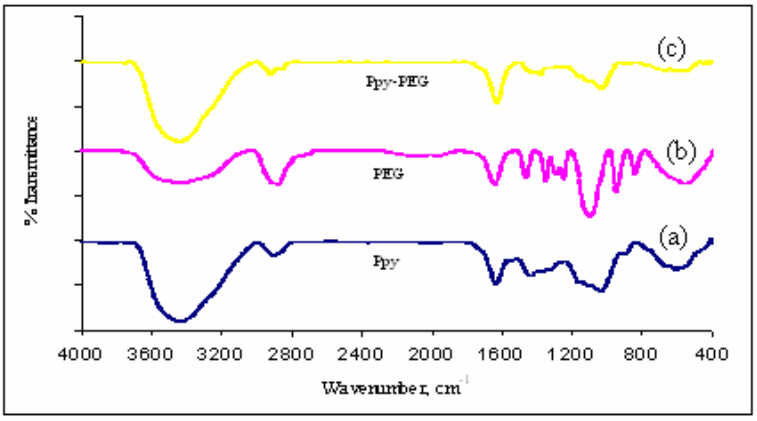


Figure 1. The FT-IR spectrum of Ppy (a), PEG (b) and Ppy-PEG composite film(c)

The Fourier transform infrared (FT-IR) spectroscopic analysis for the Ppy-PEG composite films was done by Perkin Elmer FTIR spectrophotometer (model 1725X) using KBr disc. The scanning was ranged from 4000 cm^{-1} to 400 cm^{-1}. The FT-IR absorption spectrum of only Ppy is shown in Figure 1 (a). The NH stretching band of pyrrole ring appears at 3428 cm^{-1}. The weak band at 2890 cm^{-1} is due to C-H stretching. The other bands also show the characteristic polypyrrole absorption at 1600-1100 cm^{-1}. An absorption at 1626 cm^{-1} was assigned to the C=C ring stretching of pyrrole. The C–N ring stretching band of pyrrole ring occurs at 1426 cm^{-1}. The peak at 1316 cm^{-1} is the C-H plane deformation of the pyrrole and the peak at 1168 cm^{-1} is due to C-C stretching [15-16].

The IR spectrum (Figure 1 (b)) showed the absorption spectrum of only PEG. The absorbance spectra have been normalized to the CH_2 symmetric stretching feature at 2880 cm^{-1}. The sharp band at 1110 cm^{-1} in the PEG spectrum corresponds to C-O symmetric stretching of PEG.

Figure 1 (c) shows the FT-IR absorption spectrum of Ppy-PEG composite films. There are not many differences for Ppy-PEG spectrum compared to Ppy spectrum. The FT-IR spectrum of the Ppy-PEG composite films reveal the peaks associated with pure Ppy and the polyethylene glycol peaks. The strong absorption at 3416 cm^{-1}, 1624 cm^{-1}, and 1440 cm^{-1} are characteristic peaks of Ppy. The spectrum also shows the characteristic PEG absorption at 1110 cm^{-1} due to C-O. The FT-IR result reveals the successful incorporation of PEG into the Ppy structure forming Ppy-PEG composite films.

Effect of PEG Percentage on the Conductivity of Ppy-PEG Composite Films

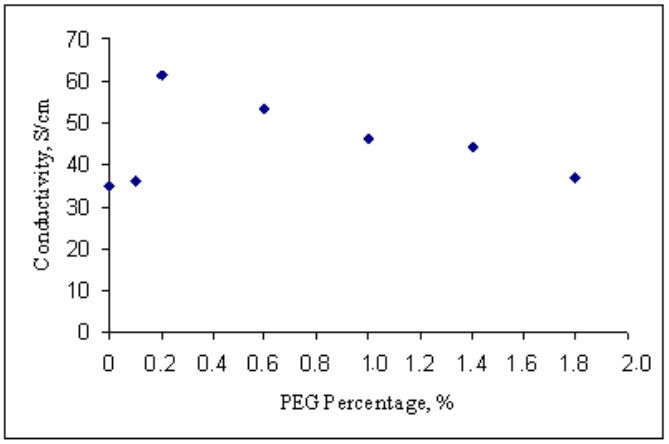


Figure 2. Conductivity of Ppy-PEG composite films versus PEG percentage used to prepare the Ppy-PEG composite films.

The conductivity of the Ppy-PEG composite films obtained from using 0.10 %, 0.20 %, 0.60 %, 1.00 %, 1.40% and 1.80 % of PEG with 0.2 M pyrrole and 0.1 M *r*-toluene sulfonate were measured. Figure 2 shows the variations of conductivity with increasing percentage of PEG. It was observed from the conductivity measurement that Ppy-PEG composite films showed the highest conductivity value of 61.3 S/cm using 0.2 % PEG. This can be explained by the increase of conjugation chain length with the increase in PEG percentage. Later, the conductivity of the composites films decreased to 37.1 S/cm. It may de due to the fact that the concentration of the electrolyte becomes too viscous with the addition of higher percentage of PEG, which slows down the rate of polymerization. Thus, further increase in percentage of PEG results in conjugation chain length to decrease.

Effect of PEG Percentage on the Molecular Order of Ppy-PEG Composite Films

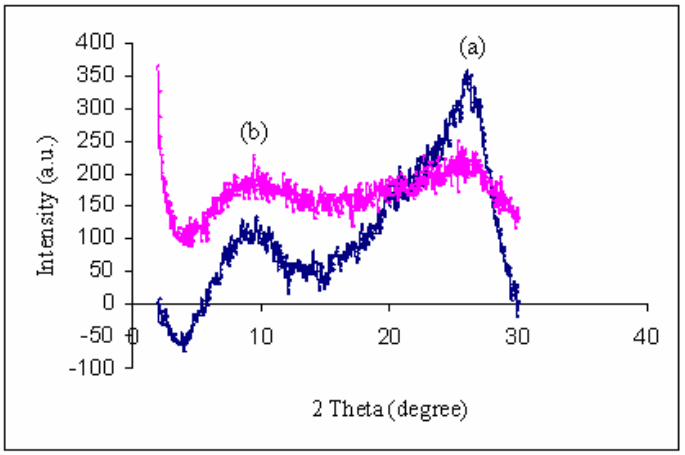
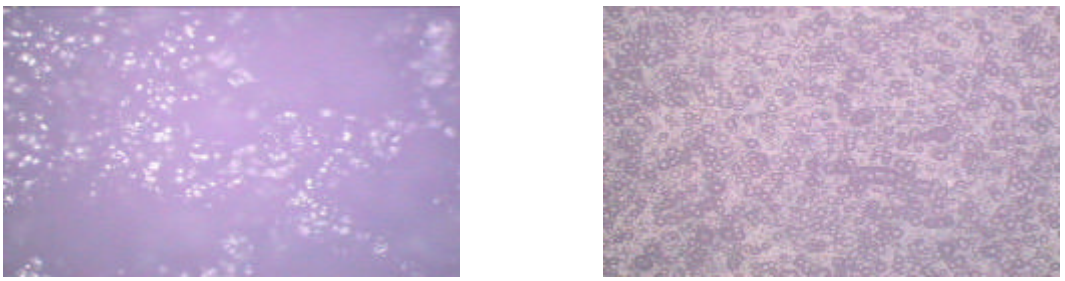


Figure3. The XRD diffractograms of Ppy-PEG composite film prepared from (a) Ppy and (b) 0.20 % Ppy-PEG, respectively.

The effect of PEG on the molecular order of the prepared films has been carried out by XRD analysis. Figure 3 shows the X-ray diffraction pattern for the composite films obtained from using (a) Ppy and (b) 0.20 % PEG. All these spectra appear almost similar and the broad peaks indicate that the films are amorphous [17-18]. They overlap with each other in the same 2θ regions.

Prigodin and Epstein [19] stated that in polypyrrole conducting polymer, single chains are arranged in the space in a very complicated way. Usually, the higher the degree of order, the higher is the conductivity. But the degree of order is not the only factor responsible for the conductivity increase as there are other important factors like conjugation chain length and doping level, which play a vital role in conductivity increase [20-23].

Effect of PEG Percentage on the Morphology of Ppy-PEG Composite Films



a) Polypyrrole b) 0.20 % Ppy-PEG

Figure 4: The optical micrographs of the solution side of Ppy-PEG composite films produced from using a) Polypyrrole and b) 0.20% Ppy-PEG in the pyrrole solution. (Magnification: 20 X)

The surface morphology of the film facing the solution side gives globular morphology (Figure 4). As the PEG used to prepare the composite films, the globular morphology becomes more evident with spherical ball shapes. Since the concentrations of monomer pyrrole and the dopant are unchanged in producing the Ppy only and Ppy-

PEG composite films and only the PEG is added, this implies that it is the PEG percentage, which is playing the vital role in Ppy-PEG composite film formation causing these changes in surface morphology.

Effects of PEG Concentration on the Mechanical Properties of Ppy-PEG Composite Films

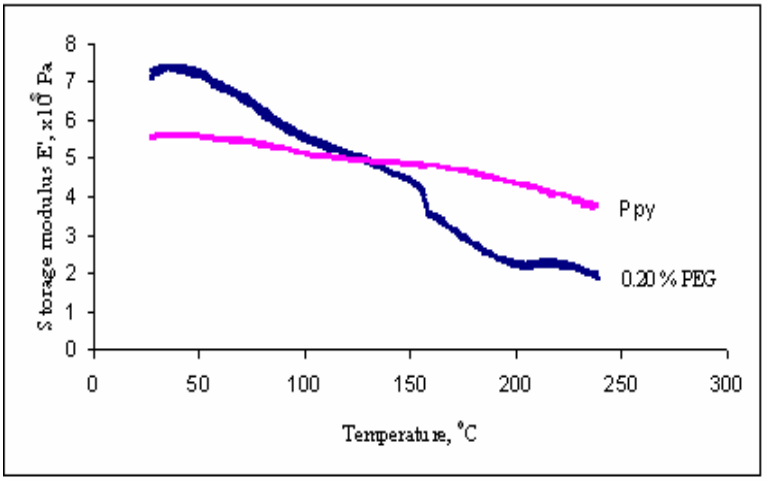


Figure 5: The storage modulus as a function of temperature for Ppy-PEG composite films prepared from using (a) Ppy, (b) 0.20 % Ppy-PEG

Figure 5 shows the temperature dependence of storage modulus (E') of Ppy-PEG composite films prepared from 0.20 % PEG percentage. The continuous decrease in storage modulus (E') has been observed from 35 ºC with the rise in temperature. The sharp steady decrease in storage modulus (E') with the increase in temperature was observed from 154 ºC to 162 ºC. Later, the storage modulus (E') decreased continuously with the increase in temperature.

The storage modulus (E') of Ppy film decreases steadily with the increase in temperature all through the whole investigated temperature range from 25 °C to 250 °C. This indicates that the Ppy film remains all through in the glassy state and does not exhibit any transition (glass-rubbery) in the investigated temperature range of 25 °C to 250 °C. Thus, it shows that the Ppy film is hard and brittle and is not soft and does not show any flexibility in the backbone chain of the polymer.

This shows that the Ppy-PEG composite film is much stiffer than the Ppy film. The effect of PEG in Ppy-PEG film clearly shows that PEG in Ppy-PEG composite film is responsible for offering flexibility in the polymer backbone as the Ppy-PEG film shows the transition (glass-rubbery) with the increase in temperature. The enhancement of storage modulus (E') of Ppy-PEG composite film shown in Figure 5 indicates that the Ppy-PEG composite film is much stifferthan Ppy film without PEG.

Conclusions

Constant potential electrochemical syntheses of Ppy-PEG composite films were achieved by one-step electrochemical polymerization. PEG are introduced into the Ppy polymer films in order to impart enhanced mechanical properties to the Ppy-PEG composite films and at the same time not impairing the conductivity appreciably. The enhanced mechanical properties of the Ppy-PEG composite films are the direct consequence of incorporating PEG in the polypyrrole structure. The conductivity of the composite films prepared from using 0.20 % PEG was found to exhibit the highest conductivity (61.28 S/cm) among all the prepared composite films measured at room temperature. The FT-IR analysis reveals the successful incorporation of PEG into the PPy structure forming Ppy-PEG composite films. XRD measurements proved that the Ppy-PEG composite films are amorphous. The surface morphology of the Ppy-PEG composites films is globular.

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