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Electronic Conducting Polymer Composite Films with Enhanced Mechanical Properties

H. N. M. Ekramul Mahmud,[a] Anuar Kassim,[a*] Zulkarnain Zainal[a] and Wan Mahmood Mat Yunus[b]

[a] Department of Chemistry, Faculty of Science and Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.
[b] Department of Physics, Faculty of Science and Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.

* Corresponding author, E-mail: anuar@fsas.upm.edu.my

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ABSTRACT: An effort has been made to produce polypyrrole-carboxymethylcelllulose (PPY-CMC) conducting polymer composite film on Indium Tin Oxide (ITO) glass electrode from an aqueous solution containing pyrrole monomer, *p*-toluenesulfonate electrolyte and carboxymethylcellulose (CMC) insulating polymer. The conductivity of the prepared composite film was found to increase with the increase in CMC concentration in pyrrole solution. The optical microscopic study showed the influence of CMC concentration in the pyrrole solution on the morphological changes of the prepared film. The dynamic mechanical analysis (DMA) on the prepared PPY-CMC film revealed the higher plastic property of the PPY-CMC composite film due to the addition of CMC in the polypyrrole structure. The electromagnetic interference (EMI) shielding effectiveness of PPY-CMC film in the frequency range of 8-12 GHz showed a high shielding effectiveness above 41 db, which supported its probable use in various electromagnetic interference shielding applications.

KEYWORDS: Polypyrrole; Carboxymethylcellulose; Conducting polymer; Dynamic mechanical analysis; Electromagnetic interference.

INTRODUCTION

Numerous studies have been performed on the conjugated polymers such as polypyrrole, polyaniline, polythiophene and polyphenylene, since the discovery of the conducting properties of polypyrrole in 1979[1]. These polymers are capable of exhibiting a significant level of electrical conductivity, hence termed as conducting polymers. They have versatile promising applications in the field of energy storage[2], electronic and optical devices[3], sensors[4], and much more. Much research efforts have been generated to produce composites or blends of conducting polymer film with some insulating polymers in order to overcome the drawbacks such as poor processability and lack of essential mechanical properties exhibited by these polymers[5]. In this technique, a host of insulating polymers (namely, poly(styrenesulphonate)[6], polycarbonate[7], poly(vinyl chloride)[8], nitrile rubber[9], polyimide[10] and poly(vinyl alcohol)[11]) have been combined with any conducting polymer (such as polypyrrole, polyaniline, polythiophene) in an aqueous or organic medium to produce conducting polymer composites which will have the conducting properties of the conducting polymer and some mechanical properties of the host insulating polymer.

Few research efforts on carboxymethylcellulose (CMC), a bio-degradable polymer, have been reported as the insulating polymer for preparing polypyrrole-carboxymethylcellulose (PPY-CMC) composite film[12-13]. All these attempts have been focused on the cyclic voltammetry and morphological studies of PPY-CMC composite film[12-13] only, but no research reports are available on their conductivity or mechanical properties.

In this communication, we report the electrochemical preparation and the characterization of PPY-CMC composite film and its application in electromagnetic interference (EMI) shielding applications.

METHODS

The conducting polymer composite films of polypyrrole (PPY) and carboxymethylcellulose (CMC) were electrochemically prepared on indium-tin-oxide (ITO) glass electrode by the oxidation of pre-distilled pyrrole (Fluka) monomer with *p*-toluene sulfonate (Fluka) dopant in the presence of sodium salt of CMC (Fluka) in an aqueous medium in a one-compartment cell using a potentiostat (Model: PS 605, USA) at 1.2 volt (vs SCE). The solution containing 0.4 M pyrrole monomer and 0.1 M *p*-toluene sulfonate dopant with varying amount of CMC in the range of 0.01 M - 0.04

M (beyond 0.04 M concentration of CMC, the solution would become too viscous to produce any film) was electrochemically polymerized at room temperature for 2 hours to form polypyrrole-carboxymethylcellulose (PPY-CMC) composite film of 24-44 mm thickness. The composite film thus produced on the ITO glass surface as an insoluble film were rinsed thoroughly with distilled water, peeled off from the electrode and dried in the oven. For the comparison purposes, PPY film without CMC was produced from using 0.4 M pyrrole and 0.1 M *p*-toluene sulfonate dopant in an aqueous solution at room temperature for 2 hours.

Polymer Characterization

The PPY-CMC conducting polymer composite film prepared by electrochemical method was characterized by conductivity measurement, optical microscopy, dynamic mechanical analysis and electromagnetic interference (EMI) shielding behavior. The electrical d.c. conductivity of the PPY-CMC composite film was measured by the four-probe technique. Before measuring the conductivity, the conductivity meter was calibrated by using standard silicon wafer with standard reference material no 2545 (National Institute of Standard and Technology, USA). The optical micrographs of the film were taken using an inverted trinocular microscope. The dynamic mechanical analysis(DMA) was done using Perkin Elmer (Pyris Diamond) DMA. The electromagnetic shielding effect of the PPY-CMC film and the PPY film was measured by network analyzer (Hewlett Packard) in the frequency range of 8-12 GHz.

RESULTS AND DISCUSSION

The physical appearance of the produced PPY-CMC polymer composite film was flexible, smooth, shiny and black in color. The film was found to be strong compared with the normal PPY film.

Conductivity

The electrical d.c. conductivity of the prepared PPY-CMC conducting composite film was measured at room temperature by the four-point probe technique taking the average value of several readings at various position on the film. The highest conductivity of the PPY-CMC film measured at room temperature was found to be 38.5 S/cm. The conductivity increased from 12.4 S/cm to 38.5 S/cm with an increase in CMC concentration from 0.01 M to 0.03 M in the pyrrole solution and later, the conductivity slightly decreased to 35.5 S/cm with further increase in CMC concentration at 0.04 M (Figure 1). The solution became more viscous using 0.04 M CMC, which may have caused the conductivity to decrease since it hindered the movement of ions. The gradual increases in conductivity with the increase in CMC concentration, while keeping the dopant concentration and the monomer pyrrole concentration unchanged, suggested that CMC helps increase the doping level of the PPY-CMC composite film. We propose that CMC may have acted as a co-dopant with *p*-toluene sulfonate since a positive charge[12] on CMC may have taken part in the charge compensation of pyrrole repeat units along with *p*-toluenesulfonate dopant. The conductivity was found to be the same for both sides of the film, indicating the homogeneous film formation of PPY-CMC composite.

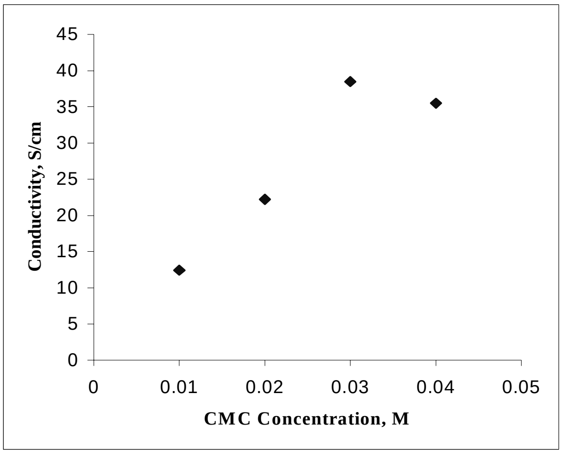
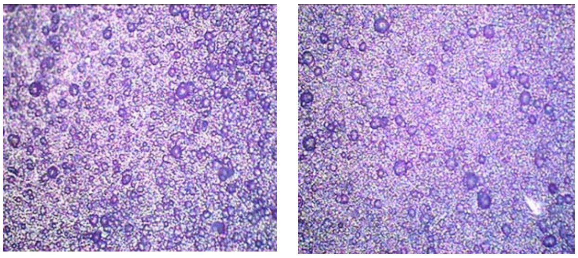


Fig 1. Variation of electrical conductivity of the PPY-CMC film with the CMC concentration in pyrrole solution.

Optical Microscopic Study

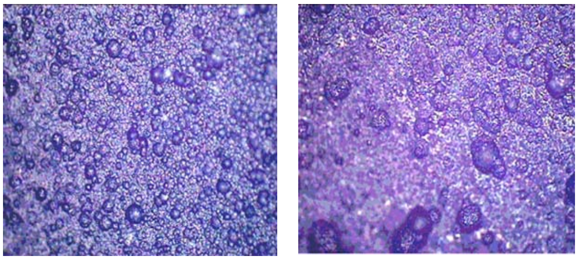
The morphological study on PPY-CMC composite filmusing optical microscopy showed that the increase in CMC concentration in the pyrrole solution, changed the morphology of the prepared PPY-CMC film (Figures 2 and 3). The surface morphology of the film facing the solution side gave globular morphology. As the concentration of CMC increased, the globular morphology became more evident with bigger spherical ball shapes. This indicated that with the increase in CMC concentration, polymerization reaction became more intense giving a globular morphology with bigger spherical ball shapes. All of the of PPY-CMC film was produced with the same concentration of pyrrole monomer (0.4 M) and *p*-toluene sulfonate dopant (0.1 M) but with different concentration of CMC (ranging from 0.01 M to 0.04 M), resulting in different surface morphology for both the solution side and the electrode side of the films. This indicated that the CMC concentration alone played a vital role in film formation with polypyrrole.

The electrode side of the film surface appeared much smoother compared to the solution side surface.



A: 0.01 M CMC (Magnification: 20X).

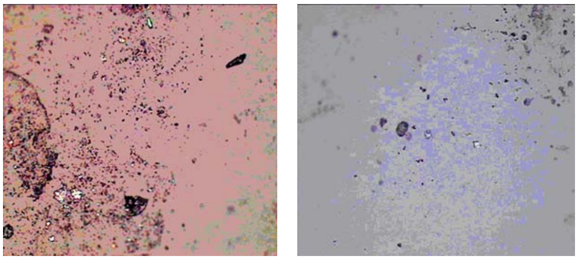
B: 0.02 M CMC (Magnification: 20X).



C: 0.03 M CMC (Magnification: 20X).

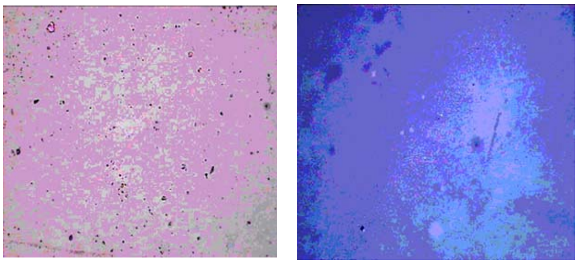
D: 0.04 M CMC (Magnification: 20X).

Fig 2. The optical micrographs of the surface morphology of solution side of the PPY-CMC composite film produced with A) 0.01 M CMC, B) 0.02 M CMC, C) 0.03 M CMC and D) 0.04 M CMC in the pyrrole solution.



A: 0.01 M CMC (Magnification: 20X).

B: 0.02 M CMC (Magnification: 20X).



C: 0.03 M CMC (Magnification: 20X).

D: 0.04 M CMC (Magnification: 20X).

Fig 3. The optical micrographs of the surface morphology of the electrode side of the PPY-CMC composite film produced with A) 0.01 M CMC, B) 0.02 M CMC, C) 0.03 M CMC and D) 0.04 M CMC in the pyrrole solution.

This was due to the fact that the polymerization was initiated on the electrode side and proceeded towards the solution side with the reaction time making the polymer thicker with rough globules on the surface of solution side. The surface morphology of the electrode side was very smooth with almost no cracks at all for the film produced with the highest concentration of CMC (0.04 M CMC) while the surface of the film produced with the lowest concentration of CMC (0.01 M CMC) has cracked with less smooth part (Figure 3). There was no phase separation apparent either on the electrode side or on the solution side of the films, supporting the homogeneous film formation of polypyrrole with CMC.

FT-IR Study

The infrared absorption spectrum of the PPY-CMC composite film, the polypyrrole (PPY) film and the CMC are shown in Figure 4. The broad strong band at 3448 cm^{-1} in the CMC spectrum corresponded to the stretching vibrations of the intra-molecular hydrogen bond (½$_{OH}$). The band at 2922 cm^{-1} indicayed the stretching vibrations of the C-H bonds (ν_{CH}). The strong peak at 1626 cm^{-1} belonged to the stretching vibration of the carboxylic group (ν_{COO^-}). The broad medium peak at 1060 cm^{-1} showed the bending vibrations of the ether (glycosidic) linkage ($\delta_{C\text{-}O\text{-}C}$). The spectrum of the polypyrrole film showed that the N-H stretching band of pyrrole ring appeared at 3446 cm^{-1}. The other characteristic pyrrole ring stretch absorption bands were observed between 1600-1100 cm^{-1}. The C=C ring stretching band of pyrrole occured at 1540 cm^{-1}. The band at 1446 was due to C-N stretching of pyrrole ring. The bands at 1306 cm^{-1} and 1170 cm^{-1} were due to C-H vibrations and C-C stretching, respectively. The band at 1034 cm^{-1} was due to bending vibrations of C-H

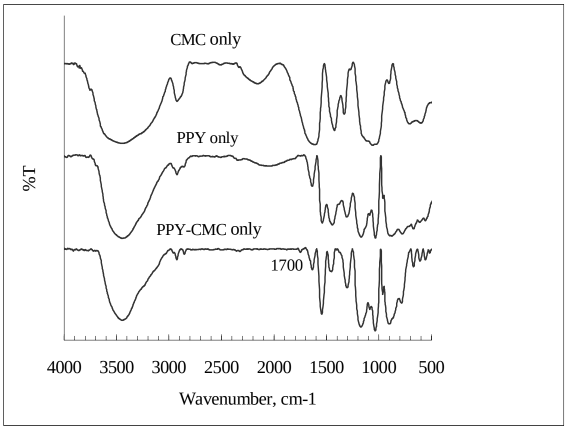


Fig 4. FT-IR spectra of CMC, the PPY film and the PPY-CMC composite film.

bond and N-H bond of pyrrole ring. The bands at 876 cm^{-1}, 776 cm^{-1} and 672 cm^{-1} represented the out-of-plane deformation of the C-H bond.

The spectrum of PPY-CMC composite film revealed all the major bands associated with the PPY film and the fresh CMC. A very weak band at 1750 cm^{-1} assigned to $n_{C\text{-}O}$ observed in the spectrum of PPY-CMC composite film, could not be observed in the spectra of either CMC or PPY film. This peak, although very weak, was an evidence for the involvement of carbonyl group of CMC in the formation of a chemical bond with polypyrrole. Similarly a very weak peak was also found in the literature for carbonyl group in the polypyrrole structure[14]. The small peak at 1088 cm^{-1} in the PPY-CMC spectrum showed the bending vibrations of the ether (glycosidic) linkage ($\delta_{C\text{-}O\text{-}C}$) of CMC. This same nature of peak was not observed in the PPY spectrum (Figure 4), rather a small peak appeared in the PPY spectrum at 1090 cm^{-1} due to the bipolaron structure of PPY.

Mechanical Properties

The DMA of the PPY-CMC composite film and the PPY film was measured by measuring the storage and loss moduli (E' and E'', respectively) and the loss tangent (tan δ) of the film with the aid of a dynamic mechanical analyzer in the temperature range of 25 to 250 °C with a heating rate of 2 °C per minute and at a frequency of 1 Hz. The E' of the PPY-CMC composite film showed a strong increment in E' over the investigated temperature range due to the addition of CMC into PPY structure. The PPY film without CMC showed a very low E’ against the measured temperature range (Figure 5). The large enhancement of E' of the PPY-CMC film indicated that the PPY-CMC film exhibited much higher elastic property than the PPY filmdid. This showed that CMC had a very strong effect on the elastic properties of polypyrrole conducting polymer.

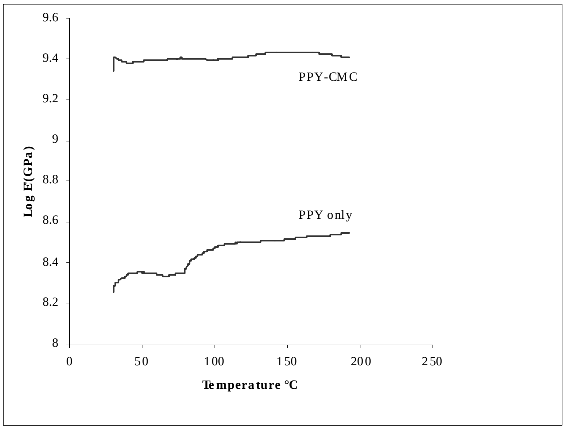


Fig 5. Temperature dependence of storage modulus (E') for the PPY-CMC film and the PPY film.

Electromagnetic Interference Shielding Effectiveness

Studies on the elelctromagnetic interference (EMI) shielding effectiveness of the PPY-CMC composite filmwere carried out in the frequency range of 8-12 GHz. The prepared PPY-CMC composite films offered an average shielding effectiveness of around 41 db (Figure 6) while the PPY film showed an average shielding effectiveness around 37 dB (Figure 7). Thus the PPY-CMC composite films offered the higher electromagnetic shielding effectiveness over the PPY film in any electromagnetic shielding applications.

CONCLUSIONS

This present communication shows that the PPY-CMC composite film with very good mechanical properties and conductivity can be prepared electrochemically from an aqueous pyrrole solution containing *p*-toluene sulfonate dopant and CMC. CMC appeared to act as a co-dopant with the main dopant *p*-toluene sulfonate, since keeping the dopant (*p*-toluene sulfonate) concentration unchanged, the conductivity

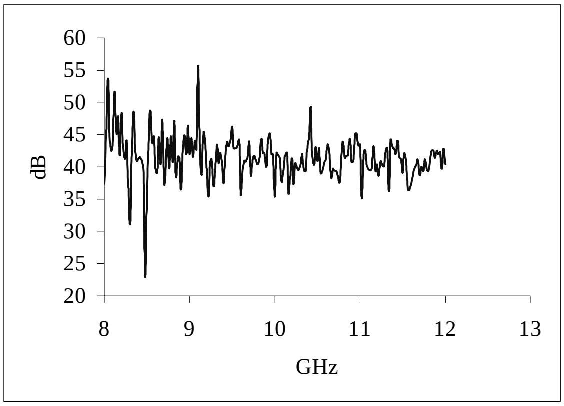


Fig 6. The electromagnetic interference shielding effectiveness of the PPY-CMC film in the frequency range of 8-12 GHz.

Fig 7. The electromagnetic interference shielding effectiveness of the PPY film in the frequency range of 8-12 GHz.

of the prepared PPY-CMC film increased with the increase in CMC concentration in the pyrrole solution suggesting that CMC helps increase the doping level. The optical microscopic study showed that the increasing concentration of CMC resulted in the globular morphology of the film on the solution sides. The electrode sides of the films were much smoother which were also influenced by the different concentrations of CMC. The DMA of the PPY-CMC film and the PPY film showed that CMC improved the plastic property of the PPY-CMC composite film. The studies on the EMI shielding effectiveness of the prepared PPY-CMC composite film showed/ that these materials can be used in any electromagnetic shielding applications since it can offer a high electromagnetic shielding effectiveness of around 41 db.

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