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Organic Conductor Films: Fabrication and Characterization

H. N. M. Ekramul Mahmud*[1] **and Anuar Kassim**[2]

*[1]Department of Chemistry, Faculty of Science, UM 50603 Kuala Lumpur.
[2]Department of Chemistry, Faculty of Science and Environmental Studies, UPM
43400 Serdang, Malaysia.

Email: ekramul@um.edu.my

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ABSTRACT

Polypyrrole-poly(vinyl alcohol) (PPy-PVA) conducting polymer composite films were prepared on Indium Tin Oxide (ITO) glass electrode from an aqueous solution containing pyrrole monomer, *p*-toluenesulfonate electrolyte and poly(vinyl alcohol) insulating polymer by electrochemical method. The prepared composite films were characterized by conductivity and electromagnetic interference (EMI) shielding measurements, dynamic mechanical analysis (DMA) and optical microscopy. The conductivity data of PPy-PVA shows that with the increase in PVA concentration in aqueous pyrrole solution used to prepare the films, the conductivity of the prepared PPy-PVA composite films increased upto a certain level and later it showed a decreasing trend with further increase in PVA concentration used to prepare the composite films. The dynamic mechanical analysis (DMA) shows the evidence of the enhanced mechanical properties of PPy-PVA composite film over PPy film. The optical micrographs show the changes of morphology of the prepared composite films with the PVA concentration. The results of electromagnetic interference (EMI) shielding effectiveness measured in the microwave range of 8-12 GHz show that a shielding effectiveness of 45.67 dB was exhibited by PPy-PVA composite films.

Key words: Polypyrrole, Polyvinyl alcohol, conducting polymer, electrochemical polymerization, dynamic mechanical analysis.

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INTRODUCTION

Conducting polymers, which can exhibit significant level of electrical conductivity upon doping, include polyacetylene, polyaniline, polypyrrole, polythiophene and polyphenylene etc., have got versatile promising applications in the field of energy storage (Novak et al., 1997), sensors (Nicolas et al., 2001), electronic and optical devices (Potember et al., 1987) and so on. Much research interests have been generated in the development of conducting polymers, which can be prepared either by chemical or electrochemical polymerization (Toshima et al., 1995).

Among all the conducting polymers, polypyrrole (PPy) 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 (Rodriguez et al., 1997), 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 blends or composites of polypyrrole polymer with other insulating polymers having desirable mechanical properties (Niwa et al., 1984; Otero et al., 1996). In this technique, a host of insulating polymers, namely, poly (styrene sulphonate) (Otero et al., 1996), polycarbonate (Wang et al., 1990), poly(methyl methacrylate)

(Lacroix 1987), rubber (Bardet et al., 1991), polyimide (Iroh et al., 2002), poly(vinyl alcohol) (Gangopadhyay et al., 2001; Street et al., 1985 ; Lindsey and Street 1984; Lin et al, 1999; Wang et al., 1993; Nicho et al., 2000) 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 host polymer.

Considering some advantages of poly(vinyl alcohol) (PVA) including its flexible molecular chains, high strength, good adhesion to electrodes and its ductile nature, some works on the electrochemical preparation of PPy-PVA has already been reported in the literature (Gangopadhyay et al., 2001; Street et al., 1985 ; Lindsey and Street 1984; Lin et al, 1999; Wang et al., 1993; Nicho et al., 2000). These efforts were made by producing polypyrrole films over a pre-coated electrode with PVA. This method is referred as two-step polymerization technique.

Apart from the previous efforts, we wish to report on the electrochemical preparation of PPy-PVA composite films by taking pyrrole, *p*-toluene sulfonate and PVA directly into the solution to get PPy-PVA composite films on the bare ITO glass electrode in aqueous medium. This one step polymerization technique allows a homogeneous film formation of PPy with PVA to take place showing an equal conductivity on both the electrode and solution side of the electrode. This present communication shows the enhanced mechanical properties exhibited by PPy-PVA composite film over PPy film along with the electromagnetic interference (EMI) shielding effectiveness of the composite films in the microwave range of 8-12 GHz.

EXPERIMENTAL

The composite films of polypyrrole (PPy) and poly (vinyl alcohol) (PVA) were electrochemically prepared by the oxidation of pre-distilled pyrrole (Fluka) monomer with *p*-toluene sulfonate dopant in the presence of polyvinyl alcohol 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 saturated calomel reference electrode (SCE).

The aqueous solution containing 0.2 M pyrrole and 0.1 M *p*-toluene sulfonate dopant was electrochemically polymerized using polyvinyl alcohol ranging from 3×10^{-4} M to 18×10^{-4} M at room temperature for 2 hours to form polypyrrole-poly(vinyl alcohol) (PPy-PVA) composite film of 22-44 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. For comparison purposes, PPy film was produced from using 0.2 M pyrrole and 0.1 M *p*-toluene sulfonate dopant in aqueous solution at room temperature for 2 hours.

RESULTS AND DISCUSSION

Electrical conductivity

The conductivity of the prepared conducting composite films was measured at room temperature by four-probe technique taking the average value of several readings at various points of the films. 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). Figure 1 shows the electrical d.c. conductivity of PPy-PVA composite films prepared from using various concentrations of PVA in the aqueous pyrrole solution containing 0.2 M pyrrole and 0.1 M *p*-toluene sulfonate. It shows that the conductivity of PPy-PVA composite films increases as the PVA concentration in the pyrrole solution increases from 3×10^{-4} M to 12×10^{-4} M, and then, the conductivity shows a decreasing trend with further increase in PVA concentration in the solution used for preparing the film. This is due to the fact that with the increase in PVA concentration upto 12×10^{-4} M, the conjugation chain length (number of pyrrole monomer units) of PPy increases causing the conductivity increase.

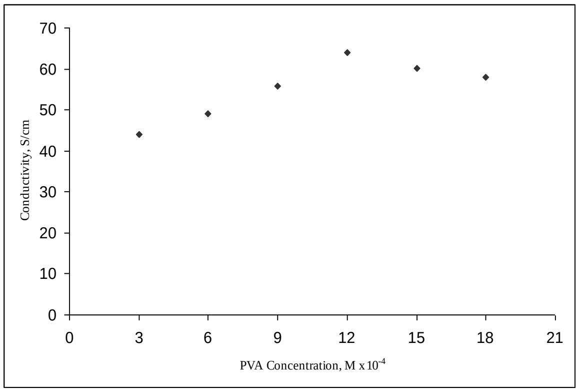


Figure **1.** Conductivity of PPy-PVA films versus PVA concentration used to prepare PPy-PVA films.

DYNAMIC MECHANICAL ANALYSIS

The mechanical properties of PPy-PVA composite film and PPy film produced from without PVA were evaluated by dynamic mechanical analysis (DMA). The analysis was carried out with in the temperature range of 25 °C to 250 °C with a heating rate of 2 °C per minute at a frequency of 1 Hz. The comparison result on the storage modulus (E') of PPy-PVA composite film prepared from using the minimum amount of PVA (3×10^{-4} M) and the PPy film prepared from without PVA is shown in Figure 2. It shows that a strong increment in storage modulus ($E^{|}$) developed for the PPy-PVA composite film over the investigated temperature range (25 °C to 250 °C) while the PPy film produced from the same amount of pyrrole and same amount of *p*-tolulene sulfonate without PVA shows a lower storage modulus (E') investigated in the same temperature range.

The storage modulus (E') of PPy-PVA composite film decreased till 104 °C with the increase in temperature while the storage modulus (E') of PPy film increased with the increase in temperature all over the whole investigated temperature range (25 °C to 250 °C) and did not decrease at all. 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 (25 °C to 250 °C) and thus the PPy film is hard and brittle and is not soft and does not show any flexibility in the backbone chain of the polymer. On the other hand, the storage modulus (E') of the PPy-PVA composite film produced from using 3x10^{-4} M PVA decreased continuously with the increase in temperature from 51 ºC to 104 ºC (Figure 2).

The rubbery state appeared to emerge from 86 ºC and the storage modulus (E') showed a slight increase in the rubbery state with the increase in temperature from 104 ºC and then leveled off. This behavior of storage modulus in the rubbery state indicates the molecular weight increase of the polymer film (Nielsen et al., 1994).

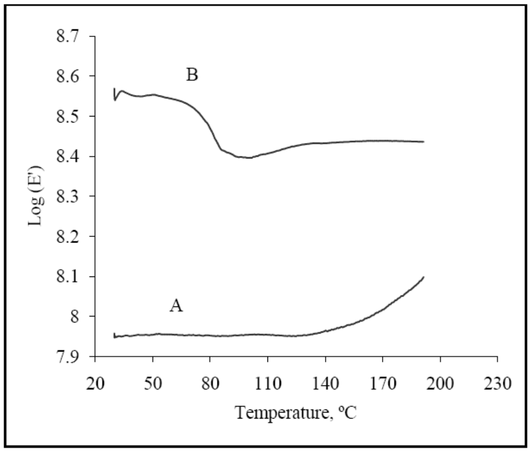


Figure 2: Storage moduli (E') of A) PPy film and B) PPy-PVA film against temperature.

The effect of PVA on the mechanical properties of PPy-PVA composite films clearly shows that the presence of PVA in PPy-PVA composite film is responsible for offering flexibility in the polymer backbone as the PPy-PVA composite film shows the transition (glass-rubbery) with the increase in temperature. The enhancement of storage modulus (E$^|$) of PPy-PVA composite film shown in Figure 2 indicates that PPy-PVA composite film is much stiffer than PPy film. The tan δ curve of the PPy-PVA film produced from using 3x10^{-4} M PVA shows that the sharp tan δ peak at 86 °C (Figure 3) represents the glass transition temperature (T_g) of the film since the storage modulus (E') showed a steady decrease at this temperature in the glass-transition region.

The broad tan δ peak at 43 °C appears as a secondary damping peak. This secondary damping peak of PPy-PVA film represents some molecular relaxation in the amorphous region of the polymer film in the glassy state. The broad peak at 144 ºC after glass-transition temperature in the rubbery state is associated with some ordered structure within the main amorphous structure of the polymer film.

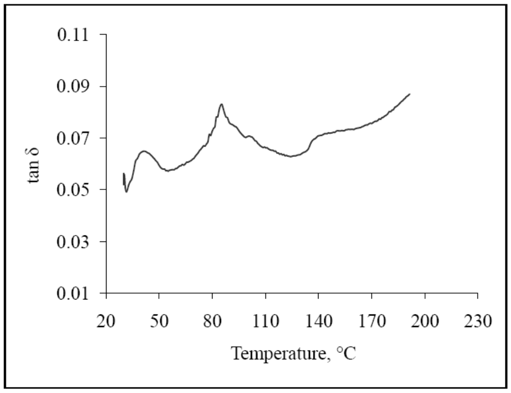


Figure 3: Temperature dependence of tan δ for PPy-PVA film produced from using 3 x 10^{-4} M PVA.

Figure 4 shows the tan δ curve of the PPy film without PVA. There is no glass transition temperature evident since the storage modulus (E') of the film increased with the increase in temperature and the film remained in the glassy state all through with the increase in temperature. Therefore, the tan δ peak at 91 °C is referred to as the secondary damping peak which is due to some molecular relaxation in the polymer.

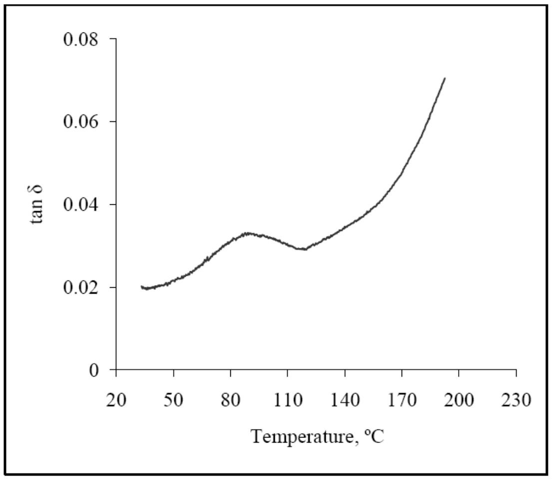


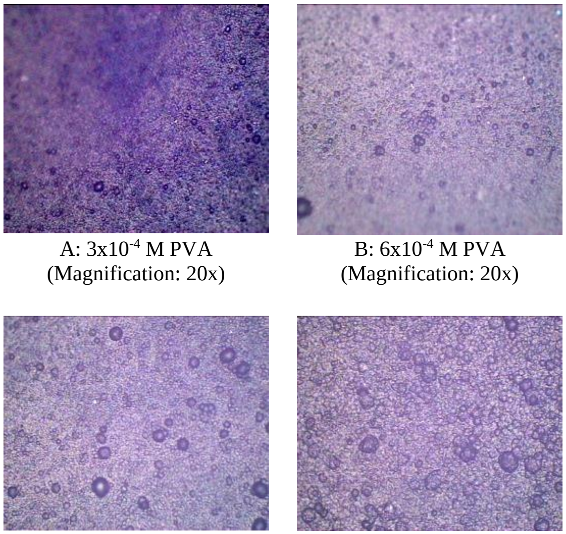
Figure 4: Temperature dependence of tan δ for PPy film without PVA.

OPTICAL MICROSCOPIC STUDY

The morphological study on polypyrrole- poly(vinyl alcohol) composite films shows that with the increase in PVA concentration in the pyrrole solution, the morphology of the prepared PPy-PVA films changes, which were visualized in optical micrographs (Figures 5 and 6). The surface morphology of the film facing the solution side gives globular morphology. As the concentration of PVA increases, the globular morphology becomes more evident with bigger spherical ball shapes. This indicates that with the increase in PVA concentration, polymerization reaction becomes more intense giving a globular morphology with bigger spherical ball shapes forming from the aggregation of smaller balls. It can be noted that all the composite films of PPy-PVA were produced from using the same concentration of pyrrole monomer (0.2 M) and the same concentration of *p*-toluene sulfonate dopant (0.1 M) but with different concentration of PVA ranging from $3x10^{-4}$ M to $18x10^{-4}$ M, offered different surface morphology for both the solution side and the electrode side of the films. This proves that the concentration of PVA plays a vital role in film formation with polypyrrole.

The electrode side of the film surface appeared much smoother compared to the solution side surface. This is 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 the solution side. The surface morphology of the electrode side shows that the surface was very smooth and looked much covered with the existence of some craters for the film produced from using the highest concentration of PVA ($18x10^{-4}$ M) while the surface of the film produced from using the lowest concentration of PVA ($3x10^{-4}$ M) has got smooth surface almost all through with no such craters (Figure 6).

The micrographs show that with the increase in PVA concentration in the solution, these craters gradually appeared. This is due to the fact that the polymerization reaction occurred much more with the increase in PVA concentration causing these craters to occur (Figure 6). All these micrographs showed no phase separation either on the electrode side or on the solution side of the films and thus it supports the homogeneous film formation of PPy with PVA.

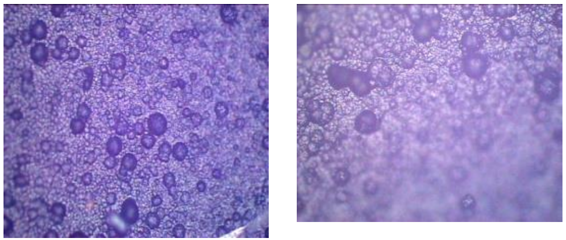


A: $3x10^{-4}$ M PVA (Magnification: 20x)

B: $6x10^{-4}$ M PVA (Magnification: 20x)

C: $9x10^{-4}$ M PVA (Magnification: 20x)

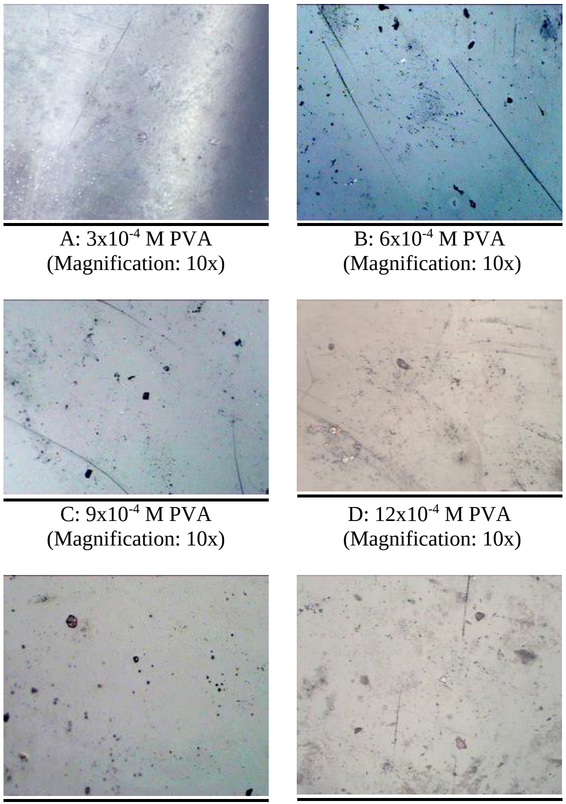
D: $12x10^{-4}$ M PVA (Magnification: 20x)



E: $15x10^{-4}$ M PVA (Magnification: 20x)

F: $18x10^{-4}$ M PVA (Magnification: 20x)

Figure 5: The optical micrographs of PPy-PVA composite films on the solution side produced from using A: $3x10^{-4}$ M PVA, B: $6x10^{-4}$ M PVA, C: $9x10^{-4}$ M PVA, D: $12x10^{-4}$ M PVA, E:$15x10^{-4}$ M PVA and F:$18x10^{-4}$ M PVA in the pyrrole solution.



A: $3x10^{-4}$ M PVA (Magnification: 10x)

B: $6x10^{-4}$ M PVA (Magnification: 10x)

C: $9x10^{-4}$ M PVA (Magnification: 10x)

D: $12x10^{-4}$ M PVA (Magnification: 10x)

E: $15x10^{-4}$ M PVA (Magnification: 20x)

F: $18x10^{-4}$ M PVA (Magnification: 20x)

Figure 6: The optical micrographs of PPy-PVA composite films on the electrode side produced from using A: $3x10^{-4}$ M PVA, B: $6x10^{-4}$ M PVA, C: $9x10^{-4}$ M PVA, D: $12x10^{-4}$ M PVA, E:$15x10^{-4}$ M PVA and F: $18x10^{-4}$ M PVA in the pyrrole solution.

Shielding effectiveness (SE) of PPy-PVA composite films

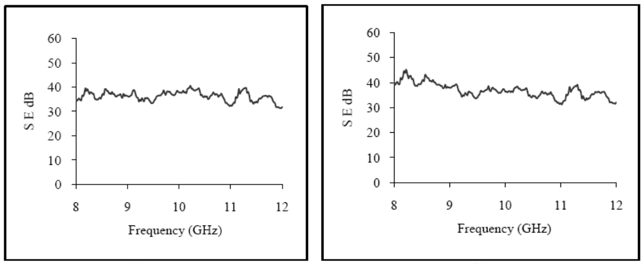
The electromagnetic interference shielding effectiveness (SE) of PPy-PVA composite films have been evaluated in the microwave frequency range of 8-12 GHz. Figure 7 shows the average shielding effectiveness of PPy-PVA composite films produced from $3x10^{-4}$ M to $18x10^{-4}$ M PVA. The composite films synthesized from $3x10^{-4}$ M, $6x10^{-4}$ M, $9x10^{-4}$ M, $12x10^{-4}$

M, 15x10^{-4} M and 18x10^{-4} M PVA showed an average shielding effectiveness of 36.26 dB, 37.0 dB, 40.09 dB, 45.67 dB, 44.64 dB and 40.79 dB, respectively.

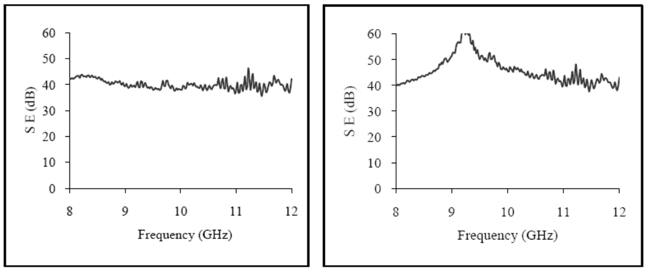
Table.1 summarizes the shielding effectiveness (dB) of all the PPy-PVA composite films. It shows that with the increase in PVA concentration from 3x10^{-4} to 12x10^{-4} M, the shielding effectiveness of the films also increases from 36.26 dB to 45.67 dB. The total attenuation of microwave energy corresponding to the above dB also increases from 98.43 % to 99.4 %. With further increase in PVA concentration from 12x10^{-4} M to 18x10^{-4} M, a very little decrease in shielding effectiveness (dB) of the PPy-PVA composite films was observed. The corresponding total attenuation of the microwave energy also showed a very little decrease.

This is due to the fact that the reflection in EMI shielding effectiveness requires the existence of mobile charge carriers (electrons or holes), which interact with the electromagnetic radiation. So, the higher the conductivity (the more the mobile charge carriers), the higher is the reflection and thus, higher is the shielding effectiveness.

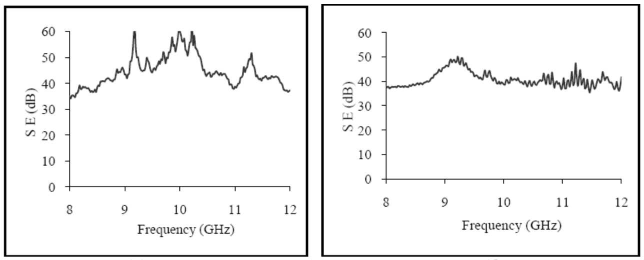
This result of EMI effectiveness of PPy-PVA composite films is fully analogous with the conductivity results of PPy-PVA composite films produced from various concentrations of PVA that with the increase in PVA concentration from 3x10^{-4} M to 12x10^{-4} M, the conductivity increased and then with further increase in PVA concentration from 12x10^{-4} M to 18x10^{-4} M, the conductivity decreased.



(a) (b)



(c) (d)



(e) (f)

Figure 7: Shielding effectiveness analyzed in the frequency range of 8-12 GHz for PPy-PVA composite films synthesized from (a) 3x10^{-4} M, (b) 6x10^{-4} M, (c) 9x10^{-4} M, (d) 12x10^{-4} M,(e) 15x10^{-4} M and (f) 18x10^{-4} M PVA.

Table 1 : The shielding effectiveness of PPy-PVA Composite films prepared from various concentrations of PVA

Conc. of PVA, M	S. E. (dB)	Trans. %	Refl. (%)	Abs. (%)	Total Atten. %	Cond. (S/cm)
3 x 10^{-4}	36.26	1.57	91.27	7.16	98.43	42
6 x 10^{-4}	37.0	1.45	91.47	7.08	98.55	49
9 x 10^{-4}	40.09	1.0	91.97	7.03	99.0	55
12 x 10^{-4}	45.67	0.6	92.55	6.85	99.40	64
15 x 10^{-4}	44.64	0.71	92.74	6.55	99.29	60
18 x 10^{-4}	40.79	0.96	92.78	6.26	99.04	58

Note: S. E. = Shielding effectiveness. Trans= Transmission, Refl = Reflection Abs = Absorption, Atten = Attenuation, Cond = Conductivity, dB = Decibel

CONCLUSIONS

We wish to report on the successful electrochemical preparation of polypyrrole-poly(vinyl alcohol) (PPy-PVA) composite films by direct or one-step polymerization method in aqueous medium. The conductivity of PPy-PVA composite films increased with the increase in PVA concentration in the pyrrole solution, which suggests the increase in conjugation

Length, and later, the conductivity showed a decreasing trend with further increase in PVA concentration, which again indicates the conjugation length decrease. The dynamic mechanical analysis of PPy-PVA composite film and PPy film suggests that the enhanced mechanical properties of the PPy-PVA composite film over PPy film is due to the incorporation of PVA in PPy structure to form PPy-PVA composite film.

The optical microscopic study exhibits the globular morphology of the films for its solution sides while the electrode sides are rather smoother. Since the monomer and the dopant concentrations remained same for all the cases, it is the PVA concentration which played the key role in making changes in the globular morphology from smaller to bigger spherical ball shapes. The surface morphology of the electrode side of the films is also influenced by the different concentrations of PVA.

The overall results of the EMI shielding effectiveness of PPy-PVA composite films prepared from various concentrations of

PVA showed that the concentration of PVA used to prepare the composite conducting film has a significant effect on the electromagnetic shielding behavior measured in the frequency range of 8-12 GHz. The EMI shielding effectiveness of 45.67 dB seems to be very attractive in any electromagnetic interference (EMI) shielding applications where a minimum shielding effectiveness of 35 dB is required.

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