

# Fourier Transform Infrared Study of Polypyrrole–Poly(vinyl alcohol) Conducting Polymer Composite Films: Evidence of Film Formation and Characterization

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**ABSTRACT:** The electrochemical preparation of polypyrrole (PPY)–poly(vinyl alcohol) (PVA) conducting polymer composite films on an indium–tin oxide glass electrode from an aqueous solution containing a pyrrole monomer, a *p*-toluene sulfonate electrolyte, and a PVA insulating polymer is reported. The prepared PPY–PVA composite films were characterized by Fourier Transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and conductivity measurements. The FTIR study showed that the composite of PPY and PVA formed through bond formation between PVA and the *p*-toluene sulfonate dopant anion. The conductivity data of PPY–PVA showed that with increasing PVA concentration in the pyrrole solution, the conductivity

of the prepared PPY–PVA film increased up to a certain level due to an increase in conjugation length, and later, it decreased with further increases in the PVA concentration in the solution due to a decrease in conjugation length. This was supported by the FTIR band intensity  $I_{1560}/I_{1480}$ . The TGA results show that the PPY–PVA polymer composite film was thermally more stable than the PPY film. A shielding effectiveness of 45.6 dB was exhibited by the PPY–PVA composite film in the microwave frequency range. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4107–4113, 2006

**Key words:** conducting polymers; electrochemistry; polypyrroles

## INTRODUCTION

Conducting polymers are polymers that can exhibit a significant level of electrical conductivity comparable to metals. The versatile and promising applications of conducting polymers, such as polyaniline, polypyrrole (PPY), polythiophene, and polyphenylene, in the field of energy storage,<sup>1</sup> sensors,<sup>2</sup> electronic and optical devices,<sup>3</sup> and so on, have generated much research interest in the development of conducting polymers, which can be prepared either by chemical or electrochemical polymerization.<sup>4</sup>

Among conducting polymers, PPY has received much attention because 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;<sup>5</sup> it still has some drawbacks, such as poor pro-

cessability and a lack of essential mechanical properties. Efforts to overcome these drawbacks have led to numerous studies on the synthesis of PPY by both electrochemical and chemical routes. Among them, a significant strategy for the achievement of both high electrical conductivity and desirable mechanical properties has been the preparation of blends or composites of PPY polymer with other insulating polymers with desirable mechanical properties.<sup>6,7</sup> The polymer blends or composites can be prepared either by electrochemical or chemical polymerization. In this technique, a host of polymers, namely, poly(styrene sulfonate),<sup>7</sup> polycarbonate,<sup>8</sup> poly(methyl methacrylate),<sup>9</sup> rubber,<sup>10</sup> polyimide,<sup>11</sup> poly(vinyl alcohol) (PVA),<sup>12–17</sup> and so on, have been combined with PPY in aqueous or organic media to produce PPY polymer composites that have the conducting properties of PPY with some of the superior mechanical properties of the host polymer.

With regard to some advantages of PVA, including its flexible molecular chains, high strength, good adhesion to electrodes, and its ductile nature, some studies on the electrochemical preparation of PPY–PVA have already been reported in the literature.<sup>12–17</sup> Efforts were made to produce PPY films over a pre-coated electrode with PVA.

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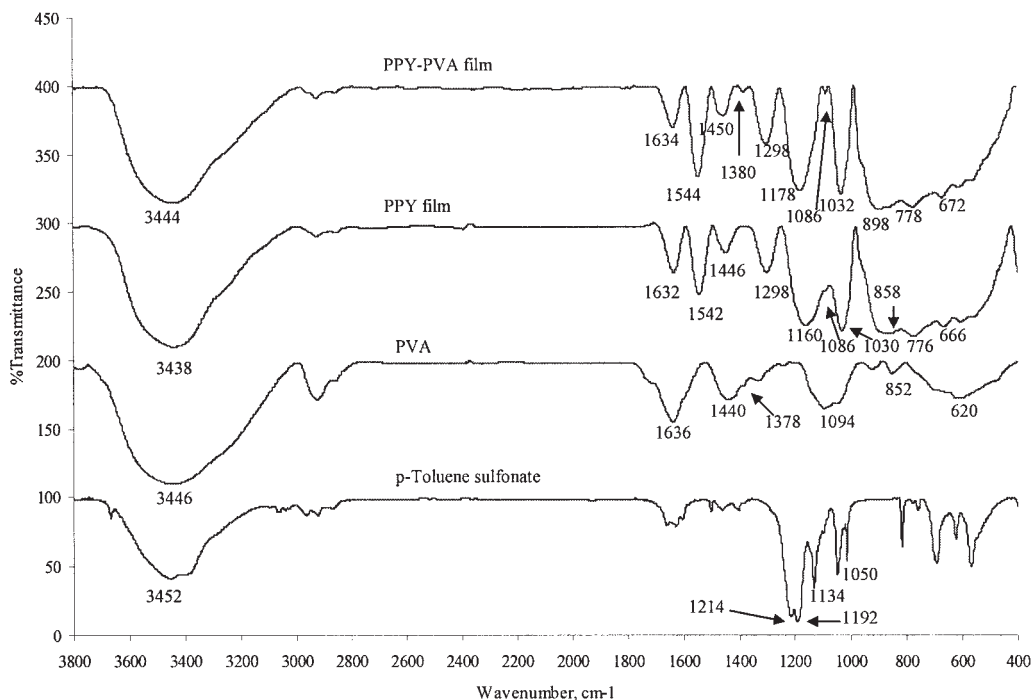


Figure 1 FTIR spectra of the PPY-PVA, PVA, and PPY films.

Apart from the previous efforts,<sup>12-17</sup> we studied the electrochemical preparation of PPY-PVA composite films by placing pyrrole, *p*-toluene sulfonate, and PVA directly into solution to produce PPY-PVA composite films on a bare indium-tin oxide (ITO) glass electrode in an aqueous medium. In this article, evidence for the formation of PPY-PVA composite films are shown through Fourier transform infrared (FTIR) spectroscopic study.

## EXPERIMENTAL

The PPY-PVA composite films were electrochemically prepared by the oxidation of predistilled pyrrole (Fluka, Switzerland) monomer with *p*-toluene sulfonate (Fluka) dopant in the presence of PVA (Fluka; molecular weight = 72,000) in an aqueous medium. The electrochemical synthesis was carried out in a one-compartment cell with a potentiostat. An ITO glass electrode was used as the working electrode (anode), and a carbon rod was used as the counterelectrode (cathode). The anodic potential of the working electrode was measured as 1.2 V against a saturated calomel reference electrode (SCE) instead of the application of 0.8 V (vs SCE), which is generally used for the deposition of PPY. This was because a higher potential of 1.2 V (vs SCE) favored the polymerization of pyrrole in the presence of PVA, a viscous additive, to form the PPY-PVA composite films. A higher potential than 0.8 V (vs SCE) has also been reported in the literature<sup>18,19</sup> for the preparation of various PPY composite films.

The aqueous solution containing 0.2M pyrrole and 0.1M *p*-toluene sulfonate dopant was electrochemically polymerized with PVA ranging from  $3 \times 10^{-4}$  to  $18 \times 10^{-4}$  M at room temperature for 2 h to form PPY-PPA composite films 22–44  $\mu\text{m}$  thick. The composite films thus produced on the ITO glass surface as insoluble films were rinsed thoroughly with distilled water and then peeled off the electrode. They were then dried in an oven at 60°C for 24 h. For comparison purposes, a PPY film was produced with 0.2 M pyrrole and 0.1 M *p*-toluene sulfonate dopant in an aqueous solution at room temperature for 2 h.

## RESULTS AND DISCUSSION

### FTIR study

The physical appearance of the obtained PPY-PVA films was strong compared to normal PPY films and was flexible and smooth with a greenish black color. The IR absorption spectra of the PPY-PPA polymer composite film, PPY film, PVA, and *p*-toluene sulfonate are shown in Figure 1.

### PVA

The broad band at 3438 cm<sup>-1</sup> in the PVA spectrum corresponded to the O—H group of PVA. The band at 1440 cm<sup>-1</sup> represented the in-plane deformation of the O—H and C—H bonds. The weak band at 1376 cm<sup>-1</sup> was due to CH<sub>2</sub> wagging. The band appearing at 1094

TABLE I  
Assignments of FTIR Absorption Bands of PVA, PPY, and the PPY-PVA Films

Assignment <sup>16,21</sup>	PVA wave number (cm <sup>-1</sup> )	PPY wave number (cm <sup>-1</sup> )	PPY-PVA wave number (cm <sup>-1</sup> )
$\nu$ (O—H) of PVA and $\nu$ (N—H) of pyrrole ring	3446 br, vs	3438 br, vs	3444, br, vs
$\nu$ (C=C) of pyrrole (aromatic type); for PVA, no band could be assigned	1636	1632	1634
$\nu$ (C=C) of pyrrole		1542 s	1544 s
$\delta$ (O—H) and $\delta$ (C—H) of PVA and $\nu$ (C—N) of pyrrole	1440 s	1446 s	1450 s
CH <sub>2</sub> wagging of PVA	1378 w	—	1380 w
$\delta$ (O—H) with CH wag (PVA); $\nu$ (C—C) of pyrrole	1330 s	1298 s	1298 s
$\nu$ SO <sub>2</sub> of <i>p</i> -toluene sulfonate; $\nu$ (C—C) of pyrrole		1160 s	1178 s
$\delta$ (O—H) and $\nu$ (C—O) of PVA; $\delta$ (C—H) of pyrrole	1094 m	1086 sh	1086 w
$\delta$ (C—H) and $\delta$ (N—H) of pyrrole		1030 s	1032 s
PVA skeletal band and $\gamma$ (C—H) of pyrrole	852 s	858 m	898 m
$\gamma$ (C—H) of pyrrole		776 m	778 m
O—H twisting of PVA and $\gamma$ (C—H) of pyrrole	620 br	666 m	672 m

$\nu$  = stretching;  $\delta$  = in-plane deformation;  $\gamma$  = out-of-plane deformation; br = broad; v = very; s = strong; sh = shoulder; m = medium; w = weak.

cm<sup>-1</sup> was due to C—O stretching and O—H bending. The PVA skeletal band occurred at 852 cm<sup>-1</sup>. The band at 620 cm<sup>-1</sup> corresponded to O—H twisting of PVA.

#### PPY film

The N—H stretching band of the pyrrole ring appeared at 3438 cm<sup>-1</sup>. The other characteristic pyrrole ring stretch absorption bands were observed between 1600 and 1100 cm<sup>-1</sup>. The C=C ring stretching band of pyrrole occurred at 1632 and 1542 cm<sup>-1</sup> for aromatic and quinonoid structures, respectively. The band at 1446 was due to C—N stretching of the pyrrole ring. The peak at 1298 cm<sup>-1</sup> was due to CH vibration, and the peak at 1160 cm<sup>-1</sup> was due to C—C stretching. The separate spectrum of *p*-toluene sulfonate showed four peaks at 1214, 1192, 1134, and 1050 cm<sup>-1</sup>, which corresponded to the three S—O groups and one S-phenyl vibration.<sup>20</sup> The peak at 1160 cm<sup>-1</sup> in the PPY spectrum was also due to the S—O group of *p*-toluene sulfonate. The in-plane deformation of the C—H bond occurred at 1030 cm<sup>-1</sup>. The bands at 858, 776, and 666 cm<sup>-1</sup> represented the out-of-plane deformation of the C—H bond.

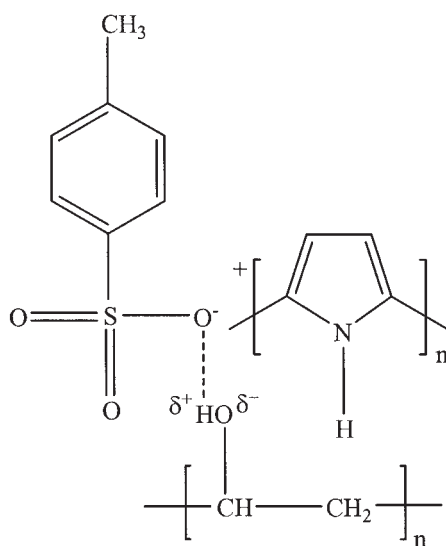
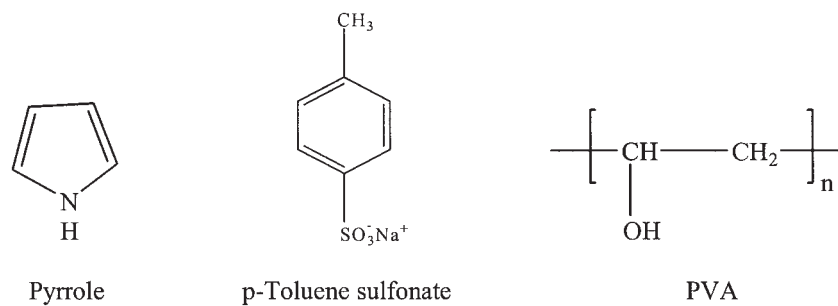
#### PPY-PVA composite film

All of the major bands associated with the PPY film and PVA were found in the spectrum of the PPY-PVA composite film. Table I shows the band assignments of the spectra of PPY-PVA, PPY, and PVA. There were some noticeable features in the spectra of PPY-PVA, PPY, and PVA. Figure 1 shows that the band at 1160 cm<sup>-1</sup> in the PPY spectrum was due to the sulfonate group of *p*-toluene sulfonate anion and C—C stretching. In the PPY-PVA spectrum, no band was observed

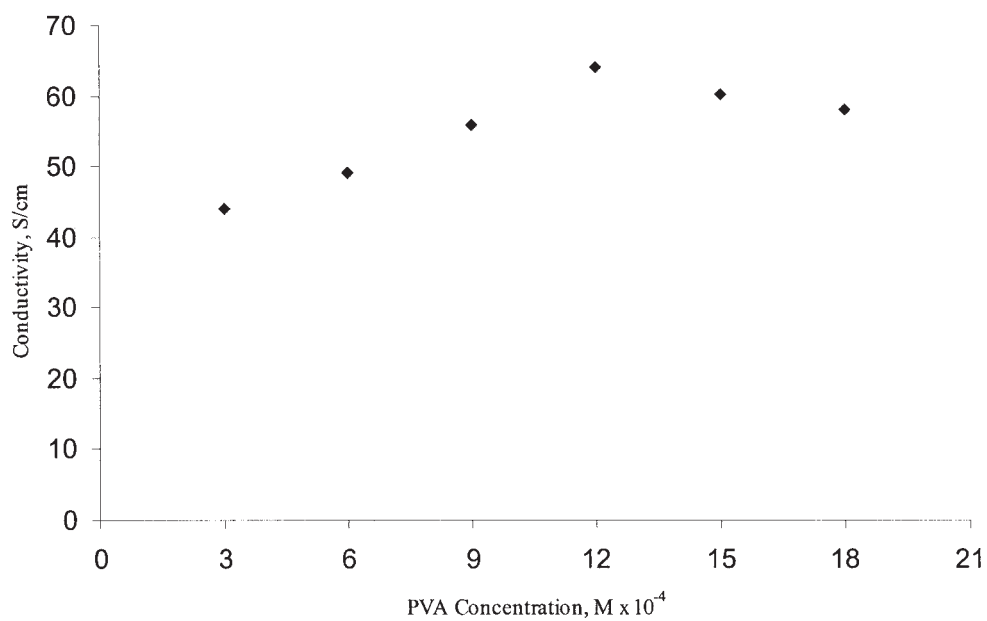
around 1160 cm<sup>-1</sup>; rather, a shifted band at 1178 cm<sup>-1</sup> was observed. Because of this shift in band position from 1160 cm<sup>-1</sup> to a higher wave number at 1178 cm<sup>-1</sup>, we assumed that the sulfonate group of *p*-toluene sulfonate of the PPY film had an interaction with PVA through hydrogen bonding of the —OH group of PVA. Figure 2 shows the probable reaction scheme.

In the PPY-PVA spectrum, the band 1086 cm<sup>-1</sup> was assigned to C—H bending of pyrrole, which was again associated with the bipolaronic structure.<sup>21</sup> The C—O stretching band of PVA overlapped at this band position in the PPY-PVA spectrum. On the other hand, in the PPY spectrum, this band due to C—H bending of pyrrole appeared as a very weak shoulder at 1086 cm<sup>-1</sup> with very little sign of bipolaronic structure. Further, the evidence for the formation of the PPY-PVA composite film also came from this FTIR band analysis in the range 850–900 cm<sup>-1</sup>. In the PPY spectrum, the band at 852 cm<sup>-1</sup> indicated the C—H in-plane deformation, whereas this C—H in-plane deformation was observed at a higher wave number (898 cm<sup>-1</sup>) in the PPY-PVA spectrum. Again, in the PVA spectrum, this band (852 cm<sup>-1</sup>) was due to the C—C—O in-phase stretching band, the skeletal band of PVA. The band at 898 cm<sup>-1</sup> in the PPY-PVA spectrum was the overlapping of the skeletal band of PVA and the band due to the C—H in-plane deformation of pyrrole. This indicated that a change had certainly occurred in the skeletal position of PVA in PPY-PVA structure, which caused the shift in the skeletal band position of PVA from 852 cm<sup>-1</sup> (in the PVA spectrum) to 898 cm<sup>-1</sup> (in the PPY-PVA spectrum). Thus, this change in band position also suggested that PPY had chemical interactions with PVA to form PPY-PVA.

In addition to the aforementioned evidences, the spectroscopic analysis in the band range 600–700 cm<sup>-1</sup> also provided us with some more information



**Figure 2** Schematic representation of PPY-PVA film formation.



**Figure 3** Conductivity of the PPY-PVA films versus PVA concentration used to prepare the PPY-PVA films.

TABLE II  
FTIR Band Intensity Ratio ( $I_{1544}/I_{1450}$ ) in Terms of PVA Concentration Used to Prepare the PPY-PVA Films

PVA concentration (M) used to prepare the PPY-PVA film	$I_{1544}/I_{1450}$	Electrical conductivity of the PPY-PVA film (S/cm; at room temperature)
$3 \times 10^{-4}$	4.65	44.12
$6 \times 10^{-4}$	3.38	49.02
$9 \times 10^{-4}$	2.18	55.70
$12 \times 10^{-4}$	1.45	64.0
$15 \times 10^{-4}$	1.93	60.03
$18 \times 10^{-4}$	3.38	58.05

for the formation of the PPY-PVA composite film. The broad band at  $620 \text{ cm}^{-1}$  due to the O—H twisting of PVA in the PVA spectrum shifted to  $672 \text{ cm}^{-1}$  in the PPY-PVA spectrum, whereas a band at  $666 \text{ cm}^{-1}$  found in the PPY spectrum was due to C—H vibration. So, the disappearance of the O—H twisting band at  $620 \text{ cm}^{-1}$  and the shifting of the C—H vibration band of PPY from  $666$  to  $672 \text{ cm}^{-1}$  in the PPY-PVA spectrum suggested some molecular interaction of PVA with *p*-toluene sulfonate doped PPY. The same disappearance of the O—H twisting band of PVA has been reported in the literature for PPY-PVA films prepared by both electrochemical<sup>16</sup> and chemical methods.<sup>17</sup> The authors of these studies,<sup>17</sup> with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as the oxidant in the chemical method, believed that the band at  $678 \text{ cm}^{-1}$  was due to some new Fe—O stretching band.

Furthermore, the peak at  $1376 \text{ cm}^{-1}$ , which was due to  $\text{CH}_2$  wagging of PVA appeared in both the PPY-PVA and PVA spectra but was totally absent in the PPY spectrum. Thus, we found some strong spectroscopic evidence in favor of the formation of the PPY-

PVA composite film where PVA and PPY were connected through the *p*-toluene sulfonate dopant anion.

### Electrical conductivity

The conductivity of the prepared conducting composite films was measured at room temperature by a four-probe technique, with the average taken of several readings at various points of the films. Before the conductivity was measured, the conductivity meter was calibrated with a standard silicon wafer with standard reference material no. 2545 (National Institute of Standards and Technology, USA). Figure 3 shows the electrical direct-current conductivity of the PPY-PVA films prepared with various concentrations of PVA in the pyrrole and electrolyte aqueous solution. It shows that the conductivity of PPY-PVA composite films increased as the PVA concentration in the pyrrole solution increased from  $3 \times 10^{-4}$  to  $12 \times 10^{-4} \text{ M}$ , and then, the conductivity decreased with further increases in PVA concentration in the solution used to prepare the films. This was due to the fact that with increasing PVA concentration up to  $12 \times 10^{-4} \text{ M}$ , the conjugation chain length (number of pyrrole monomer units) of PPY increased, which caused the conductivity to increase. The qualitative measurement of the conjugation length was obtained from the work of Tian and Zerbi,<sup>22</sup> where they showed that the bands in the IR spectrum at  $1560$  and  $1480 \text{ cm}^{-1}$ , corresponding to the oxidation state of the polymer, and the skeletal band of the polymer, respectively, were specially affected by the changes in the extent of delocalization in the polymer chain. One can visualize these changes by taking the ratio of integrated absorption intensity of the  $1560 \text{ cm}^{-1}$  (C=C stretching band) to the integrated absorption intensity of the  $1480 \text{ cm}^{-1}$  band (C—N stretching band). This band ratio of  $I_{1560}/I_{1480}$  is

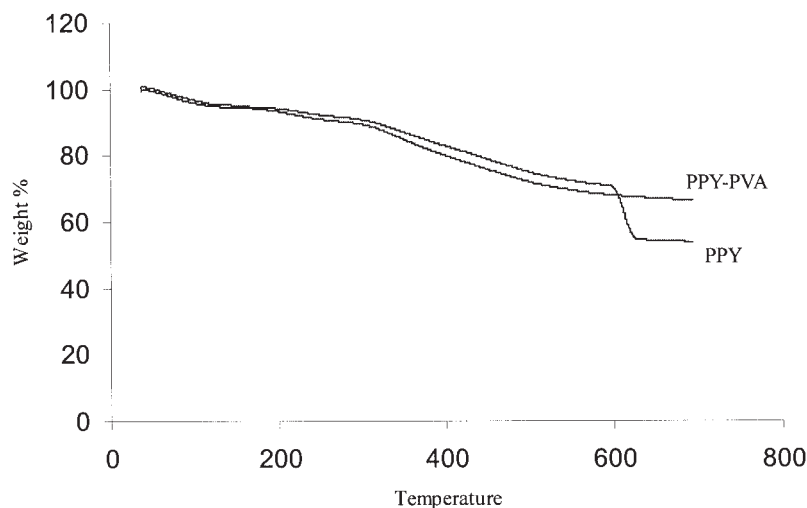
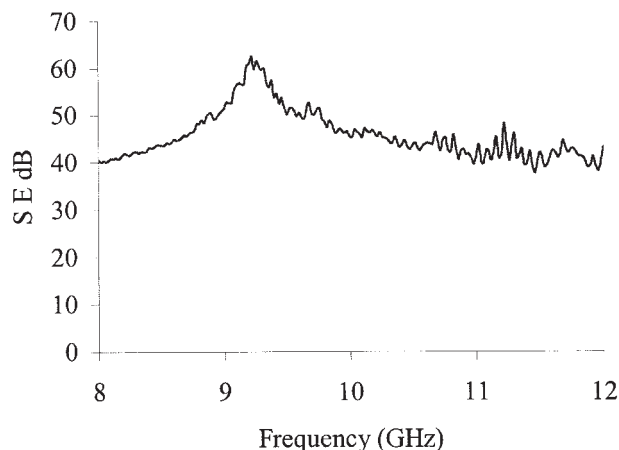


Figure 4 TGA of the PPY-PVA and PPY films.





**Figure 5** SE of the PPY-PVA composite film in the microwave range 8–12 GHz.

inversely proportional to the extent of delocalization.<sup>22</sup> Table II shows the values of this band ratio of  $I_{1544}/I_{1450}$  for the PPY-PVA composite films obtained from with various concentrations of PVA in the pyrrole and electrolyte aqueous solution. It shows that with increasing PVA concentration in the solution up to  $12 \times 10^{-4} M$ , the value of  $I_{1544}/I_{1450}$  decreased, which was again related to the increase in conductivity (Fig. 3). Later, with further increases in PVA concentration, the value of  $I_{1544}/I_{1450}$  increased, which suggested a decrease in the conjugation length, which was again related to the conductivity decrease.

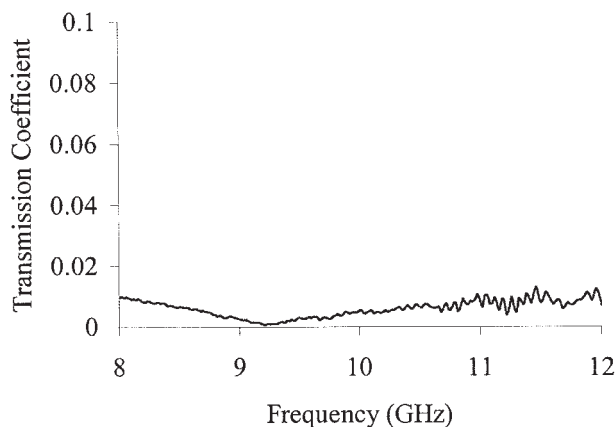
#### Thermogravimetric analysis (TGA)

The TGA results of the PPY-PVA and PPY films are shown in Figure 4. It shows that an initial weight loss of 5.57% occurred at 151°C for the PPY-PVA composite film, whereas at 132°C, a weight loss of 5.33% occurred for the PPY film. The major decomposition started at 268°C for both the PPY-PVA composite and PPY films. Finally, a residue of 66.37 wt % remained at 693°C for the PPY-PVA film, whereas the PPY film showed a residue of 53.76 wt % at 691°C. TGA showed that the PPY-PVA composite film was thermally more stable than the PPY film. The heating was carried out from 35 to 700°C at a heating rate of 10.0°C/min.

#### Electromagnetic interference (EMI) shielding effect

Studies on the possible application of the PPY-PVA composite film were carried out for EMI shielding effectiveness (SE) in the microwave frequency range 8–12 GHz by a network analyzer (Hewlett Packard, USA).

A high EMI SE of 45.6 dB, corresponding to a transmission of 0.6% of the microwave energy, was exhibited by the PPY-PVA composite film (Fig. 5). The

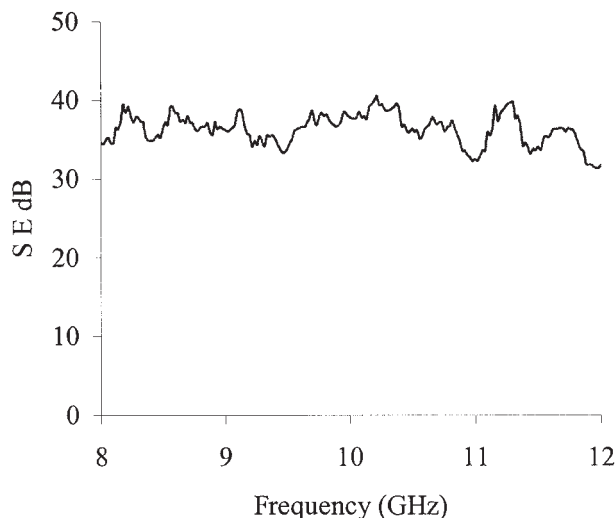


**Figure 6** Transmission coefficients of the PPY-PVA composite film in the microwave range 8–12 GHz.

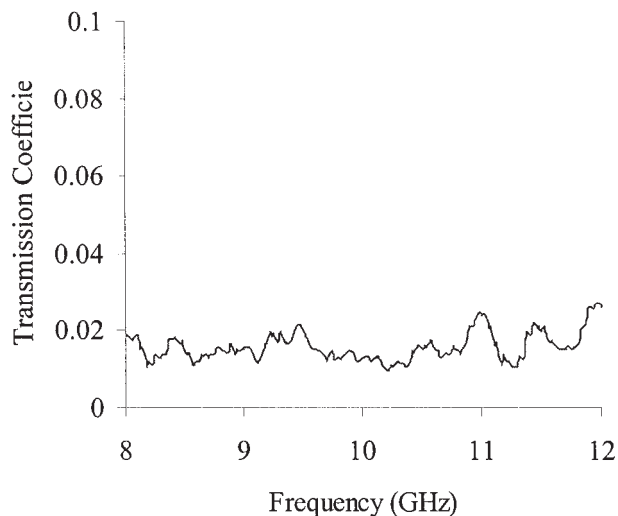
transmission coefficients of the film are shown in Figure 6. The SE of the PPY film without PVA is shown in Figure 7. It shows an average SE of 37 dB, corresponding to a transmission of 1.6% of the microwave energy. The transmission coefficients of the film are shown in Figure 8. The total shielding attenuation of the PPY-PVA composite film in the microwave range was 99.4%, whereas the PPY film without PVA showed an attenuation of 98.4%. Thus, the higher SE exhibited by the PPY-PVA composite film over PPY film in the microwave frequency range 8–12 GHz was due to the incorporation of PVA in the PPY structure.

#### CONCLUSIONS

Here, we have reported the successful preparation of PPY-PVA composite films by a potentiostatic method in an aqueous medium. The FTIR study showed that



**Figure 7** SE of the PPY film without PVA in the frequency range 8–12 GHz.



**Figure 8** Transmission coefficients of the PPY film without PVA in the frequency range 8–12 GHz.

the composite of PPY and PVA formed through the *p*-toluene sulfonate dopant anion, where PVA was attached to the *p*-toluene sulfonate dopant anion. The conductivity of the PPY-PVA composite films increased with increasing PVA concentration in the pyrrole solution, which suggested an increase in conjugation length, and later, the conductivity decreased with further increases in PVA concentration, which again indicated a conjugation length decrease. The TGA results revealed that due to the incorporation of PVA in the PPY structure, the PPY-PVA composite film was thermally more stable than the PPY film. The EMI shielding behavior of the PPY-PVA composite film showed that the higher SE of 45.6 dB with a total shielding attenuation of 99.4% in the microwave range makes the PPY-PVA composite film attractive for any EMI shielding applications.

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