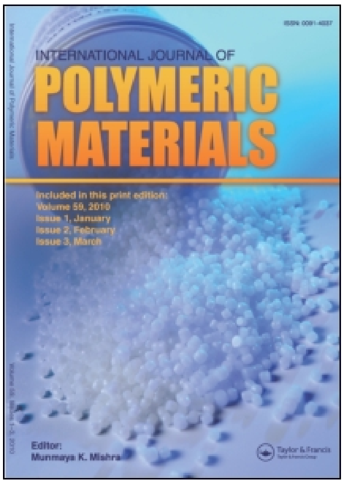

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Synthesis and Characterization of Ppy-PVS, Ppy-pTS, and Ppy-DBS Composite Films

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Composite films of polypyrrole-poly(vinyl sulphonic acid) (Ppy-PVS), polypyrrole-p-toluene sulphonic acid (Ppy-pTS) and polypyrrole-dodecylbenzene sulphonic acid (Ppy-DBS) were synthesized on ITO coated glass, using electrochemical polymerization. The synthesized films were characterized using electrochemical technique, electrical conductivity, UV-Vis spectroscopy, FTIR spectra, and scanning electron microscopy (SEM). This study reveals that Ppy-PVS composite films provide a polymer matrix with very good mechanical and environmental stability, uniform surface morphology, and higher conductivity, which are suitable for the immobilization of biocomponent.

Keywords: composites, electrochemical polymerization, galvanostatic, polypyrrole

INTRODUCTION

In recent years, conducting polymers have been extensively studied for various technological applications [1–6]. Among the conducting

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polymers, polypyrrole (Ppy) has been widely studied because it can be easily polymerized, with ease of membrane formation, high conductivity, and chemical stability [7–13]. The Ppy can be easily synthesized by electrochemical oxidation of the monomer with formation of doped conducting films. The electrochemically deposited Ppy films are dependent on many parameters such as nature of the solvent, type of dopant, temperature, pH, and potential/current used during the electrodeposition, and so on [14–16]. Doping other materials can increase the stability of Ppy matrix and its mechanical strength. The materials, which can be doped with Ppy, are Nafion, polyvinyl alcohol, poly(methylmethacrylate), poly(styrene sulphonate), dodecylbenzene sulphonic acid, p-toluene sulphonic acid, and poly(vinyl sulphonic acid) [17–19]. It has been reported that the use of polyelectrolyte in polymerization solution with pyrrole causes an increase in growth rate, higher compactness of the synthesized film, and improved environmental stability [20–21]. The stability of polymer matrix depends on anions. The anions play an important role during the electrosynthesis. The anions are divided into three groups: (a) small inorganic anions, such as NO_3^-; (b) medium sized anions (mainly organics), such as dodecylsulphonate, p-toulenesulphonate, and (c) large polymeric anions, such as polyvinylsulphonate [22].

In general, the mobility of anions in Ppy films depends on the size of the anions; small anions have good mobility, medium anions have average or bad mobility, and large polyanions are not able to leave the Ppy film at all. The ion exchange properties and stability of polypyrrole (Ppy)-polyvinylpyrrolidone (PVP), polypyrrole (Ppy)-polyvinyl alcohol (PVA), and polypyrrole (Ppy)-polystyrene sulphonate (PSS) composites have been studied by some authors [22–23]. However, it is still important to find high-quality polymers and effective dopants showing their desirable properties.

The present work systematically studied the effect of dopants PVS, pTS, and DBS on the electrical conductivity, environmental stability, surface morphology, and optical properties of Ppy films synthesized by electrochemical polymerization. The synthesized composite films were characterized using galvanostatic electrochemical technique, electrical conductivity, UV-Visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

EXPERIMENTAL

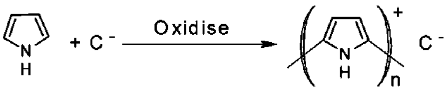
The electrochemical deposition of polypyrrole was carried out by using a galvanostatic technique at room temperature (27°C) in a one-compartment, three-electrode glass cell. ITO coated glass plate was used as a working electrode, platinum foil as a counter electrode, and Ag/AgCl as a reference electrode. The electrolyte solution was prepared in deionized water with 0.1 M pyrrole (98%) (Spectrochem), which was first distilled and kept refrigerated until use. The dopants, 0.1 M DBS, 0.1 M pTS (Loba Chemie) and 0.025 M PVS (Aldrich), were used. The applied current density, 1 mA/cm^2, and pH 3.0 were kept constant during the synthesis of the composite films. After synthesis the polymer coated electrodes were rinsed thoroughly in deionized water, dried in cold air and then used for subsequent characterization.

The synthesized composite films were subjected to characterization by galvanostatic electrochemical technique, electrical conductivity measured by Keithley 6514 Electrometer, FTIR spectra obtained by using Shimadzu FTIR-8400 series, using KBr pellets in the region 350–4000 cm^{-1}, UV spectra recorded using UV Visible 1601 spectrophotometer, Shimadzu in the range of 400–1100 nm, and scanning electron micrographs recorded, using JEOL JSM-6360A SEM machine.

RESULTS AND DISCUSSION

The conducting Ppy film can be electrochemically synthesized according to the following (Scheme 1) reaction:

The oxidation of pyrrole yields a charged polymer film with incorporated anions (Scheme 1). The pyrrole units have positive charges, which are balanced by anions that are incorporated into the polymer matrix during polymerization. In order to synthesize high-quality polymer films by electrochemical polymerization, the authors first studied the effect of electrolyte and monomer concentration, current density and pH on the electrical, optical and morphological properties of Ppy-PVS, Ppy-pTS, and Ppy-DBS composite films. It was found that 0.1 M concentration of pyrrole, 0.1 M of DBS, 0.1 M of pTS, and 0.025 M of PVS with 1 mA/cm^2 current density at pH 3.0 resulted in high conductivity with very good surface morphology. The potential time curves of the galvanostatically synthesized composite films Ppy-PVS, Ppy-pTS, and Ppy-DBS are shown in Figure 1. In fact, the behavior of the galvanostatic synthesis overshoot during the first few seconds probably indicates difficult formation of dimers and



SCHEME 1 Polymerization reaction of pyrrole in the presence of C$^-$ as the counterion, which may be the PVS, pTS, or DBS.

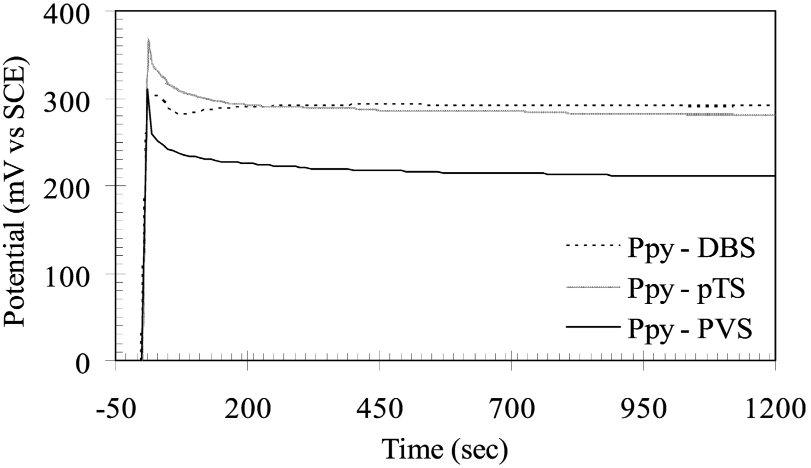


FIGURE 1 Potential-time curve of various composite films for 3.0 pH, 1 mA/cm^{-2} current density and $T = 27°C$.

oligomers. After this, the potential remains constant, suggesting that building up of the film proceeds according to the same reaction along the full thickness of the polymer. The authors have recorded the lowest polymerization potential for composite Ppy-PVS as compared to the other two composites Ppy-pTS and Ppy-DBS and follows the order Ppy-PVS > Ppy-pTS > Ppy-DBS. It has been reported that the transport of anions in the polymer body during oxidation or reduction depends on the anion species. Smaller anions are emitted from the polymer in the oxidation state by reduction [24] whereas larger size anions stick to the polymer even during a vigorous reduction process [25]. Therefore, the larger anion size of PVS causes to enhance the growth rate, compactness, and ultimately the stability of polymer matrix. The pTS and DBS (medium anion size) are less stable within the polymer matrix as compared with PVS. This can be confirmed from surface morphology. The synthesized composite film Ppy-PVS plays a unique role as a charge controllable membrane in which the fixed charges are controlled electrochemically by an internal electronic state. The electrical conductivity of the synthesized composite films Ppy-PVS, Ppy-pTS, and Ppy-DBS is 2.412×10^{-3} S/cm, 1.272×10^{-3} S/cm and 1.244×10^{-3} S/cm, respectively, as illustrated in Table 1. It shows very good resemblance with polymerization potential recorded during polymerization. The composite Ppy-PVS is advantageous for immobilization of biocomponents and useful in the electrostatic rejection of anions [26]. The sulphonate ions of the

TABLE 1 Relation between the Electrical Conductivity and the Plateau Potential of Different Composite Films

Sr No.	Composite film	Plateau potential (mV)	Electrical conductivity (S/cm)
1	Ppy-PVS	211	2.412×10^{-3}
2	Ppy-pTS	282	1.272×10^{-3}
3	Ppy-DBS	291	1.244×10^{-3}

Ppy-PVS composite films provide a charged surface for electrostatic interactions between enzymes and the surface [27].

UV-Vis spectra of synthesized Ppy films are shown in Figure 2. In case of Ppy-PVS, the spectrum shows stronger absorption at around 960 nm (bipolaron) and weaker absorption at around 460 nm (π-π^*) than those with Ppy-pTS and Ppy-DBS. The stronger absorption bands are assigned as bipolaron charge transfer bands and indicate high conductivity for the composite Ppy-PVS followed by Ppy-pTS and Ppy-DBS, which is consistent with the polymerization potential. This indicates that higher sulphonate group introduction to the polymer system may induce more doping of the Ppy backbone because the sulphonate group can be anionically charged so that it can stabilize the doped state of the Ppy more effectively, leading to the highest conductivity among this series. The absorption spectra observed for synthesized composite films are in good agreement with the earlier reported work [28–29].

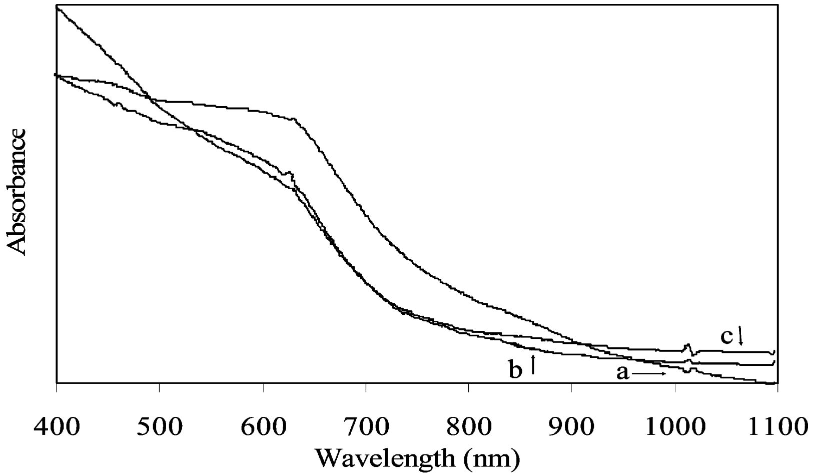


FIGURE 2 UV-Vis. spectra of composite film (a) Ppy-DBS, (b) Ppy-pTS, and (c) Ppy-PVS.

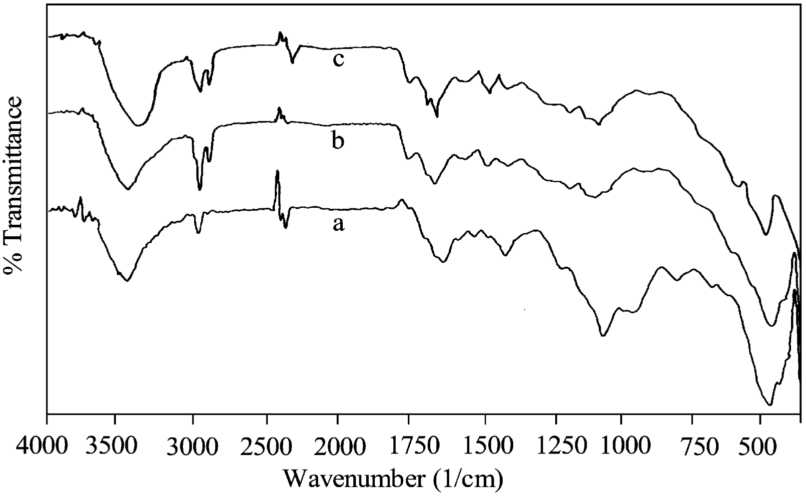


FIGURE 3 FTIR spectra of composite film (a) Ppy-DBS, (b) Ppy-pTS, and (c) Ppy-PVS.

The FTIR spectra of synthesized composites Ppy-PVS, Ppy-pTS, and Ppy-DBS are shown in Figure 3. All three spectra show a broad peak at 3430 cm^{-1} corresponding to N−H stretching. The incorporation of the counter anion in the polymer is evidenced by the peaks at 2924 and 2850 cm^{-1} assigned to aliphatic $-CH_3$ and $-CH_2$, related to the sulphonate anion. Further evidence of the presence of this anion in the polymer film is revealed by peaks at 1380 and 1600–1640 cm^{-1}, which may be assigned to SO_2 stretch in sulphonates. The vibration bands are observed at 1728–1784 cm^{-1} (C=O), 1527–1548 cm^{-1} (N−H bending). These bands correspond to the characteristic bands for Ppy; it shows very good agreement with earlier reported work [30–32]. Thus, the FTIR spectral results confirm the formation of polypyrrole.

The scanning electron micrographs submitted to the editor, but not shown here of synthesized composites films Ppy-PVS, Ppy-pTS, and Ppy-DBS show that the surface morphology is more uniform, with globular or cauliflower-like structure, in the case of Ppy-PVS composite film than those of Ppy-DBS and Ppy-pTS. It is in very good agreement with earlier reported work [33–36].

CONCLUSION

The electrochemical, electrical, optical, and morphological properties of composites films Ppy-PVS, Ppy-pTS, and Ppy-DBS (at 1 mA/cm^2

current density and 3.0 pH) have been successfully studied. The characterization study reveals that the composite Ppy-PVS films provide good and stable polymer matrix as compared with Ppy-pTS and Ppy-DBS. The Ppy-PVS composite film shows the highest conductivity 2.412×10^{-3} S/cm with lower polymerization potential and higher absorption peak (bipolaron) around 960 nm in UV spectrum. The FTIR spectrum of composite Ppy-PVS film confirms the presence of organic groups as well as occurrence N–H stretching. The surface morphology of the Ppy-PVS films indicates the formation of uniform and globular polymer matrix, which is suitable for immobilization of biocomponents.

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