Thin conducting polypyrrole film on insulating surface and its applications

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Abstract. An electrically conductive plastic material was obtained by the polymerization of pyrrole on insulating polymeric materials and nylon cloth impregnated with the oxidant by vapour phase technique, resulting in a uniform, smooth and adherent coating of conducting polymer having a surface resistance ranging from $200\ \Omega/\square$ to $20\ \text{k}\Omega/\square$, which makes it suitable for applications as an antistatic material.

Keywords. Polypyrrole; conducting composite; antistatic material.

1. Introduction

Conjugated conducting polymers such as polyacetylene, polypyrrole, polythiophene and polyaniline have been the subject of intensive research due to their peculiar electronic properties and for their use in optoelectronic devices (Paul *et al* 1985), display devices (Kitani *et al* 1986; Kobayashi *et al* 1989) and as an active electrode material in primary and secondary batteries (MacDiarmid *et al* 1985). The factor motivating much of the work on the synthesis of conducting polymers is the need to find newer materials having a wider range of properties such as flexibility and processibility of polymer and conductivity of that of metals to suit many technological applications. The interest in polyacetylene stems from its flexibility and high electrical conductivity when doped with suitable dopants (Chiang *et al* 1978). However, the intrinsic mechanical properties of polyacetylene are degraded slowly on exposure to oxygen making it brittle and hence has little technological applications. The problem of unprocessibility of these conductive polymers has been tackled by synthesizing copolymer. For example, polybenzene is unprocessable but its copolymer with naphthalene is melt and solution processible (Trivedi and Srinivasan 1988). Similarly the polyaniline has been made soluble by doping with bulky aromatic protonic acids (Dhawan and Trivedi 1990, 1991, 1993) which is suitable for obtaining thin film conducting devices. The present work aims at obtaining an adherent conducting film on insulating surfaces having a reasonably good conductivity with thermal stability. These conducting polymer coated insulating plastics have valuable applications for the shielding of electromagnetic interference in electronic equipment and for electrostatic charge dissipation and for storing of electronic components. These conductive plastics can be a better substitute for existing conducting composites consisting of insulating polymers with very high loadings of metallic fillers such as Ag, Ni, Cu, Al powders or carbon black where uniform conductivity of the composite is a major problem mainly due to the heterogeneity of the system, which is inherent because these metallic composites are prepared by mechanical mixing of the polymers with metals or C black. There have been many efforts worldwide to improve the

mechanical properties of electrically conducting polypyrrole with the aim of utilizing this polymer in many growing technologies. There are numerous reports of electrochemically and chemically prepared composites with polyvinyl alcohol (PVA), polyvinyl chloride (PVC), methylcellulose, polyethylene etc. as host matrix and polypyrrole as conducting component (Lefrant 1992; Dubois *et al* 1989; Yosomiya *et al* 1986; Lindsey and Stret 1984; DePaoli *et al* 1985; Bjorklund and Liedberg 1986; Wong 1992). Similarly efforts have also been directed at obtaining a conducting polyaniline coating on fabrics (Trivedi and Dhawan 1991, 1992, 1993) with the sole aim of utilizing these materials for EMI shielding.

This paper describes a commercially viable process for the polymerization of pyrrole on insulating surfaces like nylon, terylene and glass fabric and polymer matrix like polyvinyl alcohol (PVA) by vapour phase polymerization which can find industrial applications as antistatic material like that of metal coated insulating surfaces and carbon fibre.

2. Experimental

Pyrrole was distilled before use. All other chemicals were of AnalaR grade. The impregnation of insulating polymer surfaces such as polyester film, polyvinyl alcohol film, glass fibre, etc. was carried out using decimolar solution of ferric chloride in diethyl ether (b. pt 34–36°C) containing requisite amount of HCl to obtain a light green solution of FeCl_4^- . This green solution was sprayed on the surface of the insulating material in a closed chamber to give a uniform coverage (4–7 nm thick) of ferric chloride.

These sensitized surfaces were then exposed to pyrrole (0.1 mol) in diethyl ether under a mild vacuum (300 mm). Pyrrole on evaporation gave a uniform blue film of conducting polypyrrole. The conductivity of the polypyrrole film on the surface depends upon the exposure time.

Any excess of ferric chloride was removed from the conducting film by washing them with either benzene, diethyl ether or methylene chloride containing 2% hydrochloric acid. The methodology of obtaining conducting polypyrrole film on insulating surfaces is given below.

The cyclic voltammetric response of the composite film on the electrode surface (Pt, 0.25 cm²) was recorded on a Tacussel Bipad potentiostat coupled with PARC 175 programmer.

The electrical resistivity ($\Omega/\square$) of these surfaces was determined by two-probe method by measuring the resistance by placing two copper foils one inch apart. The tensile strength of the composite was determined by Instron equipment. Scanning electron micrographs were obtained using a JEOL SEM.

The static charge of the insulating fabric and conducting fabric was measured using Para Electronics static charge meter (SCM 1) mounted on an energy stand with a distance of 2.5 cm from energy dish whose capacitance at this distance was 23 pF.

The static charge in coulombs was calculated using the following relationship,

$$Q = C \cdot V,$$

where C is the standard capacitance of the base plate and V the voltage indicated on the static charge meter.

The static energy E was calculated using the relationship,

$$E = 1/2 CV^2 \text{ (in joules).}$$

3. Results and discussion

Oxidation of pyrrole to conducting polypyrrole by ferric salts represents a versatile alternative to the usual anodic oxidation. The present procedure of obtaining polypyrrole coating on plastic and on fabric by the oxidation of pyrrole with actively generated FeCl_4^- provides a novel method of getting highly conductive film.

The electrochemical stoichiometry of the pyrrole polymerization suggests a mechanism which involves a combination step of two radical cations. In the present case, these cations of intermediate stability get adsorbed on the surface of insulating polymeric surface and these cations in a further radical coupling reaction lead to the formation of stable and adherent electrically conductive film ($1\text{--}10\ \mu$). The polymerization mechanism can be written as given below.

The results of the elemental analysis of polypyrrole grafted on fabric (after scraping from the surface) are given in table 1.

Table 1. Elemental analysis of polypyrrole grafted on fabric.

PPy	C	H	N	Cl
Calculated (%)	64.9	4.6	18.9	11.5
Found (%)	64.3	4.9	19.0	11.6

The elemental analysis data showed that the composition of polypyrrole on fabrics and on polymeric surfaces and of electrochemically grown polymer is almost identical.

The overall stoichiometry of the polymerization indicates the following reaction path:

The cyclic voltammograms of the electrochemically deposited polypyrrole from aqueous KCl medium and of chemically grown PPy on PVA film on platinum substrate (as the direct CV response of the PPy-PVA composite film was marred by broad peak) were recorded under identical conditions (figure 1). It is interesting to observe that electrochemically grown PPy film gave a cyclic voltammogram with E_{pa} at 0.17 V vs SCE in KCl medium while the chemically grown PPy-PVA film on Pt substrate shows a shift in the anodic peak potential value to 0.4 V vs SCE which implies that orientation of the innermost polypyrrole-polyvinyl alcohol composite film is different than electrochemically grown polypyrrole film because a film directly in contact with electrode surface is responsible for the electron transfer across the electrolyte. Similar type of behaviour was observed for the polypyrrole grown on

Figure 1. Cyclic voltammograms of (a) PVA film, (b) PVA-PPy composite film, and (c) PPy film on Pt electrode in KCl medium vs saturated calomel electrode (SCE) at a scan rate of 50 mV/sec.

Figure 2. Effect of polymerization time on the surface resistance ($\Omega/\square$) of the grafted substrate.

polyvinyl alcohol film electrochemically. However, with these experiments it is difficult to pinpoint the exact orientation of polypyrrole with polyvinyl alcohol.

In the present study it has also been observed that the rate of formation of conducting polypyrrole, PPy, on the insulating surface depends not only on the concentration of the monomer but also on the activity of the freshly prepared FeCl_4^- . On the FeCl_4^- impregnated surfaces, the polymerization is complete within 30 min to yield blue to black PPy film covered surfaces. Figure 2 shows the variation of the resistivity of the PPy grafted substrate at room temperature with polymerization time. The resistivity of the PPy grafted substrate is minimum at 30 min and gradually decreases with time. This time limit is arrived at by carrying out series of experiments by measuring the resistivity of the polypyrrole grafted substrates at various time intervals.

Principal absorption bands observed in the FTIR spectra of PVA film polypyrrole and PPy-PVA composite film are given in table 2.

All the characteristic IR absorption bands due to polypyrrole are observed in PPy-PVA composite film with a slight shift in the position of absorption band. For example, a band at 3400 cm^{-1} due to $-\text{NH}$ str in PPy has shifted to 3412 cm^{-1} and 1529 cm^{-1} band due to $\text{C}=\text{C}$ str has been observed at 1545 cm^{-1} (figure 3). Likewise the characteristic bands of PVA at 1652 and 921 cm^{-1} are observed at 1634 and 920 cm^{-1} in PVA-PPy composite. The band at 3330 cm^{-1} in PVA is not observed in the composite probably due to some type of interactions of PVA with PPy through H-bonding. The IR absorption bands in PVA- FeCl_3 are observed at 3280 , 2974 , 1710 , 1650 , 1450 , 1320 , 1120 , 910 and 840 cm^{-1} . The bands at 1710 and 1320 cm^{-1} are possibly due to complexation of Fe^{3+} with PVA. However, on incorporation of polypyrrole in this FeCl_3 -PVA film these extra bands at 1710 and 1320 cm^{-1} vanish indicating that these bands in FeCl_3 -PVA are not due to any degradation of PVA matrix.

The UV-visible spectrum of a thin composite film (figure 4) reveals broad absorption bands at 423 and 659 nm . Since polyvinyl alcohol is transparent in this region (figure 4, curve a) and PVA- FeCl_3 film gives an absorption band at 390 nm (figure 4, curve b), these bands can be assigned due to polypyrrole. The optical absorption spectrum of PPy film shows two broad bands at ca 1.0 and 3.0 eV which were attributed to an interband transition and to the bipolaronic bands. The origin of the shift in the

Table 2. Assignment of IR bands.

PVA film	Polypyrrole	PPy-PVA composite
3330 (-OH str), 2974 (-CH)	3400 (-NH str)	3412 (-NH str)
1652 (>CH-OH) 1422 (-CH δ ip), 1094 (C-O str)	3100 (C-H str), 1529 (C=C and C-C str)	2925 and 2856 (-CH) 1634 (>CH-OH)
921 (-CH op)	1445 (C-N str)	1545 (C=C and C-C str)
	1295 (C-H and N-H def)	1461 (C-N str)
	1242 (C-N str and C-H def) 1050 (-CH def)	1297 (C-H and N-H def) 1113 (C-O str) 920 (-CH op)

Figure 3. FTIR spectrum of PVA-PPy composite film. **Figure 4.** UV-visible spectra of (a) PVA film, (b) PVA-FeCl₃ film, and (c) PVA-PPy composite film.

absorption from 1.0 eV to 659 nm (≈ 1.8 eV) of the composite remains to be determined and may be possibly due to polymer segments of different chain length grown on PVA film.

SEM micrograph of the polyvinyl alcohol–polypyrrole composite film shows a globular structure (figure 5) with a morphology similar to that of electrochemically deposited polypyrrole film with the difference that electrochemically grown PPy morphology is more uniform (figure 5e). However, featureless morphology is observed for blank polyvinyl alcohol film (figure 5a). Figure 5d shows the SEM of polypyrrole grafted on terylene fibre which indicates almost regular deposit of the polypyrrole which makes it suitable as a good antistatic material.

The mechanical properties of the PPy–PVA composite film are far better than those of the PPy film prepared either by electrochemical or chemical methods.

Figure 5. For caption, see p. 378.

Figure 5. SEM of (a) PVA film, (b) PVA–PPy composite film, (c) blank terylene cloth, (d) PPy deposited on terylene cloth by vapour phase technique, and (e) electrochemically deposited polypyrrole.

Table 3. Mechanical properties of the composite film.

Composite composition	Tensile strength (kg/cm ²)	Extension at break (%)	Resistance (Ω/□)
PVA	246.6	194.7	3.0×10^7
PVA (10% glycerol)	62.2	486.1	0.8×10^6
PVA:FeCl ₃			0.3×10^5
PVA:PPy	78	376.5	200

The composite films are flexible and can be creased without breaking. The various mechanical properties of PVA and PVA–PPy composite film are recorded in table 3.

The thermogravimetric analysis data for the conductive PPy composite (figure 6) recorded on a Perkin-Elmer 7 series thermal analysis system show that the composite

Figure 6. TGA curve of PPy composite.

is stable up to 150°C and after that a continuous weight loss is observed up to 450°C implying the breakdown of the host polymer PVA matrix. The DTA curve of the composite also shows first inflection at 205°C followed by major transformations at 296°C.

There is a complete dissipation of the electrostatic charge on employing the polypyrrole coated fabrics, as measured by the static charge meter SCM 1 (capacitance 23 pF) mounted on an energy stand at a distance of 2.5 cm from energy dish.

4. Conclusions

The present study indicates that it is possible to obtain a uniform and highly conducting composite by impregnating the insulating polymeric surfaces with active FeCl_4^- and exposing it with the monomer by vapour phase deposition. The polypyrrole coated fabric and PPy-PVA composite can find applications as antistatic material for electrostatic charge dissipation.

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