Electroanalytical Studies on Electrically Conducting Polyaniline:Polyethyleneterephthalate Composite Films

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ABSTRACT: Polyaniline (PANI):polyethyleneterephthalate (PET) composite was prepared by chemical polymerization of aniline diffused in the PET matrix. Thus prepared composite films were characterized by fourier-transform infrared spectroscopy and scanning electron microscopy and their electrical properties and the thermo-oxidative stability was studied by thermogravimetry and differential thermal analysis. The stability in terms of DC electrical conductivity retention was studied in an oxidative environment by two slightly different techniques viz. isothermal and cyclic techniques. DC electrical conductivity of composite films was found to be stable up to 90°C for most of the composites under ambient conditions. The composite films were employed as cathode material in secondary cells containing 1*M* $ZnCl_2$ solution. The studies were carried out on the charge/discharge cycles under a constant current load 140 mA. The composite films showed similar behavior in electrolyte solution and cell response is reversible. To determine the diffusion coefficient for the chloride ions diffusion into the composite films electrochemically, galvanostatic pulse method was used. The diffusion coefficient was estimated to be $\sim 3.28 \times 10^{-12}$ cm^2 s^{-1}. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1366–1375, 2010

Key words: polyaniline:polyethyleneterephthalate composites; electrical conductivity; diffusion coefficients

INTRODUCTION

The continuously growing interest in conducting polymers is due to their potential application in various fields such as batteries, sensor, and electrochromic display because polymers are lightweight, processible, and electrically conductive. The main characteristics of Li-PANI secondary batteries compared with conventionally Li secondary battery were the longer cyclic life, less self discharge rate, low manufacturing cost and shape flexibility. Since the specific capacity of Li-conducting polymer secondary batteries is small, these are used as power source and for small electronic devices.

Many investigations have been concerned with the possibility of applying polyaniline to solid-state rechargeable Li-ion battery as a positive material.[1,4] It was found that PANI/PEO-$LiClO_4$ polymer electrolyte in a solid-state lithium battery exhibited a good electrochemical reversibility and cyclability at 50–80°C.[2] Barthet et al.[5] prepared polyaniline composite with PEO-based polymer electrolyte as a binder for fabrication of a solid-state secondary lithium battery. Recently, Chen et al.[6] prepared a bilayer film by employing polyaniline powder as a positive active material and plasticized PEO-$LiClO_4$ as a binder and polymer electrolyte. It was found that the contacting surface area between PANI and polymer electrolyte was greatly improved by using polymer electrolyte as the binder.

In this work, we have used cathode active material of PANI:PET composite films for self constructed rechargeable cell, a PANI composite film obtained by the chemical polymerization of aniline in the PET matrix. The several characterization techniques that electrochemical properties of PANI are improve in composite systems due to the apparent synergism between the host matrix and the polymer.[7,9] We are proposing the use of zinc chloride as electrolyte, with the composite films of PANI:PET as cathode material in open circuit cell. The conductive composite of PET fibers and fabrics are used as protective materials against electromagnetic interference, antistatic materials, antidust, and antibacterial cloths.[10] The PET is a cheap and easily available engineering polymer of good mechanical properties. It also has good environmental stability and resistance to chemicals. Therefore, it is used to incorporate the strength incorporation of PET on electrical properties of PANI was studies.

EXPERIMENTAL

Materials and instruments

The materials used were aniline (99%, CDH, India), polyethyleneterephthalate (Century de'Smat Co.,

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India), hydrochloric acid (35%, E. Merck, India), potassium persulphate (98%, CDH), and ammonia solution (Qualigens, India). Electrically operated automatic presser machine (TSI PFA-15) and digital micro voltmeter (DMV 001 Roorke, India). Aniline was doubly distilled prior to use. The PET films were washed with toluene and dried in an air oven at 60°C for 12 h before use whereas all other materials were used as received.

Preparation of polyaniline: polyethyleneterephthalate composites

PET films were pressed by electrically operated automatic pressure machine the several thickness films were obtained 75, 100, and 125 μm these films were kept in doubly distilled aniline for soaking at room temperature. The films soaked in aniline were treated with potassium persulphate solution in HCl (1*M*) for 24 h to polymerize the aniline within the PET matrix. The films were taken out and washed with doubly distilled water, undoped by treatment with excess of aqueous ammonia (1*M*) and repeatedly washed with distilled water until the filtrate became neutral. The composite films were dried for 48 h at 45°C in an air oven and then stored in a desiccator for experiments.

Characterization

The fourier-transform infrared (FTIR) spectra of polyaniline and polyaniline:polyethyleneterephthalate (PANI:PET) composites were recorded by a Perkin–Elmer 1725 instrument. The scanning electron microscopy (SEM) studies were performed on a LEO-435 VP instrument to examine the surface morphology of the composites and their components. Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on the selected samples of composites by using a Perkin–Elmer (Pyris Dimond) instrument from $\sim$ 25 to 650°C at a heating rate of 10°C min^{-1} with a dry air flow rate of 200 mL min^{-1}.

Thermal stability of DC electrical conductivity retention

The DC electrical conductivity of the doped composite films was measured with increasing temperature (35–130°C) by using a four-in-line probe DC Electrical Conductivity Measuring Instrument (Scientific Equipments, Roorkee). DC Electrical conductivity (σ) was calculated using the following equations:

$$\rho = \rho_o / G_7(W/S) \quad (1)$$

$$G_7(W/S) = (2S/W)\ln 2 \quad (2)$$

$$\rho_o = (V/I)2\pi S \quad (3)$$

$$\sigma = 1/\rho \quad (4)$$

$G_7(W/S)$ is a correction divisor which is a function of thickness of the sample as well as probe-spacing where I, V, W and S are current (A), voltage (V), thickness of the film (cm), and probe spacing (cm) respectively.[11]

The isothermal stability of composites in terms of DC electrical conductivity retention was carried out on the selected samples at 50°C, 70°C, 90°C, 110°C, and 130°C in an air oven. The electrical conductivity measurements were carried out at an interval of 15 min. The thermal stability of the composites in terms of DC electrical conductivity retention was also studied by a cyclic measurement of the DC electrical conductivity on films with increasing temperature from 35 to 130°C. The measurements were repeated on same sample in this temperature range for five times at intervals of 45 min.

Set up of electrochemical cell

The positive electrode (working electrode) consisted of a PANI:PET composite film, Zn foil as a negative electrode (counter electrode) and Pt foil used as a reference electrode to monitor the potential of PANI:PET cathode during experiment. A 2 cm^2 area of each electrode was immersed in 40 mL of electrolyte solution in a glass beaker. The positive pole of 9-V battery was connected to counter electrode (Zn) foil by Teflon coated platinum wire and the negative pole of the battery was connected to the working electrode (PANI:PET composite film). And the reference electrode was connected to the digital microvoltmeter as shown in Figure 1.

Estimation of diffusion coefficient into and out of composite films

The various techniques available for ionic diffusion measurement have been discussed briefly by Crank and Park[12] and also reviews by Stannet[13] have discussed the diffusion process in great detail in relation to these polymers. The galvanostatic pulse technique has been used very successfully to estimate Li^+ ion diffusion in TiS_2 by Winn et al.[14]

In this method, a constant current pulse is passed through the equilibrated electrode material. This causes a change in the electrode potential against a standard electrode due to deposition of a quantity of ions equivalent to IP/F on the electrode surface. An amount of 10^{-10} to 10^{-8} mol of dopant (depending upon strength of pulse) was deposited on the

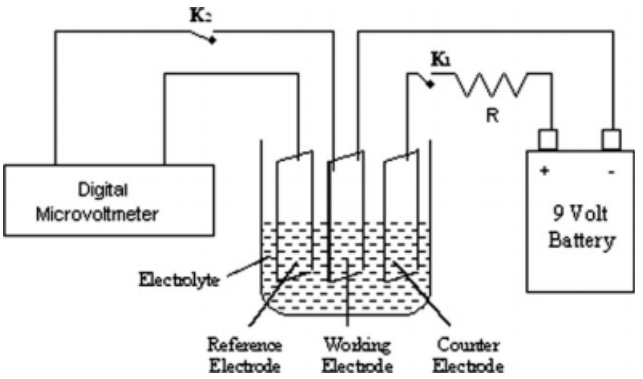

Figure 1 Set up of electrochemical cell for charging-discharging and diffusion measurements.

polymer electrode as the diffusion equation would be valid only for small changes in electrode potential i.e., small change in mole ratio (y). Clean Zn or Pt foil was used as counter electrode. Potential of this "quasi-standard" electrode may be assumed to be constant during the experiment, as equilibration does not take too long. As the deposited ions diffuse into the electrode material, the surface concentration changes and the electrode potential recovers. A plot of recovery voltage (E_t) against $t^{-1/2}$ should follow a straight line, if the diffusion behavior is governed by Fick's law. The following expression was used for the estimation of the diffusion coefficient for the ions into and out of the electrode material.

$$\exp^{((E_t-E_0)F/RT-1)} = \frac{IP}{(1-y)FAC_o\sqrt{\pi Dt}} \quad (5)$$

Plot of ($E_t - E_o$) versus $t^{-1/2}$ follows a straight line of slop,

$$S = \frac{IPRT}{(1-y)^2F^2AC_o\sqrt{\pi D}} \quad (6)$$

$$D\pi = \left(\frac{IPRT}{(1-y)^2F^2AC_oS}\right)^2 \quad (7)$$

$$D = \frac{I^2P^2R^2T^2}{(1-y)^4F^4A^2C_o{}^2S^2\pi} \text{ cm}^2\text{ s}^{-1} \quad (8)$$

RESULTS AND DISCUSSION

Preparation of composites

The method of preparation of PANI:PET composite films by soaking aniline within the PET film and then polymerizing aniline within the film is well demonstrated. A gradual increase in the weight of the composite film, as evident from Figure 2, is accompanied by the color change of the film from light green to dark green to black, which confirms the increase in polyaniline content of the composites with the increase in the period of soaking.

FTIR studies

The FTIR spectra of polyaniline and PANI:PET75, PANI:PET100 and of PANI:PET125 composites have been presented in Figure 3(a–d), respectively.

The band corresponding to out-of-plane bending vibration of C–H bond of *p*-disubstituted benzene rings appears at 824 cm^{-1}. The bands corresponding to stretching vibrations of N—B—N and N=Q=N structures appear at 1497 cm^{-1} and 1587 cm^{-1} respectively, where —B— and =Q= stand for benzenoid and quinoid moieties in the polymer. The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C—N bond appear at 1143 cm^{-1} and 1302 cm^{-1}, respectively. The FTIR spectrum supports the presence of benzenoid as well as quinoid moieties in polyaniline. The characteristic band for C=O group of the ester linkage appears at 1722 cm^{-1}. The bands at 1102 cm^{-1} and at 1262 cm^{-1} correspond to O—C— and —C(=O) —O groups in the polyethyleneterephthalate, respectively. The band corresponding to the C—H stretching of the aromatic ring of polyethyleneterephthalate

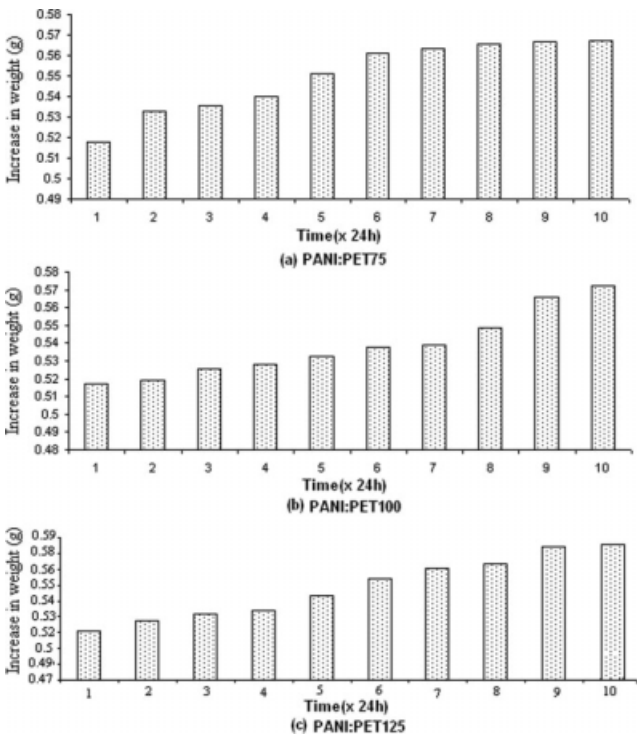

Figure 2 Increase in polyaniline content in polyaniline: polyethyleneterephthalate (PANI:PET) composites versus the time of soaking in aniline: (a) PANI:PET75; (b) PANI:-PET100; (c) PANI:PET125.

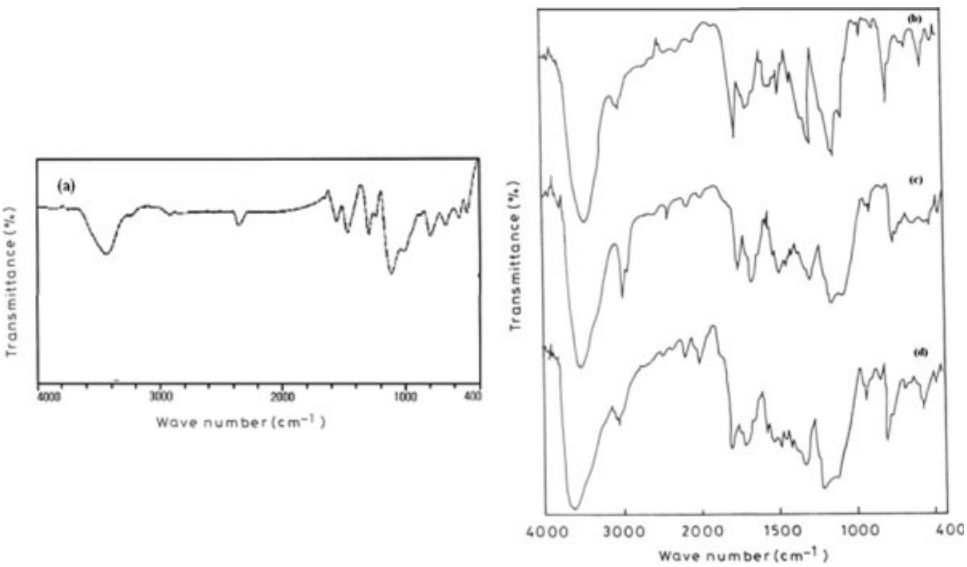

Figure 3 FTIR spectra of: (a) polyaniline; (b) PANI:PET75; (c) PANI:PET100; and (d) PANI:PET125.

appears at 3432 cm^{-1}.[15,18] As evident from the figures, all the characteristic peaks of the polyaniline and polyethyleneterephthalate are observed in the FTIR spectra of the PANI:PET composites as well.

SEM studies

Figure 4(a–c) shows the SEM photographs of PANI: PET75, PANI:PET100, and PANI:PET125 composites. Evidently, the homogeneous formation of composites of polyaniline in the PET matrix is observed.

TGA studies

In the TGA of polyaniline, the initial weight loss of around 4% by 100°C is due to the removal of moisture present in the polymer. There is extremely little weight loss (2.25%) up to 275°C, which strongly suggests that the material is thermally stable up to 275°C under oxidative conditions. The thermo-oxidative degradation starts beyond this temperature, accompanied by a massive weight loss in the polymer. A strong exothermic peak in DTA at 512°C corresponds to this degradation.

In the three PET films, the initial weight loss of around $\sim$ 1.0% up to 333°C may be attributed to the loss of moisture or other volatile materials. The films are stable up to 340°C. Then the TGA curve shows a massive weight loss on further heating, this being supported by the exothermic peaks for DTA. The weight loss is due to thermo-oxidative degradation of the PET. One small endothermic peak for DTA appears around 250°C due to the melting of the PET.

In PANI:PET composite films (PANI:PET75, PANI:PET100, and PANI:PET125) showed somewhat similar TGA/DTA thermograms (Figs. 5 and 6). The initial weight loss of $\sim$ 0.8–1.8% up to $\sim$ 135°C may be attributed to the removal of moisture or other volatile materials. A small endothermic DTA peak that appears around 250°C may be attributed to the melting of PET. Then a two-step weight loss is observed on further heating-this is due to the thermo-oxidative degradation of the polymers. The last step may be associated with the oxidative degradation exclusively of PANI, because the weight loss % in this step increases gradually with the increase in PANI content in the composites.[19,22]

Stability in terms of DC electrical conductivity retention

The PANI:PET composites were observed to show enhanced electrical conductivity on exposure to HCl, due to the charge-transfer reaction between polyaniline component of the composites and doping agents, HCl.[23,24]

$$[\mathrm{PANI(PET)}] + n\mathrm{HCl} \rightarrow [(\mathrm{PANI} - n\mathrm{H}^{+}(\mathrm{PET})][(n\mathrm{Cl}^{-})] \quad (9)$$

The electrical conductivity of the composite films was measured from 35 to 130°C and found in the semiconducting region represented in Figure 7(a–c) respectively, for PANI:PET75, PANI:PET100, and PANI:PET125 composites. All the samples, in principle, follow the Arrhenius equation for the temperature dependence of electrical conductivity up to $\sim$ 115°C. After that a deviation from the straight-line behavior in the electrical conductivity is observed. This deviation of the electrical conductivity may be

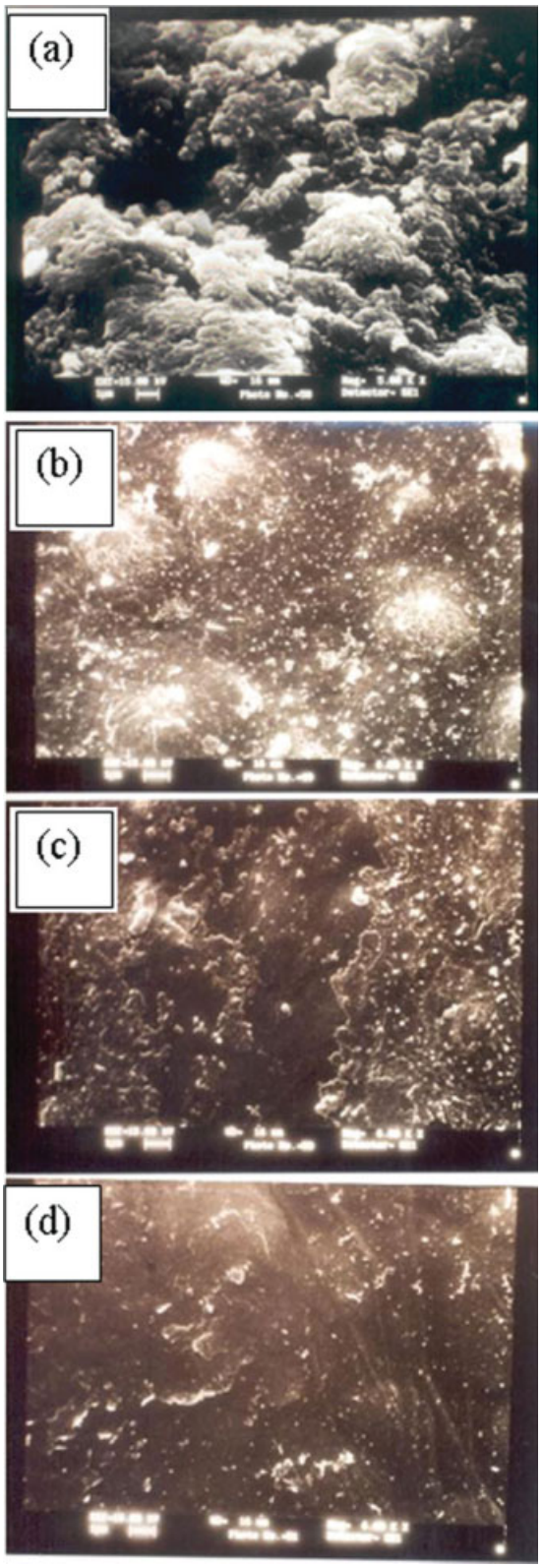

Figure 4 SEM photographs of (a) PANI, (b) PANI:PET75, (c) PANI:PET100, and (d) PANI:PET125 composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

attributed to the loss of dopant or the chemical reaction of dopant with the polyaniline component of the composites or the semiconductor to metal transition or the approaching of the glass transition of the composites. A combination of all of some of the effects may also be attributed to the decrease in electrical conductivity causing the deviation in the Arrhenius plots.

There composites have been selected to study the stability of electrical conductivity under isothermal conditions at 50°C, 70°C, 90°C, 110°C, and 130°C. The temperature of the composite films was maintained at the temperature of study and the DC electrical conductivity was measured at an interval of 15 min in the accelerated ageing experiment showing in Figure 8(a–c). It has been observed that the electrical conductivity is stable at 50°C, 70°C, and 90°C, for PANI:PET75, PANI:PET100, and PANI:PET125. That supports the fact that the composites are sufficiently stable under ambient conditions in terms of DC electrical conductivity retention below 90°C. The decrease in electrical conductivity with time of isothermal ageing at 110°C and 130°C may be attributed to the loss of dopant and the chemical reaction of dopant with polymer, i.e., degradation of polymer composites.

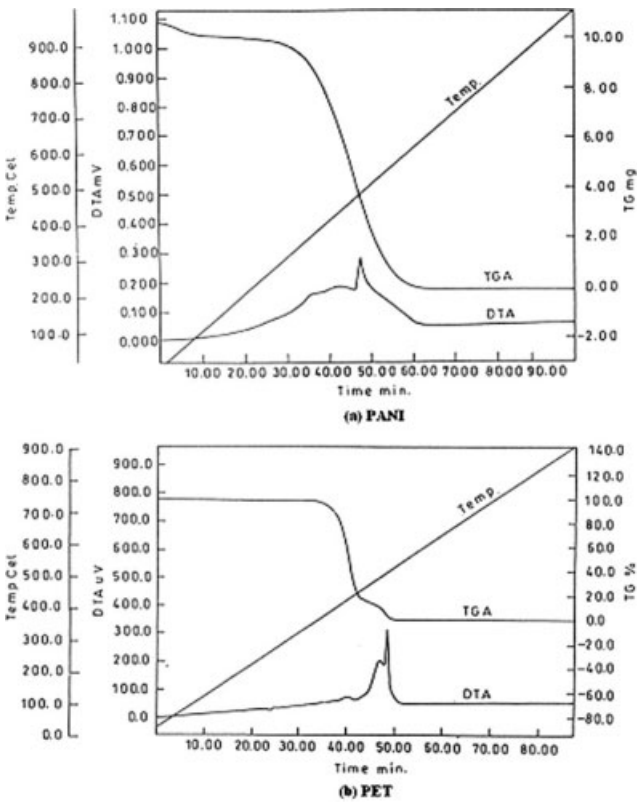

Figure 5 TGA and DTA of (a) polyaniline and (b) polyethyleneterphthalene.

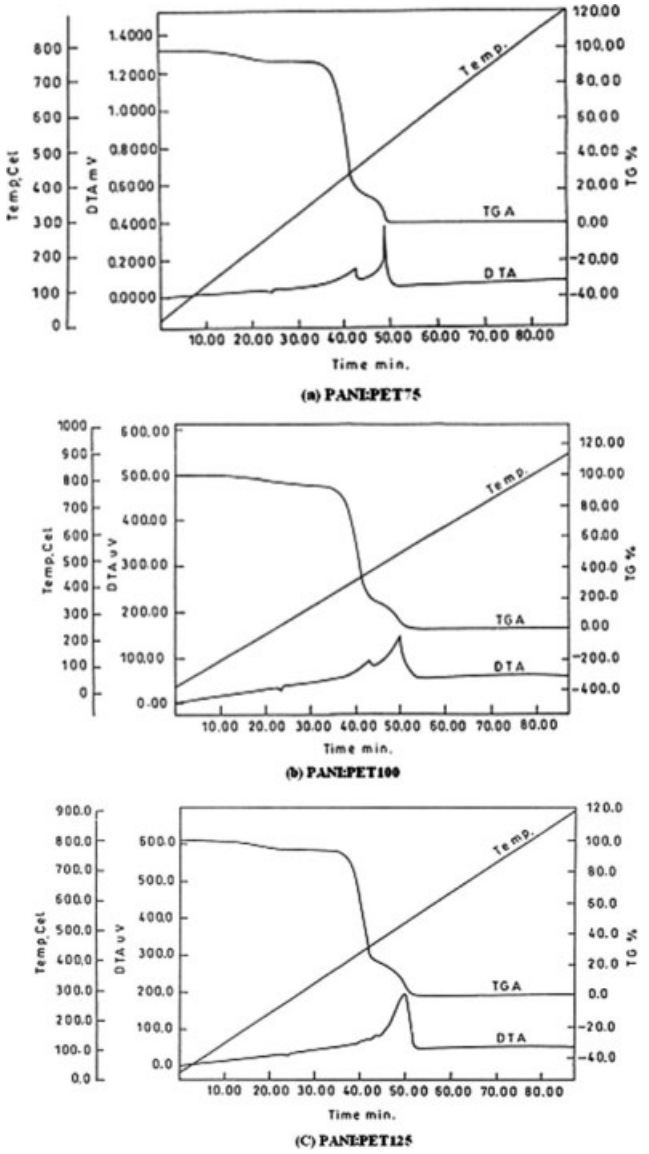

Figure 6 TGA and DTA of polyaniline:polyethyleneterphthalene composites: (a) PANI:PET75; (b) PANI:-PET100; and (c) PANI:PET125.

These three composites, PANI:PET75, PANI:-PET100, and PANI:PET125 have been selected to test the stability from 35 to 135°C in terms of the electrical conductivity retention by cyclic technique as explained in experimental. In case of PANI:PET75 the electrical conductivity decreases gradually up to cycle-5 as evident from Figure 9(a). In PANI:PET100 the electrical conductivity decreases gradually, however, a slight increase in electrical conductivity is observed in the second cycle shown in Figure 9(b). In case of PANI:PET125 composite, the electrical conductivity also decreases gradually towards cycle-5 as evident from Figure 9(c). The increase in electrical conductivity may be attributed to the annealing effect of heating on the composites, whereas the decrease may be due to the loss of dopants and the chemical reaction of dopants with polymer.

Electrochemical studies

Electrochemical cell

It consisted of Zn anode and PANI:PET75, 100, 125 composite films as cathode of working area 2 cm^2 immersed in an aqueous solution of 1*M* $ZnCl_2$ at pH 4, separately in three constructed cell. There were used for the study of the variation of charging-discharging cycles. $ZnCl_2$ electrolyte is the choice of many researchers, who use Zn as anode in various types of batteries.[25,26]

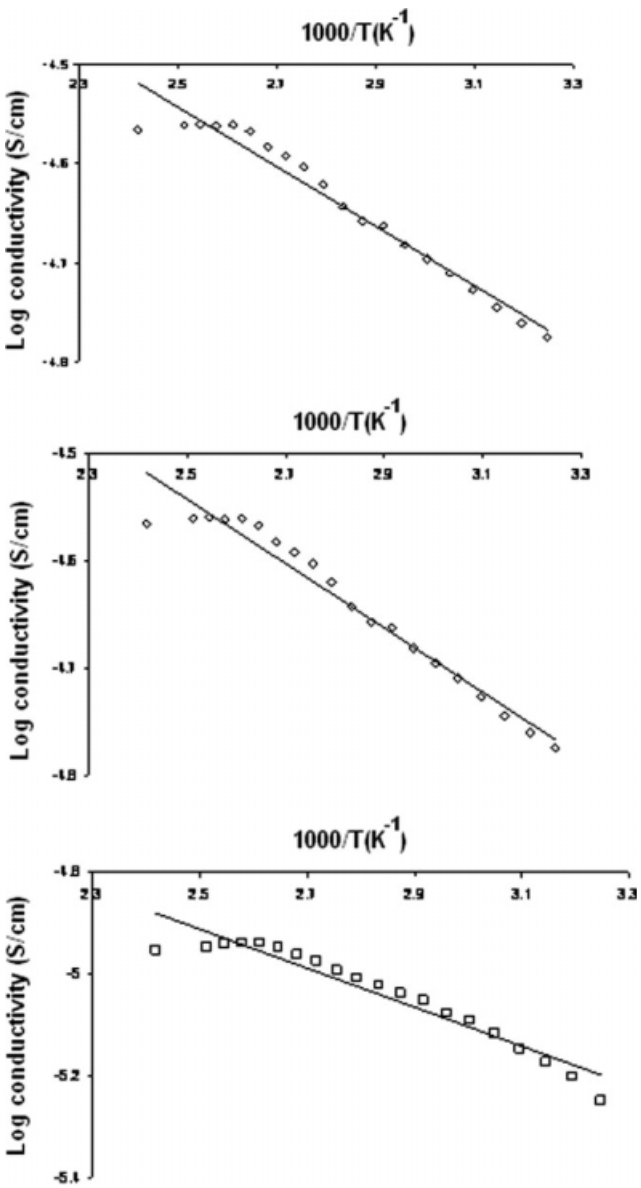

Figure 7 The temperature dependence of DC electrical conductivity of the composite films in the range of 35–130°C: (a) PANI:PET75; (b) PANI:PET100; and (c) PANI:PET125.

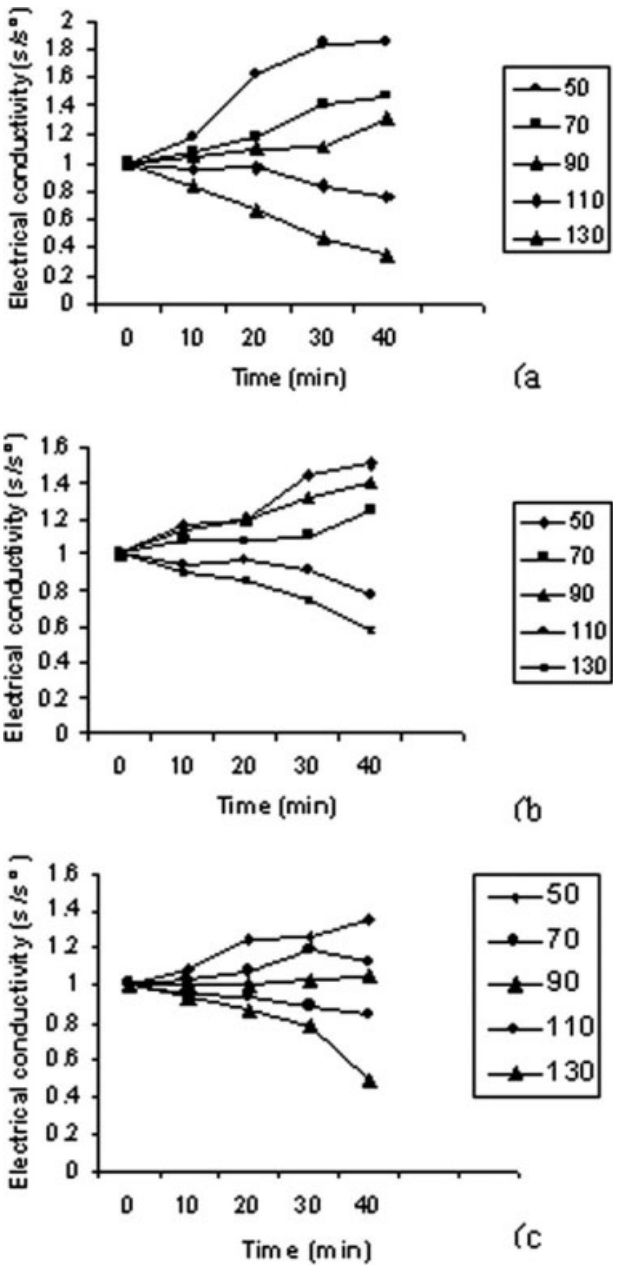

Figure 8 (a–c) DC electrical conductivity retention under isothermal conditions at 50°C, 70°C, 90°C, 110°C, and 130°C: (a) PANI:PET75; (b) PANI:PET100; and (c) PANI:PET125.

When the cell was discharged by 140 mA current using 9-V battery (When 140 mA electricity (9-V battery) passes from anode towards cathode) the voltage was first reduced sharply as shown in Figure 10 which was followed by a gradual voltage drop until the oxidized PANI form was changed to its reduced form and this discharging process completed in 60 min. The electrical conductivity by four-in-probe technique of the cathode film was found to be 2.3×10^{-4} S cm^{-1}.

On the other hand when the cell was charged again by same (140 mA electricity passes from cathode towards anode) current 140 mA, the voltage increased slowly as shown in Figure 11 and the reduced form of PANI changed to its oxidized form. There is a limit to the charging voltage. The charging process completed in 40 min and the electrical conductivity of the film was found to be 4.2×10^{-1} S cm^{-1}. Since this reaction is reversible, the cell reaction during charging is the reverse of reaction during discharging. Therefore, the over all discharging reaction of the cell is:

$$[\text{PANI} - n\text{H}^+(\text{PET})][(n\text{Cl}^-)] + n\,\text{Zn} \longrightarrow \text{PANI(PET)} + n\,\text{ZnCl}_2 \quad (10)$$

Diffusion studies on PANI:PET composite films

Diffusion of dopants into conducting composite film can also be measured electrochemically. The transport of ions into or out of a film can be followed by passing a short current pulse (5 s) to create an

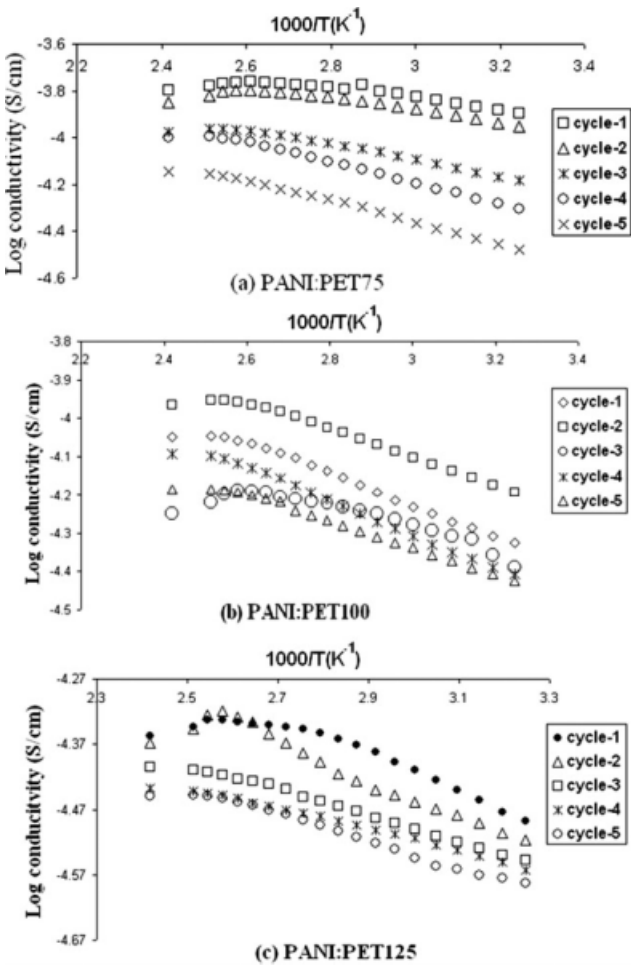

Figure 9 (a–c) DC electrical conductivity retention under cyclic thermal conditions at 50°C, 70°C, 90°C, 110°C, and 130°C: (a) PANI:PET75; (b) PANI:PET100; and (c) PANI:PET125.

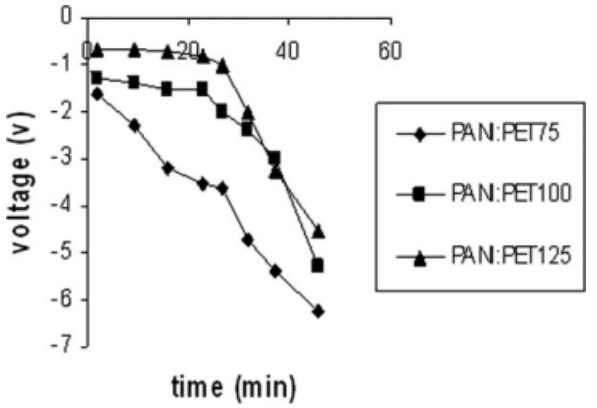

Figure 10 Electrochemical discharging of polyaniline: polyethyleneterephthalate omposite films: (a) PANI:PET75; (b) PANI:PET100; and (c) PANI:PET125 in aqueous $ZnCl_2$.

instantaneous excess, or deficit, of doping counter-ion on the surface of the film immersed in an electrolyte solution. By following the relaxation of the surface potential as the concentration of counter-ion returns to the equilibrium throughout the polymer, it is possible to determine the diffusion coefficient.[27] The diffusion coefficient was also measured as a function of doping level in the form of mol ratio of Cl^- per aniline residue. The diffusion coefficient decreases with increasing dopant ion concentration. The plot of potential versus $t^{-1/2}$ is linear and its slop yields the diffusion coefficient. The plots of the set of data from experiments on conducting composite films are given in Figure 12. Using this method, the diffusion coefficient of Cl^- into films were found to be $\sim 6.48 \times 10^{-12}$ cm^2 s^{-1}, which is lower than that previously reported values for diffusion coefficients of ions in pure polythiophene films by Foot et al.[28] as given in Table I. It may be because our conducting composite films are very compact and

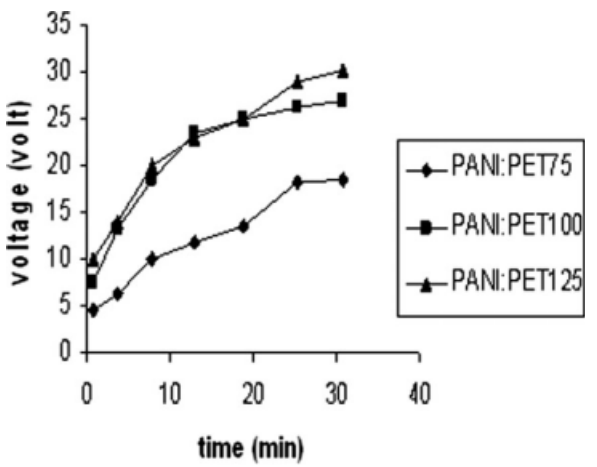

Figure 11 Electrochemical charging of polyaniline:polyethylenetrephthalate composite films: (a) PANI:PET75; (b) PANI:PET100; and (c) PANI:PET125 in $ZnCl_2$ electrolyte.

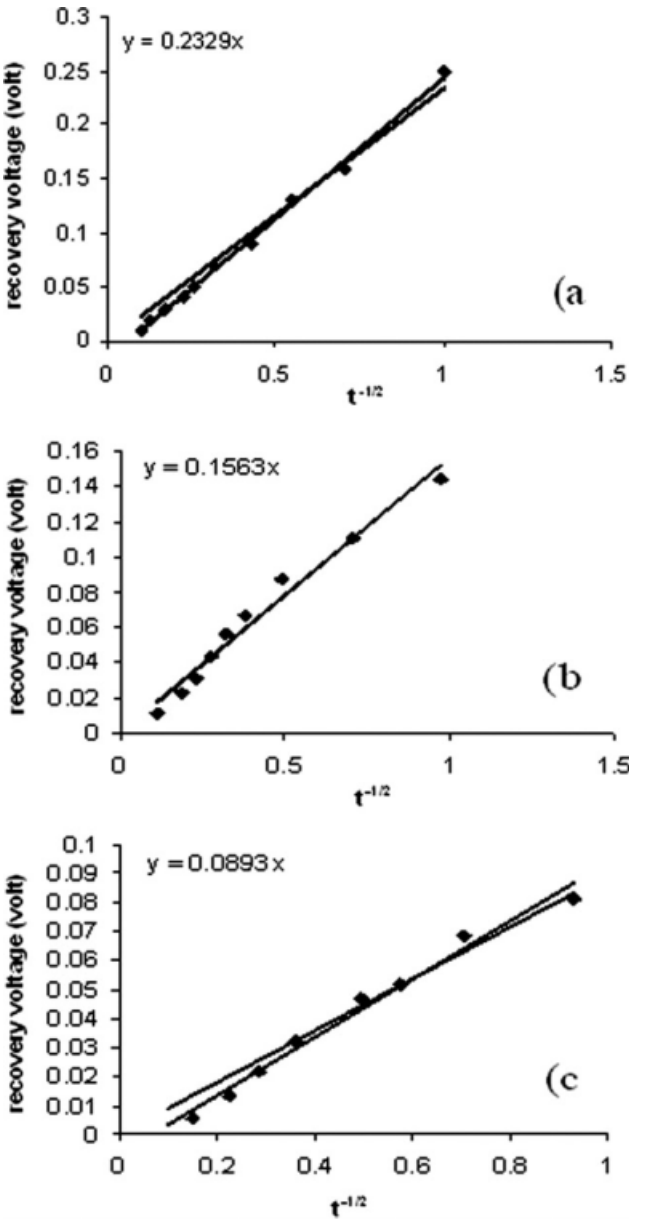

Figure 12 Diffusion behavior of (a) PET:PET75, (b) PET: PET100, and (c) PET:PET125 composite films.

made by using the insulating polymer matrix. One concern, with measurements of this type, is that undoping of a film may result either from the outward diffusion of dopant counter-ions or from the inward diffusion of polymer coions, which would then form a salt within the film. This possibility has been avoided in our composite film study by measuring with doping pulse in sample which have only been doped in one direction, either reduction or oxidation. This suggests that some of the smaller anion may also be incorporated into the film, passively as dissolved salt and then removed during the undoping step.

TABLE I
Diffusion Coefficients of Ions/Molecules in Conducting Polymers

Diffusing ion	Polymer	Measurement technique	D ($cm^2\ s^{-1}$)
BF_4^-	Polythiophene	Electrochemical	3×10^{-13}
Na^+, $ClO4^-$	Polythiophene	Electrochemical	3×10^{-13}
Li^+, AsF_6^-	Polythiophene	Electrochemical	3×10^{-13}
Na^+, SbF_6^-	Polythiophene	Electrochemical	3×10^{-13}
AsF_5	Polyacetylene	Weight uptake	3×10^{-13}
Gaseous	Polyacetylene	Weight uptake	6×10^{-13}
I_2	Polyacetylene	Weight uptake	3×10^{-12}
O_2	Polyacetylene	Electrochemical	1×10^{-14}
ClO_4^-	Polyacetylene	Electrochemical	8×10^{-14}
BF_4^-	Polyacetylene	Electrochemical	8×10^{-15}
AsF_6^-	Polyacetylene	Electrochemical	1×10^{-13}
Na^+	Polyacetylene	Electrochemical	8×10^{-13}
Cl^-	Polydicarbazole	Electrochemical	$10^{-8} - 10^{-10}$
ClO_4^-		Impedence	

CONCLUSIONS

We prepared conducting composites in the form of films by using a conducting polymer, polyaniline, in the insulating polymer matrix of polyethyleneterephthalate. The insulating polymer used in this study has good film forming properties besides other merits, whereas conducting polymer has good environmental stability and high electrical conductivity. The electrical properties of the composite materials were observed to be of good quality as almost all the composites showed a great increase in their electrical conductivity from insulator to semiconductor region after doping with hydrochloric acid. All the composite materials were successfully characterized for their electrical properties and by using FTIR, SEM, and TGA. Stability in terms of DC electrical conductivity retention was observed to be fairly good as studied by several experimental techniques. The composite formulations were found to be suitable for use in electrical and electronic applications below 90°C under ambient conditions. The films were used as electroactive cathode in the self constructed electrochemical cells to estimate the diffusion coefficient of the dopant ions into the films by galvanostatic pulse technique. The dopant diffusion rates are in the low range of $\sim 10^{-12}$ $cm^2\ s^{-1}$ these values are too low for battery application, whereas the rates of dopant diffusion values around 10^{-8} $cm^2\ s^{-1}$ are ideal for semiconductor applications. The electrochemical doping and undoping of chemically synthesized PANI:PET composite films were performed successfully for the measurement of diffusion coefficient.

The electrochemical cell model thus constructed was a wet type battery in which the electrolyte was aqueous $ZnCl_2$. The electrochemical processes of the secondary batteries involve the interconversion of chemical energy into electrical energy and vice versa. During the discharging of the cell, the anion (Cl^-) was released from the cathode, and the anode material was dissolved in the electrolyte forming cation (Zn^{2+}) and deposition of these species occurred in case of charging process. Therefore, during discharging and charging, diffusion of the anions takes place into and out of the film. Diffusion of Cl^- into the PANI:PET composite films was of Fickian type, yet the estimation study could further be improved.

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