Turk J Chem
27 (2003) , 417 – 422.
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Preparation and Characterization of Conducting Polybutadiene/Polythiophene Composites

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Received 27.11.2002

Conductive composite films of cis-1,4-polybutadiene (PBD) with polythiophene (PTh) were prepared electrochemically. Thiophene was polymerized on PBD-coated platinium electrodes. The composites with different PTh percentages showed conductivity in the order of $10^{-3}(\Omega\ \mathrm{cm})^{-1}$. The characterization of the films was performed using FTIR, scanning electron microscope and differential scanning calorimetry techniques. In order to understand the dominant transport mechanism, the temperature dependence of conductivity was investigated.

Key Words: Conducting polymers, polythiophene, polybutadiene, temperature dependence of conductivity, electrochemistry.

Introduction

The use of electrically conductive polymers has been limited in the past due to such deficiencies as poor mechanical properties and environmental and thermal instability. It has been shown that composite structure using an insulating polymer as the host matrix improves the physical and chemical properties of conductive polymers[1−10]. These composites can have practical advantages over homogeneous materials. They can demonstrate improved mechanical properties and processibility, along with a small decrease in conductivity.

We investigated[11] the conductive composites of cis-1,4-polybutadiene (PBD) with polypyrrole before. The present work covers the electrochemical synthesis and characterization of conductive composites of polythiophene (PTh) with PBD.

Experimental

PTh and PTh/PBD composites were prepared by the electrochemical polymerization of thiophene. The polymerization of thiophene was run in a three-electrode system under controlled potential conditions. The electrolysis was carried out at +1.9 V versus an Ag/Ag^+ reference electrode.

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The electrolysis system contained Pt foils as the working and counter electrodes and an Ag/Ag$^+$ electrode as the reference electrode. Acetonitrile was used as the solvent and tetrabutylammonium tetrafluoroborate was used as the electrolyte.

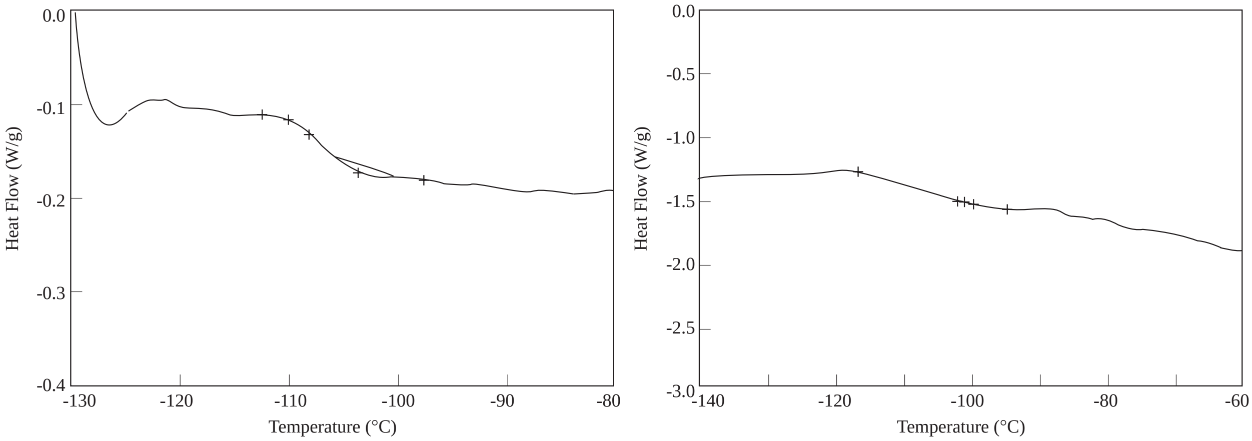
Conductivity measurements at room temperature were performed by using a four-probe technique. Films were characterized by SEM (JEOL JSM-6400 scanning microscope), DSC (TA-DSC 910S) and FTIR (Nicolet-510). The conductivity temperature variation in the range 100 K-320 K was studied by placing the sample in a closed cycle (CTI-cryogenics model 22 refrigerator) helium cryostat.

Results and Discussion

PTh/PBD composite films were produced by the electrochemical oxidation of thiophene on a PBD-coated Pt electrode. The amount of PTh deposited in the composite films was controlled by stopping the electrolysis at different time intervals. The polymerization rate was dependent on the thickness of the PBD coatings. After the polymerization had been completed, the films were washed with acetonitrile and peeled off the electrode surface. The room temperature conductivities according to the weight percent of PTh in the composites were measured. As expected, increasing the amount of the conducting polymer, PTh, increased the conductivity of composite films. This increase was in the range of 1.1-2.5 × 10^{-3} S/cm in a composition range 61%-93% of PTh.

The FTIR spectra of the PTh/PBD composite and PTh samples were analyzed. An intense band at 1080 cm^{-1} arising from the dopant ion (BF_4^-) was observed. The bands observed at 1495 cm^{-1} are due to C=C stretching, those at 1050 cm^{-1} are due to C-H in-plane bending and those at 790 cm^{-1} to the $\alpha - \alpha'$ coupling of the poly-2.5 thiophene. There is no additional peak that implies any chemical interaction between PTh and PBD.

The DSC thermograms of PBD and PTh/PBD composite films are given in Figure 1. PBD shows a glass transition temperature –107 °C. In Figure 2b, for the composite, this T$_g$ is also observed almost at the same temperature, although it is less pronounced.



a

b

Figure 1. DSC thermograms of (a) PBD and (b) PTh/PBD composite film.

The SEM micrographs of the composites show that PTh grows uniformly in PBD. PTh crests grew out of the surface of the coated electrode, producing cauliflower-like structures (Figure 2). The electrochemically prepared composite of an insulating and a conducting polymer shows differences on the solution and electrode sides of the resultant film. This may be explained by Niwa's model[12]. Under to this phenomenon, the monomer (thiophene) diffuses through the insulating film to reach the electrode and transfer an electron. The polymerization reaction naturally takes place on the electrode surface. The growing chain then diffuses back through the insulating polymer to reach the solution. The electrode side and the solution side of the films are clearly quite different. The morphology of the PTh/PBD composite film bears a similarity to the PTh film. There is no difference in the cauliflower structure of PTh because of any interaction with PBD.

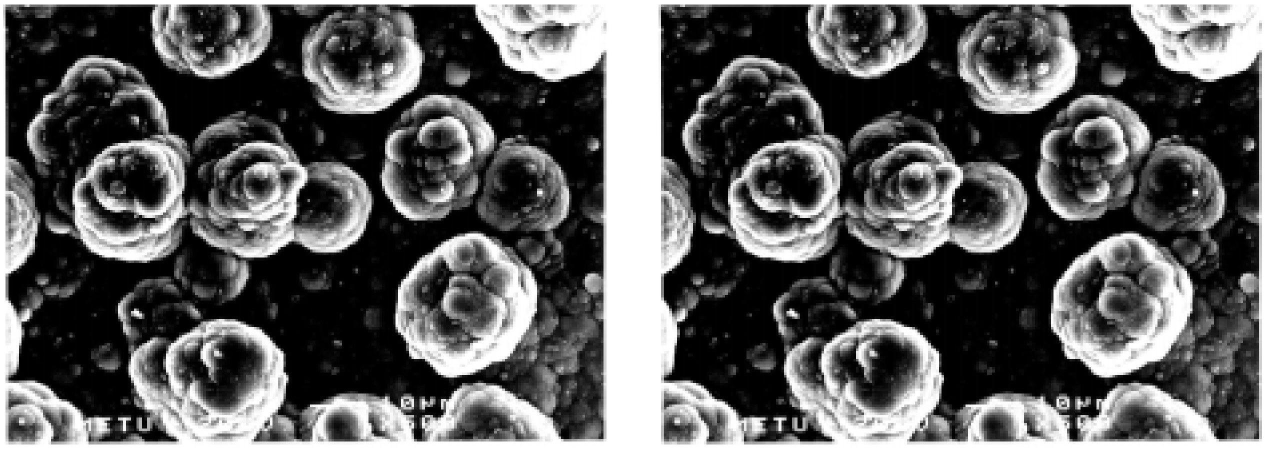


Figure 2. Scanning electron micrographs of (a) PTh/PBD composite film, solution side, (b) PTh/PBD film, electrode side.

In order to understand the dominant transport mechanism and the temperature dependence of conductivity, conductivity was measured for both films in the temperature range of 100-320 K. The variation of conductivity with temperature for both films is illustrated in Figure 3. The conductivity decreases with decreasing temperature with higher rates above 200 K, below which the σ-T variation is less pronounced (Figure 3). The conductivity variation with temperature for the PTh sample is more pronounced than that of PTh/PBD. In general, conductivity is thermally activated and varies exponentially with temperature. The conductivity temperature variations follow different slopes in different temperature regions; thus the data was analyzed as follows.

In the high temperature region, the conductivity data of the films were found to follow[13]:

$$\sigma = \sigma_0 \exp -[E_a/kT] \tag{1}$$

The semilogarithmic plots of σ-T^{-1}, illustrated in Figure 4, are linear above 220 K with conductivity activation energy E_a values of ~222 meV and ~117 meV for PTh and PTh/PBD films, respectively. These values are greater than kT, indicating that the conduction is due to the thermal excitation of charged carriers in this temperature region. Below 220 K, the conductivity activation energy values decrease to 115 meV and 35 meV for PTh and PTh/PBD films, respectively (Figure 4b). While the value 115 meV is larger than kT and assures the validity of the same approach, the value 35 meV is small, indicating that the transport mechanism for the PTh/PBD sample could not be governed by the thermal excitation transport mechanism. Thus, for PTh/PBD sample the other possible transport mechanism, hopping[9], were tested in the temperature region below 220 K. In this temperature region, the conductivity data were found to follow:

$$\sigma = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{1/4} \tag{2}$$

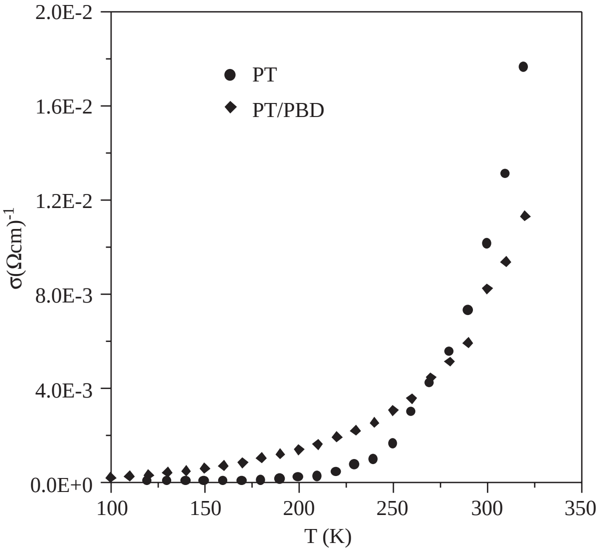


Figure 3. Temperature dependence of conductivity.

The semilogarithmic plots of $\sigma T^{1/2}$ vs $T^{-1/4}$ were linear in this temperature region, as illustrated in Figure 5, predicting the possibility of a hopping mechanism in this region.

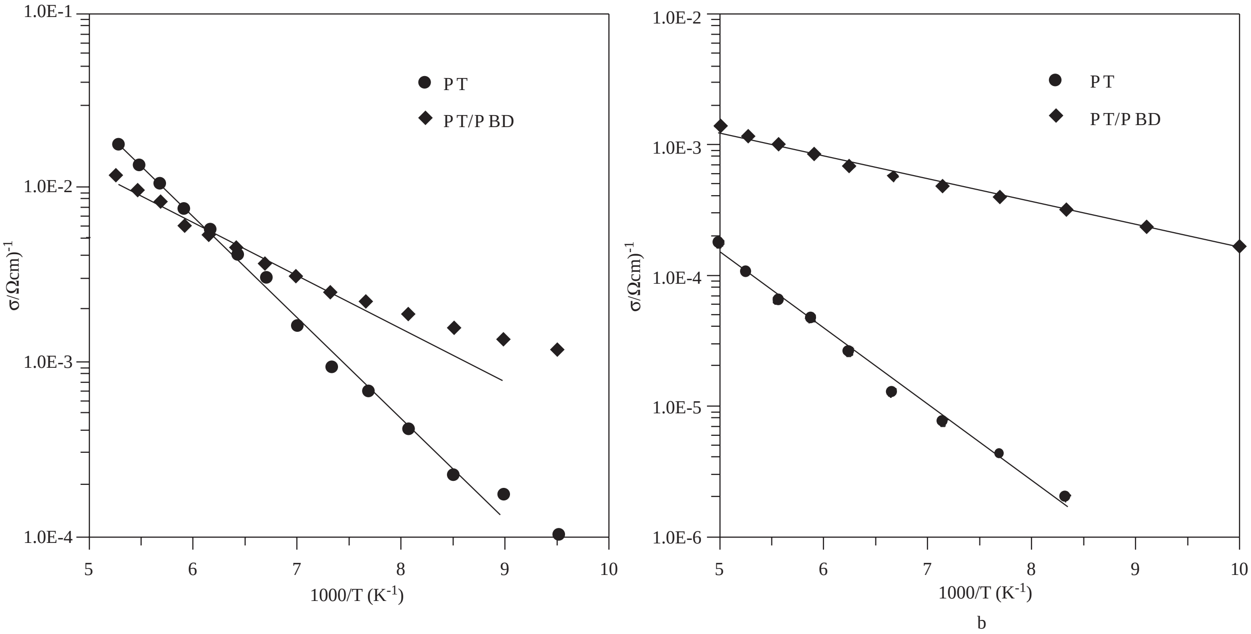


Figure 4. σ – T^{-1} variations in (a) high T region (b) low T region.

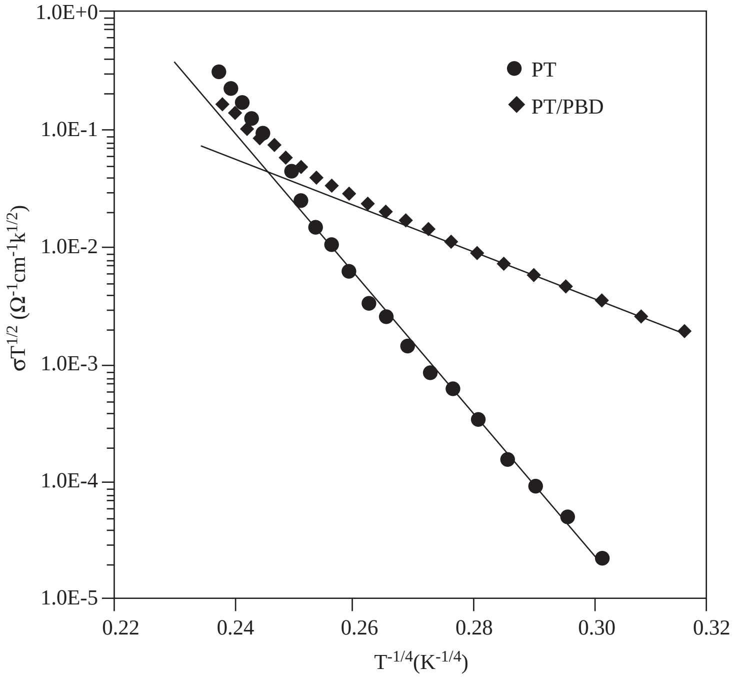


Figure 5. σ – $T^{-1/4}$ variations of PTh/PBD sample.

The above analysis shows that thermal excitation is the dominant transport mechanism in the whole temperature region for PTh films with different activation energies in two different regions (320-220 K and 210-120 K), and it is dominant for the PTh/PBD sample in the high temperature region 320-220 K. In the lower temperature region for the PTh/PBD sample, the transport is governed by the hopping mechanism.

Conclusion

PTh/PBD composite films synthesized electrochemically and characterized by FTIR, DSC and SEM techniques exhibit increasing conductivities with increasing PTh content. Analysis carried out to understand the transport mechanism implies that thermal excitation is dominant for PTh for all temperature regions, whereas the hopping mechanism is observed for the PTh/PBD composite for the lower temperature region.

Acknowledgment

The authors wish to thank Professor Çiğdem Erçelebi of the Department of Physics for her support in the conductivity measurements.

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