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Preparation of a Conducting Flexible Material from Silane Coupling Agent and Hydroxyl Terminated Polybutadiene Rubber by Hydrolysis and Condensation

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ABSTRACT

Synthesis and characterization of a flexible polymer produced from silane coupling agent (SCA) and hydroxyl terminated polybutadiene (HTPB) were performed. Mechanical properties of chemically and electrochemically prepared conducting composites synthesized from this polymer were investigated. Conductivities of the composites were also measured. Polypyrrole enhanced the mechanical properties of the chemically prepared conducting composite. Doping with iodine greatly changed the conductivity of the composite. However, the change in mechanical properties and the conductivities of the electrochemically prepared composite were not as significant when compared with the electrochemically prepared polypyrrole. Among the composites, a chemically prepared composite was highly flexible like rubber. However, the electrochemically produced composite possesses two orders of magnitude higher conductivity. Also, this composite revealed higher tensile strength and elasticity with respect to pristine polypyrrole.

Key Words: Hydroxyl terminated polybutadiene (HTPB); Silane coupling agent (SCA); Polypyrrole; Mechanical properties; Conducting composites.

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INTRODUCTION

Among the numerous conducting polymers prepared to date, polypyrrole is the most extensively studied due to its ease of synthesis. It has also attracted a great deal of attention due to the wide potential applications of conducting polymers, such as rechargeable batteries,[1,2] electroplating,[3–5] enzyme immobilization,[6–8] gas separation membranes and sensors.[9–13]

Since several other techniques have been improved to optimize the physical properties of the conducting polymers, recent investigations were focused on the improvement of processability, stability, and mechanical integrity. There are many works concerning the preparation of composites or copolymers of conducting polymers with the insulating ones. Blending conducting polymers with thermoplastic polymers is one attempt to increase their processability.[14–16] Another way to enhance the processability is to synthesize a conducting polymer within an insulating polymer.[17–21] The two main methods used to synthesize conducting composites are chemical and electrochemical polymerizations. The principle advantage of the chemical method is the possibility of mass production at a low cost. On the other hand, electrochemical methods offer materials with better conducting properties. Both techniques yield rather homogeneous products compared to blends.

The main objective of this study is to prepare a conducting polymer composite. The process contains two successive steps. The first step is to synthesize a flexible polymer from silane coupling agent and hydroxyl terminated polybutadiene. The next step involves the preparation of a conducting polymer composite via the polymerization of pyrrole inside the host polymer. In the same manner, the same composite was prepared via electrochemical methods, which involve the use of the insulating polymer as the anode material for the polymerization of pyrrole. The mechanical and electrochemical properties of the resultant products were investigated.

EXPERIMENTAL

Materials

Low molecular weight hydroxyl terminated polybutadiene (HTPB) was supplied from the Turkish Propellant industry. The relevant properties of HTPB (where the repeating group butadiene n is about 50) were as follows; viscosity at 25°C (mPa s): 6080, density (g/cm^3): 0.8975, molecular weight (g/mol): 2700, and average functionality: 1.93. The silane coupling agent (SCA) with the trade name of Polyvest 25, trimethoxy polybutadiene silane with butadiene n is about 12, was the product of the HÜLS–VEGA Group (Germany) having the viscosity at 20°C (mPa s): 1800, density (g/cm^3): 0.95, and molecular weight (g/mol): 800. Pyrrole (MERCK $>$ 98% pure) and dibutyltin dilaurate (DBTL) (MERCK $>$ 97% pure) were used as received. Reagents, iron chloride (Fluka), tetrahydrofuran (Merck) and doping agents iodine (Fluka) and *p*-toluene sulfonic acid monohydrate (PTSA) (Aldrich) were used without further purification. Other reagents were purified as given in the literature.

Preparation of a Flexible Polymer from SCA and HTPB

The HTPB and SCA were mixed in 1 : 1 ratio and molar ratio for [DBTL]/[Silane] was chosen as 0.65.[22] They were all mixed in bulk and poured into 0.9 cm × 6 cm PTFE molds. After degassing the air dissolved in the mixtures (ca. 100 mmHg) for 1 hour, they were cured at 40°C for one day. The flexible soft polymer films were obtained.

Preparation of Composite via Chemical Process

The polymer film synthesized was immersed into 25 mL of 10% (w/v) $FeCl_3$/THF solution. Two hours later, the solution was removed and 25 mL of 50% (v/v) hexane/CCl_4 solution was added. Then, 1.5 mL pyrrole was added into the solution. Five hours later, the solution was gradually removed from the system while adding ethanol. The film was removed from the system 1 hour later and left to dry for 1 day in open atmosphere. Part of the films were put in a closed container where iodine, I_2, packed in a filter paper hangs without touching films. The sublimed iodine further oxidizes the polypyrrole units and I_3^- ions incorporate the films as the secondary dopant.

Preparation of Composite via Electrochemical Process

The HTPB and SCA were mixed in 1 : 1 ratio and molar ratio for [DBTL]/[Si] was chosen as 0.025. The mixture was cured at 40°C for 10 h. A 1% solution (w/v) of this polymer was prepared in chloroform. The concentrations of pyrrole and PTSA in the electrochemical polymerization were 0.02 and 0.05 M, respectively.

The electrochemical polymerization of pyrrole inside the insulating polymer was performed on the surface of a platinum electrode. Both surfaces of a 6 cm^2 platinum foil were coated with 20 drops of previously prepared 1% polymer solution. The polymerization of pyrrole was carried out in an H-shaped electrolysis cell for 45 min at 1.1 V (vs. Ag/Ag^+) constant potential at room temperature. The working electrode was removed and washed with distilled water in order to remove the supporting electrolyte on the film. The films that face the counter electrode were subjected to mechanical tests.

Instrumentation

Nicolet 510 FTIR spectrometer and Bruker Instruments Avance Series Spectrospin DPX-400 High Performance digital FT-NMR were used for the characterization of polymers.

Tensile tests were performed using a Lloyd LS 500 computer controlled tensile testing machine with a 25 mm/min draw rate at room temperature. The gauge length was 25 mm and at least five specimens for each polymer were tested under 10 N load cell.

Electrochemical syntheses were performed by using a Wenking Model POS 73 potentiostat, which was adjusted to supply a constant potential of 1.1 V vs. Ag°/Ag^+ reference electrode. Conductivities were measured via the two-probe technique for chemically prepared composites and the four-probe technique for electrochemically prepared ones.

RESULTS AND DISCUSSION

Preparation of a Flexible Polymer from SCA and HTPB

Several attempts were performed to obtain a polymeric material from HTPB and SCA, which could provide an appreciable mechanical property and processibility. Among these attempts, a 1 : 1 ratio mixture of HTPB and SCA was kept at ambient conditions for several days to see whether a self-hydrolysis existed or not. The homogeneous mixture remained without any change in viscosity, color, and appearance. When the temperature of this mixture was increased to 80°C no polymerization was observed at the expense of thermal degradation. Similar experiments on the equal ratio mixtures were carried out by using different catalysts, such as HCl (concentrated), NaOH (concentrated) at higher temperatures. The reaction was found to be so slow that only about five days, a bulk polymerization was observed at 80°C, yet the degree of polymerization was still low and accompanied with a thermal degradation. The resultant products were soluble in some of the common solvents such as chloroform and tetrahydrofuran. The hydrolysis and condensation between HTBP and SCA at moderate temperatures with common catalysts were inefficient due to the hydrophobic nature of this SCA.

On the other hand, DBTL, which is the usual catalyst for hydrolysis and condensation of silanes, served well.[23–25] A transparent product was obtained without any thermal degradation as described in the experimental section. Although the HTPB and SCA were soluble in various solvents (chloroform, tetrahydrofuran), the resultant product was insoluble indicating that the polymer was highly crosslinked. The proposed mechanism for the hydrolysis and condensation of the HTPB and SCA in the presence of DBTL was shown in Fig. 1.

FT-IR and ^{1}H-NMR Analyses

Infrared spectroscopy and ^{1}H-NMR were used to support the proposed mechanism. Since the polymerization proceeds via hydrolysis and condensation reactions over the methoxy groups, these functional groups attached to the silicon atom were of main interest. The —CH_3 rocking of methoxy groups attached to the silicon gives a strong band at about 1190 cm^{-1}, in addition, the band around 800 cm^{-1} belongs to the symmetric Si—O—C stretching. Consistent with the proposed reaction mechanism (Fig. 1), these two characteristic bands of methoxy groups were observed in the spectrum of SCA while disappearing in the spectra of the polymers. Besides the peak around 1100 cm^{-1}, the asymmetric Si—O—Si stretching interfered with the strong asymmetric Si—O—C stretching. Yet, the decrease in peak height around 1100 cm^{-1} in the spectrum of the polymers can be attributed to the formation of Si—O—Si bond. The two peaks around 1600 and 1710 cm^{-1} which were observed in the polymer synthesized with DBTL, were not observed in the sample synthesized with HCl. Therefore, these peaks assigned for the ester groups in DBTL remained in the matrix after polymerization.

Nuclear magnetic resonance results also support the mechanism proposed. Since the resultant product was not soluble (just swells) in its best solvent, the reaction was stopped before gelation and the NMR spectrum of the soluble fraction of the polymer was taken.

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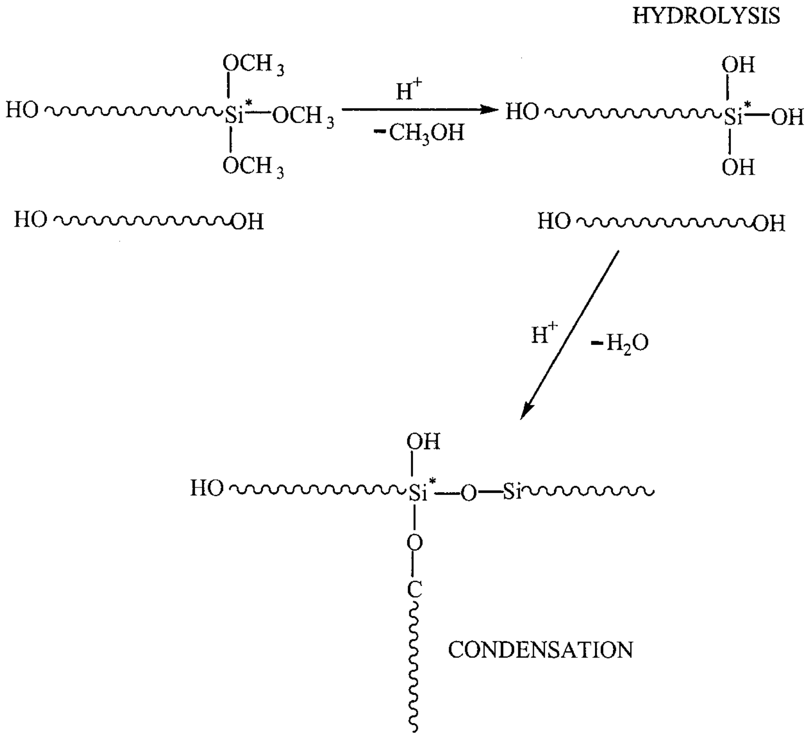

Figure 1. Proposed hydrolysis and condensation reaction mechanisms of SCA and HTPB in the presence of DBTL.

The peak around $\delta = 3.5$ ppm corresponding to singlet of methoxy functional groups in the ^{1}H-NMR spectrum of SCA disappears as the resultant polymer formed.

Characterization of Chemically Prepared Composites

Mechanical Results

The mechanical properties of pure (polymer obtained from HTBP and SCA in the presence of catalyst DBTL), slightly doped and highly doped polymers were determined and the results were collected in Table 1.

Among the others, the ultimate strength at break value of pure polymer was very low. On the other hand, the highest percentage elongation at break was determined for the pure polymer. Mechanical properties of the slightly doped polymer composite were greatly affected by the polymerization of pyrrole inside the pristine polymer. That led to a sharp change in the tensile strength for this polymer. On the contrary, elongation at break decreased to about 35% [Fig. 2(a)]. The same trend continued after doping process. Doping with iodine enhanced the strength of the composite [Fig. 2(b)]. The maximum

Table 1. Basic and mechanical properties of pure, slightly doped, and further doped polymer.

Sample	Thickness (μm)	Stress at break (MPa)	Percentage strain at break (%)	Young's modulus (MPa)	Conductivity (S/cm)
Pure polymer[a]		0.011	56.9	0.019	
Slightly doped polymer[b]	~500	0.182	34.87	0.611	6×10^{-7}
Highly doped polymer[c]	~500	1.383	21.19	12.358	6×10^{-2}

[a]Polymer obtained from HTBP and SCA in the presence of DBTL.
[b]Composite with PPy produced via $FeCl_3$, i.e., chemically.
[c]Slightly doped polymer further oxidized with I_2.

breaking stress was observed for the highly doped polymer composite. However, the decrease in percent elongation was not that significant compared to the improvement in the ultimate strength (Table 1). Furthermore, the change in modulus values was similar to the change in ultimate strength values. Young's modulus, and consequently, the stiffness and rigidity of the pure polymer were very low compared to the others. More than 30 times improvement in modulus was observed after the polymerization of pyrrole inside the pure polymer. Iodine doping further enhanced the modulus value up to 12.35 MPa (Table 1). As a result, polypyrrole inserted into the pure polymer improved the stiffness and doping with iodine further enhanced this property.

SEM Analysis

The tensile fractured surfaces of pure polymer and its composites were studied under scanning electron microscopy. Morphological changes are clearly seen in SEM pictures given in Fig. 3(a) and (b). The fractured surface of the pure polymer [Fig. 3(a)] was rather smooth even at high magnification (×10,000). This relative smoothness of the polymer fracture surface was that typically observed in rubbers, an indication that these specimens were highly crosslinked and fractured with a brittle manner. On the other hand, the typical cauliflower structures were observed in Fig. 3(b) and these homogeneously distributed cauliflower structures indicated that pyrrole was successfully polymerized inside the polymer.

Conductivity Measurements

The conducting composite films, obtained by the chemical polymerization of pyrrole in the host insulating polymer were highly flexible like rubber, despite its quite low tensile strength. The composites were allowed to dry for a day in open atmosphere and then their conductivities were measured. The chemically prepared polymers without further doping have very low conductivities. The conductivity measurements of these polymers were performed by two-probe technique in order to get an idea about the order of conductivity (Table 1).

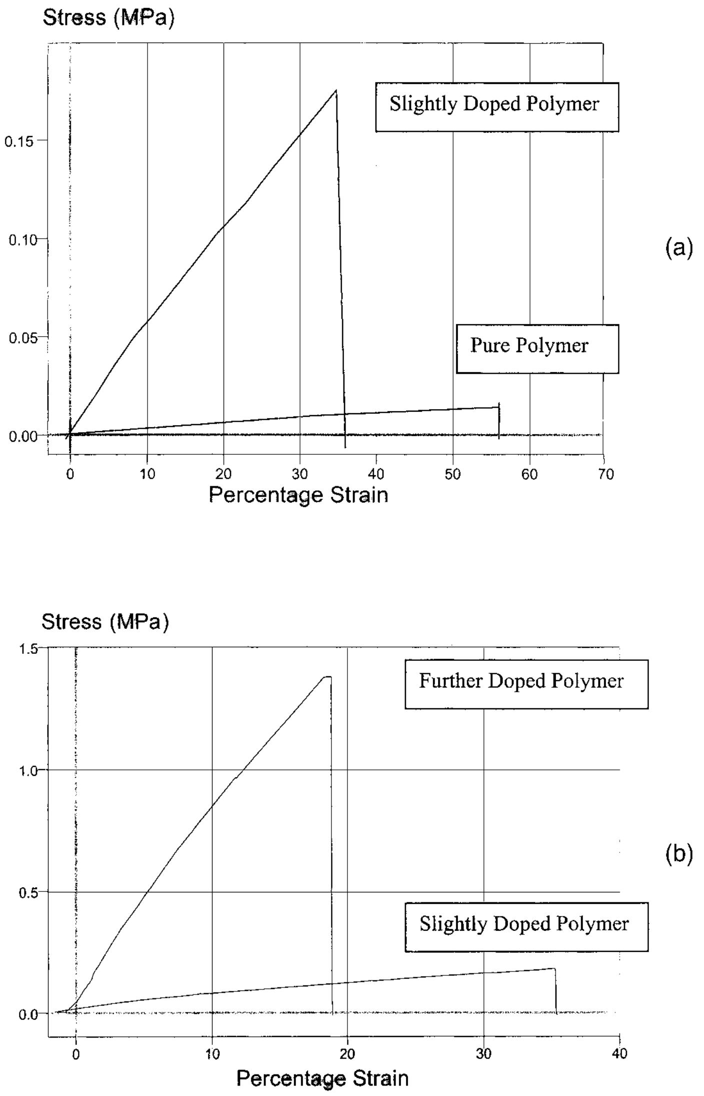

Figure 2. Stress vs. strain curves for (a) pure and slightly doped polymer and, (b) slightly and further doped polymer.

Characterization of Electrochemically Prepared Composites

Characterization of the Composite by FT-IR

The polymerization of the pure polymer was stopped before gelation and the electrode was coated by this soluble fraction. The procedure to be followed for the characterization of the composite was the preparation of the product on the surface of the electrode,

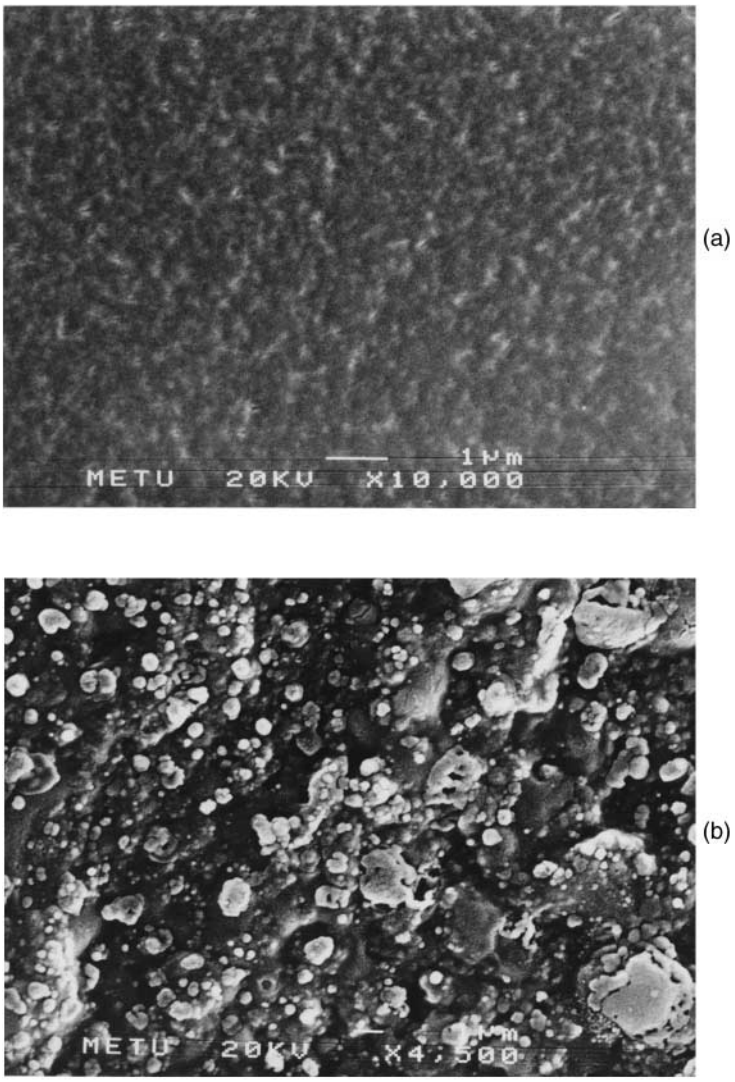

Figure 3. Fractured surface of (a) pure polymer (HTPB and SCA) and (b) chemically prepared composite polymer, where pyrrole was polymerized within polymer HTPB and SCA polymer.

washing the product with the solvent of the synthesized pure polymer and subtraction of the IR spectrum of washed product from that of unwashed one. The spectrum obtained would then be the spectrum of the pure polymer (Fig. 4). Although the peaks of PTSA surpass the other peaks, the ones at 966 $\mathrm{cm^{-1}}$ (in phase out of plane HC=CH deformation), 911 $\mathrm{cm^{-1}}$ (CH_2 wagging), 1448 $\mathrm{cm^{-1}}$ (CH_2 scissoring), and the peaks around 3000 $\mathrm{cm^{-1}}$ (CH_2) were the peaks arising from the pure polymer. The reason of very low peak intensities was most probably due to the presence of host polymer, which was not completely removed from the matrix.

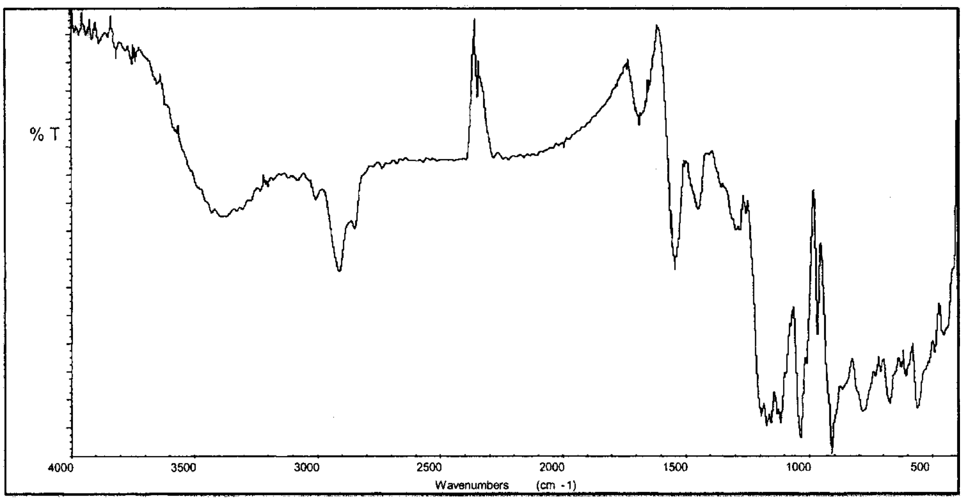

Figure 4. Subtraction of FT-IR spectrum of washed film from the unwashed one.

Mechanical Results

The ultimate strength, percent elongation at break and modulus variation in polypyrrole and its composite were shown in Table 2 and Fig. 5. In order to maintain an identical procedure for each specimen, the films were washed to eliminate the excess electrolyte on the surface, removed from the electrode surface and the mechanical tests were performed immediately. The composite possessed higher stress at break value with respect to polypyrrole. The average stress at break value for the composite was found to be 24.8 MPa, which was 18.2 for polypyrrole (Table 2). Similarly, the modulus value of the composite was found to be higher than that of polypyrrole. Although the modulus of the composite increased (Fig. 5), the conclusion could not be attributed to the stiffness because if it were the case, the composite would be more brittle than the polypyrrole. However, opposite to the polypyrrole, the composite can be folded without any fracture. These results were also consistent with the results of a recent study.[26] The average percent elongation at break of the composite was lower than that of the polypyrrole. Actually, the difference in percent elongation at break was not significantly high. There were also some composite specimens that had higher percent elongation than the average percent elongation of polypyrrole or vice versa. This was most

Table 2. Basic and mechanical properties of electrochemically prepared polypyrrole and its composite.

Sample	Thickness (μm)	Stress at break (MPa)	Percentage strain at break (%)	Young's modulus (MPa)	Conductivity (S/cm)
Polypyrrole	25–30	18.2	1.94	849.85	30
Polypyrrole composite	20–25	24.8	1.61	1251.37	1

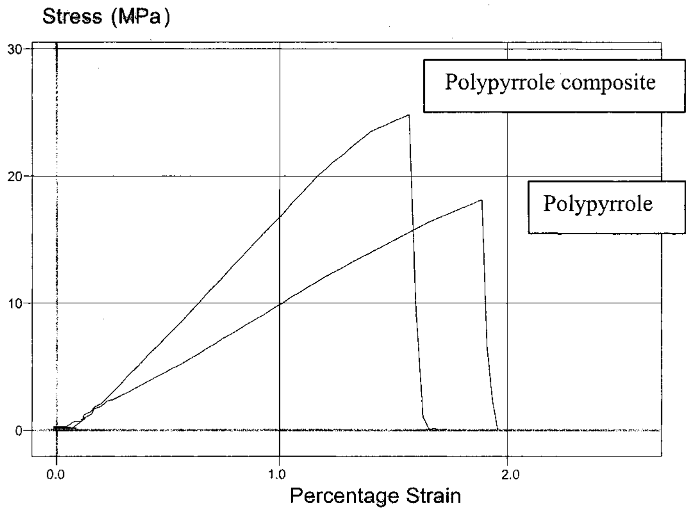

Figure 5. Stress vs. percentage of elongation of polypyrrole and its composite.

probably due to the presence of water. The products were immediately tested after the preparation of the films therefore, they were not completely dry during the test. Not being able to keep the water content constant in the films, the results obtained were not fully reliable as far as the percent elongation at break values were concerned.

SEM Analysis

The fractured surfaces in SEM pictures shown in Fig. 6(a) and (b) gave further information about the morphology and mechanical behavior of the samples. The domains observed on the surface of the film in Fig. 6(a) were the characteristic cauliflower structure of the polypyrrole. These characteristic structures on the solution side were not as big as the usually observed ones due to the short polymerization time. Furthermore, the cross sectional view of the film indicated that the film was fractured with a brittle manner, which is also consistent with the mechanical results. On the other hand, observed behavior for the composite was completely different, [Fig. 6(b)]. The surface of the film was rather smooth compared to the polypyrrole. In addition, the typical wormlike structures were observed on the fractured surface of the composite. From the cross sectional view of the composite, it can be concluded that the sample was fractured mostly in brittle manner.

Conductivity Measurements

The electrochemically prepared composite were left to dry for a day in open atmosphere and then conductivity measurements were performed by using four-probe method (Table 2).

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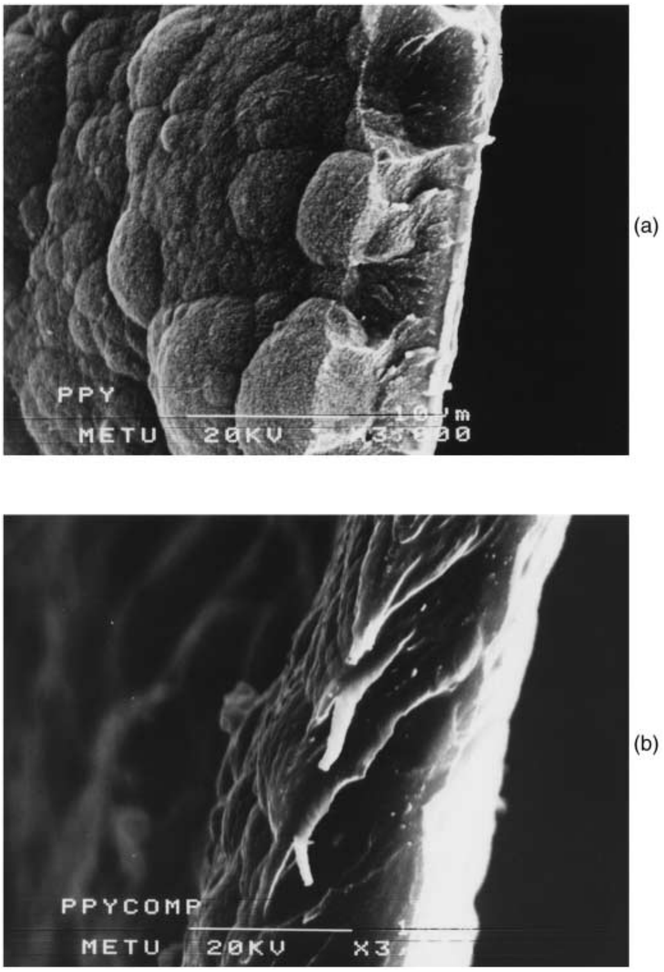

Figure 6. Fractured surface of (a) polypyrrole (electrochemically prepared PPy) and (b) electrochemically prepared composite.

There was no significant difference in the conductivities of the solution and electrode sides of the composite. On the other hand, a slight difference in the thickness of the composite and polypyrrole synthesized under the same experimental conditions was observed.

CONCLUSION

The synthesis and characterization of the composites prepared via chemical and electrochemical means were successfully performed. The polymer synthesized in the first part of the study was highly flexible like rubber. Fracture without yield and insolubility indicated that the polymer had a highly crosslinked network structure.

In-situ polymerization of pyrrole in the host polymer greatly enhanced the tensile strength of the composite with a relatively small loss in the percentage strain. The same trend was observed after doping with iodine. The doping process also resulted in a high increase in the conductivity of the chemically prepared composite.

The electrochemically prepared conducting composite possessed better mechanical properties with respect to the polypyrrole. The resultant composite film was not as fragile as the polypyrrole film. On the other hand, a slight loss in the conductivity at the expense of insulating host polymer was observed in this composite.

Although the mechanical properties and the conductivity were highly improved in the chemically prepared composite, the electrochemically prepared one possessed better properties in overall except for the elongation at break value.

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