

Flexible and Conducting Composites of Polypyrrole and Polydimethylsiloxane

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ABSTRACT: Conductive and flexible polydimethylsiloxane (PDMS)/polypyrrole (PPy) composites were synthesized electrochemically. Electrochemical syntheses were performed at +1.10 V by using *p*-toluene sulfonic acid (PTSA) as supporting electrolyte and water as solvent. Composites were characterized by cyclic voltammetry, thermogravimetric analysis, differential scanning calorimetry, scanning electron microscopy, and Fourier transform infrared spectroscopy. Conductivity measurements and mechanical tests were also performed. The observed conductivities were in the range of 3.5–7.6 S/cm, indicating that the conductivities

of PDMS/PPy composites and that of pure PPy were in the same order of magnitude. Tensile tests revealed that higher percent elongation was obtained by the addition of PDMS. Highly flexible and foldable PDMS/PPy composites were successfully synthesized, which have high conductivities and improved mechanical properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 736–741, 2004

Key words: polypyrroles; thermal properties; electrochemical synthesis; mechanical properties; conducting composites

INTRODUCTION

In recent decades, conducting polymers gained great interest because of their hi-tech applications in electronics, optoelectronics, sensors, and energy storage devices.¹ However, poor processibility and stability of conducting polymers have limited their practical applications.^{2,3} Conducting polymers are usually brittle materials; hence, many studies were conducted to improve their mechanical properties. Environmental stability and mechanical and physical properties can be additionally improved through preparation of composites or blends. Electrochemical polymerization is one of the best methods to prepare composites, in which the conducting monomer is electrochemically polymerized through a swollen insulating polymer matrix.^{4–7} The new composite gains conductivity as well as good mechanical properties from its two components. Among all known conducting polymers, polypyrrole (PPy) stands out as an excellent one because of its good environmental stability, high conductivity, and ease of synthesis.^{8–10} In the last few years, the goal of researchers has been to improve physical properties of PPy-like processibility and mechanical integrity. To achieve this goal, composites and copolymers of PPy with insulating thermoplastic were synthesized.¹¹ In preparation of conducting com-

posites, the electrochemical method is preferred because it is easy, clean, and selective.

The main objective of this study was to prepare flexible and foldable conducting polymer composites of PPy and polydimethylsiloxane (PDMS) by constant potential electrochemical synthesis. PDMS was chosen as an insulating host matrix because of its flexibility, solubility, and thermal resistivity.¹² The effect of PDMS on electrical, thermal, mechanical, and morphological properties of PPy was also investigated.

EXPERIMENTAL

Materials

Pyrrole (Py) was supplied from Acros Organics (NJ, USA). PDMS (molecular weight = 5×10^3) was purchased from Polyscience Chemical Co. (Warrington, PA). *p*-Toluene sulfonic acid (PTSA) and tetrahydrofuran (THF) were acquired from Merck (Darmstadt, Germany).

Electrochemical syntheses of the composites

Electrolyses were performed in aqueous system by using PTSA (0.05M) as the supporting electrolyte and polymerization of 100 μ L (1.44 mmol) pyrrole was achieved at +1.10 V under inert atmosphere. The electrolysis cell was an H-type three-compartment cell. Reference electrode was Ag/Ag⁺; working and counter electrodes were platinum. Working electrode was coated with different percentages of PDMS solu-

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TABLE I
Conductivities of PDMS/PPy Composites

PDMS% : PPy% (by weight)	Conductivity of electrode side (S/cm)	Conductivity of solution side (S/cm)
0 : 100	7.6	7.5
8 : 92	5.8	5.7
12 : 88	3.9	3.5

tions, which were prepared in THF. After the electrochemical synthesis, the composite films were washed with distilled water to get rid of unbounded dopant ions. Furthermore, they were washed with THF, the solvent of PDMS, and no weight loss was observed. The percentages of components were determined gravimetrically.

Conductivities of samples were measured via the four-point probe method and current-voltage measurements were performed by using a Keithley 617 Electrometer (Cleveland, OH). Cyclic voltammograms were recorded with software from Pico Electronics Ltd. (Ankara, Turkey). FTIR analyses were performed by a Nicolet DX 510 FTIR spectrometer (Madison, WI). Thermal analyses of samples were achieved by using a DuPont 2000 thermogravimetric analyzer (Wilmington, DE) and a TA-DSC 910S differential scanning calorimeter (New Castle, DE). A JEOL JSM-6400 scanning electron microscope (SEM; Tokyo, Japan) was used for morphological studies of films. Mechanical tests were performed by using a Lloyd LS 500 (Hampshire, UK) computer-controlled tensile testing ma-

chine having 100N load cell with 50 mm/min draw rate, 15 mm gauge length, and 3 mm width at room temperature.

RESULTS AND DISCUSSION

Preparation and conductivity measurements

Flexible and foldable composite films were obtained after the electropolymerization of Py onto PDMS-coated electrodes at +1.10 V. As pyrrole was being polymerized, the transparent PDMS film on platinum electrode turned black. The influence of PDMS compositions on electrical conductivities of PDMS/PPy composites was tabulated in Table I. As the insulating PDMS content was increased, the electrical conductivity of composites slightly decreased. Rather small differences in conductivity values for composites were observed. They were in the same order of magnitude with the pure polypyrrole. Almost same values were obtained for the conductivity of solution and electrode sides of composites, which reveals the homogeneity of the films. Conductivities of nonfreshed composites were also measured under atmospheric conditions and <4% loss of conductivities was observed for 1-month aged samples. This indicates the environmental stability of composite system.

Cyclic voltammetry measurements

The electrochemical behaviors of pure PPy and PDMS/PPy composites were recorded by cyclic voltammetry. The measurements were performed at

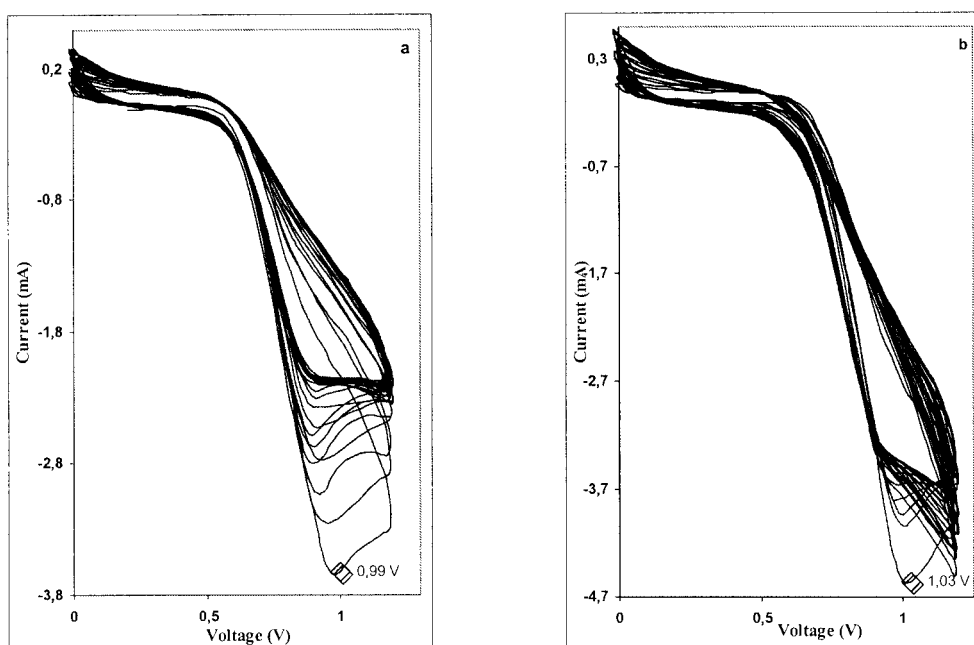


Figure 1 Cyclic voltammogram of pyrrole (a) on platinum electrode (b) on PDMS-coated electrode.

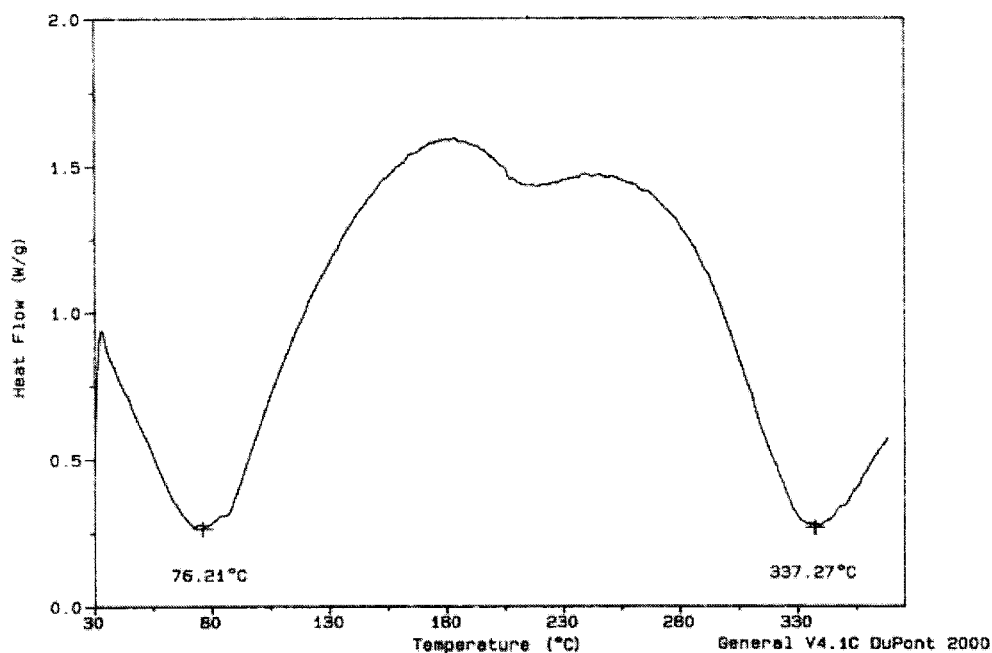


Figure 2 DSC thermogram of pure PPy.

room temperature with respect to Ag/Ag^+ reference electrode. The scan rate was 100 mV/s and the potential was scanned from 0 to +1.20 V in water-PTSA medium. Nitrogen gas was purged from the system prior to analysis to make the system inert.

Figure 1(a), showing the electrochemical behavior of Py on platinum electrode, indicates an oxidation potential for the first cycle at +0.99 V. Figure 1(b) dis-

plays the cyclic voltammogram of electrochemical polymerization of Py on a PDMS-coated platinum electrode. The anodic peak potential was observed at +1.03 V in the first cycle. Slightly higher oxidation potential is needed for pyrrole monomer to diffuse inside the PDMS matrix and to reach the electrode surface. The anodic potential was chosen as +1.10 V to synthesize PPy and PDMS/PPy composites.

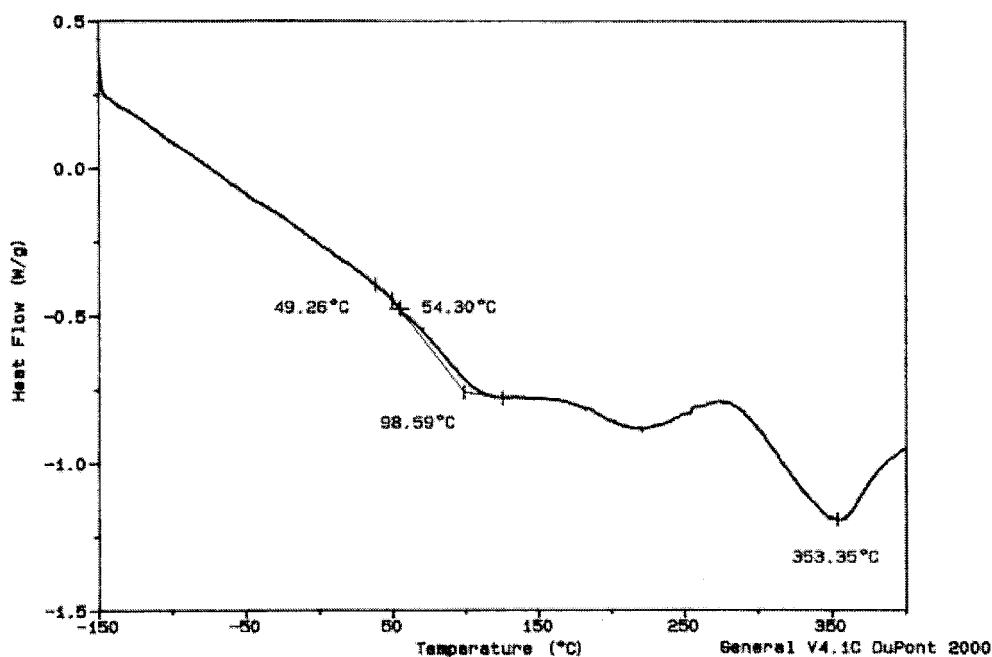


Figure 3 DSC thermogram of PDMS/PPy composite.

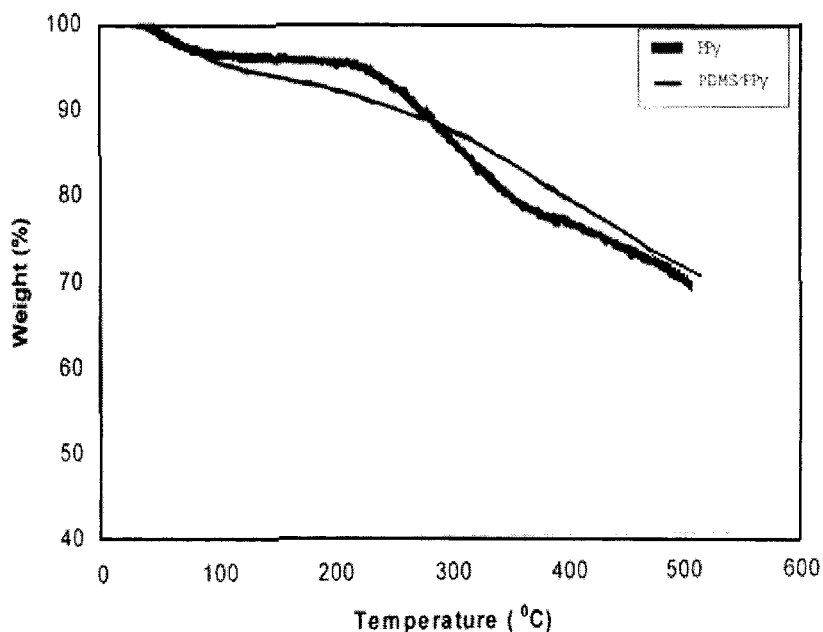


Figure 4 TGA of PTSA doped pure PPy and PDMS/PPy (5% : 95%) composite.

Thermal analyses

The thermal properties were assessed by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). DSC thermogram of pure PPy shows two endothermic transitions at 76 and 337°C (Fig. 2). The first peak is most probably due to the removal of solvent trapped in the matrix and the second one likely corresponds to the loss of the dopant anion from

the matrix, which is the decomposition temperature. PDMS/PPy (4% : 96%) composite has a decomposition temperature at 353°C, which is slightly higher than pure PPy (Fig. 3).

TGA results indicate that PDMS increases the thermal stability of preliminary polymer. The thermal behaviors of PPy and PDMS/PPy upon heating from 30 to 500°C with 10°C/min ramp were given in Figure 4. The percent weight loss of PPy was 22.5%, while that

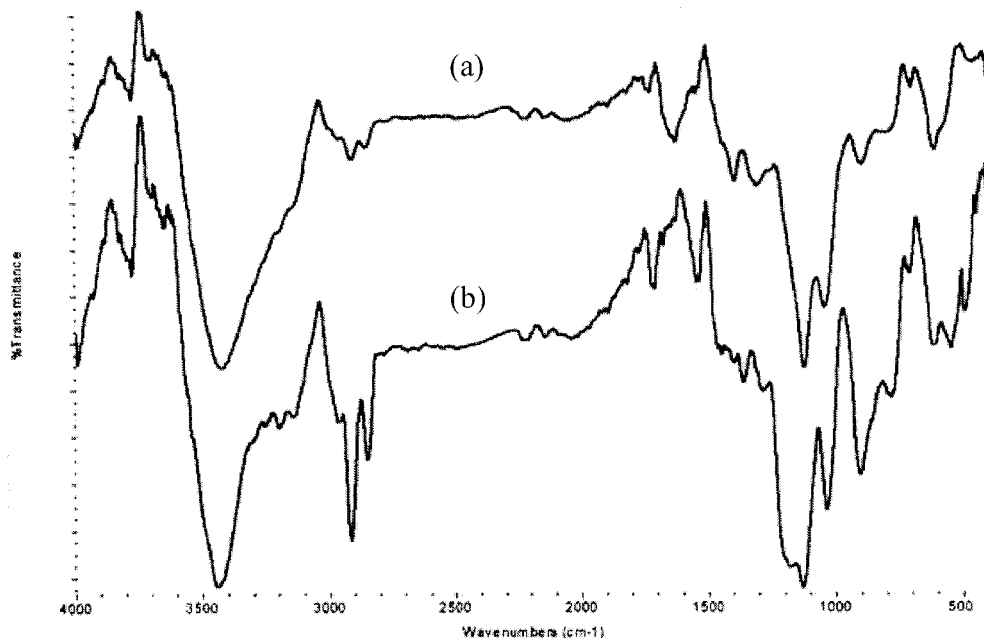


Figure 5 FTIR spectra of (a) pure PPy, (b) PDMS/PPy composite.

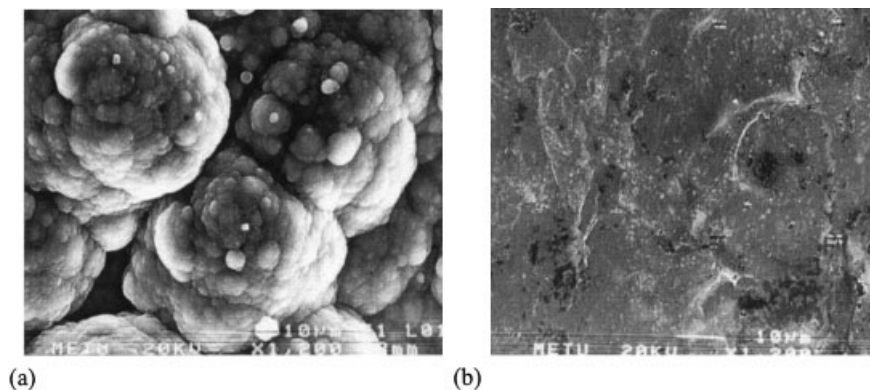


Figure 6 SEM of (a) solution side, (b) electrode side of unwashed PDMS/PPy composite.

of PDMS/PPy was 19% around 375°C, which were consistent with DSC results. Thermal analyses reveal that the PDMS/PPy composite showed a slightly more stable thermal behavior than pure polypyrrole films, which were produced under the same conditions.

FTIR analyses

FTIR analysis of pure PPy showed characteristic peaks at 1623 cm^{-1} for C=C stretching, 1533 cm^{-1} for C—N stretching, 1150 cm^{-1} for C—H in-plane bending, and 890 cm^{-1} for C—H out-of-plane bending [Fig. 5(a)].¹³ PTSA also gave peaks at the 1000–1200 cm^{-1} region.^{14–16} The composite showed the additional bands in the FTIR spectra [Fig. 5(b)], corresponding to the characteristic peaks of PDMS (i.e., 1150 and 1033 cm^{-1} for Si—O—Si asymmetric stretching, 870 cm^{-1} for Si—CH₃ rocking, 1280 cm^{-1} for Si—CH₃ bending, and 2910 cm^{-1} for CH₃ symmetric stretching).¹² The spectrum of composite showed the characteristic peaks of PDMS (at 1280 and 2910 cm^{-1}), implying that PDMS was still incorporated in the composite matrices after the washing process of the film with the solvent of PDMS.

Scanning electron microscopy analyses

Surface appearances of washed and unwashed films of PDMS/PPy composite were studied by SEM. When we compare the solution sides [Fig. 6(a) and Fig. 7(a)] and electrode sides [Fig. 6(b) and Fig. 7(b)] of washed and unwashed films, washing did not affect the appearance of both sides. This shows the existence of strong interactions between PDMS and PPy. Figure 6(b) shows the electrode side of unwashed PDMS/PPy composite, which had a flat glossy appearance. On the other hand, PPy crests grew out of the surface of the coated electrode, producing a cauliflower-like structure in the solution side of this composite [Fig. 6(a)].

Mechanical properties

Stress at break, percent strain at break, and Young's modulus of these composites were investigated and tabulated in Table II. Increments in these values were achieved by increasing the PDMS percentage in the composite. Fair improvement in stress at break and Young's modulus were observed. Percent strain at break values were increased about 60% by inserting

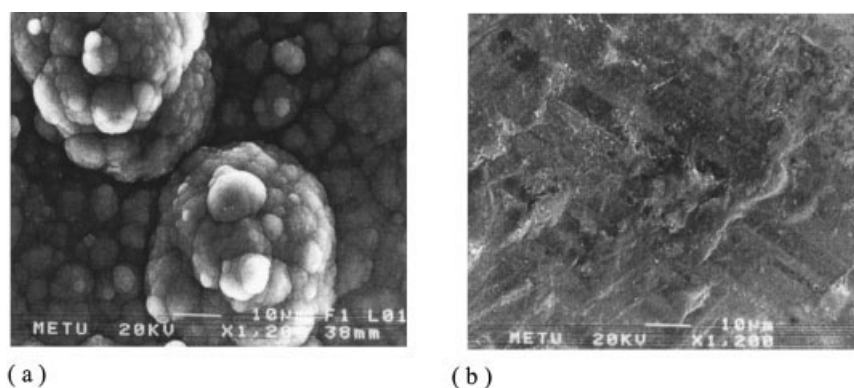


Figure 7 SEM of (a) solution side, (b) electrode side of washed PDMS/PPy composite.

TABLE II
Tensile Strength at Break, Percent Elongation at Break,
and Young's Modulus of PDMS/PPy Composites

PDMS% : PPy%	Stress at break (MPa)	Percent strain at break	Young's modulus (GPa)
0 : 100	34.5 ± 1.5	5.15 ± 0.7	0.97 ± 0.02
8 : 92	36.3 ± 7.8	6.81 ± 2.4	1.02 ± 0.03
12 : 88	38.2 ± 5.5	8.27 ± 2.6	1.14 ± 0.02

12% PDMS into the PPy matrix because of the flexibility of the PDMS.

CONCLUSION

Flexible, foldable conducting composites of PDMS and PPy were electrochemically synthesized. The presence of strong interactions between components was proved by the existence of PDMS even after washing with the solvent of PDMS (THF). This result was supported by FTIR and SEM analyses. The mechanical properties of PPy were improved by PDMS in the composites without losing its electrical conductivity. Hence, the composites gain both high electrical conductivity from the PPy component and high flexibility accompanied by good mechanical properties from the PDMS component. This superior property can be eas-

ily observed by folding up and down the composites by 180°. Thermal analyses revealed that composites have slightly higher decomposition temperatures compared to pure PPy and PDMS.

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