2010

The mechanical and the electrical properties of conducting polypyrrole fibers

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Publication Details

Foroughi, J, Ghorbani, SR, Peleckis, G, Spinks, GM, Wallace, GG, Wang, P & Dou, SX (2010), The mechanical and the electrical properties of conducting polypyrrole fibers, Journal of Applied Physics, 107(10), pp. 1-4.

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Abstract
The mechanical and the electrical properties of polypyrrole (PPy) fibers and electrochemically deposited PPy films were studied. It was found that the PPy fibers showed a significantly higher strength than the PPy films due to better orientation of the molecular structure. The electrochemically prepared PPy films had a higher electrical conductivity than that of the fibers at high temperature. At low temperature, the PPy fibers showed the higher conductivity. The conductivity results were analyzed in the frame of the three-dimensional variable range hopping model. The results showed that at room temperature the average hopping distance for the fibers was about 4 Å while for the films it increases to about 5.7 Å. This corresponds to about 1 and 2 monomer units in length for the fiber and film samples, respectively.

Keywords
mechanical, electrical, properties, conducting, polypyrrole, fibers

Disciplines
Engineering | Physical Sciences and Mathematics

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The mechanical and the electrical properties of conducting polypyrrole fibers

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(Received 25 November 2009; accepted 7 April 2010; published online 20 May 2010)

The mechanical and the electrical properties of polypyrrole (PPy) fibers and electrochemically deposited PPy films were studied. It was found that the PPy fibers showed a significantly higher strength than the PPy films due to better orientation of the molecular structure. The electrochemically prepared PPy films had a higher electrical conductivity than that of the fibers at high temperature. At low temperature, the PPy fibers showed the higher conductivity. The conductivity results were analyzed in the frame of the three-dimensional variable range hopping model. The results showed that at room temperature the average hopping distance for the fibers was about 4 Å while for the films it increases to about 5.7 Å. This corresponds to about 1 and 2 monomer units in length for the fiber and film samples, respectively. © *2010 American Institute of Physics*. [doi:10.1063/1.3425793]

Although polymers dominate the general fiber and textile industries they have had little impact on applications that require electrical conductivity or electronic properties. Conducting polymer fibers are likely to be important for electronic textile applications as they allow the possibility to incorporate desirable features like chemical sensing or actuation that are not feasible with metallic fibers. Polypyrrole (PPy) is a well known conducting polymer that is already used in a range of applications including battery electrodes,[1] gas sensors,[2] biological sensors,[3] ion-sieving, corrosion protection,[4] microwave shielding,[5,6] and artificial muscles.[1,7–12] In addition, PPy manufactured by conventional chemical and electrochemical methods is normally insoluble in ordinary organic solvents[13] and this intractability has been attributed to the presence of strong interchain interactions.[14] Consequently, PPy films are normally prepared electrochemically, with the size of the film restricted to the electrode area. However, due to the insolubility of such PPy films, fabrication of the electropolymerized conductive polymers is limited and restricted to the electrode shape and area.[15] Recently, the development of continuous PPy fibers has been achieved using di(2-ethylhexyl) sulfosuccinate (DEHS) as a dopant through a wet-spinning process.[16,17] It is well known that the electrochemical, mechanical, physical, and other properties of conducting polymers, such as PPy depend upon the synthetic conditions employed during polymerization.[18]

There have been no reports of comparisons of the electronic and mechanical properties of PPy using DEHS as a dopant to produce PPy-DEHS films and fibers. In this letter we report the effect of preparation methods on the electronic and mechanical properties of these fibers and films. It was found that the fibers showed a significantly higher strength than the films due to better orientation of molecule structure. The electrochemically prepared PPy-DEHS film had a higher conductivity than the PPy-DEHS fibers at high temperature. While at low temperature, the fibers showed the higher conductivity. These conductivity results are supported by the conductivity analyses in the frame of the three-dimensional (3D) variable range hopping (VRH) model.

The desired electropolymerized PPy films were successfully synthesized by anodic oxidation of pyrrole monomer. DEHS sodium salt (Na^+DEHS^-), ammonium peroxydisulfate, and dichloroacetic acid (98%), were supplied by Sigma-Aldrich and used as received. Pyrrole monomer (95%, Aldrich) was used after distillation.

The electrolytic cell contained 0.40 M pyrrole and 0.15 M Na^+DEHS^- in water. A stainless steel plate was used as the anode and a stainless steel mesh as the cathode. The polymerization was carried out galvanostatically using a constant current of 0.2 mA/cm^2 for 12 h at 0 °C. The resultant black film was pulled off the electrode and washed several times with distilled water, and then allowed to dry for 24 h in air at room temperature. PPy-DEHS fiber was produced as described in a previous report[16] using a wet-spinning process. The as-spun PPy-DEHS fibers were further drawn 40% and used to investigate electronic and mechanical properties. Tensile testing was carried out using TA Instruments DMA. For tensile testing, a 10 mm gauge length of fiber or film was stretched at 25 °C and at a strain rate of 500 $\mu m/min$ until the sample failed. A Leica Stereoscan 440 scanning electron microscope (SEM) was used for morphological studies of the fibers and films. The resistivity was measured using a standard four-probe method over a wide range of temperatures from 10 to 300 K (PPMS, Quantum Design).

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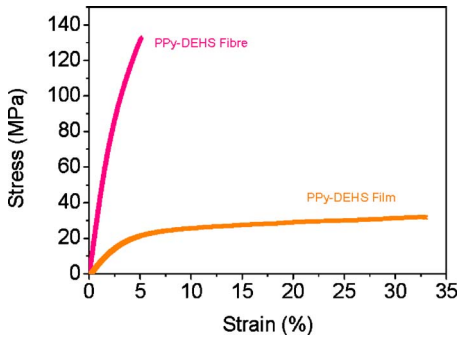

FIG. 1. (Color online) Comparison of the mechanical properties of the PPy-DEHS fiber and film.

The mechanical properties of drawn PPy-DEHS fibers and free-standing PPy-DEHS films tested at room temperature are given in Fig. 1. Analysis of these curves indicates a stress at break 136 MPa with 5% strain for the PPy fiber compared with only ~35 MPa stress with 33% strain for free-standing PPy-DEHS film. Young's modulus of the PPy fiber and film was ~4.2 GPa and ~0.60 GPa, respectively. Comparison of the results suggested that PPy-DEHS fibers have a significantly higher strength than PPy-DEHS films. This is possibly due to better orientation of the molecular structure within the fibers.

The surface morphology of the various PPy-DEHS materials are shown in Fig. 2. As can be seen from the SEM images, the fibers show a smooth and uniform surface [Fig. 2(a)]. Examination of the fiber fracture surface showed the fibers to be dense and nonporous [Fig. 2(b)]. SEM micrographs of the electropolymerized PPy-DEHS film at higher magnification indicated a layered structure [cross-section Fig. 2(c)], which may result in their lower modulus. On the surface of the growth side of the electropolymerized PPy film a nodular morphology was observed with some cauliflower shaped features [Fig. 2(d)] which are typical of such films.

The temperature dependence of the resistivity, ρ(T), of both the electrochemically prepared PPy-DEHS films and PPy-DEHS fibers are shown in Fig. 3. As can be seen in the inset of Fig. 3, the films have a higher conductivity than the

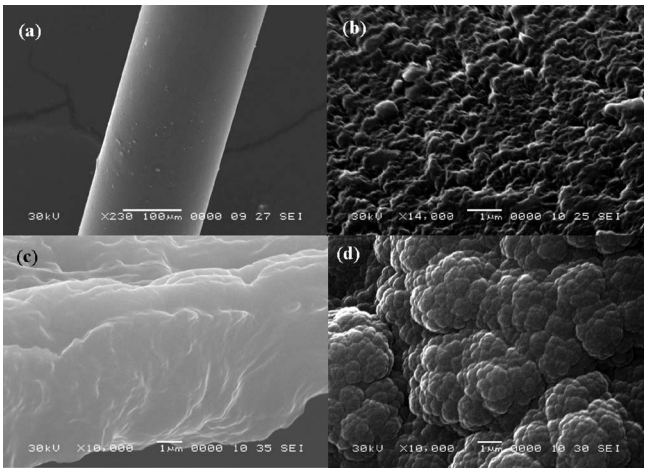

FIG. 2. SEM micrographs of PPy-DEHS fiber and film at low and higher magnification.

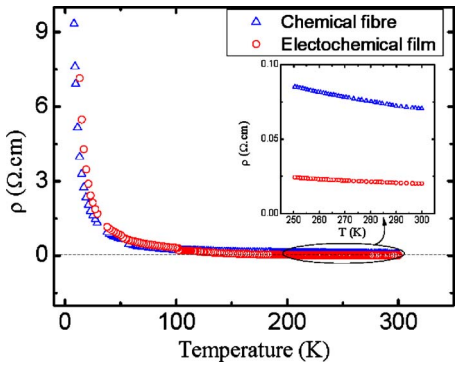

FIG. 3. (Color online) The temperature dependence of ρ(T) of the PPy-DEHS film and fiber.

fibers at high temperatures. While at low temperature, the fibers have the higher conductivity. The temperature dependence of the conductivity of conducting polymers is commonly explained by the 3D VRH model[19]

$$\sigma(T) = \sigma_0 \exp[(-T_0/T)^{1/4}], \quad (1)$$

where σ_0 is the high temperature limit of dc conductivity and T_0 is related to thermally activated hopping among localized states.

Figure 4 shows ln σ(T) versus $T^{-1/4}$. As can be seen in Fig. 4, the conductivity of the PPy-DEHS film has a different behavior as a function of temperature. At least four distinct regions were identified in the temperature dependence of conductivity. For the PPy-DEHS fiber sample, only two regions are seen. At temperatures lower than 10 K and higher than 200 K, there are deviations in the conductivity of the electrochemically prepared PPy-DEHS films. These anomalies related possibly to the less densely packed morphology of the films.

The conductivity is evaluated from the best-fitted straight lines at 10 K$\leq$T$\leq$200 K temperature interval as presented in Fig. 4. The best-fitted values of σ_0 and T_0 are shown in Tables I and II for both samples. The characteristic temperature T_0 for 3D hopping transport is given by

$$T_0 = \frac{16}{k_B L^3 N(E_F)}, \quad (2)$$

where L is the localization length and $N(E_F)$ is the density of states at the Fermi level. As T_0 is inversely proportional to L,

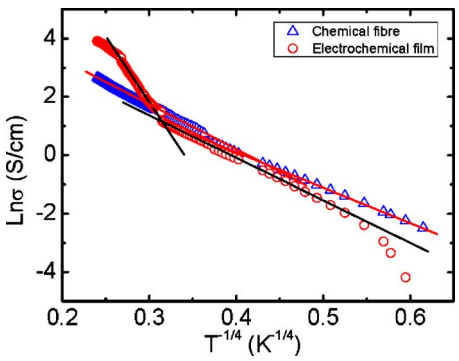

FIG. 4. (Color online) Temperature variation in dc conductivity of the PPy-DEHS fiber and film.

TABLE I. Conductivity analysis for PPy-DEHS fiber.

Temperature range (K)	T_0 (10^5 K)	σ_0 (S/cm)	$N(E_F)$ (10^{23} eV^{-1} cm^{-3})	R_{hop} (Å)	W_{hop} (meV)
$60<T\leq200$	0.58	566.8	1.19	4.2	24.1
$T\leq60$	0.43	419.9	1.59	3.9	22.4

the degree of disorder of the systems reduces with lowering of T_0. The values of $N(E_F)$ are calculated by considering the charge transport primarily arising from the conducting PPy phase and assuming localization length of the pyrrole monomer unit of about 3 Å.[20] At high temperature, the higher values of density states at the Fermi level for the PPy-DEHS fibers samples (1.19×10^{23} eV^{-1} cm^{-3}) compared to the PPy-DEHS films (0.34×10^{23} eV^{-1} cm^{-3}) indicates that charge carriers are more delocalized. This is also consistent with the increase in dc conductivity in the fibers samples. The average hopping distance R_{hop} between two sites and the activation energy W_{hop} are given by

$$R_{hop} = (3/8)(T_0/T)^{1/4}L, \tag{3}$$

$$W_{hop} = (1/4)k_BT(T_0/T)^{1/4}. \tag{4}$$

At room temperature the average hopping distance for the fibers is about 4 Å while for the films it increases to about 5.7 Å. These distances correspond to about 1 and 2 monomer units in length for the fibers and the films, respectively. The estimated activation energies for hopping are 24 meV and 33 meV for the PPy-DEHS fibers and films, respectively (as shown in Tables I and II). This is in good agreement with the average hopping distance changes.

As can be seen in Fig. 4, the conductivity within the temperature at 10 $K\leq T\leq100$ K interval is similar for both samples. This result is in good agreement with the conductivity analyses in the frame of the VRH model as shown in Tables I and II.

The transport properties of the conducting polymer can be classified in the insulating, critical, or metallic state from the slope of temperature dependence of the reduced activation energy defined as[21]

$$W = \log_{10}[d \ln \sigma(T)/d \ln T]. \tag{5}$$

The W(T) of the PPy-DEHS fiber and film are compared in Fig. 5. The slope of the PPy-DEHS fiber is negative at whole temperature range, i.e., W increases as T decreases, which indicates that the system is in the insulating regime. While for PPy-DEHS film, the slope of W as a function of temperature is positive for the temperature interval of 100 $K<T\leq200$ K and it change to negative for 10 $K<T\leq100$ K. Therefore, the PPy-DEHS film is in the metallic side of the

TABLE II. Conductivity analysis for electrochemically prepared PPy-DEHS film.

Temperature range (K)	T_0 (10^5 K)	σ_0 (S/cm)	$N(E_F)$ (10^{23} eV^{-1} cm^{-3})	R_{hop} (Å)	W_{hop} (meV)
$100<T\leq200$	24.7	9.65×10^5	0.028	10.7	61.5
$10\leq T\leq100$	0.48	0.33×10^3	1.44	4.0	23.0

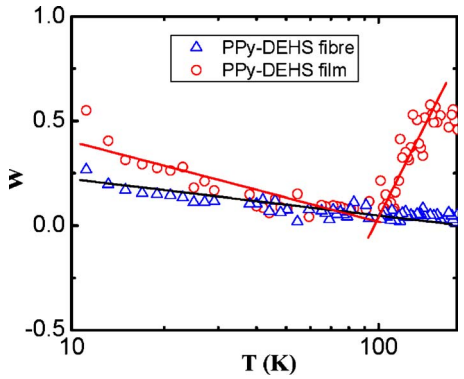

FIG. 5. (Color online) The temperature dependence of the reduced activation energy W(t) of the PPy-DEHS fiber and film.

metal-insulating transition in the first temperature interval but the system change to insulating regime at the last temperature interval. These results for the reduced activation energy are in agreement with that of the σ_0 results as shown in the both Tables I and II. While σ_0 is slowly change from the first region to the second region for the fiber samples while there is a big difference in σ_0 for film sample at both regions.

In summary, we have found that PPy-DEHS fibers and electrochemically deposited PPy-DEHS films show different mechanical and electrical properties. It was found that the fibers showed a significantly higher strength than the films possibly due to better orientation of the molecular structure. The films had a higher conductivity than the fibers at high temperature but at low temperature, the PPy-DEHS fibers showed the higher conductivity. The conductivity results are in good agreement with the conductivity analyses in the frame of the VRH model. At room temperature the average hopping distance for the fibers is about 4 Å while for the films it increases to about 5.7 Å.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Australian Research Council through its Centres of Excellence Program.

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