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Supercritical carbon dioxide processing of conducting composites of polypyrrole and porous crosslinked polystyrene

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Abstract

Conducting composites (∼3 mm in thickness) of polypyrrole (PPy) and porous crosslinked polystyrene (PCPS) were prepared by first impregnating PCPS with iodine (I_2), and then contacting it with pyrrole (Py). Both these steps were carried out with and without supercritical carbon dioxide. The use of supercritical CO_2 as a solvent for I_2 and Py facilitated the transport and deposition of these substances in the pores of the permanently porous host and produced composites with conductivities as high as 10^{-3} S cm^{-1}. Moreover, the deposition of I_2 in the pores could be controlled via the CO_2 pressure. The bulk and surface conductivities of the composite exhibited percolation behavior with respect to the amount of the I_2 deposited, whereas the volume conductivity exhibited a stepwise transition at approximately 100 wt% PPy + I_2 complex formed (with respect to the original mass of PCPS). Optical micrographs suggest that non-uniform distributions of PPy are obtained in the pores below this transition.

The percolation threshold was as low as 10 wt% so that the stability and mechanical strength of the composites were approximately the same as those of the host PCPS. This was verified by TGA and compressive strength measurements. The temperature dependence of the conductivity conformed with Mott's variable-range hopping (VRH) model for three-dimensional electronic transport. However, the data could be correlated equally well with the CELT model.

Keywords: Conductive composite; Polypyrrole; Polystyrene

1. Introduction

Intrinsically conducting polymers (ICPs) such as polypyrrole (PPy) have been extensively studied because of their potential application in electronics, light emitting diodes, smart windows, sensors, solar cells, and other devices [1]. The structure–property relationships of ICPs, however, are poorly understood and depend strongly on the synthesis method, counter ions, and other processing variables that are difficult to control experimentally [2]. It has been suggested that oriented, defect-free and crystalline ICPs can be obtained via in situ polymerization of the monomers in the void spaces of porous host materials [2–4]. Porous hosts offer an environment that favors ordering of the ICP chains and minimizes cross-linking and other undesirable interactions [2]. This has been demonstrated by preparing composites of PPy in the pores of membranes [5,6], molecular sieves [7,8] and synthetic opals [9] as well as other materials.

Ruckenstein and Park [10] prepared several ICP/porous host polymer composites using a two-step process in which the host polymer was first imbibed in an oxidant solution and then contacted with a solution of the monomer, or vice versa. Contact between the oxidant and monomers resulted in polymerization to the ICP in the pores of the host polymer. However, a sufficiently high loading of the ICP was required to reach the percolation threshold and obtain a connected network of the ICP in the composite [4,10]. The solvent appeared to play a key role in the level of conductivity attained by ensuring a uniform distribution of the ICP in the host polymer. However, control of the conductivity by manipulating the properties of the solvent was not investigated.

The present work investigates the role of one solvent, supercritical CO_2, in determining the level of conductivity in a composite made from an ICP (polypyrrole) and a permanently porous host (porous cross-linked polystyrene). Supercritical carbon dioxide is known to swell many polymers and has been used to facilitate the diffusion of small molecules in several

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porous hosts such as polyurethane [11]. However, the host polymer in the present work is not swollen by supercritical carbon dioxide because of its highly cross-linked nature. Therefore, the role of the solvent is to transport the monomer and oxidant to the void spaces (pores) of the host, and hence to facilitate the formation of a conducting network of the ICP in the host. Supercritical CO_2 is a non-toxic, environmentally benign solvent with a unique ability to diffuse rapidly through small voids because of its high diffusivity and negligible surface tension [12]. It was therefore, expected to enhance the deposition and distribution of the monomer and oxidant in the pores, thereby enhancing the connectivity of any ICP network formed, as well as the conductivity. Moreover, since the properties of supercritical CO_2 can be manipulated by relatively small changes in pressure, the ability to control conductivity by pressure was hypothesized. PPy was chosen as the ICP for investigation because it exhibits high intrinsic conductivity and good environmental stability [13]. It also has the ability to form stable and uniform coherent films on hydrophobic surfaces [14]. PCPS was chosen as the host polymer because it is easily prepared and provides a three-dimensional template for the in situ polymerization of PPy [10]. Finally, iodine (I_2) was selected as an oxidant because of its ability to form charge transfer complexes with PPy [15] and because it has appreciable solubility in supercritical CO_2 [16]. The electrical conductivity and morphology of the composites, as well as their thermal and mechanical properties, are reported below.

2. Experimental

2.1. Materials

Styrene (>99% pure), divinylbenzene (mixture of isomers), sorbitane monooleate (Span®80), 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%), and iodine (99.8%) were purchased from Aldrich (Milwaukee, WI). Pyrrole (99%) was purchased from Fisher Scientific (Hampton, NH), and stored in a refrigerator before use. Coolant grade carbon dioxide (99.99%) was obtained from Air Products and Chemicals (Allentown, PA). All chemicals were used as received.

2.2. Apparatus

High-pressure experiments involving supercritical CO_2 were conducted in a 10 mL stainless steel vessel (Model SFX-210, ISCO, Lincoln, NE) connected to a high-pressure syringe pump (Model 100DX, ISCO, Lincoln, NE). In order to liquefy CO_2 before pumping, cold water was circulated to the pump head from an immersion cooler (Model CC-100 II, Neslab Instruments, Newington, NH). The temperature in the stainless steel vessel was controlled using a pre-installed temperature controller (Model PYZ4-TCY1-4V, Fuji Electric, Saddle Brook, NJ). The system pressure was measured with a pressure gauge (Model CM-51917, Heise, Newtown, CT) calibrated using a dead weight tester (Model 380 H, Budenberg, Manchester, UK). Low-pressure experiments involving Py vapor in the absence of CO_2 were conducted in a glass dessicator covered with a blanket.

2.3. Preparation of PCPS

PCPS wafers were prepared according to the procedure reported by Ruckenstein and Park [10]. AIBN initiator (0.20 g) and divinylbenzene (4.0 g) were mixed under nitrogen flow in a 250-mL three-necked round-bottom flask equipped with a magnetic stirrer. Sorbitan monooleate (4 mL) and styrene (20 g) were added to the flask followed by water (100 mL). The mixture was vigorously stirred at room temperature for 4 h, and the resulting emulsion was poured into petri dishes and maintained at 323 K for 24 h. Excess water was removed by subsequently keeping the uncovered petri dishes on a hot plate at 373 K for 3 days. The PCPS films obtained were then cut into strips with dimensions of 1.0 cm × 2.5 cm, and of varying thickness between 0.2 and 0.4 cm. The dimensions of each strip were measured with a caliper to a precision of ±0.005 cm. Any samples exhibiting visual signs of surfactant contamination (spots on the surface) were discarded.

2.4. Preparation of PPy/PCPS composites

Since polymerization of pyrrole (Py) occurs rapidly when it is contacted with I_2 (the oxidant), a two-step process was used in the preparation of the composites. In experiments not involving CO_2, a PCPS strip was contacted first with I_2 vapor for 24 h and then with Py vapor for 24 h in a dark room. Experiments that involved supercritical CO_2 were initiated by adding 1 g of I_2, followed by a layer of glass beads and one PCPS strip, to a glass vial inside the 10-mL stainless steel vessel and then pumping CO_2 into the vessel until the pressure reached 10.5 MPa at 313 K. The vessel was left at these conditions for a specified period of time, and then depressurized to ambient pressure. I_2 has an appreciable solubility in CO_2 at 10.5 MPa and 313 K and was therefore, solubilized and transported to the pores of the PCPS by the supercritical CO_2. Upon depressurization, I_2 precipitated in the pores because it was no longer very soluble in supercritical CO_2. Charging and release of CO_2 from the vessel were therefore, done very slowly in order to avoid convection currents. After depressurization, the PCPS film was removed from the vial, dried, and weighed to determine the mass uptake of I_2. In the second step, the procedure was repeated with Py in the glass vial instead of I_2. Contact between Py and I_2 in the pores of PCPS resulted in rapid polymerization to PPy. After depressurization, the PCPS strip was left in a fume food for several days to allow unreacted I_2 and Py monomer to diffuse out of the strip before weighing and analysis. The mass gain due to the formation of PPy was calculated relative to the mass of the pristine host substrate.

2.5. Electrical conductivity measurement

The surface resistance of each composite was measured with a four-point probe (Model C4S-64/00, Cascade Microtech, Beaverton, OR) connected to a multimeter (Keithley, Model 196 System DMM). The bulk resistance was measured with a two-point probe (2-mm OD, Fluke, Everett, WA) connected to another multimeter (Model 3458A, Hewlett-Packard, Houston, TX) using sandwich geometry. Silver paint (Ernest F. Fullam, Inc., Latham, NY) was applied to the contact points in order to reduce the resistance between the probe and the sample surface. The volume conductivity [17] was measured by cutting a 0.5 cm×0.5 cm piece of the PCPS strip, and measuring the conductivity of the resulting element using a two-point probe. Differences in the three conductivities (surface, bulk, and volume) provide a measure of the distribution of PPy in the composite.

2.6. Optical microscopy

The morphology of the composite was studied by placing the sample in a Leica DMLM optical microscope (Leica Microsystems, Bannockburn, IL) after each step in the experiment. Reflected light was used to illuminate the sample, and images were captured and processed with an Image-Pro PLUS version 4.5 software.

2.7. Scanning electron microscopy

A Hitachi S800 field emission scanning electron microscope was used to image the surface and cross-sections of each sample. The sample was first cut to size and mounted on an SEM slide with double-sided adhesive tape and then sputter-coated with gold.

2.8. Thermogravimetric measurement

The thermal stability of the composite was determined using a Seiko TG/DTA Model 320 instrument (Seiko, Torrance, CA). Between 5 and 15 mg of the sample were placed in an aluminum pan under a nitrogen flow of 250 mL min^{-1} and scanned from ∼300 to 823 K at a heating rate of 20 K min^{-1}.

2.9. Compressive mechanical testing

Compressive mechanical testing was performed using a uniaxial electro-mechanical testing device (Model 650R, TestResources, Shakopee, MN) [18]. A preload of 5 N was applied to small squares of PCPS before initiating compression testing at a rate of 0.5 mm min^{-1}. Samples were tested to a strain endpoint of 50% of initial thickness. The stress–strain relationship was calculated from the measured load–displacement data and sample dimensions. The compressive modulus was determined from the largest slope in the linear elastic region of the stress–strain curve.

2.10. Temperature dependence of electrical conductivity

The change in electrical conductivity with temperature was measured using a constant-current van der Pauw technique [19]. The measurement system consisted of a programmable current source (Model 220, Keithley, Cleveland, OH), autoranging picoammeter (Keithley, Model 485), multimeter (Keithley, Model 2000), and switch system (Keithley, Model 7001). Silver wires (0.127 mm in diameter, 99.9% purity, Alfa Aesar, Ward Hill, MA) were attached to the four corners of a 1 cm^2 piece of the composite using silver-filled epoxy (410E, Epoxy Technology, Billerica, MA) and then connected to electrodes on a sampling rod inserted in a superconducting quantum interference device (SQUID) magnetometer (Model MPMS-5S, Quantum Design, San Diego, CA). After the system reached thermal equilibrium at 90 K, a program was executed to initiate measurements at 5 K intervals until the temperature reached 300 K. A total of eight measurements were made at each temperature, and the average resistance of the sample was obtained using ASTM Method F76. The electrical conductivity was calculated from the measured resistance and the thickness of the film.

3. Results

3.1. Properties of PCPS

The density of PCPS was found to be 0.204 g cm^{-3} and its porosity was 77 vol%, which implies an open-pore structure with a large internal area in which most of the pores are connected by channels [10]. Pore sizes were determined from SEM images and were in the range 1–10 μm. Additional details are provided elsewhere [17].

3.2. Properties of PPy/PCPS composites

After 24 h of contact with I_2 vapor, the color of the PCPS strip changed to purple and its mass increased by 12%. Optical images of the strip (Fig. 1(a) and (b)) clearly show that the distribution of I_2 in the strip was not uniform, with the amount of I_2 gradually decreasing from the surface exposed directly to I_2 to the opposite face. This shows that I_2 is not able to penetrate the PCPS matrix under its own vapor pressure in 24 h. Subsequent contact of the I_2-impregnated PCPS strip with Py vapor resulted in an additional mass gain of 46% and a color change to black due to the formation of PPy. However, the distribution of PPy in the matrix was also not uniform, in spite of the relatively high content of PPy in the composite (suggested by the 46% mass gain). As a result, the bulk and surface conductivities were only 3.24×10^{-7} and 1.31×10^{-8} S cm^{-1}, respectively, and no volume conductivity was detected.

Increasing the contact time to 7 days for I_2 (to allow adequate penetration) and an additional 2 days for Py vapor resulted in mass gains of 47% after I_2 contact, and 113% after Py contact, respectively. The bulk and surface conductivities increased to 9.29×10^{-4} and 1.68×10^{-5} S cm^{-1} and a volume conductivity of 5.43×10^{-6} S cm^{-1} was measured. However, the level of conductivity attained is still low, implying a failure to form a completely connected network of PPy in the pores. Fig. 2 validates this conclusion, showing that relatively large particles of PPy (Fig. 2(a)) were formed on the surface of the composite, and small granular PPy nodules

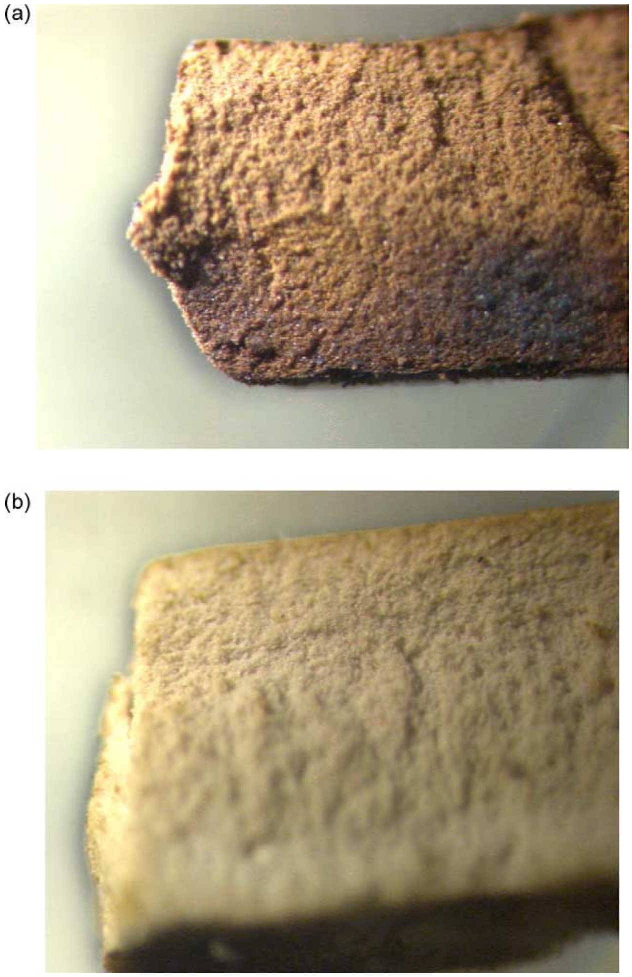

Fig. 1. Optical micrographs of the cross-section of the (a) exposed and (b) unexposed surfaces of a PCPS sample exposed to I_2 vapor (×25).

(~100 nm in diameter) were deposited on the walls of the pores (Fig 2(b)). The nodule morphology of PPy has been observed in composites prepared chemically in the absence of a solvent [20], as well as electrochemically in CO_2 modified with acetonitrile [21]. Neither of these morphologies leads to a continuous uniform network of PPy in the pores.

Since experiments without a solvent required long contact times and produce a partially formed network of the ICP, they were repeated with CO_2 as the solvent for both I_2 and Py. The CO_2 experiments were performed in the high-pressure reactor at 313 K and 10.5 MPa. A PCPS strip was first contacted with I_2 and CO_2 for a specified time interval ranging from 0.5 to 24 h, and then with Py and CO_2 for 24 h. Mass gains were recorded after each step, and the mass of I_2 and $PPy+I_2$ complex formed was calculated. The calculations assumed that all of the impregnated I_2 is incorporated in the substrate in the form of a PPy charge transfer complex [15]. This allows the amount of PPy to be estimated. The amount of $PPy+I_2$ complex formed is plotted against the amount of I_2 impregnated in Fig. 3. The relationship was found to be linear, suggesting that the polymer yield depends only on the amount of the I_2 impregnated in the substrate and that polymerization proceeds with a constant molar ratio of 4.5 Py moles to 1 mole of I_2 (calculated from the slope of the line). This ratio is in agreement with a value of ~4:1 reported by Kang et al. [22] for PPy complexes synthesized in acetonitrile. Similar values have also been reported for PPy complexes in polyurethane foams [23].

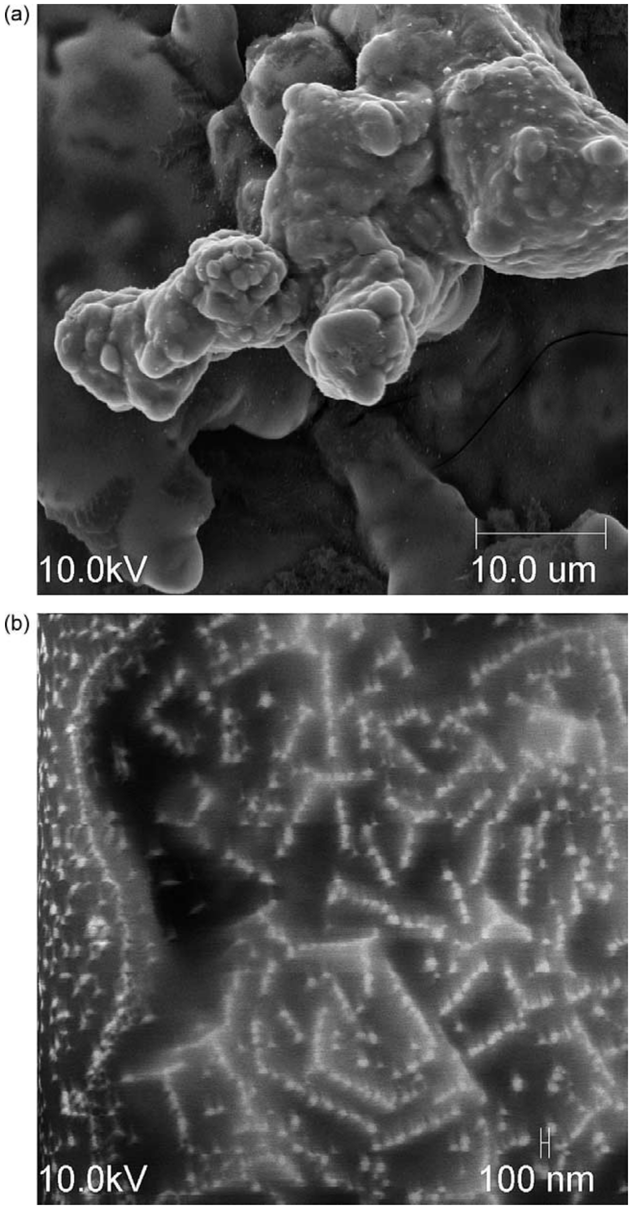

Fig. 2. SEM micrographs of the (a) surface (×1500) and (b) cross-section (×3000) of a PPy/PCPS composite.

The bulk, surface, and volume conductivities of the composites are plotted versus the amount of $PPy+I_2$ complex in Fig. 4. These conductivities exhibit percolation behavior, although the percolation threshold is higher (~10 wt%) than in experiments conducted in the absence of CO_2. The bulk conductivity attained values as high as 10^{-3} S cm^{-1}. Therefore, the use of CO_2 appears to facilitate the transport and deposition of the oxidant and monomer to the pores, leading to a more uniform distribution of the conducting polymer in the host. The volume conductivity exhibited a stepwise transition with respect to the substrate mass at around 100 wt% $PPy+I_2$.

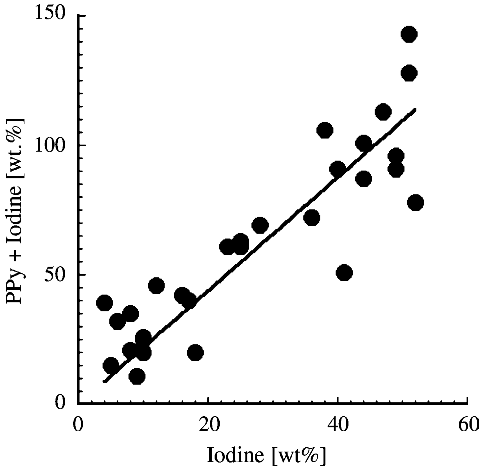

Fig. 3. Amount of conductive PPy + I_2 complex in the PPy/PCPS composite as a function of amount of I_2 impregnated.

At high loadings, the degree of connectivity of the conducting polymer network is probably sufficient to provide uniform conductivity in all directions. Therefore, the distribution of PPy in the composite must not have been uniform below the transition point. This was confirmed by examining cross-sections of the composite under an optical microscope and noting that at low loadings (below the transition point), a gradual color change from the surface to the center of the composite could be observed.

A reverse preparation procedure was also evaluated with the impregnation of Py monomer for 24 h, followed by contact with I_2 and supercritical CO_2 for 24 h. The mass gains after each step were 83 and 49%, respectively. The smaller mass gain in the second step can be attributed to diffusion of Py out of the substrate before the I_2 reaches the pores. An SEM picture of the composite showed that dense layers of PPy were formed near the surface of the composite whereas thin layers of PPy were deposited on the pore walls. The final bulk and surface conductivities were 1.52×10^{-5} and 1.31×10^{-6} S cm^{-1}, respectively.

A final experiment was conducted with a PCPS strip being contacted with I_2 and CO_2 at 313 K and 10.5 MPa for 4 h, followed by exposure of the impregnated strip to Py vapor at room temperature (300 K) for 48 h. The mass gains were 29% and 90 wt% after each step. The distribution of PPy in the composite was uniform and the bulk and surface conductivities attained values of 7.01×10^{-5} and 5.63×10^{-6} S cm^{-1}, respectively.

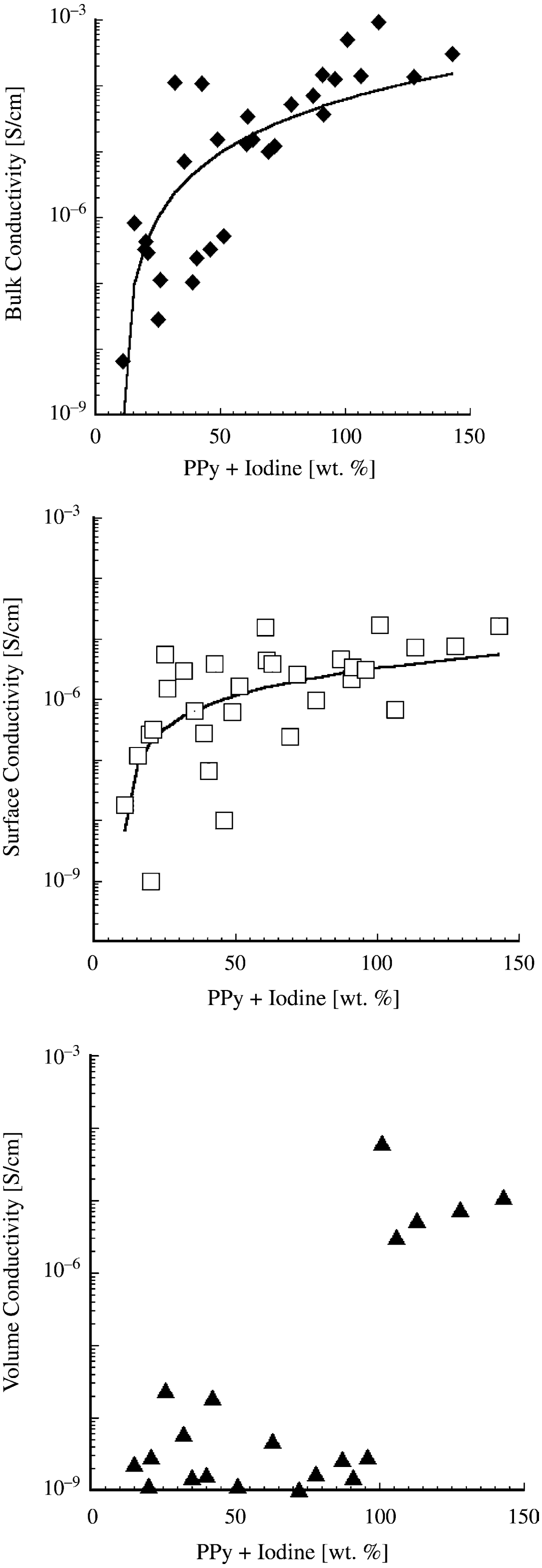

Fig. 4. Bulk, surface, and volume conductivities of PPy/PCPS composites.

3.3. Partitioning of I_2 between PCPS and the supercritical fluid phase

The partitioning of I_2 between the PCPS substrate and the fluid phase was estimated from the amount of I_2 deposited in the PCPS strips and the solubility data (amount in the CO_2 phase) of Fang et al. [16]. The 'partition coefficient' (defined as the mass fraction of I_2 in the polymer divided by the mass fraction of I_2 in the CO_2) was found to decrease with CO_2 density at 313 K due to an increase in the solubility (and therefore, weight fraction) of I_2 in the CO_2 phase. This is quite common behavior for heavy solutes in supercritical CO_2. The decrease in the 'partition coefficient' implies that the amount of I_2 deposited in the polymer decreases with pressure. Fig. 3 shows that a decrease in the amount of I_2 in PCPS will

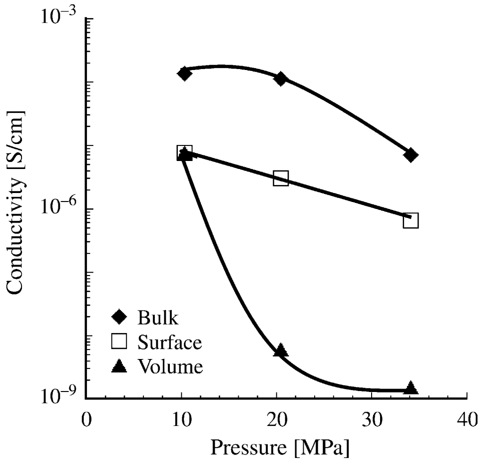

Fig. 5. Electrical conductivity of PPy/PCPS composites at 313 K as a function of CO_2 pressure.

result in a decrease in the conductivity of the composite. The conductivity plots are shown in Fig. 5 and demonstrate that the conductivity does, indeed, decrease with pressure. Hence, it may be possible to control the conductivity by manipulating CO_2 pressure.

3.4. Thermal stability

Thermal stability of several samples was determined by TGA analysis and mass changes as a function of temperature are plotted in Fig. 6. The onset of weight loss near room temperature can be attributed to water vaporization, since PPy is hygroscopic and can absorb water during storage [24]. The weight loss becomes dramatic above 600 K, corresponding to substrate decomposition. The calculated decomposition temperatures are 634 K for PCPS and 689 K for the PCPS/PPy composite. The latter value compares well with a value of ∼660 K reported by Omastova et al. [25]. These authors noted that the higher decomposition temperature of the composite may be due to a PPy layer covering the surface of the PCPS and partially preventing its decomposition. The composite also exhibited weight loss around 473 K, probably due to I_2 vaporization.

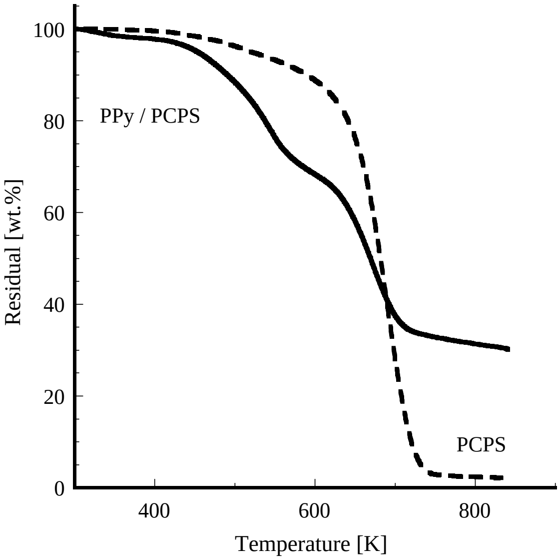

Fig. 6. Thermogravimetric analysis of PCPS and its composite with PPy.

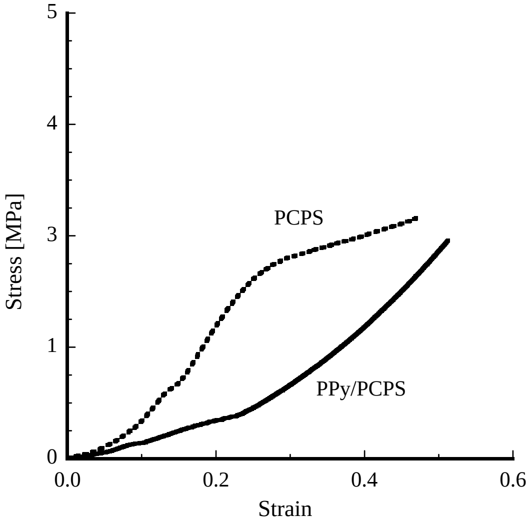

Fig. 7. Compressive stress–strain curve of PCPS and its composite with PPy.

3.5. Compressive strength

The compressive stress–strain relationships for several samples are shown in Fig. 7. The yield stress of the PCPS was ∼2.1 MPa at a strain of 0.28, which is close to that of polystyrene foams (0.9–2.5 MPa) calculated by the equation of Gibson and Ashby [26]. The PCPS/PPy composites did not exhibit a distinct yield point but did exhibit fluctuations in the stress–strain behavior at low strain (∼0.1). This may correspond to failure of weak cells. The stress at the onset of these fluctuations was ∼0.9 MPa at a strain of 0.15, which is the lower limit of yield stress in polystyrene foams.

Since there was a linear portion prior to yield in each stress–strain curve, the slope of this linear portion was used to calculate Young's modulus—estimated at 13.9 MPa for PCPS

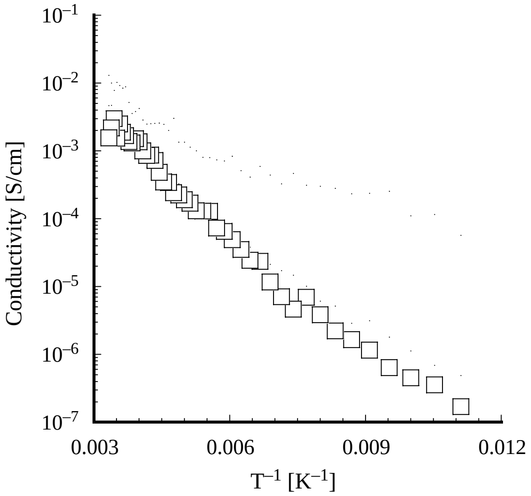

Fig. 8. Arrehenius plot of conductivity.

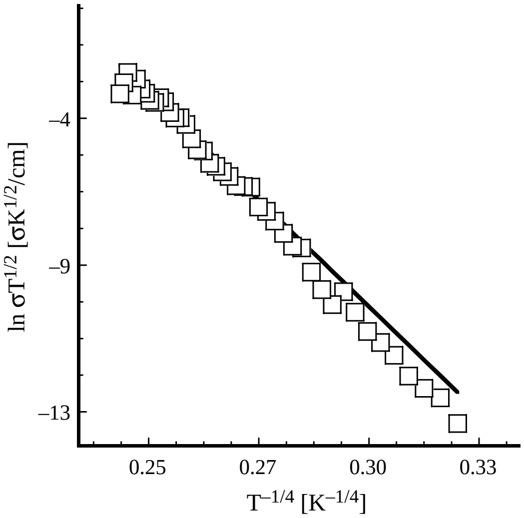

Fig. 9. Plot of ln $\sigma T^{1/2}$ as a function of $T^{-1/4}$.

and 22.7 MPa for PCPS/PPy composites. The higher value for the composite may be due to a uniform coating of stiff and ordered PPy.

3.6. *Effect of temperature on electrical conductivity*

The dc electrical conductivity of the composite is plotted as a function of the reciprocal temperature in Fig. 8. The slope suggests that the activation energy E_A depends on the temperature and therefore, hopping conduction rather than band conduction may dominate the mechanism of conduction in the composite [27]. The applicability of the Mott's variable-range hopping (VRH) model [28] was investigated in which the temperature dependence of conductivity is given by

$$\sigma(T) \propto T^{1/2}\exp\left[-\left(\frac{T_0}{T}\right)^{-1/(n+1)}\right]$$

where n (=1, 2, and 3) is the number of dimensions in which hopping occurs, and T_0 is a constant. Fig. 9 shows a plot of ln $\sigma T^{1/2}$ as a function of $T^{-1/4}$ and shows good agreement between the VRH model and the data of this work, indicating three-dimensional hopping as the dominant mechanism of electrical conductivity in PPy/PCPS composites. However, the data could be equally well correlated using an exponent of 1 or 2, as well as the charge-energy-limited tunneling (CELT) model of Sheng and Abeles [29] and Sheng et al. [30].

4. Conclusions

Composites (~3 mm in thickness) of PPy with electrically insulating PCPS were prepared using a two-step batch method in which PCPS was first impregnated with I_2 and then with Py resulting in the in situ polymerization to PPy in the pores of PCPS. The use of supercritical CO_2 as a solvent for both I_2 and Py facilitated the transport and deposition of these substances in the pores leading to composites with higher levels of conductivity (as high as 10^{-3} S cm^{-1}). Moreover, the pressure could be used to vary the partitioning of I_2 between the supercritical phase and the host polymer, and hence control the deposition of I_2 in the pores. The amount of PPy + I_2 complex formed was found to be linearly proportional to the amount of I_2 impregnated in the substrate. Since this amount is related to the level of conductivity in the composite, this work shows that the manipulation of pressure during the impregnation step can potentially be used to control the level of conductivity of the composite. The bulk and surface conductivities of the composite exhibited percolation behavior with respect to the amount of the PPy + I_2 complex formed. However, the percolation threshold was higher (~10 wt%), and the bulk and surface conductivities lower by one or two orders of magnitude than those of the composite prepared with $FeCl_3$ at similar PPy concentrations. The volume conductivity exhibited a stepwise transition around 100 wt% of PPy + I_2 complex with respect to the substrate weight, when the degree of connectivity of the PPy network is apparently sufficient to have uniform conductivity in all directions. A disadvantage of using iodine as the oxidant is that it tends to diffuse out of the substrate because of its volatility, a process that is accelerated in the presence of supercritical carbon dioxide. This counter-diffusion can lead to the formation of a conducting surface layer, and hence a non-uniform distribution of PPy.

The percolation threshold was as low as 10 wt% suggesting that the stability and mechanical strength of the composites would approximately be that of the PCPS. This was verified by TGA and compressive strength measurements. The temperature behavior of the conductivity conformed with Mott's variable-range hopping (VRH) model suggesting three-dimensional electronic transport. However, the data could also be correlated equally well with the CELT model.

Acknowledgements

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