Macromolecules **1997,** *30,* 7611−7613

Synthesis of Conductive Polypyrrole/Polyurethane Foams via a Supercritical Fluid Process

Yueping Fu, Daniel R. Palo,
Can Erkey,* and R. A. Weiss*

Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut 06269

Received July 17, 1997
Revised Manuscript Received September 26, 1997

Introduction

In the past fifteen years, significant progress has been made on organic conducting polymers with novel electrical, optical and electrochemical properties.[1−8] Among the intrinsically conducting polymers, polypyrrole (PPy) has received much attention, because it is relatively stable in air and exhibits reasonably high conductivity, $\sim 10^2$ S/cm. PPy may be readily synthesized by either oxidative chemical or electrochemical polymerization of pyrrole, though PPy films are insoluble, hard, and brittle.

One way to overcome the poor mechanical properties of PPy and exploit its inherent electrical conductivity is to blend it with another polymer. That approach has prompted the development of composite materials in which the electrically conducting polymer is dispersed into an insulating polymer matrix either directly or by an *in-situ* polymerization. *In-situ* polymerization of pyrrole may be accomplished by exposing a polymer host containing a suitable oxidant to pyrrole vapor, and that procedure has been used to prepare conductive blends based on a variety of different polymer matrices. The subject was recently reviewed.[9]

To incorporate the oxidant into the polymer matrix, an aqueous or organic solvent is generally used to swell the polymer and facilitate the penetration of the oxidant. After *in-situ* polymerization, the conductive composite is washed with a solvent to remove unwanted reaction byproducts. The process generates large amounts of solvent contaminated with metal salts, and the disposal of the waste is a major economic and environmental concern. That problem may be eliminated by using nontoxic supercritical fluids (SCFs) as solvents. Supercritical carbon dioxide ($SCCO_2$) is particularly attractive since it is nontoxic, nonflammable, and environmentally acceptable and has a moderate critical temperature and pressure. Moreover, carbon dioxide leaves no residue in the treated polymer. Such properties combined with high diffusivities of solutes in $SCCO_2$ may be exploited to impregnate polymers with a wide variety of chemicals.[10−13]

In the present study, we investigated the use of $SCCO_2$ in the *in-situ* polymerization of pyrrole within a preformed polyurethane foam. The major objective was to determine the technical feasibility of replacing organic solvents with $SCCO_2$ for impregnating the oxidant into the foam and for removing the byproducts of the pyrrole polymerization reaction from the foams.

Experimental

Pyrrole was distilled and stored in a refrigerator. Trifluoromethane sulfonic acid (TFMSA), CF_3SO_3H, was obtained from Aldrich Chemical Co. Ferric triflate (TF), $Fe(CF_3SO_3)_3$, was prepared by neutralizing TFMSA with ferric hydroxide, $Fe(OH)_3$, and FT was used as the oxidant for the pyrrole polymerization. $Fe(OH)_3$ was synthesized by mixing a 0.31 M aqueous ferric chloride ($FeCl_3{\cdot}6H_2O$) solution with a stoichiometric amount of a 3.7 M aqueous sodium hydroxide (NaOH) at room temperature with vigorous stirring. A brown precipitate of $Fe(OH)_3$ was allowed to settle for 2−3 h, and the supernatant liquid was siphoned off. The $Fe(OH)_3$ was then washed with water two or three times and then filtered. $Fe(CF_3SO_3)_3$ was prepared by mixing stoichiometric quantities of TFMSA and $Fe(OH)_3$ in methanol for 3 h at 50 °C. $Fe(CF_3SO_3)_3$ was isolated by evaporating the methanol solvent and drying the residue under vacuum. Polyurethane (PU) foams with a density of 0.3 g/cm^3 were obtained from Rogers Corporation (Rogers, CT).

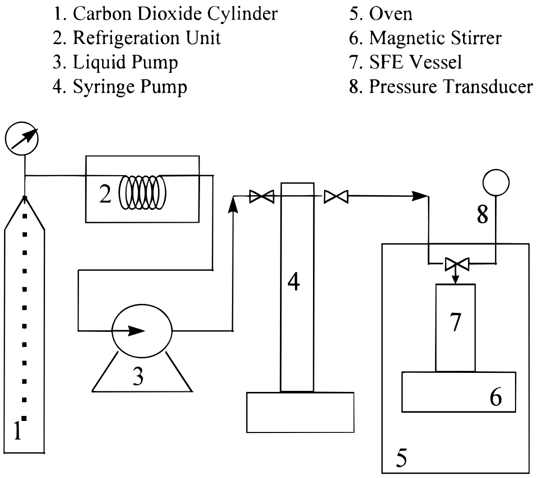

Figure 1. Schematic diagram of the apparatus.

PU foam specimens, 15 × 5 × 2 mm were impregnated with $Fe(CF_3SO_3)_3$ dissolved in $SCCO_2$ in a batch process. A schematic diagram of the $SCCO_2$ impregnation setup is given in Figure 1. For a typical experiment, 100 mg of $Fe(CF_3SO_3)_3$, the foam, and a magnetic stir bar were placed into a supercritical fluid extraction vessel (Valco, SFED.625−5) with an internal volume of 10 cm^3. The vessel was sealed and placed on a magnetic stirrer in a constant temperature oven (Thelco, 2DG). Liquid CO_2 was charged into the vessel using a high-pressure syringe pump (ISCO, 260D) equipped with a cooling jacket. The temperature was monitored with a T-Type thermocouple (Omega Engineering) inserted into the oven and a thermocouple meter (DP41-TC-MDSS, Omega Engineering) accurate to ±0.1 °C. After a measured period of time, the carbon dioxide was slowly vented, and the impregnated amount of oxidant was determined from the change of mass of the foam. The soak time was varied between 0 and 24 h at 45 °C and 238 atm. The PU foams containing various amounts of $Fe(CF_3SO_3)_3$ were then exposed to pyrrole vapor in a dessicator under a pressure of ca. 1 Torr for 4 h. Following the polymerization, the composite foams were washed with methanol several times to remove unreacted oxidant and byproducts, dried in air for 1−2 h, and then put under vacuum for 24 h. The *in-situ* polymerization process did not affect the structure of the PU foam.

Conductivity measurements were made with a four-probe fixture consisting of four parallel copper wires separated by 4 mm that were pressed onto the PU specimen. A constant current supplied by a Keithley 224 Programmable Current Source was applied through the outer wires, and the voltage drop across inner wires was recorded with a Keithley 197A Autoranging Microvolt DMM meter. Thermogravimetric analysis (TGA) was done with a Perkin-Elmer TGA-7 using a nitrogen atmosphere and a heating rate of 20 °C/min.

Results and Discussion

Pyrrole has a relatively low oxidation potential and can be polymerized with an oxidizing agent such as $FeCl_3$.[13] Fe(III) salts such as $FeCl_3$ provide a convenient

---

* Authors to whom inquiries should be addressed.

S0024-9297(97)01074-7 CCC: $14.00

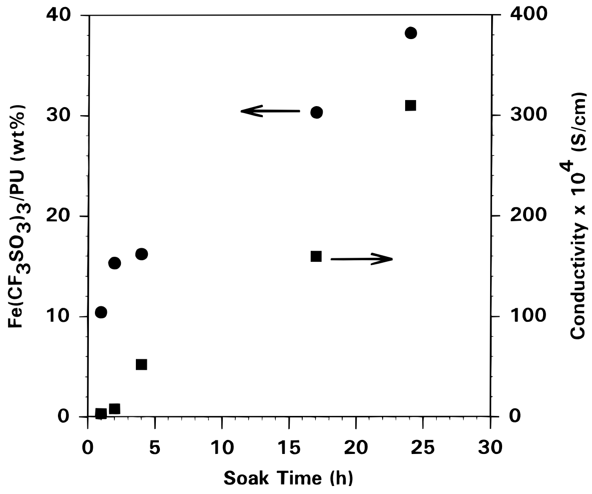

Figure 2. Variation of $Fe(CF_3SO_3)_3$ uptake and conductivity with soak time in $SCCO_2$ at 45 °C and 238 atm.

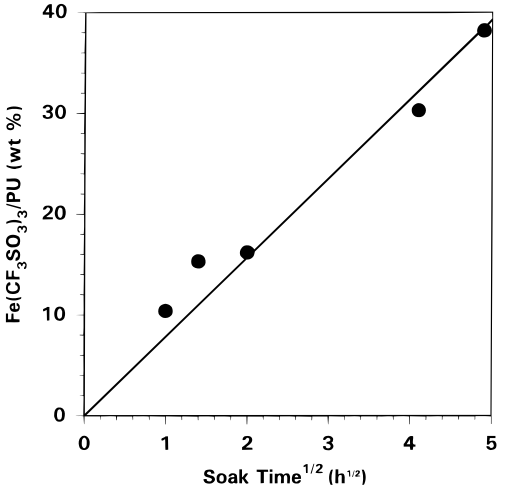

Figure 3. Variation of $Fe(CF_3SO_3)_3$ uptake with square root of soak time in $SCCO_2$ at 45 °C and 238 atm.

means for oxidatively polymerizing pyrrole and incorporating the "dopant" counterions for the conductive polymer. Since most inorganic salts are insoluble in $SCCO_2$, ferric triflate was used as the oxidant. The triflate ion has recently been utilized in asymmetric catalytic hydrogenation of enamides in $SCCO_2$ as a counteranion to solubilize cationic catalysts.[14] $Fe(CF_3SO_3)_3$ is also a suitable oxidant for the chemical polymerization of pyrrole and generates highly conductive PPy.[15]

The solubility of $Fe(CF_3SO_3)_3$ in $SCCO_2$ at 45 °C and 238 atm is ca. 0.01 wt % as measured using a flow technique. The details of the experimental setup and procedure are given elsewhere.[16] The reasonably high solubility may be attributed to the trifluoromethane groups.

Figure 2 plots the uptake of $Fe(CF_3SO_3)_3$ by the PU foams and the conductivity of the resulting PPy/PU foams composites as a function of soak time in the saturated oxidant/$SCCO_2$ solution. The sorption data are replotted in Figure 3 as a function of the square root of immersion time. The linear relationship observed in Figure 3 indicates Fickian diffusion of $Fe(CF_3SO_3)_3$ into the polymer matrix. The increase in oxidant concentration with immersion time was accompanied by an increase in conductivity of the resultant composite foam, which increased monotonically with the immersion time and reached a value of 0.03 S/cm for an immersion time of 24 h.

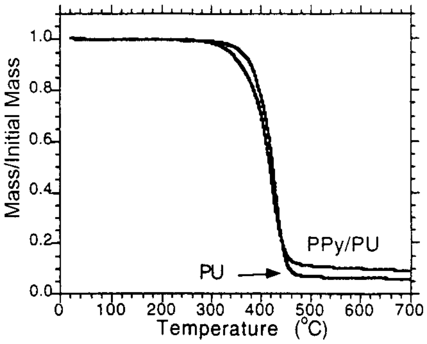

Figure 4. TGA of neat PU foam and a conductive PPy/PU foam.

The amount of PPy produced in the composites was estimated to be ca. 3 wt % for the most conductive sample. Normally, for a dense material filled with spherical conductive particles, the percolation threshold for conductivity is ca. 16 vol %.[17] For PPy/polymer composites, vol % and wt % values are about the same since the densities of most organic polymers are fairly similar. The unusually low percolation threshold concentration for the foam may be attributed in part to the incorporation of PPy only into the polymeric cell walls of the foam, i.e., the struts. However, even if one considers only the concentration of PPy within the PU phase, the concentration is lower than what would be expected for percolation of particles. That suggests that the rodlike PPy molecules may have been preferentially aligned parallel to the walls of the foam cells, though globally within the sample there was no preferred orientation of the PPy and the conductivity of the foam was isotropic. Lower percolation volume fractions have been reported when the conductive polymer phase was anisotropic or if specific interactions occurred between the components of the blend. [18,19]

TGA results under nitrogen for a neat PU foam and a conductive PPy/PU foam are shown in Figure 4. Both samples lost less than 3% mass below 300 °C. The major degradation process occurred for both materials between 300 and 400 °C. Although the PPy/PU composite appeared to begin to degrade at a temperature 10−20 °C lower than the neat PU foam, that difference was probably not significant, given that experimental factors such as sample thickness and viscosity can affect the volatiles removal rate in a dynamic TGA experiment. In effect, there is probably no significant difference between the two TGA thermograms shown in Figure 4, which would indicate that the *in-situ* polymerization process had no deleterious effect on the stability of the PU foam. The composite sample lost about 3% less mass at the highest temperatures than the PU foam, which can be attributed to the concentration of PPy in that specimen. The residual mass in the PU foam is due to the catalyst and additives used in the foam process.

The removal of the *in-situ* polymerization byproducts, i.e., $Fe(CF_3SO_3)_2$ and unreacted $Fe(CF_3SO_3)_3$, with $SCCO_2$ was also evaluated. Strips of the composite foams were packed into a 5-cm^3 vessel and $SCCO_2$ was passed through the vessel at 45 °C and 238 atm. That $SCCO_2$ wash process, however, was less effective than organic solvents at removing the reaction byproducts, presumably due to lower solubility of the products in $SCCO_2$ than in methanol. Research is currently underway on the synthesis and testing of a variety of other oxidants that are expected to exhibit higher solubility in $SCCO_2$ due to the presence of CO_2-philic groups.

References and Notes

(1) *Handbook of Conducting Polymers*; Skotheim, T. J., Ed.; Marcel Dekker: New York, 1986.
(2) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183.
(3) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
(4) Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209.
(5) *Conjugated Polymers and Related Materials*; Salaneck, W. R., Lundstron, I., Ranby, B., Eds.; Oxford University Press: Oxford, New York, 1993.
(6) *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Kluwer Academic Publishers: Dordrecht, 1989.
(7) *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics*; Bredas, J. L., Chance, R. R., Eds.; Kluwer Academic Publishers: Dordrecht, 1989.
(8) *Conjugated Polymers*; Bredas, J. L., Silbey, R., Eds.; Kluwer Academic Publishers: Dordrecht, 1991.
(9) DeJesus, M. C.; Fu, Y.; Weiss, R. A. *Polym. Eng. Sci.*, in press.
(10) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice;* Butterworth-Heinemann: Boston, MA, 1994.
(11) Howdle, S. M.; Ramsay, J. M.; Cooper, A. I. *J. Polym. Sci. B—Polym. Phys.* **1994**, *32*, 541.
(12) Berens, A. R.; Huvard, G. S.; Korsmeyer, R. W.; Kunig, F. W. *J. Appl. Polym. Sci.* **1992**, *46*, 231.
(13) Genies, E. M.; Bidan, G.; Diaz, A. F. *J. Electroanl. Chem.* **1983**, *149*, 101.
(14) Morgenstern, D. A.; LeLacheur, R. M.; Morita, D. K.; Borkowsky, S. L.; Feng, S.; Brown, G. H.; Luan, L.; Gross, M. F.; Burk, M. J.; Tumas, W. In *Green Chemistry: Designing Chemistry for the Environment*. Anastas, P. T., Williamson, T. C., Eds.; American Chemical Society: Washington, DC, 1996.
(15) Walker, J. A.; Warren, L. F.; Witucki, E. F. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1285.
(16) Palo, D. R.; Erkey, C. *J. Chem. Eng. Data*, submitted for publication.
(17) Levon, K.; Margolina, A.; Patashinsky, A. Z. *Macromolecules* **1993**, *26*, 4061.
(18) Andreatta, A.; Heeger, A. J.; Smith, P. *Polym. Commun.*, **1990**, *31*, 275.
(19) Balberg, I.; Anderson, C. H.; Alexander, S.; Wagner, N. *Phys. Rev. B* **1984**, *30*, 3933.

MA9710747