

# Preparation of Conducting Composites of Polypyrrole Using Supercritical Carbon Dioxide

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**ABSTRACT:** Supercritical carbon dioxide, saturated with pyrrole, was brought into contact with oxidant-impregnated films of poly(chlorotrifluoroethylene) (PCTFE), crosslinked poly(dimethylsiloxane) (PDMS), poly(methyl methacrylate) (PMMA), and porous crosslinked polystyrene (PS) in order to form conducting composites via the *in situ* polymerization of pyrrole. The two nonporous hosts—PCTFE and crosslinked PDMS—did not form conducting composites with polypyrrole (PPy). On the other hand, the electrical conductivity of the PPy composites with carbon dioxide-

swollen PMMA and porous PS ranged from  $1.0 \times 10^{-4}$  S/cm to  $3.0 \times 10^{-5}$  S/cm. In these two cases, the level of pyrrole polymerized on the surface or in the pores of the host polymer was sufficient to attain the interconnected conducting polymer networks necessary for electrical conductivity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1113–1116, 2003

**Key words:** polypyrrole; composites; conducting polymers; morphology

## INTRODUCTION

The conducting polymer field has expanded rapidly in recent years, and many intrinsically conducting organic polymers have been synthesized for applications such as electrochromic and electro-optic devices, packaging materials, actuators, batteries, sensors, and catalysts.<sup>1,2</sup> However, limited mechanical stability and poor processibility of these organic conductors, especially in the highly conducting state, must be overcome before some of the potential uses of these polymers can be realized. One way to overcome these limitations is by the formation of composites with insulating polymers that have high mechanical strength. Blends have been formed by dispersing the electrically conducting polymer into a non-porous insulating polymer host, either directly or via *in situ* polymerization.<sup>3,4</sup> However, this requires an organic solvent to swell the host polymer and to facilitate the penetration of the oxidant and the monomer into the host substrate. On the other hand, the deposition of the conducting polymer into a porous polymer matrix to form a conducting composite can be achieved relatively easily,<sup>5</sup> although organic solvents may still be required to impregnate the host with an oxidant.

Processing with supercritical fluids offers an attractive alternative to conventional processing with organic solvents.<sup>6</sup> The organic solvent can be replaced

by an inexpensive, environmentally benign solvent such as carbon dioxide, which also offers high mass transport rates and, possibly, *in situ* removal of unreacted monomer and other impurities. In addition, temperature and pressure can be controlled to change the solvent properties. Because of these advantages, supercritical fluids have been used as solvents in polymerizations<sup>7,8</sup> and in the preparation of conductive composites.<sup>9,10</sup>

Conductive composites of polypyrrole (PPy) and polyurethane foams (PU) have been prepared by impregnating the host PU with a suitable oxidant (e.g. ferric chloride or ferric triflate), followed by exposing the foam to pyrrole vapor.<sup>9–11</sup> A solvent such as methanol is used to transport an oxidant such as ferric chloride into the foam.<sup>11</sup> Supercritical carbon dioxide can be used as the solvent when ferric triflate is the oxidant because of the latter's appreciable solubility in the supercritical fluid.<sup>10</sup> Reported conductivities of the composite foams ranged from  $10^{-7}$  to  $10^{-1}$  S/cm, depending on the concentration of the oxidant in the host.<sup>9–11</sup> However, supercritical carbon dioxide does not appreciably swell PU, and no attempt was made to utilize its properties to transport pyrrole into the host.

In this work, supercritical carbon dioxide was used as a transporter as well as reaction medium for the *in situ* polymerization of pyrrole into a host polymer, poly(methyl methacrylate) (PMMA), which is appreciably swollen by carbon dioxide; and into another host, crosslinked polystyrene (PS), which can be obtained with fairly uniform pores that allow uninhibited penetration by carbon dioxide.<sup>5</sup> Two other host polymers, poly(chlorotrifluoroethylene) (PCTFE), and

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crosslinked poly(dimethylsiloxane) (PDMS), were also examined because, although nonporous, they are known to absorb high levels of supercritical carbon dioxide.<sup>6,12</sup> Pyrrole has significant solubility in supercritical carbon dioxide,<sup>9,10</sup> and its partitioning between the supercritical phase and the host polymer phase would be expected to play a role in the level of conductivity attained by the composites. Each host was first impregnated with ferric chloride, which acts as a catalyst/oxidant to facilitate the polymerization of pyrrole.

## EXPERIMENTAL

### Materials

Coleman grade carbon dioxide (99.9% purity) and nitrogen were purchased from Air Products (Bethlehem, PA) and used as received. Ferric chloride was purchased from Aldrich and also used as received. Acetonitrile was purchased from Fisher, nitrobenzene from Aldrich (Milwaukee, WI), and chloroform was purchased from J.T. Baker (Phillipsburg, NJ). All solvents had a stated purity greater than 99 wt % and were used as received. Polymer host substrates used in these experiments were purchased or synthesized as discussed in a previous work.<sup>12</sup>

### Experimental

The apparatus consisted of an ISCO SFX 2–10 vessel connected to two ISCO 260D and 500D pumps for pressurizing the carbon dioxide to supercritical conditions. A cooler with a circulating system (Precision Scientific model 254) was used to circulate coolant to the pumps. Temperature was controlled with a temperature controller (Fuji PYZ4-TCY1-4V), calibrated with a digital thermometer (Fluka model 2180A). A pressure gauge (Heise CMM 51848) was used to measure the pressure in the vessel. The Heise gauge was calibrated with a dead weight tester (Budenburg model 380H).

### Ferric chloride impregnation

Ferric chloride (anhydrous) solutions in acetonitrile, chloroform, and nitrobenzene were prepared by adding 1 g of ferric chloride to 25 mL of solvent. Films of the host polymers (4.0 cm × 0.5 cm × 0.03–0.29 cm) were weighed and then soaked in the solutions for various time intervals. The mass gain of each film was recorded as a function of time, and the samples with the maximum mass gain were identified for further study. The samples were subsequently dried in a vacuum for several hours to remove any residual solvent. PMMA was soluble in these solvents, so the impregnation of ferric chloride into this polymer was at-

**TABLE I**  
**Properties of PPy/Host Composites**

Host polymer	FeCl <sub>3</sub> (wt %)	PPy (wt %)	Conductivity (S/cm)
PCTFE	0.2	1.0	0
PDMS	0.6	2.1	0
PMMA	—	5.3	$1.0 \times 10^{-4}$
PS	8.1	13.4	$3.0 \times 10^{-5}$

tempted by placing ferric chloride and PMMA in a cell pressurized with supercritical carbon dioxide at 313 K and 10.5 MPa. At the conclusion of the experiment (corresponding to maximum swelling of the polymer), ferric chloride could be detected in a thin layer on the outer surface of the PMMA under an optical microscope.

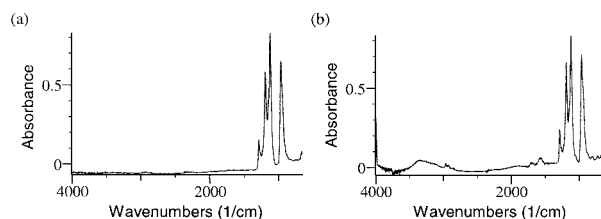
### Composite experiments

The ferric chloride impregnated host polymers, together with a small amount of pyrrole, were placed in the ISCO SFX 2–10 reaction vessel maintained at 313 K. The vessel was pressurized with carbon dioxide until a pressure of 10.5 MPa was attained, and then maintained at these conditions for a length of time necessary for the host polymer to absorb the maximum amount of carbon dioxide (determined in a separate set of experiments<sup>12</sup>). The carbon dioxide, saturated with pyrrole, diffused into the host polymer to locations where ferric chloride was also present, thus facilitating the polymerization of pyrrole. The vessel was then quickly depressurized and the host polymer samples weighed to obtain the mass gain due to PPy. The actual amount of PPy was determined by elemental analysis, and the electrical conductivity of the composite was measured with a four-point probe.

## RESULTS AND DISCUSSION

### Elemental analysis

The amounts of ferric chloride and PPy in the host substrates were determined by an elemental analysis of iron and chlorine or nitrogen in the sample. The weight percents of ferric chloride and PPy in the composites are presented in Table I. Chloroform, nitrobenzene, and acetonitrile were the solvents that yielded the greatest amount of uptake of ferric chloride in PCTFE, PDMS, and PS, respectively. PMMA samples contained only trace amounts of ferric chloride (most of the ferric chloride being found in a surface layer, as discussed above). The elemental analysis of PMMA is therefore not presented in Table I. The composites of PPy with PCTFE and PDMS contained very little PPy because the host polymers are nonporous and absorbed only small amounts of ferric chloride.



**Figure 1** FTIR-ATR of (a) PCTFE and (b) PCTFE/PPy composite.

### FTIR-ATR

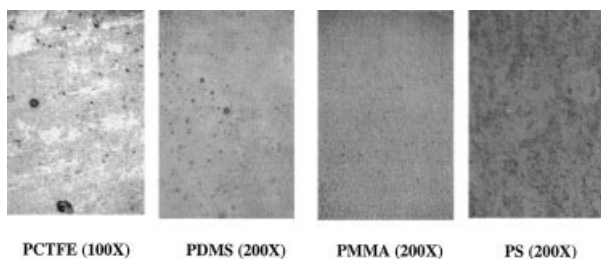
IR spectra were obtained using a Nicolet IR microscope for all hosts and composites.<sup>12</sup> Figure 1 shows the IR spectra of PCTFE and PPy/PCTFE. The composite spectrum exhibits an additional peak at  $1550\text{ cm}^{-1}$ , which is generally assigned to the ring vibrations of PPy.<sup>13</sup> Similar results were obtained with the other samples.

### Morphology

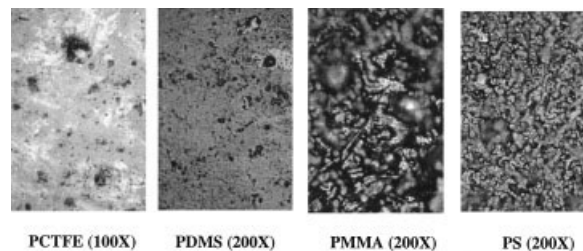
Optical micrographs of the host substrates after soaking in ferric chloride solutions are shown in Figure 2. The host substrates were all transparent prior to soaking except for PS, which was opaque. All substrates changed color after soaking, although clear areas can still be seen in the PCTFE and PDMS samples, due to the absence of ferric chloride in the transparent regions. The micrographs also show some very dark spots, which can be attributed to an excess of ferric chloride. The distribution of ferric chloride was found to be much more uniform in PMMA and PS, which is desirable because it leads to more uniform composites.

Figure 3 shows optical micrographs of the composites obtained in this work. The treated PPy/PCTFE sample was mostly clear, except for some yellow spots due to ferric chloride. By contrast, the PPy/PDMS sample was almost entirely black, with a few clear spots where no PPy or ferric chloride was present. In both of these hosts, low resistivity domains of PPy were separated by high resistivity domains<sup>14</sup> where no PPy was present.

PPy/PMMA and PPy/PS composites were found to exhibit connected black domains of PPy separated by



**Figure 2** Micrographs of polymer hosts after ferric chloride absorption.



**Figure 3** Micrographs of PPy/Host composites.

thin insulating layers. This connected domain morphology appears to be essential for electrical conductivity, as discussed by several authors.<sup>15–17</sup>

### Electrical conductivity

Electrical conductivities were determined with a four point probe and are shown in Table I. PPy/PCTFE and PPy/PDMS composites exhibited negligible overall electrical conductivity. The amount of PPy in these composites was small, resulting in the absence of connected domains. PPy/PMMA composites exhibited the highest electrical conductivity, although most of this was due to surface conductivity resulting from a thin layer of PPy on the surface of PMMA. PPy/PS composites exhibited almost the same electrical conductivity as PPy/PMMA composites, and furthermore the conductivity appeared to be uniform throughout the sample. The PPy/PS samples also showed uniformly distributed and connected domains of PPy under an optical microscope. Microporous polymers therefore appear to be ideal host polymers for the preparation of conducting composites.<sup>5,17</sup> The conductivities obtained in the present work ( $10^{-4}\text{ S/cm}$ ) are in the mid-range of the conductivities obtained ( $10^{-7}$  to  $10^{-1}\text{ S/cm}$ ) by Weiss and co-workers<sup>9–11</sup> in the case of PPy/PU composites prepared by exposing oxidant-impregnated PU foam to pyrrole vapor. A major advantage of using carbon dioxide saturated with pyrrole, rather than pyrrole vapor, in the experiments is that the penetrating and swelling abilities of carbon dioxide can be utilized to increase the kinetics of the process.

### CONCLUSIONS

Supercritical carbon dioxide was used as a transport and reaction medium in the *in situ* polymerization of pyrrole in PMMA, PS, PDMS and PCTFE. The nonporous PPy/PDMS and PPy/PCTFE composites were not conducting, partly because the host polymers did not absorb appreciable quantities of the oxidant in a prior step. On the other hand, PPy/PMMA and PPy/PS composites exhibited conductivities in the semi-conducting range. In these two cases, the level of PPy on the surface or in the pores of the host polymer

was sufficient to attain interconnected conducting polymer networks necessary for electrical conductivity.

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