

# Continuous Vapor Phase Polymerization of Pyrrole. I. Electrically Conductive Composite Fiber of Polypyrrole with Poly(*p*-phenylene terephthalamide)

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## SYNOPSIS

Electrically conductive polypyrrole (PPy)/poly(*p*-phenylene terephthalamide) (PPTA) composite fibers have been prepared by continuous vapor phase polymerization at a speed of 0.5 ~ 1.5 m/min. The main parameters have been examined, and the conducting fibers with the best properties of electrical conductivity 0.68 s/cm, tensile strength 2731 N/mm<sup>2</sup>, and the elongation at break 4.8% were obtained by using FeCl<sub>3</sub>·6H<sub>2</sub>O as the oxidizing agent. The results of elemental analysis, wide-angle X-ray diffraction analysis and SEM of the composite fibers are also reported. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

An electrical conductive composite can be produced by different methods, such as electrochemical oxidative polymerization of the monomer of the conducting polymer in some insulating or conducting polymer matrix,<sup>1-3</sup> the conducting polymer is blending with the insulating polymer in the solid or in liquid phase,<sup>4,5</sup> block polymerization or graft polymerization of the conducting polymer with the insulating polymer,<sup>6</sup> and surface treatment of the insulating polymer by conductive materials in the vapor or liquid phase.<sup>7-10</sup>

Electrically conductive polymeric materials have many important potential applications, such as EMI shielding, conductive coating, gas-separation membranes, rechargeable batteries, and antistatic agent.<sup>11</sup> Among these, polypyrrole (PPy) is preferred for its high conductivity and stability under environmental conditions. However, it has poor mechanical properties and processibility. In recent years, several attempts have been made to overcome these drawbacks and the fabrication of PPy/poly(*p*-phenylene terephthalamide) (PPTA) composite fibers has received a great deal of attention.<sup>8,9,11-13</sup> But

all these polymerization methods are uncontinuous, have long reaction times (20 min ~ 1.5 h), and need more reagents, which limit their application.

In our laboratory, we have done the stepwise process to produce PPy/PPTA composite fibers.<sup>13</sup> In this paper the electrically conductive PPy/PPTA composite fibers are prepared by continuous vapor phase polymerization. Drawing by a rolling motor at a speed of 0.5 to ~ 1.5 m/min, it is faster than all of the stepwise processes.<sup>13</sup> PPTA fibers are pretreated by acetone and FeCl<sub>3</sub>·6H<sub>2</sub>O aq. solution, then react with Py/H<sub>2</sub>O vapor in the reacting tube under nitrogen atmosphere. After drying, PPy/PPTA composite fibers with the best properties of electrical conductivity 0.68 s/cm, tensile strength 2731 N/mm<sup>2</sup>, and the elongation at break 4.8% were obtained. The results of wide-angle X-ray diffraction and SEM show that amorphous PPy diffused into the interior of PPTA fibers, which is similar to the result described by Carr et al.<sup>9</sup>

## EXPERIMENTAL

### Material

Pyrrole (Py) was obtained from Tokyo Chemical Industries Ltd. and distilled prior to use, b.p. 129 to ~ 131°C. PPTA fiber was obtained from the Institute of Synthetic Fibers in Shanghai, China. Acetone and FeCl<sub>3</sub>·6H<sub>2</sub>O were used as received.

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**Table I Influence of the Concentration and Temperature of Oxidizing Agent on the Composition and Electrical Conductivity of the Composite Fibers**

Exp. No.	Oxidizing Agent		Elemental Analysis					PPy/Repeat Unit = $\delta$ : 1	$\sigma$ (s/cm)	
	Temp. (°C)	Conc. (w/w)	C	H	N	O	Cl			C/N <sup>a</sup>
1	40	10	18	15.22	2.60	3.28	0.05	14/2.022	0.167	0.076
2	40	40	18	15.95	2.61	3.44	0.15	14/2.03	0.187	0.220
3	40	60	18	16.76	2.61	3.82	0.47	14/2.03	0.187	0.682
4	20	40	18	12.44	2.51	3.25	0.21	14/1.953	0.005	0.287

<sup>a</sup> PPTA fiber C/N = 14/1.951. Time of oxidizing process: 60 s.

### Preparation of PPy/PPTA Composite Fibers

Drawing by a rolling motor, PPTA fibers were first passed through acetone to dissolve the surface oil layer that was put on while spinning, then were passed through  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  aq. solutions of different concentration (5, 10, 20, 40, and 60% w/w) at different temperatures (20, 30, 40, and 60°C). After swelling and drying, they were reacted with Py/ $\text{H}_2\text{O}$  vapor in a reacting tube under nitrogen atmosphere. Finally PPy/PPTA electrically conductive composite fibers were obtained at a speed of approximately 0.5 to  $\sim$  1.5 m/min. This process could be finished within 1 to 3 min.

### Characterization

The electrical conductivity was measured using the conventional four point probe method under ambient laboratory conditions. All the data were obtained from an R8340 ultra high resistance meter (Advantest) having a range from  $10^{-3}$  to  $10^{12}$   $\Omega$ . Mechanical properties were obtained on an Instron 1122 material testing machine at room temperature with a draw speed of 100 mm/min. SEM photographs were taken on a Hitachi S-530 scanning electron microscope. The wide-angle X-ray diffraction meter, Cu target, was 40 kV, 30 mA, scanning speed 2°/min.

## RESULTS AND DISCUSSION

### Influence of the Concentration and Temperature of the Oxidizing Agent on the Composition and Electrical Conductivity of the Composite Fibers

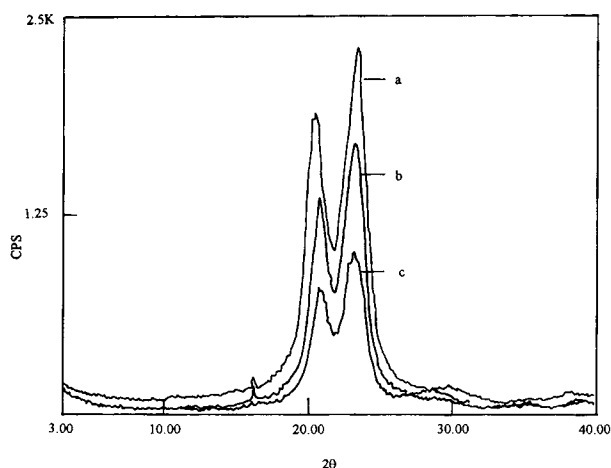
Table I shows that the concentration and temperature of the oxidizing agent have some effects on the composition and electrical conductivity of PPy/PPTA composite fibers. In our previous work, the best conductivity datum is  $10^{-2}$  s/cm; even the stepwise process lasted for 20 min.<sup>13</sup>

While the oxidizing agent is at different temperatures (same concentration), such as for experiments 2 and 4, the molecular ratio of PPy in the Kevlar matrix is much higher at high temperature than at low temperature; even the electrical conductivity is similar. We think that the difference in the components of the PPy/PPTA fibers was attributed to the difference in swelling, and the Py polymerized first to make the conducting passage-way contributed more to the final electrical conductivity, while the PPy formed latter contributed almost little.<sup>14</sup>

While the oxidizing agent is at different concentrations at the same temperature, such as experiments 1, 2, and 3, the molecular ratios of PPy in the Kevlar are almost the same. But the content of Cl and the electrical conductivity of the composite

**Table II Mechanical Properties of PPy/PPTA Composite Fibers**

Exp. No.	Oxidizing Temp. (°C)	Agent Conc. (w/w)	Tensile Strength (N/mm <sup>2</sup> )	Elongation at Break (%)
1	40	10	2644	4.4
2	40	40	2731	4.8
3	40	60	2450	4.1
PPTA fiber			2655	4.5



**Figure 1** X-ray diffraction pattern: (a) PPTA fiber  $2\theta = 20.68^\circ, 22.98^\circ$ ; (b) PPy/PPTA fiber: oxidizing agent 10%,  $40^\circ\text{C}$ ,  $2\theta = 20.78^\circ, 23.16^\circ$ ; (c) PPy/PPTA fiber: oxidizing agent 60%,  $40^\circ\text{C}$ ,  $2\theta = 20.7^\circ, 23.22^\circ$ .

fibers are increased with increasing concentration of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . We think that the increase of electrical conductivity was in accordance with the theory supposed by Martin et al.<sup>15</sup> The increasing concentration of oxidizing agent improved the polymerization rate; the polymer chain length, conjugation length, and doping level of PPy also rose, resulting in an increase of electrical conductivity of the PPy/PPTA composite fibers. Since the concentration of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  we used was very high, Py easily formed a thick layer on the surface of the PPTA fiber at the beginning of the polymerization, which prevented the further diffusion of Py into the interior

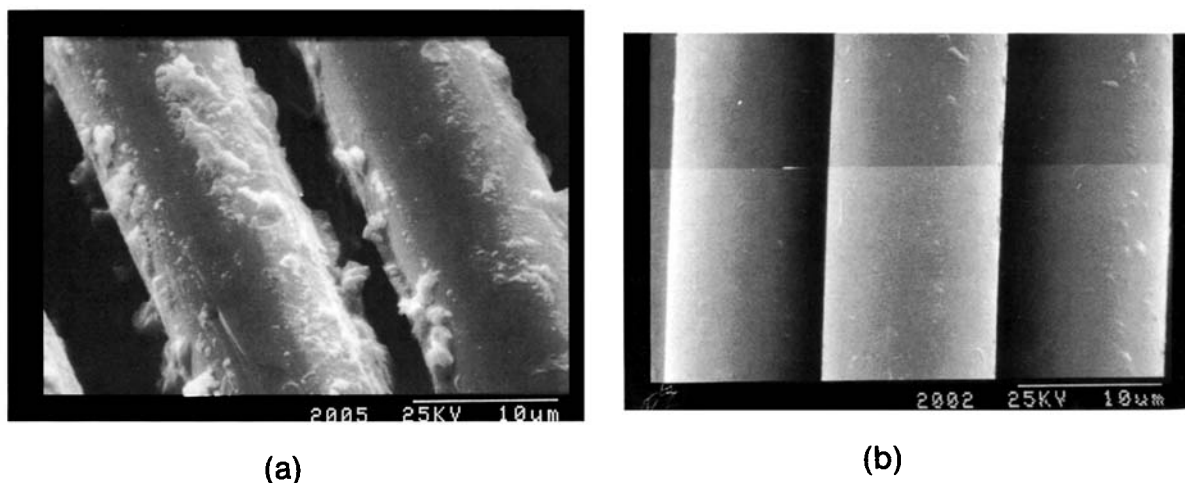
of the PPTA fiber to polymerize. The molecular ratio of PPy with the Kevlar matrix was then determined by the diffusing speed of Py and showed little difference. This can be provided by the SEM photographs.

### Mechanical Properties of the Composite Fibers

The mechanical properties of the PPy/PPTA composite fibers made from the continuous vapor phase polymerization method shows some difference from that of PPTA fibers. When using 40%  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  at  $40^\circ\text{C}$ , the tensile strength is  $2731 \text{ N/mm}^2$  (Table II), which is even higher than that of the PPTA fibers. In our previous work by a stepwise composite process the tensile strength of the composited fibers is lower than of the matrix fiber, and the elongation at break is also lower.<sup>13</sup>

### Wide-Angle X-Ray Diffraction

Figure 1 shows the result of wide-angle X-ray diffraction analysis, the two main peaks at  $23^\circ$  and  $20.7^\circ$  corresponding to the x-ray reflections of the PPTA crystal. After Py polymerized, the peak positions shift little, which indicates that the crystalline structure did not change, and the PPy formed was mainly amorphous. The intensity of the reflection peaks decrease while the concentration of the oxidizing agent increased, which indicates that the crystallinity of the crystal decreased. This is because the polymer chain length of amorphous PPy rose with the increase in the concentration of the oxidizing agent; this affected the crystallinity of PPTA.



**Figure 2** SEM image of surface morphology of the (a) PPTA fiber and (b) PPy/PPTA fiber ( $\times 3000$ ).

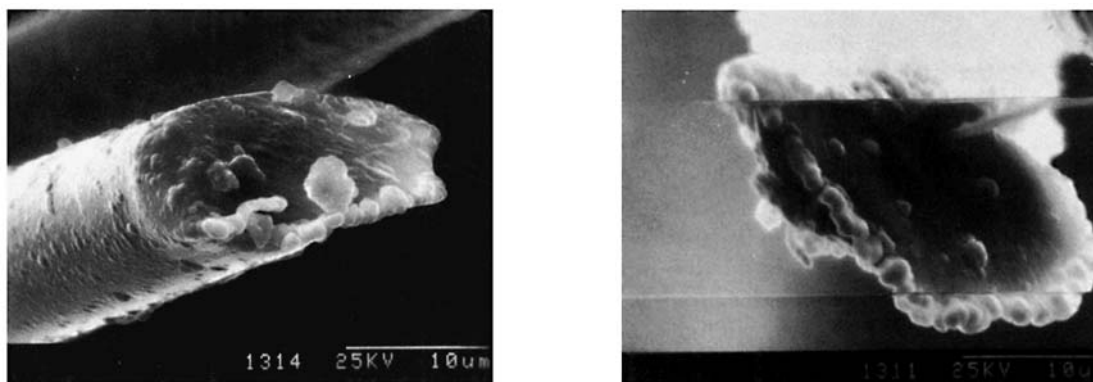


Figure 3 SEM image of the cross section of a PPy/PPTA fiber.

### SEM

The surface morphology of the PPy/PPTA composite fiber shows that the surface of PPTA was covered by a smooth PPy layer with a thickness of  $0.4 \mu\text{m}$  (Fig. 2). The cross-sectional morphology of the PPy/PPTA composite fiber (Fig. 3) shows a layer of spherulike PPy coated on the surface of the PPTA fiber; some PPy was also diffused into the interior of the PPTA fiber, which indicates that the polymerization taken place not only on the surface but also into the interior of the PPTA fiber.

### Stability

To examine the stability of electrical conductivity of the composite fibers, we placed the composite fiber in atmospheric circumstances for several months or dipped it into some organic solvents, such as acetone, alcohol, toluene, or ethyl acetate for 24 h. Then we measured the electrical conductivity of the dry fibers (Table III).

The results show that the PPy/PPTA composite fiber has good stability in atmospheric circumstances, and can be treated by the other organic solvents except acetone with little decrease in electrical conductivity.

### Comparison of Continuous Vapor Phase Polymerization of Py with Other Polymerization Methods

In comparison with other polymerization methods mentioned in other papers,<sup>9,12,13</sup> we find our method shows some advantages over them (Table IV). The electrical conductivity of PPy/PPTA composite fibers prepared by our continuous vapor phase polymerization method is far higher than the range  $10^{-6}$  to  $\sim 10^{-4}$  s/cm required for antistatic, and the fibers show good stability; a very important advantage is saving time. We think it can have some potential applications.

### CONCLUSION

1. We suggest a fast method to prepare electrically conductive PPy/PPTA composite fibers in a continuous vapor phase polymerization method with the best properties of electrical conductivity ( $\sigma$ ) 0.68 s/cm, tensile strength 2731 N/mm<sup>2</sup>, and the elongation at break 4.8%.
2. Wide-angle X-ray diffraction analysis and SEM show that amorphous PPy not only

Table III Stability of PPy/PPTA Fibers in Atmospheric Circumstances and Some Organic Solvents<sup>a</sup>

	Composite Fiber	Atmospheric Circumstances		Acetone	Alcohol	Toluene	Ethyl Acetate
		2 Months	3 Months				
$\sigma$ (s/cm)	0.68	0.14	0.13	0.045	0.26	0.37	0.21

<sup>a</sup> Concentration of oxidizing agent, 60%; swelling temperature, 40°C.

Table IV Comparison of References with Our Work

Preparing Method	$\sigma$ (s/cm)	Mechanical Properties	React Time (min)	Reference
Electrochemical flow cells	24.3	Flexible	20	12
Chemical oxidizing method	2.4	—	90	9
Vapor phase polymerization	1.33	85% as PPTA fibers	30	13
Continuous vapor phase polymerization	0.68	The same as PPTA	1 ~ 3	This work

coated the surface of PPTA fibers but also diffused into the interior of PPTA fibers.

3. Our method can prepare stable PPy/PPTA electrically conductive composite fibers quickly (0.5 to ~ 1.5 m/min) and continuously. It shows some advantages over other preparation methods and has some potential applications.

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