

# Conducting Composite Film Based on Polypyrrole and Crosslinked Cellulose

WUSHENG YIN,<sup>1</sup> JUN LI,<sup>2</sup> YONGMING LI,<sup>2</sup> JINGPIN WU,<sup>2</sup> TIREN GU<sup>2</sup>

<sup>1</sup> Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

<sup>2</sup> Department of Chemistry, Beijing University of Aeronautics and Astronautics, Beijing, People's Republic of China, 100083

Received 12 December 1999; accepted 15 November 2000

**ABSTRACT:** Polypyrrole/crosslinked cellulose conductive composite films were prepared by vapor-phase polymerization of pyrrole on the silicon crosslinked cellulose network using anhydrous ferric chloride as oxidant. The properties of the composite film depend on their synthetic conditions such as the amount of ferric chloride and tetraethyl orthosilicate crosslinker, the reaction time, the solvent, etc. Interestingly, it was found that the conductivity was strongly affected by the nature of the solvents and their amount in pyrrole solution. When the weight ratio of methanol/pyrrole is 1 : 1, the conductivity was as high as 1.1 S/cm, increased by two orders of magnitude compared to that without solvent, and the mechanical properties was good. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1368–1373, 2001

**Key words:** polypyrrole; conducting composite; crosslinked cellulose

## INTRODUCTION

Polypyrrole (PPy) exhibits high conductivity and good environmental stability, so it has drawn considerable attention as a substitute for metallic conductors or semiconductors in a wide variety of electrical and electronic devices.<sup>1,2</sup> However, polypyrrole is, like many other conductive polymers, insoluble in ordinary solvents and infusible because of decomposes before melting. For this reason, the conventional methods for polymer processing, such as melt processing and solution casting, could not usually be applied to these materials. Extensive investigations have been carried out to improve the processability of polypyrrole. These include synthesizing soluble N- or ring-substituted derivatives, i.e., introducing flex-

ible side substitutes to the main rigid chain.<sup>3</sup> or grafting conducting polymer chains to a nonconducting polymer.<sup>4</sup> PPy films have also been prepared by electrochemical polymerization on the surface of an electrode,<sup>5–7</sup> or by the interfacial oxidative polymerization method.<sup>8</sup>

Of all the methods, fabrication of polypyrrole-based composites has been received a great deal of attention.<sup>9–11</sup> The method involves synthesis of polypyrrole on a suitable insulating matrix. In recent years, chemical oxidative polymerization and electrochemical synthesis have been successfully developed to produce several interesting conducting-polymer composite films, such as polypyrrole-poly(vinyl chloride) (PPy-PVC), polypyrrole-poly(vinyl alcohol) (PPy-PVA), polypyrrole-poly(ethylene terephthalate) (PPy-PET), PPy-cellulose, PPy-PU(polyurethane) as well as PPy-PMMA(methyl methacrylate).<sup>12–17</sup> However, few conductive composites based on polypyrrole and a crosslinked matrix have been reported.

Correspondence to: W. Yin, Olde Carriage House Apts. C-4, Clinton, NY 13323.

*Journal of Applied Polymer Science*, Vol. 80, 1368–1373 (2001)  
© 2001 John Wiley & Sons, Inc.

In our group, several conducting IPNs have been synthesized.<sup>18,19</sup> PPy/PMAA (Poly(methyl acrylate-co-acrylic acid)) IPN was prepared by vapor-phase polymerization of pyrrole on crosslinked PMAA,<sup>18</sup> which exhibited good conductivity and processability. The polyaniline(PANI)/crosslinked cellulose IPN produced exhibited better conductivity than that of the PANI/cellulose acetate despite the polyaniline content of the IPN as low as 20%. In this work, we have synthesized another conductive composite film based on polypyrrole and crosslinked cellulose, within which the crosslinked matrix not only enhanced the physical properties and processability of the rigid conducting polymer, but also could keep the rigid conducting polymer in good conductive state due to the weaker interaction between the crosslinked matrix and the conducting polymer in comparison to the linear matrix. We found the conductivity was enhanced by two orders of magnitude in comparison to that with linear cellulose matrix. The conductivity was greatly dependent on the solvent in pyrrole solution. Therefore, the detail of the effect of reaction conditions such as the amount of ferric chloride and tetraethyl orthosilicate (TEOS), reaction time, as well as the solvents on the properties of the films was investigated in this work.

## EXPERIMENTAL

### Materials

Pyrrole was purchased from Aldrich Chemical Corp., distilled under vacuum, and stored in a refrigerator before use. Tetraethyl orthosilicate, anhydrous ferric chloride, and anhydrous ethyl alcohol were purchased from Beijing Chemical Industry and used without further purification. All solvents were used as received. Sodium carboxymethyl cellulose (Molecular weight: viscosity, 500800cP; PH, 68) was purchased from Chinese Medicine & Pharmaceuticals Corp.

### Preparation of Carboxymethyl Cellulose

Sodium carboxymethyl cellulose was dissolved in alcohol/deionized water (35:65) and slightly heated with vigorous stirring until sodium carboxymethyl cellulose was completely dissolved. Then the solution was acidified with HCl to pH < 2, precipitated with methanol, and finally filtered to obtain carboxymethyl cellulose.

### Preparation of Conductive Composite Film

The well-defined amount of freshly obtained carboxymethyl cellulose and TEOS were dissolved in 15g of 35% alcohol aqueous solution. The mixture was refluxed for 1 h, cooled, then the ferric chloride was added with stirring for more than 30 min. The solution was poured into Teflon substrate plate and placed at room temperature under a moisture atmosphere for 48 h. The final film was peeled off, and the preparation of free-standing conductive composite films was carried out at  $-8^{\circ}\text{C}$  by exposing crosslinked cellulose films containing  $\text{FeCl}_3$  to pyrrole vapor or the mixed vapor of pyrrole/solvent solution for the given time. After the oxidative polymerization was completed, the films were washed several times with methanol until the solvent remained colorless, and then the film was pressed with glass plates and dried *in vacuo* for more than 12 h.

### Measurement

The electrical conductivity of the composite films was measured at room temperature by the standard four-probe method. The content of polypyrrole in the composite films was measured using standard element analysis instrument. The phase morphological characteristics of the samples were studied by scanning electron microscopy (SEM). The specimens for SEM were frozen in liquid nitrogen, fractured, mounted, and coated with gold. They were then observed with HITACHI S-530.

## RESULTS AND DISCUSSION

The vapor-phase polymerization of pyrrole has been utilized for the preparation of composite of PPy and other conventional polymers such as poly(vinyl chloride),<sup>12</sup> poly(vinyl alcohol),<sup>13</sup> and polyacrylonitrile.<sup>20</sup> It was found that the rate of polymerization and the conductivity of the resultant composite were strongly dependent on the amount of  $\text{FeCl}_3$  in the polymer film. In this work, the effect of the amount of  $\text{FeCl}_3$  on the properties of the films is listed in Table I. It can be seen that both the conductivity and the PPy content in the conductive composite film increase with increase in the oxidant content within the range of oxidant content investigated. On the other hand, the higher the content of PPy in the film, the more brittle the film.

**Table I Effect of the Amount of Ferric Chloride on the Properties of the Films<sup>a</sup>**

Feeding Amount of Ferric Chloride (g)	PPy <sup>b</sup> (%)	Conductivity (S/cm)		Remarks on the Films
		Air Surface	Bottom Surface	
1.5	1.9	$1.0 \times 10^{-2}$	$9.2 \times 10^{-3}$	smooth, strong, brittle
1.0	<0.5	$8.8 \times 10^{-3}$	$5.4 \times 10^{-3}$	smooth, strong, less brittle
0.5	<0.5	$1.8 \times 10^{-3}$	$2.3 \times 10^{-3}$	smooth, strong, less brittle
0.1	0	Under detected		smooth, strong, tough

<sup>a</sup> The conductive composite films were prepared under the following conditions: 0.8 g sodium carboxymethyl cellulose, 0.2 g TEOS, reaction time: 24 h.

<sup>b</sup> Calculated on the basis of the elemental analysis.

Table II presents the effect of the amount of TEOS on the properties of the films. In this work, TEOS was not only used as crosslinker but also self-condensed to form the SiOSi network. The crosslink network includes two kinds of networks, namely, the SiOSi network and the SiOC-(cellulose) network. The content of PPy increases and then decreases with the amount of TEOS used, as is seen in Table II. It can be also found that 10/90 is the best ratio of TEOS/Na-CMC (sodium carboxymethyl cellulose), the conductivity is as high as  $10^1$  S/cm, increased by two orders of magnitude compared to that without TEOS. This is because PPy is in a better conductive state due to its interaction with the crosslinked matrix weakened by the formation of the network at 10/90 TEOS/Na-CMC compared to that without TEOS. The crosslink density of the matrix is increased with the increase in the ratio of TEOS/Na-CMC, and this limits the formation of polypyrrole in good conductive state at the high ratio of TEOS/Na-CMC. On the other hand, the content of polypyrrole is decreased at the higher ratio of TEOS/Na-CMC (40/60). The above two effects cause the decrease in the conductivity at the high ratio of

TEOS/Na-CMC. In addition, there is no obvious difference between the conductivity of the air surface and the bottom surface, although the structure of the air surface of the crosslinked matrix is different from that of the bottom, as caused by the migration of siloxane to the surface with lower surface energy.<sup>21</sup> In comparison to the linear structure of the matrix, the crosslink structure of the matrix can retard the volume shrinkage of the composite film. The serious shrinkage of the composite film appeared at 40% TEOS, which was caused by the formation of the SiO<sub>2</sub> gel via hydrolysis and condensation of TEOS.<sup>22</sup>

Many works have reported the effect of reaction time of oxidative polymerization on the conductivity. Generally, the conductivity increases and then decreases or remains unchanged with increase in the reaction time.<sup>10</sup> Table III shows that the conductivity decreases with increase in the reaction time. The fact that the conductivity first increases with increase in the reaction time was not observed because the reaction time investigated in this work is much longer. During the exposure of the crosslinked cellulose film containing FeCl<sub>3</sub> to pyrrole vapor, at least two processes

**Table II Effect of the Amount of TEOS on the Properties of the Films<sup>a</sup>**

Weight Ratio of TEOS/Na-CMC	PPy <sup>b</sup> (%)	Conductivity (S/cm)		Remarks on the Films
		Air Surface	Bottom Surface	
0/100	0.5	$8.8 \times 10^{-3}$	$5.4 \times 10^{-3}$	strong, brittle, shrank
10/90	0.9	$1.5 \times 10^{-1}$	$1.9 \times 10^{-1}$	strong, less brittle, smooth
20/80	1.9	$2.8 \times 10^{-3}$	$8.3 \times 10^{-3}$	strong, brittle, smooth
40/60	<0.5	$1.8 \times 10^{-2}$	$2.1 \times 10^{-2}$	strong, most brittle, seriously shrank

<sup>a</sup> The conductive composite films were prepared under the conditions: ferric chloride: 1.5 g reaction time: 24 h.

<sup>b</sup> Calculated on the basis of the elemental analysis.

**Table III Effect of the Reaction Time on the Properties of the Films<sup>a</sup>**

Reaction Time (h)	Conductivity (S/cm)		Remarks on the Films
	Air Surface	Bottom Surface	
24	$1.0 \times 10^{-2}$	$9.2 \times 10^{-3}$	brittle, most strong, smooth
48	$7.8 \times 10^{-4}$	$7.4 \times 10^{-4}$	brittle, strong, smooth
72	$3.6 \times 10^{-4}$	$1.5 \times 10^{-3}$	most brittle, less strong, coarse
120	$3.5 \times 10^{-4}$	$5.8 \times 10^{-4}$	most brittle, less strong, coarse

<sup>a</sup> The conductive composite films were prepared under the following conditions: 0.8 g sodium carboxymethyl cellulose, 0.2 g TEOS, ferric chloride: 1.5 g.

may take place: (1) the diffusion of pyrrole vapor into the film; (2) the oxidative polymerization of pyrrole by  $\text{FeCl}_3$ . Generally speaking, the diffusion-oxidative polymerization process may take place. When the reaction time is long, the amount of polypyrrole becomes high enough, a network has been generated in the neighborhood of the surface of the film. The network forms a shield near the crosslinked cellulose film surface that prevents the diffusion of pyrrole. However, for very long reaction times, for example, 48 h, some pyrrole still penetrates through the surface layer and reacts with  $\text{FeCl}_3$  behind the layer, but produces some loose PPy with low bulk density aggregated near the surface of the film.<sup>11</sup> This not only increases the thickness of the film but also makes the conductive coarse, and the conductivity, thus, first decreases with the reaction time. With a further increase in the reaction time, the conductivity almost remains unchanged due to no

further oxidative polymerization of pyrrole. In addition, the polypyrrole with low bulk density also results in the decrease in the strength of the film for the longer reaction time.

Table IV lists the effect of solvent on the properties of the films, which were prepared by changing the solvent in the pyrrole solution. The value of conductivity is affected by the nature of the solvents used and changes from 10 to  $10^{-2}$  S/cm, increased by one to two orders of magnitude in comparison to that without solvent ( $10^{-2}$  S/cm, see Table I). The long-chain amine and octanol are almost not volatile at  $-8^\circ\text{C}$ , but lead to the decrease in the vapor pressure of pyrrole in comparison to that without solvent. Therefore, the ratio of oxidative polymerization of pyrrole is slow so that the polypyrrole that has good conductivity is easily produced. However, the conductivity is increased by only a little compared to that without solvent, indicating the conductivity is affected

**Table IV Effect of the Solvent in Pyrrole Solution on the Properties of the Films<sup>a</sup>**

Solvent	PPy <sup>b</sup> (%)	Conductivity (S/cm)		Remarks on the Films
		Air Surface	Bottom Surface	
$\text{CH}_3\text{OH}$	4.2	1.1	1.1	less tough, strong, coarse
$\text{C}_2\text{H}_5\text{OH}$	26.4	$9.2 \times 10^{-1}$	$6.3 \times 10^{-1}$	less tough, less strong, coarse
$\text{C}_8\text{H}_{17}\text{OH}$	4.6	$1.1 \times 10^{-2}$	$1.6 \times 10^{-2}$	tough, most strong, slightly coarse
$(\text{CH}_2\text{CH}_2)_2\text{O}$	—	$8.5 \times 10^{-1}$	$7.5 \times 10^{-3}$	tough, strong, slightly coarse
$\text{C}_5\text{H}_5\text{N}$	16.2	$9.9 \times 10^{-1}$	$6.4 \times 10^{-1}$	less tough, most strong, coarse
$\text{C}_8\text{H}_{17}\text{NH}_2$	—	$3.0 \times 10^{-2}$	$4.5 \times 10^{-2}$	tough, most strong, slightly coarse
$\text{C}_{14}\text{H}_{29}\text{NH}_2$	—	$1.1 \times 10^{-2}$	$2.1 \times 10^{-2}$	tough, most strong, slightly coarse
$\text{C}_6\text{H}_6$	5.4	$6.9 \times 10^{-2}$	$2.9 \times 10^{-2}$	most tough, most strong, slightly coarse
$\text{CCl}_4$	—	$1.9 \times 10^{-2}$	$9.5 \times 10^{-2}$	tough, most strong, slightly coarse
$\text{CHCl}_3$	22	$1.3 \times 10^{-1}$	$1.0 \times 10^{-1}$	less tough, most strong, slightly coarse

<sup>a</sup> The conductive composite films were prepared under the following conditions: 0.9 g sodium carboxymethyl cellulose, 0.1 g TEOS, ferric chloride: 1.5 g reaction time: 24 h; weight ratio of pyrrole/solvent, 1:1.

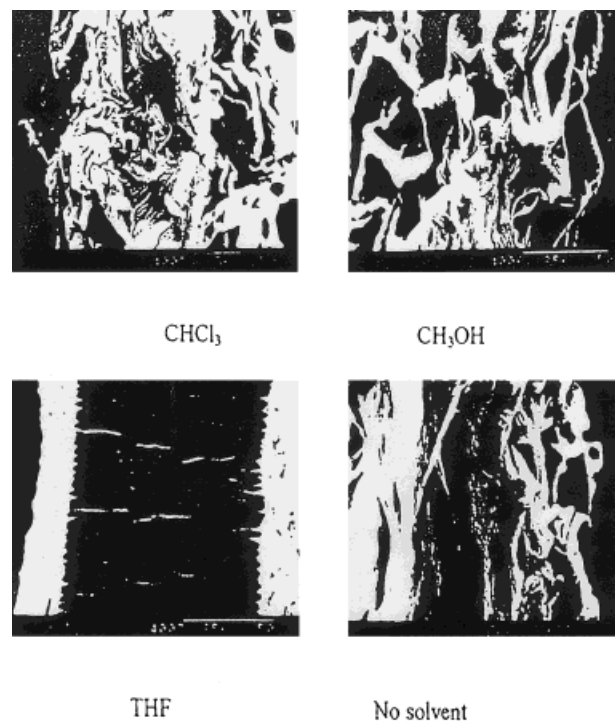
<sup>b</sup> Calculated on the basis of the elemental analysis.



very little with addition of long-chain solvent into pyrrole solution at temperatures as low as  $-8^{\circ}\text{C}$ . By addition of the volatile solvents into pyrrole, the properties of the films are not only affected by the decrease pressure in the vapor of pyrrole, but also mainly dependent on their interaction with the crosslinked matrix. Using ethanol, pyridine, and chloroform as solvents, the contents of PPy in the mixture is much higher than that without solvent (1.9%, see Table I) because these are solvent for carboxymethyl cellulose and make the crosslinked matrix swollen helping the diffusion of pyrrole into the films. Methanol and benzene are nonsolvents for carboxymethyl cellulose, so the content of PPy is enhanced slightly compared to that without solvent. The degree of increase in the PPy content is much smaller while the degree of increase in the conductivity is higher than that for those good solvents for carboxymethyl cellulose. For instance, using methanol as solvent, the conductivity is as high as 1.1 S/cm, and enhanced by two orders of magnitude compared to that without solvent ( $10^{-2}$  S/cm, see Table I), and also larger than that for these good solvents for carboxymethyl cellulose, indicating the conductivity strongly depends on the structure of PPy in the film. Regarding the remarks on the film, these are also changed correspondingly with the addition of solvent into pyrrole.

Figure 1 shows the effect of the solvents on the morphologies of the conductive films. It can easily be found that the structures of the films strongly depends on the solvent in pyrrole solution. With tetrahydrofuran (THF) or without solvent, the obtained conductive films were of "sandwich" structure, whose air and bottom surfaces are conductive, and whose middle layer is insulating.<sup>19</sup> However, the two structures are completely different. The former exhibited more complete conductive layer than the latter. With methanol or trichloromethane as solvent, the "sandwich" structure disappeared, and the conductive network structure has been formed. The conductive network has been generated more completely for methanol than that for trichloromethane, strongly suggesting the conductivity depends on the morphology of the conductive film.

Table V presents the effect of the weight ratio of methanol/pyrrole on the properties of the conductive films. First, the conductivity increases with increase in the weight ratio of methanol/pyrrole (below 1 : 1), then decreases with increase in the weight ratio of methanol/pyrrole. The conductivity shows a maximum value (1.1 S/cm) at



**Figure 1** SEM of the composite films with different solvents, the preparation of the films described as in Table IV.

1 : 1 (weight ratio) of methanol/pyrrole. During the diffusion of the mixed vapor of methanol/pyrrole into the free film containing oxidizing agent, several processes may take place: (1) the swelling of the free film by the vapor of pyrrole/methanol solution; (2) the oxidative polymerization of pyrrole by  $\text{FeCl}_3$ . Methanol can function as solvent during the oxidative polymerization and further diffuse into the insider layer of the film; (3) the further diffusion of pyrrole into the film and the  $\text{FeCl}_3$ /methanol solution from inside towards the surface of the film. The conductivity strongly depends on the diffusion rate of  $\text{FeCl}_3$  and pyrrole as described in the other work.<sup>23</sup> The fact that the conductivity increases and then decreases with the weight ratio of methanol/pyrrole may be explained by the too large diffusion rate of pyrrole and  $\text{FeCl}_3$ , which causes the formation of PPy with low density.

In conclusion, the conducting composite film based on polypyrrole and crosslinked cellulose has been synthesized, which combined high conductivity with good mechanical properties. The conductivity increases with increase of the amount of oxidant, decreases with increase of the reaction time, also strongly depends on the

**Table V** Effect of the Weight Ratio of Methanol/Pyrrrole on the Properties of the Films

Methanol/Pyrrrole (Weight Ratio)	Conductivity (S/cm)		Remarks on the Films
	Air Surface	Bottom Surface	
0/1	$1.0 \times 10^{-2}$	$9.2 \times 10^{-3}$	tough, strong, slightly coarse
1/3	$3.8 \times 10^{-2}$	$7.7 \times 10^{-2}$	tough, most strong, slightly coarse
1/1	1.1	1.1	less tough, strong, slightly coarse
3/1	$2.5 \times 10^{-1}$	$2.3 \times 10^{-1}$	tough, most strong, slightly coarse

<sup>a</sup> The conductive composite films were prepared under the following conditions: 0.9 g sodium carboxymethyl cellulose, 0.1 g TEOS, ferric chloride: 1.5 g reaction time: 24 h.

amount of TEOS as well as changes with the nature and the content of solvent in pyrrole solution. The structure of conductive film strongly depends on the solvent in pyrrole solution.

## REFERENCES

- Bhat, N. V.; Yasmin, S. *J Appl Polym Sci* 1995, 55, 1827.
- Kittlesen, G. P.; Wihte, H. S.; Wrighton, M. S. *J Am Chem Soc* 1984, 106, 7389.
- Li, S.; Cao, Y.; Xue, Z. *Synth Met* 1987, 20, 141.
- Dao, L. H.; Lelerc, M. *Synth Met* 1989, 29, E377.
- Diaz, A. F.; Paoli, M.; Kanazawa, K. K. *J Chem Soc Chem Commun* 1979, 635.
- Kuwabata, S.; Okamoto, K.; Ikeda, O.; Yoneyama, H. *Synth Met* 1987, 18, 101.
- Peres, R. C. D.; Pernault, J. M.; DePaoli, M. A. *J Polym Sci A Polym Chem* 1985, 23, 1687.
- Nakata, M.; Taga, M.; Kise, H. *Polym J* 1992, 24, 437.
- Ruckenstein, E.; Yang, S. *Polymer* 1993, 34, 4655.
- He, F.; Omoto, M.; Yamaoto, T.; Kise, H. *J Appl Polym Sci* 1995, 55, 283.
- Nakata, M.; Kise, H. *Polym J* 1993, 25, 91.
- Ojio, T.; Miyata, S. *Polym J* 1986, 18, 95.
- Lindsey, S. E.; Street, G. B. *Synth Met* 1984, 10, 67.
- Li, C.; Song, Z. *Synth Met* 1991, 40, 23.
- Bjorklund, R. B.; Lundstrom, I. *J Electron Mater* 1984, 13, 211.
- Bi, M.; Bei, Q. *Synth Met* 1987, 22, 145.
- Moreta, M.; Hashida, I.; Mishimura, M. *J Appl Polym Sci* 1988, 36, 1639.
- Yin, W. S.; Li, J.; Gu, T.; Wu, P. *J Appl Polym Sci* 1997, 64, 903; 63, 13.
- Yin, W. S.; Liu, C.; Li, J.; Liu, H. W.; Gu, T. *Polym Int* 1997, 42, 276.
- Bhat, N. V.; Sundaresan, E. *J Appl Polym Sci* 1989, 38, 1173.
- Yin, W. S. Ph.D dissertation, Institute of Chemistry, Academia Sinica, 1995.
- Novak, B. M.; Ellsworth, M.; Wallow, T. *Polym Prep* 1990, 31, 698.