

# Conducting Composite Films Based on Polypyrrole and Crosslinked Poly(styrene-butyl acrylate-hydroxyethyl acrylate)

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**ABSTRACT:** Polypyrrole/crosslinked poly(styrene-butyl acrylate-hydroxyethyl acrylate) (PSBH) conductive composite films were designed to obtain high conductivity and good mechanical properties, and were prepared by vapor-phase polymerization of pyrrole within the silicon-crosslinked PSBH network using anhydrous ferric chloride as oxidant. The properties of the conducting composite film, such as conductivity, were strongly dependent on their synthetic conditions, such as the amount of ferric chloride and tetraethyl orthosilicate and the nature and weight ratio of the solvent in pyrrole solution. Above all, the most interesting point was the effect that solvent in pyrrole solution had on the conductivity. Using methanol as solvent, the conductivity was as high as 15 S/cm, increased by two orders of magnitude as compared with that without solvent. The conducting composite exhibited good mechanical properties (tensile strength, 10.3 MPa; Young's modulus, 178.9 MPa; elongation yield, 170%). © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2293–2298, 1997

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

## INTRODUCTION

Because polypyrrole (PPy) exhibits high conductivity and good environmental stability, it has drawn considerable attention as a substitute for metallic conductors or semiconductors in a wide variety of electrical and electronic devices, such as electrochromic displays, modified electrode catalysis, and shielding material for electromagnetic fields.<sup>1–3</sup> However, PPy is, like many other conductive polymers, insoluble in ordinary solvents and infusible because it decomposes before melting. Currently, many investigations have focused on the preparation of conductive PPy composites with the object of improving PPy processability. Chemical oxidative polymerization and electrochemical synthesis have been successfully

developed to prepare conductive PPy composite films, such as PPy-poly(vinyl chloride) (PVC), PPy-poly(vinyl alcohol) (PVA), PPy-poly(ethylene terephthalate), PPy-cellulose, and PPy-polyurethane, as well as PPy-poly(methyl methacrylate).<sup>4–9</sup> However, few conductive composites based on rigid conductive polymers and crosslinked flexible matrices have been reported in the literature.<sup>10,11</sup>

In our laboratory, the conductive polymer composites based on rigid conducting polymers and crosslinked flexible matrices have been synthesized.<sup>12,13</sup> PPy-poly(methyl acrylate-co-acrylic acid) (PMAA) and PPy-poly(methyl acrylate-co-hydroxyethyl acrylate) (PMA-HEA) were prepared by vapor-phase polymerization of pyrrole on the crosslinked PMAA and crosslinked PMA-HEA, respectively, which exhibited good conductivity and processability. In this study, we have synthesized another new conductive polymer composite using the silicon crosslinked poly(styrene-

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**Table I** Recipe for the Emulsion Copolymerization of S-BA-HEA

Ingredient	S	BA	HEA	APS	SHS	DBSA	OP-10	H <sub>2</sub> O
Amount (g)	15	30	4	0.3	0.15	0.1	0.2	120

butyl acrylate-hydroxyethyl acrylate) (PSBH) as a matrix for improvement of the mechanical properties of the conducting composite. In comparison with the former research,<sup>13</sup> the PSBH-PPy composite film exhibited not only higher conductivity but also better mechanical properties. Here we have investigated the details of the effects of reaction conditions [such as the amount of ferric chloride and tetraethyl orthosilicate (TEOS), reaction time, and the solvents in the pyrrole solution] on the properties of the composite films.

## EXPERIMENTAL

### Materials

Pyrrole was purchased from Fluka Chemika, Germany, distilled under vacuum, and stored in a refrigerator before use. TEOS, anhydrous ferric chloride and tetrahydrofuran (THF), styrene (S), butyl acrylate (BA), HEA, ammonium persulfate (APS), and sodium hydrogen sulfite (SHS), as well as OP-10 (10 units of oxyethylene containing alkyl phenol) were purchased from Beijing Chemical (Beijing, China) and used without further purification. Dodecyl benzene sulfonic acid (DBSA) was purified through a rotary evaporator. All other solvents were used as received.

### Synthesis of PSBH

S, BA, HEA, and mixed surfactant (OP-10 and DBSA), as well as deionized water, were added to a three-neck flask and emulsified prior to polymerization. The emulsion copolymerization was carried out in a 250-mL three-neck flask equipped with a reflux condenser, stirrer, and thermometer. A typical recipe used to prepare the copolymer latex is shown in Table I. The emulsified solution containing APS and 20 g of SHS aqueous solution were added dropwise at the same time for about 2 h. The reactor was maintained at 60°C in a thermostated water bath and the polymerization was carried out under an inert nitrogen atmosphere for 6 h. To terminate the reaction, the copolymer was precipitated in 5% NaCl solution at 50°C and

the precipitate was dried in an oven to constant weight. The composition and hydroxyl group content of the copolymer were characterized with nuclear magnetic resonance. The molar ratio of S-BA-HEA was 3 : 4 : 0.3.

### Preparation of Conductive Composite Films

The well-defined amount of copolymer and TEOS, 0.01 g deionized water, and 0.01 g DBSA were dissolved in 10 g THF. The mixture was refluxed for 1 h and cooled. Then a certain amount of ferric chloride was added to the solution with vigorous stirring for more than 30 min until the ferric chloride was completely dissolved. The solution was poured into a Teflon substrate plate, placed at room temperature under air atmosphere for 48 h, and cured at 100°C for 1 h. The final film was peeled off, and the preparation of freestanding conductive composite films was carried out at -8°C by exposing crosslinked PSBH films containing FeCl<sub>3</sub> to pyrrole vapor for a given time. After the oxidative polymerization was completed, the films were washed several times with methanol until solvent remained colorless, pressed with glass plates, and dried in vacuum 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 PPy content of the composite films was measured using a standard element-analysis instrument. The phase morphologic 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 a Hitachi S-530. The tensile testing was performed at room temperature with an Instron Testing Instrument (model 3710-016) with a crosshead speed of 40 mm/min.

## RESULTS AND DISCUSSION

Most papers have reported the preparation of rigid conducting polymer composites (involving

**Table II Effect of the Amount of TEOS on the Properties of the Films**

TEOS/PSBH (wt/wt)	PPy <sup>a</sup> (%)	Conductivity (S/cm)		Remarks on the Films
		Air Surface	Bottom Surface	
0/100	1.4	$1.1 \times 10^{-1}$	$6.5 \times 10^{-1}$	smooth, flexible, strong
10/90	3.0	$5.6 \times 10^{-2}$	$2.7 \times 10^{-2}$	smooth, flexible, strong
20/80	4.4	$7.7 \times 10^{-1}$	$6.9 \times 10^{-1}$	smooth, little brittle, strong
40/60	6.1	$5.6 \times 10^{-2}$	$1.5 \times 10^{-2}$	smooth, brittle, less strong

The conductive composite films were prepared under the following conditions: 1.2 g ferric chloride; reaction time: 24 h. Other conditions as described in the Experimental section.

<sup>a</sup> Calculated on the basis of the element analysis.

PPy) using conventional linear polymers such as PVA and PVC as matrix; the effect of the nature of the matrix on the properties of the films has also been reported.<sup>14</sup> However, the effect of the structure of crosslinked matrix on the properties of the films is still not clear. In this work, the effect of the amount of crosslinker TEOS on the properties was investigated and is shown in Table II. Although the content of PPy increases with increased amounts of TEOS, the conductivity does not increase simply with increased TEOS. The TEOS' effect is more complex for a PSBH system than that for PMA/HEA,<sup>13</sup> suggesting that the conductivity is affected not only by the crosslink density but also by the flexible chain structure. However, the conductivity of the film with the crosslinked PSBH (20/80) matrix is the same order of magnitude as that with a linear PSBH matrix ( $10^{-1}$  S/cm), indicating that PPy with higher conductivity can be obtained in the case with larger steric hindrance in the crosslink structure of the matrix. To circumvent the larger steric hindrance and form a consecutive conductive network, PPy was forced to grow in interpenetration with the crosslinked matrix. In addition, the film

becomes more brittle and less strong with increased PPy content.

Table III lists the effect of the amount of ferric chloride on the properties of the films. As expected, both the conductivity and physical properties of the composite films are strongly dependent on the oxidant concentration. The conductivity decreases with increases in the amount of ferric chloride used in this study. The tendency of conductivity to increase with increased ferric chloride is not observed because the onset amount of ferric chloride is larger. Similar results have been reported for other oxidative polymerization systems of pyrrole.<sup>14</sup> The decrease in conductivity at higher oxidant concentrations may be explained by the decrease in the content and the bulky density of PPy because the oxidative polymerization of pyrrole occurs rapidly. Alternatively, excess amounts of the oxidant led to the loss of regularity in the PPy structure and the overoxidative reaction of PPy, namely, the decrease in the length of conjugation and the structural defects in the composite film. The film becomes slightly brittle at 2.0 g ferric chloride in spite of the decrease in the content of PPy, indicating that PPy has low

**Table III Effect of the Amount of Ferric Chloride on the Properties of the Films**

Feeding Amount of FeCl <sub>3</sub> (g)	PPy <sup>a</sup> (%)	Conductivity (S/cm)		Remarks on the Films
		Air Surface	Bottom Surface	
0.8	5.5	1.2	2.6	smooth, flexible, most strong
1.2	4.4	0.97	0.87	smooth, slightly brittle, strong
1.6	2.3	1.3	1.0	smooth, flexible, strong
2.0	1.4	$1.3 \times 10^{-2}$	$1.4 \times 10^{-2}$	smooth, slightly brittle, strong

The conductive composite films were prepared under the following conditions: 0.8 g PSBH; 0.2 g TEOS; reaction time: 24 h. Other conditions as described in the Experimental section.

<sup>a</sup> Calculated on the basis of the element analysis.

**Table IV** Effect of Reaction Time on the Properties of the Films

Reaction Time (h)	Conductivity (S/cm)		Remarks on the Films
	Air Surface	Bottom Surface	
24	$2.3 \times 10^{-2}$	$6.5 \times 10^{-1}$	smooth, flexible, strong
48	$5.6 \times 10^{-1}$	1.8	smooth, flexible, strong
96	$1.4 \times 10^{-1}$	2.1	smooth, flexible, strong

The conductive composite films were prepared under the following conditions: 0.8 g PSBH; 0.2 g TEOS; ferric chloride: 1.2 g. Other conditions as described in the Experimental section.

bulky density, in agreement with the former result.

Table IV shows the effect of the oxidative reaction time on the properties of the films. The electrical conductivity increases and then remains almost unchanged with increasing reaction time. The surface conductivity of the film increases by an order of magnitude when the reaction time increases from 24 to 48 h. When the reaction time increases from 48 to 96 h, the surface conductivity remains almost unchanged. This may be explained as follows: the oxidative polymerization of pyrrole vapor process includes the diffusion step and the oxidative polymerization step. If the reaction time is long enough, the conductive PPy network is generated in the neighborhood of the surface of the matrix film. The network may form a shield near the matrix surface, which prevents the diffusion of pyrrole and thus prevents the additional oxidative polymerization. Moreover, the other properties of the composite films remain unaltered with reaction time, suggesting that no sig-

nificant change takes place in the structures of the films, in agreement with the above result.

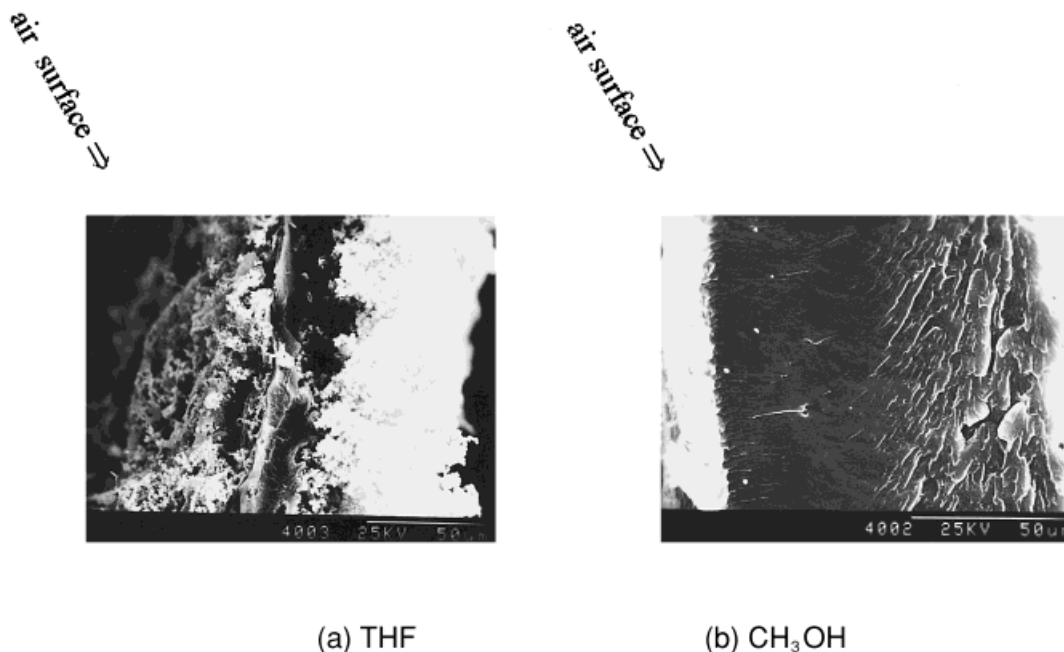
Table V presents the effect of the solvent in pyrrole solution on the properties of the films. It can be found that the PPy content in the films decreases with the addition of strong polar solvents such as CH<sub>3</sub>OH and CHCl<sub>3</sub> with low boiling points to pyrrole solution, and that the PPy content in the films increases with addition of weak or nonpolar solvents such as THF and C<sub>6</sub>H<sub>6</sub>, compared with that without solvent (4.4%, see Table III). However, the conductivity does not increase regularly with the content of PPy, especially when the content of PPy is high enough to form a conductive network. Using C<sub>2</sub>H<sub>5</sub>OH and CHCl<sub>3</sub> as solvent, the conductivity is as low as 10<sup>-2</sup> S/cm and 10<sup>-3</sup> S/cm, respectively, since the PPy content was too low to form a consecutive conductive network. Although when methanol was used as solvent the content of PPy was much lower than that when THF or C<sub>6</sub>H<sub>6</sub> was used as solvent, the conductivity of the air surface is higher (15 S/

**Table V** Effect of the Solvent in Pyrrole Solution on the Properties of the Films

Solvent	PPy <sup>a</sup> (%)	Conductivity (S/cm)		Remarks on the Films
		Air Surface	Bottom Surface	
CH <sub>3</sub> OH	2.6	15	$1.9 \times 10^{-1}$	most flexible, strong, smooth
C <sub>2</sub> H <sub>5</sub> OH	< 0.8	$3 \times 10^{-2}$	$2.7 \times 10^{-2}$	flexible, most strong, smooth
C <sub>8</sub> H <sub>17</sub> OH	4.6	$1.3 \times 10^{-1}$	$6.9 \times 10^{-1}$	most flexible, less strong, smooth
(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O	14.6	1.3	1.2	most flexible, strong, smooth
C <sub>5</sub> H <sub>5</sub> N	5.2	$1.9 \times 10^{-1}$	$9.7 \times 10^{-1}$	most flexible, strong, smooth
C <sub>8</sub> H <sub>17</sub> NH <sub>2</sub>	—	$8.0 \times 10^{-2}$	$5.3 \times 10^{-2}$	most flexible, less strong, smooth
C <sub>14</sub> H <sub>29</sub> NH <sub>2</sub>	—	$4.5 \times 10^{-3}$	$6.5 \times 10^{-1}$	most flexible, less strong, smooth
C <sub>6</sub> H <sub>6</sub>	14.8	$4.4 \times 10^{-2}$	1.3	most flexible, most strong, smooth
CCl <sub>4</sub>	—	$1.4 \times 10^{-2}$	$1.6 \times 10^{-1}$	most flexible, less strong, smooth
CHCl <sub>3</sub>	0.9	$6.5 \times 10^{-3}$	$7.1 \times 10^{-3}$	most flexible, strong, smooth

The conductive composite films were prepared under the following conditions: 0.8 g PSBH; 0.2 g TEOS; ferric chloride: 1.2 g; reaction time: 24 h; weight ratio of pyrrole/solvent, 1 : 1. Other conditions as described in the Experimental section.

<sup>a</sup> Calculated on the basis of the element analysis.



**Figure 1** Effect of solvents on SEM of the films: (a) THF; (b) methanol.

cm), showing that conductivity is strongly dependent on the morphology and structure of PPy in the film.

Figure 1 shows SEM of the films with different solvents. There is an obvious characteristic of “sandwich” structures in the films, namely, the air and the bottom surface are conductive layers, and the middle is the insulating layer of the matrix.<sup>10</sup> Using THF as solvent, the thickness of the conductive layer is 50 to 70  $\mu\text{m}$ , which displays a “relaxative snow” structure. Using methanol as solvent, the thickness of the conductive layer is 15 to 20  $\mu\text{m}$ , which exhibits fine structure. This suggests that the conductivity is dependent mainly on the relatively fine structure of the conductive layer rather than the thickness of the conductive layer.

We also found that some of the bottom surface conductivity is different from the corresponding air surface conductivity. For example, using methanol as solvent, the air surface conductivity is 15 S/cm and the bottom is  $1.9 \times 10^{-1}$  S/m. This may be caused by the different diffusion rate of the solvent in the two layers and the different effect of the solvent on the morphology of the matrix, which is caused by the different structure in the two layers.<sup>15</sup> The films become more flexible, smoother, or even stronger with addition of solvent to pyrrole solution, suggesting that homogeneous PPy in the matrix is helpful in improving the properties.

Table VI lists the effect of the weight ratio of methanol/pyrrole on the properties of the films. The conductivity of the air surface and the bottom

**Table VI** Effect of the Weight Ratio of Methanol/Pyrrole on the Properties of the Films

Methanol/Pyrrole (weight ratio)	Conductivity (S/cm)		Remarks on the Film
	Air Surface	Bottom Surface	
0/1	$7.7 \times 10^{-1}$	$6.9 \times 10^{-1}$	flexible, strong, smooth
1/3	$4.4 \times 10^{-1}$	1.2	flexible, strong, smooth
1/1	15	$1.9 \times 10^{-1}$	flexible, strong, smooth
3/1	$3.1 \times 10^{-1}$	$2.8 \times 10^{-1}$	flexible, strong, smooth

The conductive composite films were prepared under the following conditions: 0.8 g PSBH; 0.2 g TEOS; ferric chloride: 1.2 g; reaction time: 24 h; other conditions as described in the Experimental section.

**Table VII Mechanical Properties of Conductive Composite Films**

Code	FeCl <sub>3</sub> (g)	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at Break Point (%)
T <sub>20</sub> F <sub>1</sub>	0.8	10.3	178.9	170
T <sub>20</sub> F <sub>3</sub>	1.6	4.2	46.8	162.5

T<sub>20</sub>F<sub>1</sub> and T<sub>20</sub>F<sub>3</sub> were prepared as described for 0.8 g and 1.6 g ferric chloride; respectively, in Table II.

surface changes with the weight ratio of methanol/pyrrole with the same tendency that the conductivity increases and then decreases with the weight ratio of methanol/pyrrole, giving maximum conductivity of 15 S/cm and 1.2 S/cm at 1 : 1 and 1 : 3 methanol/pyrrole ratios, respectively. The weight ratio of methanol/pyrrole for the air surface conductivity to reach the maximum value is larger than that for the bottom. This may be explained as follows: the conductivity is dependent mainly on the amount of ferric chloride in the matrix and the pyrrole content in the vapor phase. When the amount of ferric chloride and the content of pyrrole in the vapor phase are high, a film with low bulky density is obtained which exhibits poor conductivity. During the process of methanol evaporation, ferric chloride could segregate in the air surface of the film; as a result, the amount of ferric chloride in the air surface would be higher than that in the bottom. Therefore, PPy with good conductivity was generated only at larger weight ratios of methanol/pyrrole, namely, at low contents of pyrrole in the vapor phase.

The mechanical properties of the conductive composite are listed in Table VII. When the amount of ferric chloride is 0.8 g, the conductive composite film exhibited better mechanical properties. The tensile strength, Young's modulus, and elongation at break point of the film are 10.3 MPa, 178.9 MPa, and 170%, respectively. When the amount of ferric chloride is 1.6 g, the tensile strength, Young's modulus, and elongation at break point are 4.2 MPa, 46.8 MPa, and 162.5%, respectively. Although the PPy content is higher in the composite film at 0.8 g ferric chloride (see Table III), Young's modulus and elongation at break point increase, indicating that rigid PPy can reinforce the flexible matrix. The structural defects caused by the higher amount of oxidant (1.6 g) lead to a decrease in the mechanical properties, further supporting the results shown in Table III.

## CONCLUSIONS

In summary, conductive composite films based on crosslinked PSBH and PPy have been synthesized which combine high conductivity and good mechanical properties. When the content of PPy was sufficient, the films' properties were strongly dependent on the morphologies of PPy in the composite films rather than on the content of PPy. The addition of solvent to pyrrole solution affected not the morphology but the content of PPy in the composite. The structural defects in the composite caused a decrease in mechanical properties.

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