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CONDUCTIVE COMPOSITE FILMS BASED ON POLYPYRROLE AND CROSSLINKED POLY(STYRENE/BUTYL ACRYLATE/ACRYLIC ACID)

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Abstract—A new conductive composite film based on polypyrrole and crosslinked poly(styrene/butyl acrylate/acrylic acid) (PSBA) was synthesized by vapor phase polymerization of pyrrole within the silicon crosslinked PSBA using anhydrous ferric chloride as oxidant. These films had high conductivity and good mechanical properties. They were very flexible and strong (e.g. elongation yield: 94.7%, tensile strength: 6.2 MPa), and the maximum conductivity achieved was 2.2 S cm^{-1} and the lowest surface resistance was 74 $\Omega\,cm^{-2}$. The factors affecting the properties of the conductive composite film were investigated in detail. The surface resistance and the conductivity were strongly affected by the over-oxidative reaction of polypyrrole which took place mainly at the outermost surface layer of the film. The mechanical properties, however, were largely unaffected. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Since the discovery of conductive polyacetylene doped with iodine in 1977 [1], electrically conducting polymers such as polypyrrole (PPy) [2], polyaniline [3], polythiophene [4] and their derivatives, have been extensively studied because of their potential uses in chemical detectors, batteries, and biosensors, catalysis and for corrosion protection, etc. These materials exhibit high conductivities and some of them also exhibit good environmental stability. However, their practical use has been hampered by the fact that many of these conjugated polymers are insoluble and infusible due to the delocalized π-bonds along their macromolecular chains. One way to overcome this disadvantage is to produce composites in which the conductive polymer constitutes the conductive component and the insulating polymer component contributes to the flexibility.

The conducting composite films were mostly prepared by blending, electrochemical and chemical methods. Some of the examples are PPy/PVA (poly(vinyl alcohol)) [5], PPy/polyether-polyester [6], PPy/polyacrylonitrile [7], PPy/PVC(poly(vinyl chloride)) [8], random copolymers of 3-methylthiophene (3-MT) and methyl methacrylate (MMA) [9, 10], grafting of aniline on chitosan [11], etc. However, each of these methods has its limitation. In the blending method, phase separation is generally the cause of the problem; whereas for the electrochemical method, the main drawback is in the size of the film produced which is limited by the area of the electrode used; and in the chemical method, the regularity of the conductive structure is generally reduced due to the insertion of insulating polymer segments into the conductive backbone, and the conductivity suffered.

We have previously synthesized and studied some conductive interpenetrating polymer networks (IPNs) which combine high conductivity, good processibility and mechanical properties. Polypyrrole/crosslinked poly(styrene/butyl acrylate/hydroxyethyl acrylate), for example, has a conductivity of 10^1 S cm^{-1}, and good mechanical properties with a tensile strength of 10.3 MPa and elongation yield of 170% [12] at a low content of polypyrrole. By controlling the synthetic conditions, conductive "micro-fiber" of polypyrrole could be obtained [13]. Furthermore, it is found that the addition of tetraethyl orthosilicate(TEOS) can improve the stability of conductive composite due to the aggregation of the Si–O–Si network formed via the hydrolysis and condensation of TEOS in the surfaces of the composite film [14]. We now report a new conductive composite based on polypyrrole and silicon crosslinked poly(styrene/butyl acrylate/acrylic acid). The major factors affecting the properties of the conductive films will be discussed.

EXPERIMENTAL

Materials

Pyrrole, purchased from Aldrich Chemical Co., was distilled under vacuum and stored in a refrigerator before use. TEOS, anhydrous ferric chloride and tetrahydrofuran,

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Table 1. Recipe for the emulsion copolymerization of styrene/butyl acrylate/acrylic acid

Ingredient	S	BA	AA	APS	SHS	DBSA	OP-10	H_2O
Amount (g)	15	30	4	0.3	0.15	0.1	0.1	120

styrene (S), butyl acrylate (BA), acrylic acid (AA), ammonium persulfate(APS), sodium hydrogen sulfite (SHS) as well as OP-10 (10 units of oxyethylene containing alkyl phenol) were purchased from Beijing Chemical industry and used without further purification. The solvents in dodecyl benzene sulfonic acid (DBSA) was removed with rotary evaporator. All other solvents were used as received.

Synthesis of PSBA

Styrene, butyl acrylate, acrylic acid, mixed surfactant (OP-10 and DBSA) as well as deionized water were added in 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, a stirrer, and a thermometer. A typical recipe used to prepare the copolymer latex is shown in Table 1. The emulsified solution containing APS and a 20 g 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. The reaction was terminated by precipitating the copolymer in 5% NaCl solution at 50°C. The precipitate was washed and dried in an oven to constant weight. The composition and carboxyl group content of the copolymer were characterized with NMR. The molar ratio of styrene/butyl acrylate/acrylic acid was 1:1.9:0.3.

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. A fixed amount of ferric chloride was then added into the solution with vigorously stirring for more than 30 min until the ferric chloride was completely dissolved. The solution was poured onto a Teflon substrate plate at room temperature under air atmosphere for 24 h, and then the final film was peeled off. The preparation of free-standing conductive composite films was carried out at −8°C by exposing crosslinked PSBA films containing $FeCl_3$ to pyrrole vapor for a given time. After the oxidative polymerization was complete, the film was washed several times with methanol until the solvent remained colorless. The film was then 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 tensile testing was performed with an Instron Testing Instrument (model 3710-016) at room temperature with a cross-head speed of 40 mm min^{-1}.

RESULTS AND DISCUSSION

The properties of the conductive films prepared were found to be greatly influenced by the amount of TEOS as shown by the results presented in Table 2. The conductivity was found to decrease and the surface resistance increase with the increase of TEOS content initially. The 20/80 TEOS/PSBA sample had the maximum conductivity of 10^0 S cm^{-1}. The minimum conductivity of 10^{-3} S cm^{-1} was registered by the 40/60 sample. The corresponding surface resistances were $\sim 10^2\ \Omega\ cm^{-2}$ and $\sim 10^4\ \Omega\ cm^{-2}$ respectively. The decrease in the conductivity with the increase in TEOS content is consistent with the previous results [12, 15] and has been attributed to the increase in the crosslink density of the network. Our present results have additionally shown, when the content of TEOS had further increased to 50/50 TEOS/PSBA, the decreasing trend reversed and the conductivity increased instead. This reversal of trend may be attributed to the following reason. At low content of TEOS, only small Si–O–Si networks were produced and they dispersed in the matrix. When the TEOS content had increased and reached a certain level, the Si–O–Si networks formed became large enough to constitute a continuous phase. These networks aggregated and migrated to surfaces with low surface energy [16]. Hence the surface resistance decreased and the conductivity increased for sample 50/50 TEOS/PSBA. The mechanical properties of the films was also affected by the content of TEOS. Initially as the TEOS content increased, the film became increasingly brittle due to the increase in crosslink density. When the TEOS/PSBA ratio reached 50/50, in tandem with the reversal in the conductivity, the film became hard and strong, consistent with the argument that large enough Si–O–Si networks had now been formed to constitute a continuous glassy phase in the matrix. Generally, the films had good mechanical properties. For example, the sample with 20/80 TEOS/PSBA ratio shown in Table 2 had a tensile strength of 6.2 MPa, an elongation at break of 94.7% and a Young modulus of 90.7 MPa.

The effect of ferric chloride on the properties of the films is shown in Table 3. As expected, the conductivity was found to increase and then decrease with the increase in the amount of $FeCl_3$.

Table 2. Effect of the amount of TEOS on the properties of the conductive films*

TEOS/PSBA (wt/wt)	Surface resistance ($\Omega\ cm^{-2}$)		Conductivity (S cm^{-1})		Remarks on the films
	Air surface	Bottom surface	Air surface	Bottom surface	
10/90	2.2×10^3	4.1×10^2	1.6×10^0	6.8×10^{-1}	flexible, strong
20/80	8.3×10^2	1.2×10^3	1.9×10^0	1.9×10^{-1}	flexible, strong
30/70	5.0×10^3	1.1×10^3	1.7×10^{-1}	9.0×10^{-2}	flexible, strong
40/60	4.5×10^4	1.6×10^4	1.6×10^{-3}	1.7×10^{-3}	brittle, weak
50/50	5.9×10^2	3.4×10^2	7.4×10^{-1}	5.9×10^{-1}	hard, strong

*The conductive composite films were prepared under the conditions: 1.5 g ferric chloride; 0.01 g H_2O; 0.01 g DBSA; reaction time: 24 h.

Table 3. Effect of the amount of ferric chloride on the properties of the films*

Feeding amount of chloride (g)	Surface resistance ($\Omega\,cm^{-2}$)		Conductivity ($S\,cm^{-1}$)		Remarks on the films
	Air surface	Bottom surface	Air surface	Bottom surface	
0.5	6.0×10^3	8.4×10^2	1.5×10^{-1}	1.6×10^{-1}	flexible, strong
0.8	9.6×10^1	7.4×10^1	2.2	1.7	flexible, stronger
1.5	2.2×10^3	4.1×10^2	1.6	6.8×10^{-1}	flexible, strong
1.9	1.6×10^4	5.6×10^3	6.8×10^{-1}	1.7×10^0	flexible, strong
2.2	2.6×10^4	1.1×10^3	1.6×10^{-1}	1.7×10^{-2}	flexible, strong

*The conductive composite films were prepared under the conditions: 0.9 g PSBA, 0.1 g TEOS, 0.01 g H_2O, 0.01 g DBSA; reaction time: 24 h.

The decrease in conductivity with higher concentration of $FeCl_3$ has been attributed to the over-oxidative reaction and the formation of PPy with low bulky density. The maximum conductivity found in this study was $2.2\,S\,cm^{-1}$. The surface resistance was also found to increase with increasing amount of $FeCl_3$. This effect was more pronounced. When the amount of ferric chloride was at 2.2 g, the surface resistances were two or three orders of magnitude higher than the sample with 0.8 g $FeCl_3$ ($74\,\Omega\,cm^{-2}$). This rather drastic change in the surface resistance clearly indicated that the over-oxidative reaction of PPy and the formation of PPy with low bulky density took place mainly in the outermost surface layer of the conductive film. It is important to note that all the conductive composite films were flexible and strong.

The effect of reaction times on the properties of the films is shown in Table 4. For the sample with reaction time of 24 h, the conductivity reached a maximum at $2.2\,S\,cm^{-1}$. This was two orders of magnitude higher than the sample with 8 h reaction time. Furthermore, the conductive film not only remained flexible but was also stronger, resulting from the reinforcement effect of the rigid conductive PPy formed. Further reaction time however, had little additional effect on the conductivity. This can be explained as follows: when the reaction time was long enough, the sufficiently compact PPy network which had already been generated at the surface of the matrix film could then function as a shield to hinder further diffusion of pyrrole. As a result, additional oxidative polymerizations of pyrrole was impeded and little change in the conductivity was observed. However in the range where there was little change in conductivities, the surface resistance continued to increase. It increased by $1 \sim 2$ orders of magnitude with the reaction time changing from 24 h to 72 h. These results suggested that the over-oxidative reaction took place mainly at the outermost surface layer of the film. The over-oxidative reaction of PPy at the surface would undoubtedly be strongly dependent on the residual amount of $FeCl_3$ present. It is believed the residual $FeCl_3$ could have migrated to the surface due to its better affinity to the more polar silicon networks. This would give rise to the higher concentration of $FeCl_3$ near the surface. Significantly, all the conductive films were flexible and strong despite the morphology changes of the films.

The properties of the conducting films obtained by the vapour diffusion process were found to be profoundly affected by the nature of the solvent used in the preparation of the pyrrole solutions (Table 5). Depending on the type of the solvent used, the conductivity was found to varied from 10^0 to $10^{-4}\,S\,cm^{-1}$ and the surface resistance from 10^2 to $10^7\,\Omega\,cm^{-2}$. When methanol or chloroform was used as solvent, the conductivity and the surface resistance were about $2.0\,S\,cm^{-1}$ and $10^1\Omega\,cm^{-2}$, respectively. Comparing these values with those obtained using neat pyrrole with conductivity of $1.6 \sim 6.8 \times 10^{-1}\,S\,cm^{-1}$ and surface resistance of $4.1 \times 10^2 \sim 2.2 \times 10^3\Omega\,cm^{-2}$ (see Table 3), there was only a marginal change in the conductivity, but the surface resistance had decreased by a significant level of $1 \sim 2$ orders of magnitude. However, the films remained flexible and became even stronger. This could be attributed to the reinforcement effect of the compact PPy which was favourably formed in the presence of methanol and chloroform [12]. When pyridine was used as solvent, however, the conductivity was found to decrease significantly, by $1 \sim 3$ orders of magnitude. Correspondingly, the surface resistance increased by $1 \sim 4$ orders of magnitude. These results are consistent with the report that pyridine inhibits the electropolymerization of pyrrole. The study by Morse *et al.* [17] has shown that the key step in the intervention involves the pyridine acting as base to remove the proton from the nitrogen atom of the first-formed radical cation, yielding insulative film at equimolar pyridine/

Table 4. Effect of reaction times on the properties of the films*

Reaction time (h)	Surface resistance ($\Omega\,cm^{-2}$)		Conductivity ($S\,cm^{-1}$)		Remarks on the films
	Air surface	Bottom surface	Air surface	Bottom surface	
8	3.3×10^2	3.2×10^3	3×10^{-2}	5.9×10^{-1}	flexible, strong
24	9.6×10^1	7.4×10^1	2.2	1.7	flexible, stronger
46	1.4×10^2	8.6×10^1	1.8	1.6	flexible, strong
58	1.3×10^2	1.1×10^2	1.8	1.1	flexible, stronger
72	4.2×10^3	5.5×10^2	1.2	1.2	flexible, stronger

*The conductive composite films were prepared under the conditions: 0.9 g PSBA, 0.1 g TEOS, 0.01 g H_2O, 0.01 g DBSA, ferric chloride: 0.8 g.

Table 5. Effect of solvents in pyrrole solutions on the properties of the conducting films*

Solvent	Surface resistance (Ω cm^{-2})		Conductivity (S cm^{-1})		Remarks on the films
	Air surface	Bottom surface	Air surface	Bottom surface	
CH_3OH	1.2×10^1	1.1×10^1	1.1	1.4	stronger, flexible
$(CH_2CH_2)_2O$	6.7×10^2	5.6×10^2	0.8	0.9	strong, flexible
C_5H_5N	1.0×10^7	4.0×10^3	6.0×10^{-4}	4.4×10^{-2}	strong, flexible
$CHCl_3$	1.0×10^1	1.1×10^1	2.1	2.1	stronger, flexible

*The conductive composite films were prepared under the conditions: 0.9 g PSBA, 0.01 g H_2O, 0.01 g DBSA, 0.1 g TEOS, ferric chloride: 1.5 g; reaction time: 24 h; volume ratio of pyrrole/solvent: 1:1.

pyrrole ratio.* It is envisaged that similar proton abstraction process may be at work in the present system studied. However, more works are needed before the effect of solvent could be fully understood.

SUMMARY

The conductive composite film based on PPy and the silicon crosslinked PSBA had been synthesized by vapour diffusion method. The film had high conductivity and good mechanical properties. The conductivity and surface resistance were strongly dependent on the amount of oxidant and TEOS, reaction times as well as the nature of solvents in pyrrole solutions. By increasing the amount of oxidant or the reaction time, the over-oxidative reaction of polypyrrole were found to take place within the outermost surface of the film and thus strongly affected the surface resistance.

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