Surface Structure of Conductive Polypyrrole-Containing Composites

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ABSTRACT: The surface structures of polypyrrole/silicon crosslinked poly(styrene/butyl acrylate/hydroxyethyl acrylate) (PSBH) conductive composite films were investigated by X-ray photoelectron spectroscopy and scanning electron microscopy. It was found that the conductive composite films were of a "sandwich" structure, and the surfaces greatly differ in chemical compositions and phase morphologies from the bulk. The Si and N contents exhibit opposite gradient change with the measured depth of the two surface layers in the composite films, namely, the decrease in Si content and the increase in N content with increase in the depth of the surface layers. However, the N^{$\delta+$}/N ratios in polypyrrole decreased with the measured depth of the conductive composite film. It was also found that the conductive composite film based on silicon crosslinked matrix exhibits more environmental stable than that based on linear matrix. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 95–101, 1999

Keywords: polypyrrole; PSBH; conductive composite; X-ray photoelectron spectroscopy

INTRODUCTION

In the past decade the conductive composites based on rigid conductive polymers and matrices have received considerable attention due to their good processability, mechanical properties, and stability in atmospheric environment.¹⁻⁴ For example, blending of polypyrrole with other polymers,¹ synthesis of block copolymers containing polypyrrole or polyaniline, introducing flexible side substitutes to the main rigid chain,³ or grafting conducting polymer chains to a nonconducting polymer⁴ and electrochemical polymerization of pyrrole on a modified electrode by polyacetylene⁵ or other insulating polymers have been exten-

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sively reported. The electrochemical polymerization method and chemical polymerization method have been successfully developed to prepare the composites of polypyrrole with excellent properties of stability and flexibility. Among these, many conductive polypyrrole composites such as polypyrrole/PVA, polypyrrole/PVC have been prepared by interfacial polymerization or vapor polymerization methods. However, few investigations on the surface structure of the conductive composite films have been reported. To understand the stability of the composite of polypyrrole/poly(vinyl alcohol), the several states of O and Cl atoms have been measured by XPS.⁶ Regarding other conductive composite films, especially those prepared by interface polymerization or vapor polymerization such as polypyrrole/poly(vinyl chloride), polypyrrole/polyurethane, their structures have not been investigated.

Table I Atomic Sensitivity Coefficient (ASC)

Element	Si	Ν	0	С
ASC	0.25	0.42	0.61	0.24

We have previously reported the preparation of conducting composite films of polypyrrole by exposing silicon crosslinked network matrix films containing ferric chloride to pyrrole vapor^{7–9} and conducting interpenetrating polymer networks (IPNs) of polyaniline by *in situ* polymerization of aniline within the silicon crosslinked matrix.¹⁰ Our composite films are, moreover, very flexible, with good mechanical properties and high conductivity. In the previous work,¹¹ the surface structures of PSBH/polysiloxane IPN films are investigated with XPS, and it is found that the surface composition is different from the bulk. In this article, we report the surface structure of polypyrrole/silicon crosslinked PSBH.

EXPERIMENTAL

Materials

Styrene (S), butyl acrylate (BA), and hydroxyethyl acrylate (HEA) were distilled under vacuum before use. Sodium hydrogen sulfite, ammonium persulfate, tetrahydrofuran (THF), tetraethyl orthosilicate (TEOS), and *p*-nonaphenol polyethyleneoxy (10) ether (OP-10) were used as received. The solvents in dodecyl benzene sulfonic acid (DBSA) were removed with the use of rotary evaporator. Synthesis of crosslinked poly(styrene/ butyl acrylate/hydroxyethyl acrylate) (PSBH) (molar ratio, 3: 4: 0.3) has been previously described.¹²

Preparation of Conductive Composite Films

Fixed amounts of PSBH and TEOS, 0.01 g deionized water and 0.01 g DBSA were added into 10 g THF. The mixture was refluxed for 1 h, then 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, placed at room temperature under air atmosphere for 48 h, then cured at 100°C for 1 h. The final film was then peeled off. The conductive composite film was prepared by exposing the crosslinked PSBH film containing FeCl_3 to pyrrole vapor for 24 h at -8° C. The films were washed several times with methanol until the solvent remained colorless, and then pressed with glass plates and dried in vacuum for more than 12 h.

Oxidation of the Conductive Composite Films

The conductive composite films were exposed in air at 80°C for various lengths of time. The electrical conductivity was measured at room temperature by the standard four-probe method.⁷

Measurements

Electron Microscopy

The phase morphological characteristics of the samples were studied by scanning electron microscopy (SEM) using the model HITACHI S-530. The specimens for SEM were frozen in liquid nitrogen, fractured, mounted, and coated with gold.

X-ray Photoelectron Spectroscopy (XPS) Measurements

The surface composition of the films was studied by X-ray photoelectron spectroscopy (XPS) using a Kratos XSAM-800 instrument. AlKa X-rays were used as the source, operated at 12 kV and 15 mA. Base pressure in the analysis chamber was maintained at 10^{-9} Torr. The samples were mounted on the sample holder using adhesive tape. To assess the compositional gradient in the surface layers, the XPS spectra were taken at several different electron take-off angles, 80, 45, and 0°. The depth of analysis increases with decrease in the electron take-off angle. The ratio of Si(N)/(Si+O+C+N) was used to characterize Si and N gradient change with the depth of analysis. Atomic sensitivity coefficients are shown in Table I.

RESULTS AND DISCUSSION

The synthesis of the conductive composite film based on poly(styrene/butyl acrylate/hydroxyethyl acrylate) and polypyrrole by vapor phase polymerization was in accordance to that described previously.⁷ In the present study, by SEM and XPS techniques, the surface structure and composition of the conductive film was found to be different from its bulk. Furthermore, results from XPS analysis have shown, surprisingly, that the content of polypyrrole increases rather than de-



Figure 1 Angular-dependent Si and N relative contents for $T_{10}F_2$ (a) air surface; (b) bottom surface. (Synthetic conditions for $T_{10}F_2$: 0.9 g PSBH, 0.1 g TEOS, 1.2 g FeCl₃, the other same as described in Experimental.)

creases with the increase in the measured depth within the surface layers of the conductive film. Figure 1(a) and (b) and Figure 2(a) and (b) clearly show that the content of Si atom decreases, and the content of N atom increases with an increase in the measured depth of the film, an observation that had not been expected. This rather unexpected finding that polypyrrole contents are less near the surfaces is believed to be related to the concomitant increase in the Si content. More Si found in the two surfaces of the film is due to the migration of Si as a result of poor compatibility between the Si—O—Si network and polypyrrole.⁸ In addition, from Figure 1(a) and (b) and Figure 2(a) and (b) it is clear that the Si—O—Si network is richer in the air surface than that in the bottom surface of the film. For $T_{10}F_2$, the Si content increases from 2.2 to 16.5% in the air surface layer, compared to that from 2.8 to 10.8% in the bottom layer with the take-off angle increasing from 45 to 80°, respectively. It should be stressed that the difference in the Si and N contents are fairly large, varying from the outer to the inner sur-



Figure 2 Angular-dependent Si and N relative contents for $T_{20}F_2$ (a) air surface; (b) bottom surface. (T_{20}F_2 with 20% TEOS (PSBH + TEOS = 1 g), the other conditions same as $T_{10}F_2$.)

faces, as shown by the results with the take-off angle changing from 45 to 80° .

Figures 3 and 4 show N1s XPS spectra for the air surface of $T_{20}F_2$ at 45 and 0°, respectively. The N1s core level spectra were resolved into two components corresponding to neutral amine at about 399.5 eV, and protonated, positively charged N sites at around 401.6 eV.^{13,14} It was found that the N^{δ^+}/N ratios decreased with the measured depth of the conductive composite film (Table II). These results indicate that the content of nitrogen in the so-called doped state was higher near the surface of the film. It was calculated that, based on the $N^{\delta+}/N$ ratios, the percentage of pyrrole in doped state varied from 12.5-20%, depending on the take-off angle, resulting from the corresponding changes in structure and composition from the outside to the inside in the film and the diffusion effect of pyrrole and ferric chloride during the oxidative polymerization. It has been reported from the other conductive composite systems that the percentage of pyrrole in doped state is 25-33%.^{6,15} This further indicates the percentage of $N^{\delta+}$ strongly depended on the structure of the insulating matrix. Based on the above



Figure 3 N1s core-level spectra for the air surface of $T_{20}F_2$ at 45°.



Figure 4 N1s core-level spectra for the air surface of $T_{20}F_2$ at 0°.

results, we can conclude that the polymerization of pyrrole occurs on the silicon crosslinked PSBH-transition metal salt film according to the following reaction:

$$nC_4H_5N + (2.1-2.2)n \text{ FeCl}_3 \text{ (Silicon crosslinked}$$

 $PSBH) \rightarrow [C_4H_3N^{0.1-0.2+}Cl_{0.1-0.2}^{--}]n$
 $+ 2n \text{ HCl} + (2.1-2.2)n \text{ FeCl}_3$

Table IIIa and b list the change of the conductivity with the exposure time. For T_0F_2 without the addition of TEOS in the preparation of the ma-

Table II	The N^{δ}	⁺ /N Ratios	of the Co	onductive
Composit	e Films	Obtained	from XPS	5 Spectra

	T ₁₀	$T_{10}F_2$		$T_{20}F_2$	
Take-Off Angle (°)	Air Surface	Bottom Surface	Air Surface	Bottom Surface	
$\begin{array}{c} 45\\0\end{array}$	$1:5.4 \\ 1:6.6$	$1:6.9 \\ 1:7.2$	$1:4.0 \\ 1:7.0$	1:5.1 1:6.3	

_		Conductivity (S/cm)				
Exposure Time (h)	T_0F_2	$T_{10}F_2$	$T_{40}F_2$	$T_{20}F_1$	$T_{20}F_{3}$	
0^{b}	$6.7 imes10^{-1}$	$1.2 imes10^{-1}$	$1.6 imes10^{-2}$	$6.4 imes10^{-1}$	$7.7 imes10^{-1}$	
6	$4.8 imes10^{-1}$	$2.4 imes10^{-1}$	$9.2 imes10^{-3}$	$5.5 imes10^{-1}$	$2.7 imes10^{-1}$	
12	$3.1 imes10^{-1}$	$9.0 imes10^{-2}$	$7.0 imes10^{-3}$	$2.6 imes10^{-1}$	$2.6 imes10^{-1}$	
33	$1.1 imes10^{-1}$	$8.0 imes10^{-2}$	$2.8 imes10^{-3}$	$2.3 imes10^{-1}$	$1.6 imes10^{-1}$	
130	$1.0 imes10^{-1}$	$5.0 imes10^{-2}$	$1.9 imes10^{-3}$	$1.3 imes10^{-1}$	$9.0 imes10^{-2}$	
216	$9.2 imes10^{-3}$	$1.4 imes10^{-2}$	$3.7 imes10^{-4}$	$1.7 imes10^{-2}$	$3.0 imes10^{-2}$	

Table IIIa Effect of Exposure Time in Air on the Conductivity of the Air Surfaces in the Films^a

trix, the conductivity decreases by two orders of magnitude from 4.9 imes 10⁻¹ S/cm to 4.9 imes 10⁻³ S/cm after exposure to air at 80°C for 216 h. With the addition of TEOS, the conductivity of these samples decreased less than that of T_0F_2 after the same exposure. This is particularly evident for $T_{10}F_2$. Its conductivity was found to decrease only one order of magnitude compared to that without exposure, indicating the addition of TEOS can improve the stability of the conducting polymer within the insulating crosslinked matrix. However, further increase of TEOS in the preparation of the matrix, i.e., $T_{40}F_2$, did not improve further the stability of the conductive film. This may be resulted from the different chemical composition and phase structure. From Table IIIa and b it can be seen that $T_{20}F_1$ and $T_{20}F_3$ show similar changes with exposure time, suggesting the environmental stability was not influenced by the amount of oxidative agent.

The SEM micrographs of T_0F_2 , $T_{10}F_2$, and $T_{40}F_2$ are shown in Figure 5. It can be seen that all the three samples have the same characteristic "sandwich" structures. Fine wavy ridges are seen near the two surfaces, but are slightly more prominent in the air surfaces. These fine structures are due to the presence of polypyrrole with gradient concentrations, which have been clearly shown from the XPS results. The conductivity data have shown that the -SiOSi- network aggregated in the two surfaces can provide good environmental stability for the conductive composite films (i.e., $T_{10}F_2$ and $T_{40}F_2$). The morphology of the sample is also an important factor. For example, the bottom surface of sample $T_{10}F_2$ has a smoother and more compact structure, and it has been found to be more stable when exposed to air.

In conclusion, the migration of silicon to the air and bottom surfaces in the crosslinked PSBH/Polypyrrole was observed. In contrast, the polypyrrole content in the outer most surface was lower than that in the interior surface and the $N^{\delta+}/N$ ratio decreased with the mea-

-	Conductivity (S/cm)				
Exposure Time (h)	T_0F_2	$T_{10}F_2$	$T_{40}F_2$	$T_{20}F_1$	$T_{20}F_{3}$
0^{b}	$4.9 imes10^{-1}$	$3.0 imes10^{-1}$	$1.2 imes 10^{-2}$	$4.0 imes10^{-1}$	$5.2 imes10^{-1}$
6	$2.3 imes10^{-1}$	$1.3 imes10^{-1}$	$1.3 imes10^{-2}$	$3.5 imes10^{-1}$	$2.1 imes10^{-1}$
12	$2.0 imes10^{-1}$	$2.0 imes10^{-2}$	$2.8 imes10^{-2}$	$2.8 imes10^{-1}$	$2.4 imes10^{-1}$
33	$1.1 imes10^{-1}$	$2.5 imes10^{-1}$	$4.7 imes10^{-3}$	$2.7 imes10^{-1}$	$1.5 imes10^{-1}$
130	$9.0 imes10^{-2}$	$1.3 imes10^{-1}$	$1.2 imes10^{-3}$	$1.8 imes10^{-1}$	$7.0 imes10^{-2}$
216	$4.9 imes10^{-3}$	$3.2 imes10^{-2}$	$3.2 imes10^{-3}$	$2.0 imes10^{-2}$	$2.0 imes10^{-2}$

Table IIIb Effect of Exposure Time in Air on the Conductivity of the Bottom Surfaces in the Films^a

^a The synthetic conditions of the films: T₀F₂, T₄₀F₂ with 0%, 40% TEOS, respectively; T₂₀F₁, T₂₀F₃ with 0.8 g, 1.6 g FeCl₃, respectively; the others same as described in $T_{10}F_2$. ^b The conductive composite films have been stored in desiccator for 3 months.





Figure 5 SEM micrographs for T_0F_2 , $T_{10}F_2$, and $T_{40}F_2$.

sured depth of the conductive composite film, resulted from the migration of silicon to the surface. The stability of the conductive composite film could be improved with the addition of TEOS, but strongly depended on the phase morphology of the —SiOSi— network aggregated in the surfaces.

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