



# Polyimide modified with metal coupling agent for adhesion application

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## ARTICLE INFO

Available online 24 March 2009

### Keywords:

Polyimide  
Sol–gel  
Adhesion  
Metal oxide  
Coupling agent

## ABSTRACT

Polyimide hybrid metal oxide thin films used on flexible print circuit boards are prepared by the *in situ* sol–gel process. The precursor, poly (amic acid), containing 2,2'-bis[4-(4-aminophenoxy) phenyl]propane (*p*-BAPP), 3,3',4,4'-benzophenonetetracarboxylic anhydride (BTDA) and *p*-aminopropyltrimethoxysilane (APrTMOS), is synthesized, and then phenyltrimethoxysilane; PhSi(OCH<sub>3</sub>)<sub>3</sub> and tris(2,4-pentanedionato) aluminum(III); Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> are added and mixed thoroughly. Following curing, the polyimide/PhSiOx/Al<sub>2</sub>O<sub>3</sub> hybrid films exhibit high transparency and flexibility. The adhesion improvement between copper and polyimides hybrid films is investigated by peel test and the X-ray photoelectron spectroscopy (XPS) measurements are made to demonstrate that the Si elements from APrTMOS and PhSiOx migrate from the surface to the bulk of polyimide hybrids. Dynamic mechanical analysis (DMA) indicates that the glass transition temperature (T<sub>g</sub>) increases with the Al<sub>2</sub>O<sub>3</sub> content and the tanδ peak becomes broader and lower. The nano-sized Al<sub>2</sub>O<sub>3</sub> particles are highly dispersed in the hybrid film, as detected by high-resolution transmission electron microscopy (HRTEM). The polyimide/PhSiOx/Al<sub>2</sub>O<sub>3</sub> films show good peel strength with copper, as well as high T<sub>g</sub> values. They may therefore have potential applications in flexible print circuits.

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## 1. Introduction

Polyimide (PI) has been widely utilized in electric industries as materials in flexible printed circuits (FPC) and electrical packaging especially for use in high electric fields and high-temperature applications. A wide range of polyimides and inorganics have been combined to form hybrid films with perfect mechanical, electrical, magnetic and adhesive characteristics [1–6]. They combine the beneficial properties of inorganic materials – rigidity, high thermal stability and high mechanical strength with those of organic polymers – flexibility, ductility and ease of processability [7–13]. Generally, they also exhibit special properties of nanocomposites, enabling them to be used in FPCs or other special applications.

Polyimide hybrid materials have attracted considerable interest in recent years because the introduction of only small amounts of inorganic additives markedly improve their thermal stability and mechanical properties and add special features. The adhesion strength between PI and copper can be enhanced by incorporating metal oxide into PI matrix. Several investigations have been performed on the addition of inorganic additives to polyimides to improve their properties [14–18].

In this study, *p*-aminopropyltrimethoxysilane (APrTMOS) is employed to control the PI segment length and alter the PhSiOx/

Al<sub>2</sub>O<sub>3</sub> ratio of prepared hybrid films to improve their surface composition. This work explores various properties of the resultant PI/PhSiOx/Al<sub>2</sub>O<sub>3</sub> hybrid films, such as their morphology, mechanical characteristics, dimensional stability and peel strength.

## 2. Experimental

### 2.1. Materials

3,3',4,4'-Benzophenonetetracarboxylic anhydride (BTDA, 99%), from Dugessa Chemical Company, was purified by recrystallization. 2,2'-Bis[4-(4-aminophenoxy)phenyl]propane (*p*-BAPP, 98%) from Tokyo Chemical Industry was dried in a vacuum oven at 125 °C for 24 h prior to use. N, N-Dimethyl formamide (DMF, 99.5%) from Fisher Chemical Company was dehydrated using 4 Å molecular sieves. *p*-aminopropyltrimethoxysilane (APrTMOS), tris(2,4-pentanedionato)-aluminum(III); Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> additive from Tokyo Chemical Industry and the phenyltrimethoxysilane; PhSi(OCH<sub>3</sub>)<sub>3</sub> (97%) from Alfa Aesar, were used as supplied.

### 2.2. Synthesis

Fig. 1 displays the chemical structure of PI/PhSiOx/Al<sub>2</sub>O<sub>3</sub> hybrid films and the reaction process. In a three-neck flask, nitrogen gas was purged to remove the moisture before the monomer was added and

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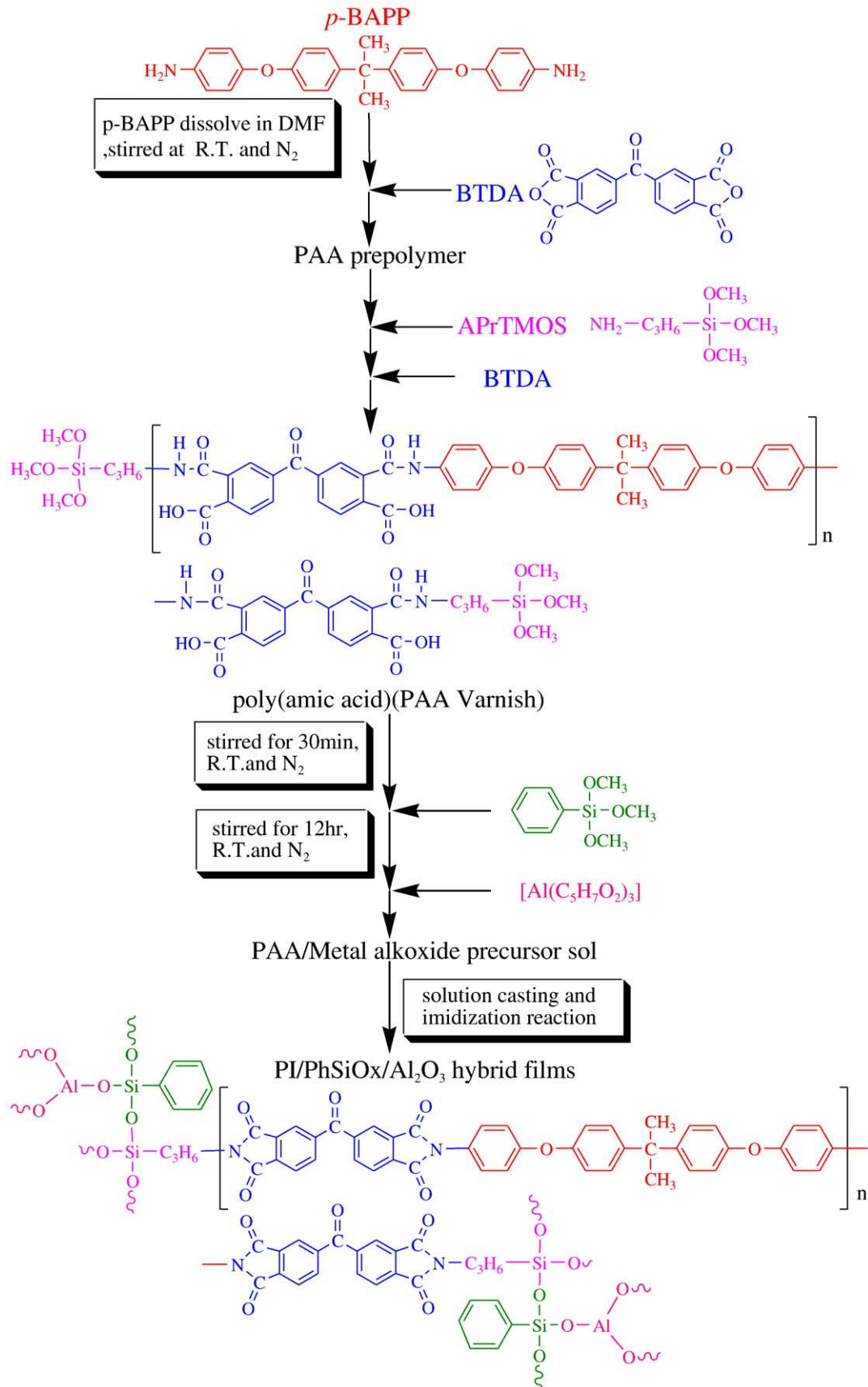


Fig. 1. The chemical structure and reaction process of PI/PhSiOx/ $Al_2O_3$  hybrid films.

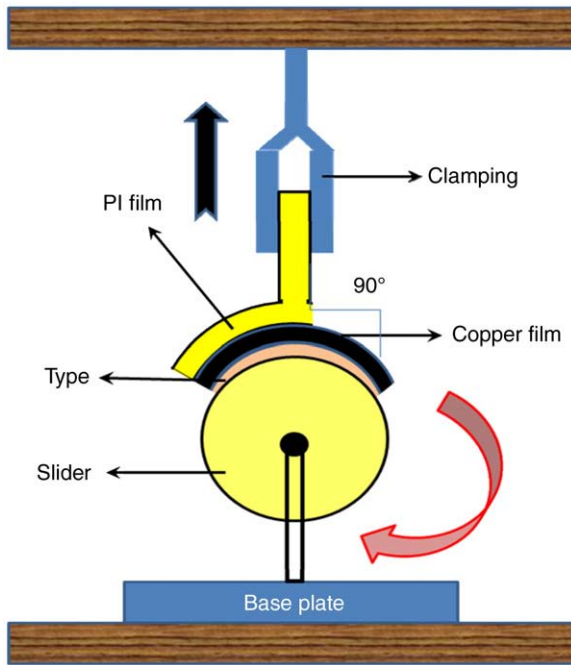


Fig. 2. The diagram of peel test.

then *p*-BAPP and DMF solvent were added directly. After the solution had been thoroughly stirred and dissolved, BTDA powder was added. APrTMOs, with a monoamine group, was added to the above solution, which was stirred for 1 h to control the PI segment chain length at 10000 g/mole. Poly(amic acid) (PAA) varnish solution with 18% solid content (w/w) were thus obtained. Coupling agents, PhSi(OCH<sub>3</sub>)<sub>3</sub> and Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub>, were added and the solution was stirred for at least 12 h to ensure that the modified PAAs were well mixed. The metal oxide concentration of hybrid with PhSiOx/Al<sub>2</sub>O<sub>3</sub> ratios of 8/2, 5/5, 2/8 were 8 wt.%, based on the assumption of complete imidization and complete conversion of PhSi(OCH<sub>3</sub>)<sub>3</sub> and Al(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> to PhSiOx and Al<sub>2</sub>O<sub>3</sub>, without no remaining residual solvent. In this investigation, the sample code is denoted PIS-*y*-ScAb, where PIS means that the film is an APrTMOs-containing PI segment with a chain length of 10000 g/mole and *y* is the 8 wt.% inorganic metal oxide content of the hybrids.

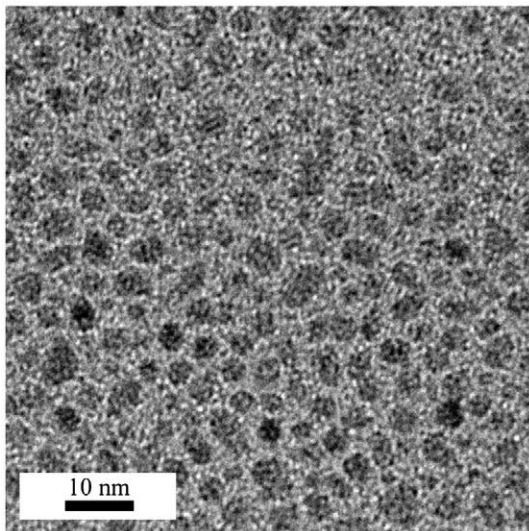


Fig. 3. Transmission electron microscope photographs of the PIS-30%-S0A10 hybrid films.

Table 1  
Characteristic of pure PI, PIS and PIS-8%-ScAb hybrid films.

Code	Item	L*	a*	b*	Appearance	C.T.E.(ppm/°C)		DMA T <sub>g</sub>
						100–200	200–300	
Pure PI		87.3	−4.5	78.3	PY <sup>a</sup>	59.6	1912	235.8
PIS		87.5	−5.7	74.2	PY	64.2	941	− <sup>c</sup>
PIS-8%-S10A0		87.1	−4.3	79.0	PY	67.7	1155	230.7
PIS-8%-S8A2		85.5	−2.5	77.1	PY	65.8	753	242.8
PIS-8%-S5A5		83.0	2.4	77.1	PY	62.1	631	249.4
PIS-8%-S2A8		77.5	9.1	77.6	PY	61.6	595	253.1
PIS-8%-S0A10		71.0	16.2	63.5	Y <sup>b</sup>	62.8	500	255.9

<sup>a</sup> Pale yellow.

<sup>b</sup> Yellow.

<sup>c</sup> No measurement.

S and A denote PhSiOx and Al<sub>2</sub>O<sub>3</sub>, respectively, and the c/b ratio is the weight ratio of PhSiOx content to Al<sub>2</sub>O<sub>3</sub> content in the hybrid films. However, pure PI contains *p*-BAPP and BTDA only. PIS-8%-S10A0 is a hybrid of PIS with 8 wt.% PhSiOx content and a PhSiOx to Al<sub>2</sub>O<sub>3</sub> content weight ratio was 10/0. PIS-8%-S2A8 represents a hybrid of PIS with 8 wt.% metal coupling agent, and a PhSiOx to Al<sub>2</sub>O<sub>3</sub> weight ratio of 2/8.

### 2.3. Measurements

The color intensity of the polymers is determined using a color meter-SP60 X-Rite/U.S.A. X-ray photoelectron spectra (XPS) are obtained using an ESCA ULVAC-PHI spectrometer in constant analyzer energy mode with pass energy of 50 eV and Al-Kα (280 eV) radiation as the excitation source. XPS analysis is performed at room temperature and at pressures under 5 × 10<sup>−10</sup> Torr. The take-off angle used in XPS was 45°; the sputter ratio was 8.5 nm/min. Dynamic mechanical analysis (DMA) was carried out using a thermal analyzer DMA-2980 from 60 to 450 °C at a heating rate of 3 °C/min. The coefficient of thermal expansion (CTE) was measured in the range of 50–350 °C using a TA instrument TMA-2940, at a heating rate of 10 °C/min. The CTE values were obtained on temperature scales between 100 and 200 °C and between 200 and 300 °C. Cryo-high-resolution transmission electron microscopic (Cryo-HRTEM) images were obtained using a JEM-2010 electron microscope. The hybrid films adhered to Cu foil substrates, which were preheated at 190 °C for 2 min and a pressure of 20 kg/cm<sup>2</sup> was applied for 5 min. The adhesion of the samples was tested using the 90° peel test method and the peel rate was 50.8 mm/min. The

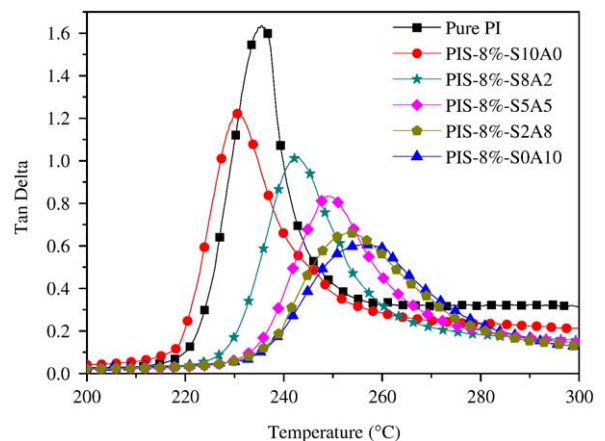


Fig. 4. Tan  $\delta$  of dynamic mechanical analysis for pure PI and PIS-8%-ScAb hybrid films.



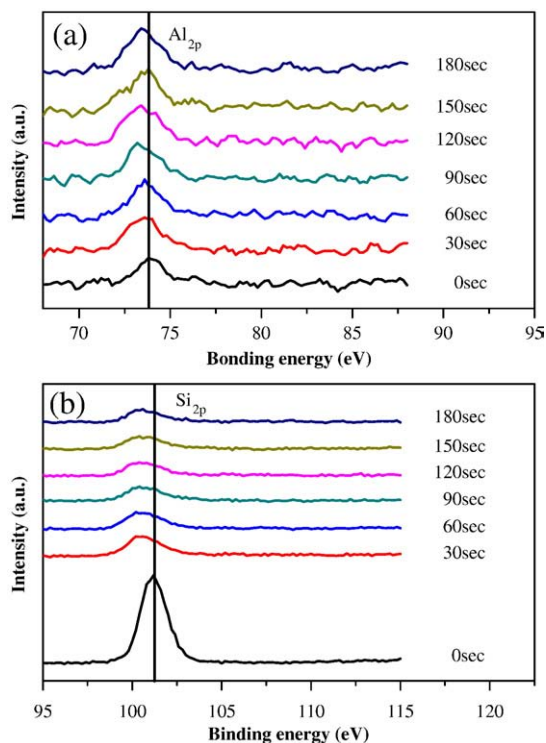


Fig. 5. XPS depth profile analysis of PIS-8%-S2A8 (a)  $Al_{2p}$  element with different times (b)  $Si_{2p}$  element with different times.

experimental value was the mean of at least ten measurements. The diagram of peel test was shown as Fig. 2.

### 3. Results and discussion

The morphology of the  $Al_2O_3$  in the PI hybrid films was investigated by TEM (transmission electron microscope micrographs). The Fig. 3 displays the TEM micrographs of PIS-30%-S0A10 hybrid films. In our work, TEM micrographs of hybrids with low inorganic content (<10 wt. %) did not reveal the size of the dispersed particles. Then, the inorganic content was increased to 30 wt.%. The  $Al_2O_3$  particles (black points) were homogeneously dispersed in the polyimide matrix and the particles were nano-sized. TEM revealed that the size of the  $Al_2O_3$  particles in the hybrid films was approximately <10 nm.

The yellowness ( $b^*$ ), redness ( $a^*$ ) and lightness ( $L^*$ ) indices determined using an X-Rite color meter specified the color of the PI/PhSiOx/ $Al_2O_3$  hybrid films. This work focuses on the lightness ( $L^*$

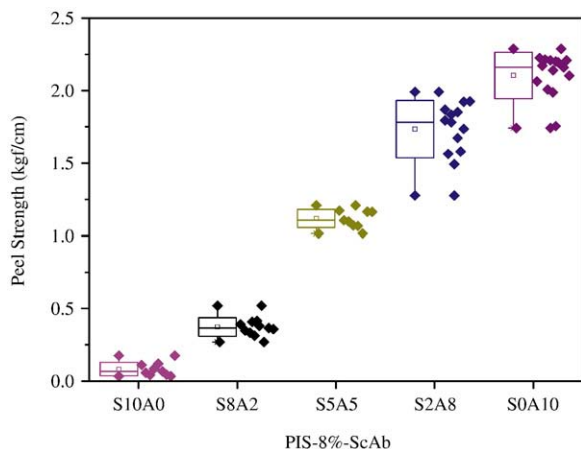


Fig. 6. Peel strength of PIS-8%-ScAb hybrid films.

value). Table 1 shows that all of the PI/PhSiOx/ $Al_2O_3$  exhibited a broad range of  $L^*$  values, from 60.6 to 87.5. The  $L^*$  value of the film varies mainly with the aluminum content and slightly with the silicon content. The  $L^*$  values of pure PI, PIS and PIS-8%-S10A0 vary slightly, being 87.1, 87.5 and 87.1, respectively, obtained by adding APrtMOS or PhSiOx to the PI matrix. The cause of this slight variation may be the formation of loose intermolecular cross-linkages between the Si-OCH<sub>3</sub> groups, and the increase in the free volume of the polymer chains. The  $L^*$  values of hybrids PIS-8%-S8A2, PIS-8%-S5A5 and PIS-8%-S2T8 with various PhSiOx/ $Al_2O_3$  contents decrease from 85.5, through 83.0 to 77.5, respectively. The changes of color intensity and optical transparency are caused by the active  $Al_2O_3$  group and the formation of the close intermolecular cross-linkages, reducing the free volume of the polymer chain.

The effect of nano-sized  $Al_2O_3$  on the coefficient of thermal expansion (CTE) of the PI hybrid films is also investigated as listed in Table 1. The CTE of the PI hybrid films declines as the  $Al_2O_3$  content increases [19], especially between 200 and 300 °C. One reason is that  $Al_2O_3$  has a low CTE of 8 ppm/°C and the decrease becomes more obvious as the  $Al_2O_3$  content increases. Another reason is that the cross-linkages that are formed during the sol-gel process improves thermal stability.

The  $\tan\delta$  curves of pure PI and PIS-8%-ScAb hybrid films determined by dynamic mechanical analysis (DMA) was shown in Fig. 4. The glass transition temperature ( $T_g$ ) increased with the  $Al_2O_3$  content, while the damping intensity decreased. The intermolecular cross-linking reaction among polyimide,  $Al_2O_3$  and PhSiOx was responsible for the increase in  $T_g$  and the decrease in damping intensity. The hybrids had higher  $T_g$  values than the pure polyimide, which increased with the  $Al_2O_3$  content. Table 1 summarizes the results. The effect of  $Al_2O_3$  on the  $T_g$  and damping intensity are stronger than on those of PhSiOx. The benzene ring of PhSiOx hinders the formation of cross-links and increases the free volume and thereby causes the  $T_g$  of PIS-8%-S10A0 film to be lower than that of pure PI.

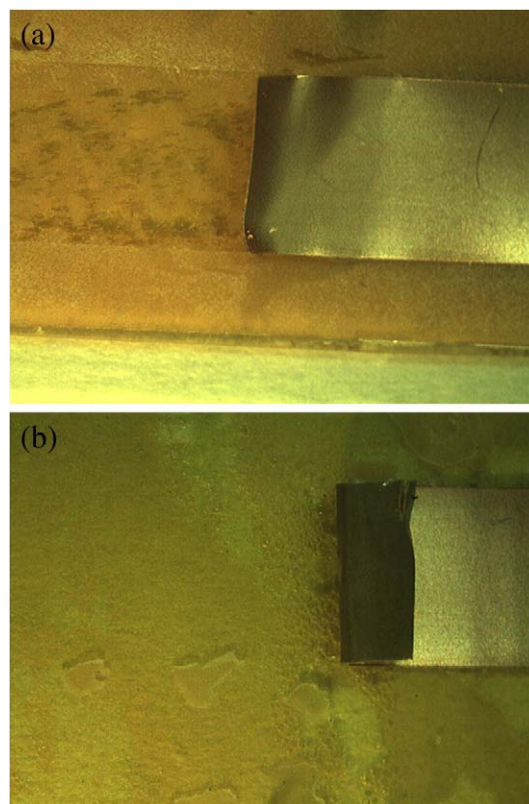


Fig. 7. (a) The breaking side is the adhesive/copper foil (A/C) side of PIS-8%-S2A8 hybrid films. (b) The breaking side is the adhesive/polymer (A/P) side of PIS-8%-S8A2 hybrid films.

Fig. 5 displays the binding energies of  $Al_{2p}$  and  $Si_{2p}$ , given by the photoelectron peaks at 73.57 eV for  $Al_{2p}$  and 101.16 eV for  $Si_{2p}$  [20–23], and the PIS-8%-S2A8 XPS spectra obtained at different sputtering times. The results imply that a small quantity of aluminum atoms and more silicon remained in the surface of the film. The shift in the  $Al_{2p}$  binding energy is a result of the aluminum atom's being in a different chemical environment. The results indicate that molecular oxygen that is present on the air-side of the film probably explains why the surface aluminum atom has a higher binding energy than that in the bulk, since the surface contains more molecular oxygen that can react with  $Al^{3+}$  to form aluminum oxide, whereas the bulk of the film lacks molecular oxygen. Accordingly, various aluminum compounds, such as Al–C, Al–O and others may be presented. Clearly, longer sputtering times increase the concentration of the aluminum species and reduce the silicon content, as shown in Fig. 5. The surface contains more silicon than aluminum. The silicon concentration decreases from the surface of the film to the bulk, while the aluminum concentration follows the reverse trend. The energy of a solid sample is thus minimized in an equilibrium state because the silicon atom has less energy than the aluminum atom, and so easily migrates to the surface, while the aluminum is easily dispersed in the bulk of the film [24].

A three-layer laminate of PI film, silicon-containing adhesive and copper foil, is used in most parts of an electrical circuit. Fig. 6 plots the peel strength of the PIS-8%-ScAb hybrid films. The peel strength increased with the  $Al_2O_3$  content in the PI film. Although silicon has a lower surface energy and more easily moves to the surface of the film than aluminum does, the silicon can draw a little aluminum to the surface simultaneously. Metallic bonds are then formed between the silicon-containing adhesive and the aluminum-containing PI film, increasing the peel strength between the hybrid film and the adhesive. A higher PhSiOx content, as detected by XPS, in the surface of the film corresponds to lower peel strength. Although silicon in the PI film attracts the silicon-containing adhesive, the benzene ring on the PhSiOx side-chain repels the metal-containing adhesive. The competition between the above contrary effects reduces the peel strength. For instance, the PIS-8%-S10A0 has a lower peel strength, 0.08 kgf/cm<sup>2</sup>, than the other films.

Fig. 7(a) shows that the breaking side is the adhesive/copper foil (A/C) side, which has higher peel strength. However, Fig. 7(b) reveals that the breaking side is the adhesive/polymer (A/P) side and that the peel strength between the copper foil and PI surface is lower. Films with a breaking surface on the A/C side are PIS-8%-S0A10, PIS-8%-S2A8. Films with a breaking surface on the A/P side are PIS-8%-S5A5, PIS-8%-S8A2 and PIS-8%-S10A0. The above mentioned results demonstrate that  $Al_2O_3$  can improve the peel strength of the film [25].

#### 4. Conclusion

In this study, PI/PhSiOx/ $Al_2O_3$  hybrid films were prepared by the *in situ* sol–gel process. The CTE of PI hybrid films decreased

progressively as the  $Al_2O_3$  content increased, especially between 200 and 300 °C. The peel strength of PIS-8%-ScAb hybrid films between hybrid film and copper foil increased with the  $Al_2O_3$  content, reaching 1.7 kgf/cm<sup>2</sup> when the  $Al_2O_3$  content exceeded that of PIS-8%-S2A8. The more PhSiOx is added into the hybrid film, the lower peel strength is obtained. This result is attributed to the benzene ring on the PhSiOx side-chain repels the metal-containing adhesive. However, the addition of  $Al_2O_3$  to the hybrid film can effectively improve the thermal properties and reduce the coefficient of thermal expansion, while maintaining the peel strength, enabling the film to be applied in flexible boards.

#### Acknowledgements

The authors would like to thank the Ministry of Economic Affairs, Republic of China, Taiwan, for financially supporting this research on the flexible polymeric materials for electronic usages (98-EC-17-A-07-S1-120).

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