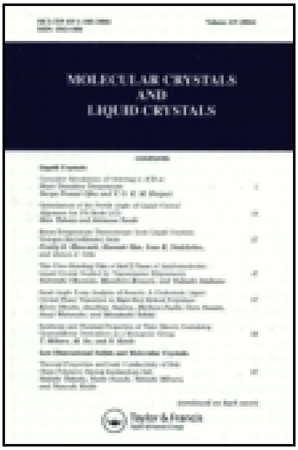

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Interfacial Characterization of POLYBENZOXAZOLE/COPPER System

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INTERFACIAL CHARACTERIZATION OF POLYBENZOXAZOLE/COPPER SYSTEM

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Poly(benzoxazoles) (PBO) are a class of high temperature organic polymers which have low dielectric constant. The interfacial characteristics of PBO/copper system have been investigated. PBO films on copper substrate were prepared by thermal conversion from poly(hydroxyamide) (PHA). PHA was synthesized by the low temperature condensation reaction of 3,3′-dihydroxybenzidine and isophthaloyl chloride in DMAc. PHA film on the copper substrate was converted to PBO by heating at 350°C. DSC, TGA, XPS, and lap-shear test were employed to characterize both PHA/copper and PBO/copper systems. The XPS results revealed that the polar groups in PHA and the heterocyclic ring in PBO had special interactions with copper at the surface. The adhesive strength of PBO/Cu was slightly greater than that of PHA/Cu system. The dielectric constant of PBO film was about 3.1 and showed no changes with frequency.

Keywords: dielectric constant (k); interfacial characterization; poly(benzoxazole); poly (hydroxyamide); X-ray photoelectron spectroscopy (XPS)

INTRODUCTION

Adsorption of polymers onto metal surface is important in applications such as adhesive bonding, corrosion protection, colloid stabilization, and many other areas [1,2]. Accordingly, understanding the interfacial

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characteristics between polymer and metal is necessary to control their chemical and physical properties.

It has been reported that the interfacial adhesive strength between polymer and metal could significantly enhanced by metal oxygen-polymer complex formation when metal atoms were vapor-deposited on oxygen-containing polymers [3,4]. When the metal atoms are deposited on oxygen containing polymer, X-ray photoelectron spectroscopy (XPS) can detect changes in the photoemission line shapes of carbon and oxygen atoms at the interface.

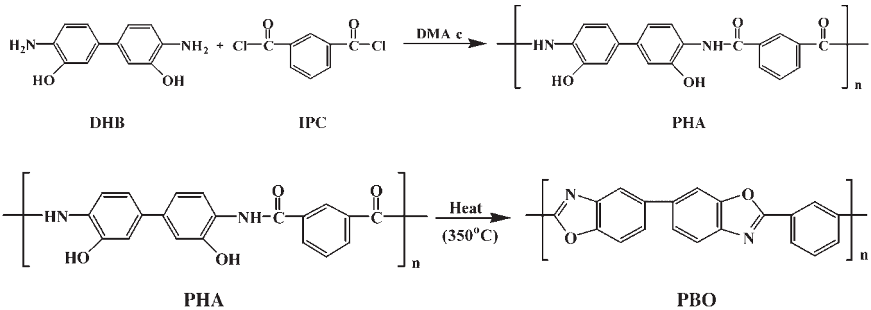
Poly(benzoxazoles) (PBO) are a class of high temperature organic polymers which have low dielectric constant. These properties enable PBO to be applicable to microelectronics. Since, in many microelectronic applications, the low dielectric materials usually contact to metals, the interfacial properties between low k materials and metals are very important. Many studies have been focused on lowering the dielectric constant of PBO. Since, in many microelectronic applications, the low dielectric materials usually contact to metals, the interfacial properties between low k materials and metals are very important. In the present study, we investigated the interfacial characteristics of PBO/copper system.

EXPERIMENTAL

Poly(hydroxyamide) (PHA) was prepared from the low temperature condensation reaction of 3,3′-dihydroxybenzidine and isophthaloyl chloride in DMAc [5–7]. 3,3′-dihydroxybenzidine (1.08 g, 0.005 mol) was dissolved in 25 ml of anhydrous DMAc. The solution was cooled to 0°C, and isophthaloyl chloride (1.02 g, 0.005 mol) was added into the solution. The solution was stirred for 1 hour at 0°C, and then for 5 hours at room temperature. PHA/DMAc solution was spin-coated on copper and then dried completely. PHA on the copper substrate was converted to PBO by heating at 350°C. PBO conversion of PHA was analyzed by DSC and TGA. The reaction Scheme 1 is the summary of the PHA synthesis and PBO conversion.

The adhesive strength was measured by the lap-shear test (ASTM D1002) at a pulling rate of 5 mm/min by using the Instron 4467. The PHA/DMAc 5 wt% solution was dropped on the end of a copper plate and then covered with another plate so that lap area would be $25 \times 15\,mm^2$. The lap-shear strength was calculated by dividing the strength by the lap area. Five sets of specimens for each polymer were tested and the lap-shear strength was averaged.

The interfacial characterization of PBO/copper system was conducted by using XPS, which was a Surface Science Instruments Spectrometer (SSI, 2803-S) equipped with a monochromatic Al K_α X-ray source at a



SCHEME 1 Synthesis of PHA and conversion of PHA to PBO.

power of 350 W. The pass energy was 187.85 eV(0.8 eV steps) and 23.50 eV(0.1 eV steps) for the survey and the high-resolution spectra, respectively. The incident angles of X-ray were 15, 45, and 75°. Each spectrum was curve-fitted by using the XPS PEAK2 software.

The dielectric constant of PBO was measured by using the HP 4194 A impedance analyzer with the frequency range of 0.1 ~ 15 MHz. The sample consists a Pt/dielectric film/Pt sandwich structure (MIM structure). The dielectric constant (k) of the film was calculated by the formula of a parallel plate capacitor:

$$k = C \times t/(k_o \times A)$$

where C is the capacitance of the MIM element, t is the thickness of the dielectric film, A is the area of the Pt-electrode and k_o ($= 8.854 \times 10^{-12}$ F/m) is the permittivity of free space.

RESULTS AND DISCUSSION

The conversion of PHA to PBO was analyzed by DSC and TGA [6,7]. As shown in Figure 1, DSC thermogram of PHA showed strong endothermic peak due to the conversion of PHA to PBO at around 300°C, while in case of PBO, (b) in Figure 1, there was no thermal transition until 450°C. TGA thermograms also showed that the conversion of PHA to PBO was completed showing no weight loss until 600°C after heat treatment (Fig 2). It means that PBO has excellent thermal stability at high temperature.

The lap-shear strength between the PBO film and the copper substrate were measured as a function of conversion of PHA to PBO as shown in Figure 3. The lap-shear strength of PBO/copper systems increases according to conversion of PHA to PBO.

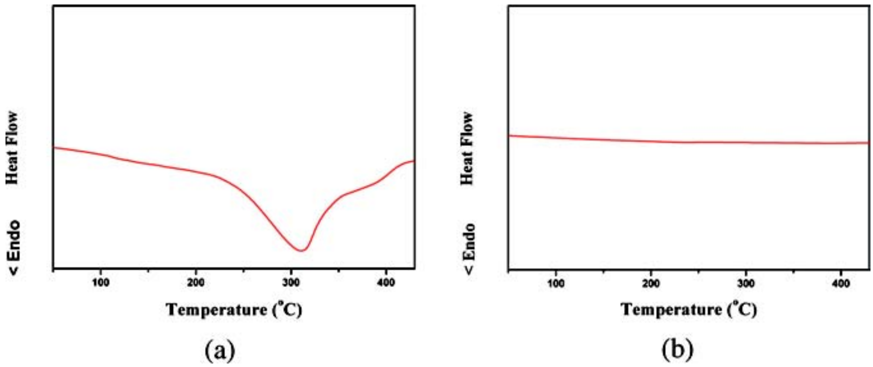


FIGURE 1 DSC thermograms of PHA before (a) and after (b) heat treatment at 350°C.

XPS was used to quantitatively analyze the amounts of the oxygen and nitrogen atoms near the interface. Figures 4 and 5 are high-resolution O 1 s spectra and N 1 s spectra obtained from the PBO bulk film and PBO/copper interface respectively. There are only one O 1 s and N 1 s peak in PBO bulk film at 533.6 eV and 440.8 eV, respectively. But In case of PBO/copper interface, there are two different types of O 1 s (530.1 eV, 531.25 eV) and N 1 s (397.4 eV, 398.8 eV) peaks. The O 1 s and N 1 s peaks of lower binding energy are result from interaction with copper. This means that oxygen and nitrogen atoms in PBO chain have specific interaction with copper at the interface. We obtained the high-resolution C 1 s spectra from the PBO bulk film and PBO/copper interface. The binding energy of the carbon

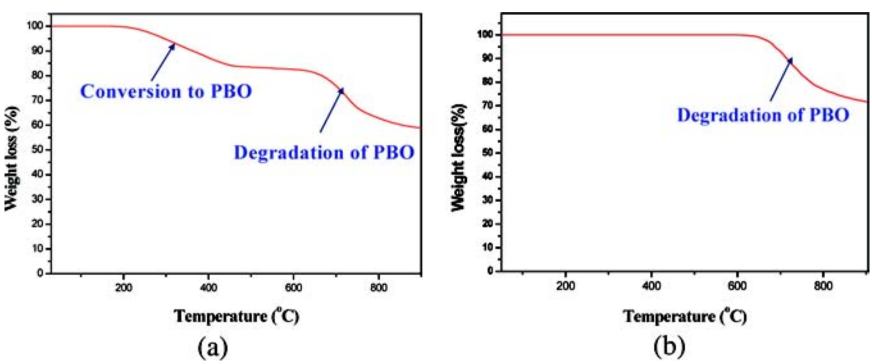


FIGURE 2 TGA thermograms of PHA before (a) and after (b) heat treatment at 350°C.

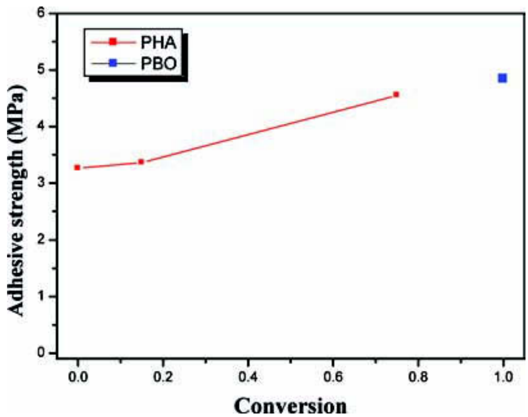


FIGURE 3 The variation of the adhesive strength of PBO according to degree of conversion.

atoms adjoining O and/or N in PBO/copper interface was shift to the lower energy than PBO bulk film. This implies that the oxygen and/or nitrogen atoms in PBO at the interface have specific interactions with copper at the interface.

The changes of dielectric constant with frequency are shown in Figure 6. It was observed that the dielectric constant did not depend on the frequency. The dielectric constant of the PBO film maintains 3.1.

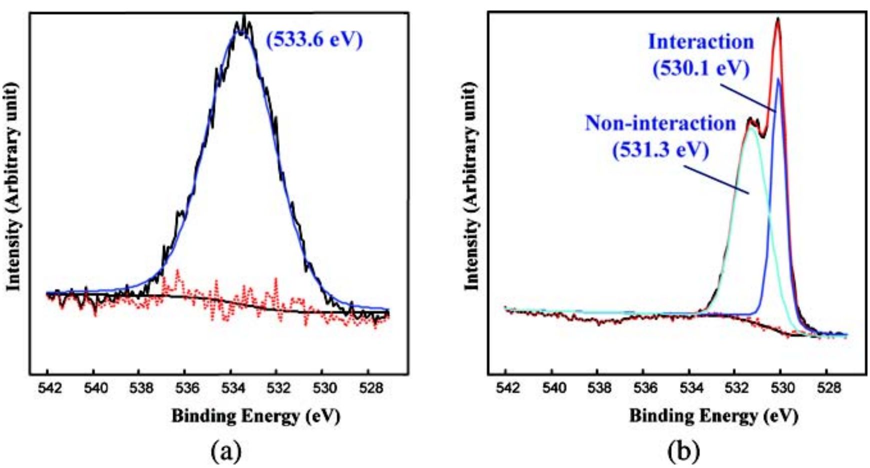


FIGURE 4 XPS high-resolution O 1 s spectra obtained from the PBO bulk film (a) and PBO/copper interface (b), respectively.

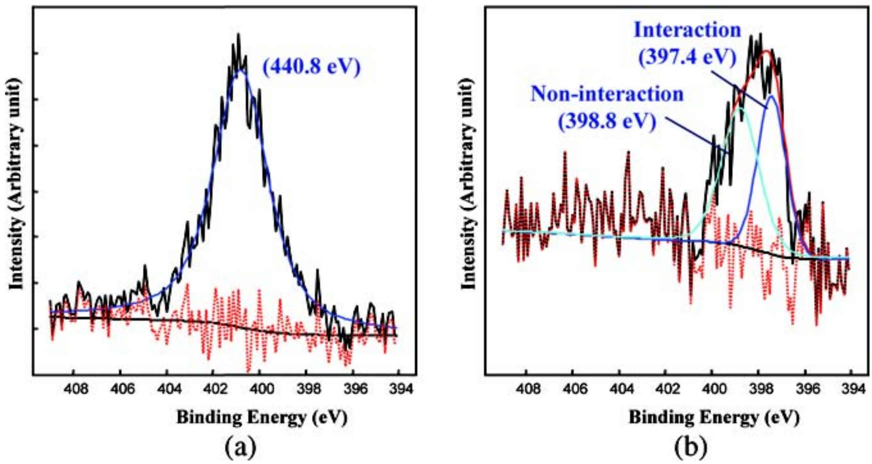


FIGURE 5 XPS high-resolution N 1 s spectra obtained from the PBO bulk film (a) and PBO/copper interface (b), respectively.

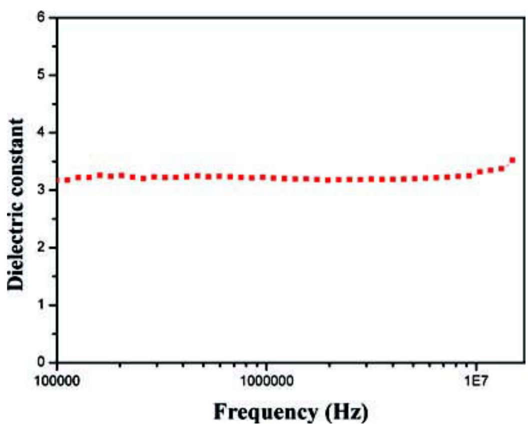


FIGURE 6 The changes of dielectric constant of PBO film with frequency.

CONCLUSION

The PHA can be converted to PBO by heat treatment at 350°C for 30 min, which was confirmed by DSC and TGA. The adhesive strength of PBO/copper system increased with the conversion of PHA to PBO. According to the XPS results, we can confirm that the amount of oxygen and nitrogen atoms interact with copper at the interface. There are only one O 1 s and N 1 s peak in PBO bulk film. For PBO/copper interface, however, there are two different types of O 1 s and N 1 s peaks. This means that oxygen and nitrogen atoms in PBO chain have specific interactions with copper at the interface. The amount of interacting oxygen and nitrogen atoms with copper increase as approaching to the interface. The dielectric constant of PBO film is about 3.1 and has no change with frequency.

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