

Miscibility behavior of polyimide (PI)/poly(arylene ether benzimidazole) (PAEBI) blends and its effects on the adhesion of PI/PAEBI/copper joints

J. Yu^{a, b}, M. Ree^{a,*}, T.J. Shin^a, X. Wang^{a, c}, W. Cai^{b,*}, D. Zhou^b, K.-W. Lee^d

^aDepartment of Chemistry, Polymer Research Institute and School of Environmental Engineering, Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang 790-784, South Korea

^bDepartment of Applied Chemistry, Harbin Institute of Technology, Harbin, Heilongjiang Province, 150001, People's Republic of China

^cDepartment of Electrical Engineering, Harbin Institute of Technology, Harbin, Heilongjiang Province 150001, People's Republic of China

^dIBM Research, T.J. Watson Research Center, Yorktown Heights, NY 10598, USA

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Abstract

Poly(amic acid) (PAA) and poly(amic diethyl ester) (PAE) precursors of poly(*p*-phenylene biphenyltetracarboximide) (BPDA–PDA), which is a representative polyimide (PI) being used widely in the microelectronic industry as an interdielectric material, were synthesized. The miscibility behavior of these precursors with poly(arylene ether benzimidazole) (PAEBI), which is known to exhibit strong cohesive adhesion to copper metal conductor, were studied in *N*-methyl-2-pyrrolidone (NMP) as well as the condensed state and the imidized state using light scattering technique. And, the miscibility effect on the adhesion strength of PI/PAEBI/copper joint, in which the locus of failure is known to be within the PI layer, was investigated by 90° peel test. The PAA precursor was miscible completely with PAEBI in the NMP solution as well as in the condensed state via the strong interaction between carboxylic acid groups of the precursor and imidazole groups of PAEBI. However, imidization-induced phase-separation took place during thermal imidization of the PAA precursor, leading to domains of 0.7–1.4 μm for the imidized blends containing 30–70 wt % PI. The other blend compositions still were optically transparent. In contrast, the PAE precursor was miscible with PAEBI in the NMP solution with a limited concentration of <11.3–14.5 wt %, but immiscible almost completely in the condensed state, causing phase-separation. The phase-separation occurred further during thermal imidization, producing domains of 0.8–3.0 μm. In particular, the 50/50 (=PAEBI/PAE, wt/wt) blend had domains of >3.6 μm. Only the 90/10 blend film was optically transparent. The difference in the miscibilities of PAEBI with the polyimide precursors was reflected on the adhesion strength of PI/PAEBI/copper joint. The PAA precursor gave a relatively high peel strength, compared to the PAE precursor. In addition, the PAEBI having a relatively low intrinsic viscosity provided a high peel strength in the adhesion joint. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(arylene ether benzimidazole); Polyimide; Precursor polymer

1. Introduction

Aromatic polyimides have played an increasingly important role as dielectric layers in a variety of microelectronic devices because of providing a unique combination of properties, such as low dielectric constant, high thermal stability, high chemical resistance, and good mechanical properties [1–5]. For applications in a multilevel thin film package, most aromatic polyimides (PIs) are processed in soluble precursor forms because of their insolubility and then converted to the PIs by imidization at high temperatures [4,5]. For the overall integrity of microelectronic package, adhesion at all the interfaces including PI/copper metal and PI/substrates must be strong and tolerant of cyclic

thermal stresses. However, aromatic PIs are generally known to exhibit a poor adhesion to copper metal which is widely used as an electric conductor in the microelectronic devices [6–10]. For example, for a poly(4,4'-oxydiphenylene pyromellitimide) (PMDA–ODA) film on copper prepared by spin-coating of its poly(amic diethyl ester) (PAE) precursor solution and subsequent thermal imidization, a peel strength in the 90°-peel test is obtained to be only ≤100 J/m² which is a weak adhesion for the microelectronic applications [8–10]. The weak adhesion is obtained for the interface of PMDA–ODA polyimide to copper prepared from the poly(amic acid) (PAA) precursor which is another type of precursor polymer [8–10]. Further, the PAA precursor is known to react with copper during the imidization process, consequently generating copper oxide particles which diffuse into the PI film [8–10]. The diffusion

* Corresponding authors.

E-mail address: ree@postech.ac.kr (M. Ree)

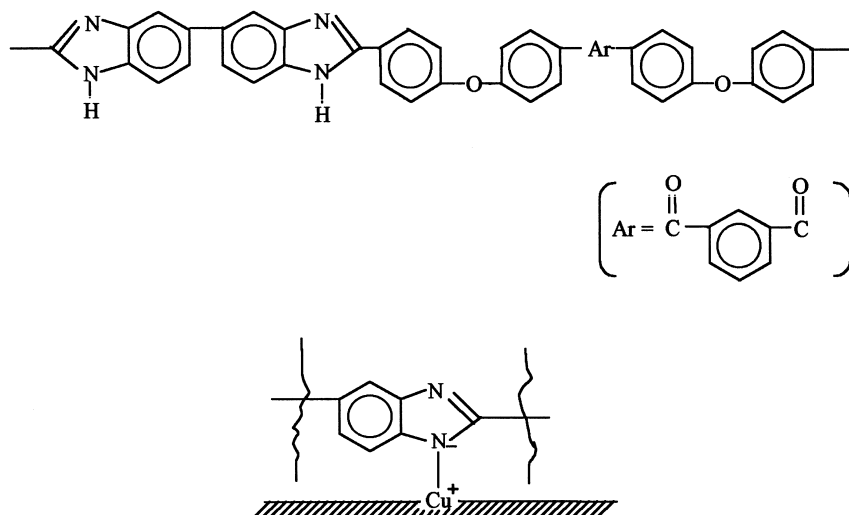


Fig. 1. Chemical structure of PAEBI and its proposed complex formation with copper via reaction of its imidazole group with copper.

of copper oxide particles causes the dielectric constant of the PI film to increase [11].

In order to prevent the reaction of PAA precursor with copper as well as to improve adhesion of PI to copper, Lee and his coworkers [10] have recently introduced a new fabrication process using poly(arylene ether benzimidazole) (PAEBI) as a copper capping material. In their fabrication process, a thin layer of the capping polymer was coated onto a copper/PI substrate, followed by a relatively thick layer of a PI dielectric. Here, the thin capping polymer layer forms a stable copper complex via the reaction of copper with the N–H group of benzimidazole unit in the PAEBI polymer (see Fig. 1), preventing the permeation of PAA precursor solution into the copper layer during the fabrication of the PI dielectric layer. Thus, no copper oxide precipitates in the PI layer was detected in the cross-sectional transmission electron microscopic measurement. Further, the capping polymer layer plays as an adhesion promoter, enhancing the adhesion of PI layer to copper. Using PAEBI as a capping material, a relatively high peel strength of 600–700 J/m² was obtained for the interface of poly(*p*-phenylene biphenyltetracarboximide BPDA–PDA) to copper.

For the BPDA–PDA/PAEBI/copper joint, the locus of failure by 90°-peeling was found to be within the BPDA–PDA layer. Thus, the adhesion may be dependent further upon the miscibility between the PI and PAEBI layers even though the PAEBI layer provides a strong adhesion to copper via the complexation. A good miscibility of polyimide to PAEBI may provide a high stability for the PI/PAEBI/copper joint. In contrast, a poor miscibility of PI to PAEBI may provide a low stability for the PI/PAEBI/copper joint. In practice, the PI layer is fabricated in a soluble precursor form because of its insolubility in common solvents, so that the miscibility of precursor polymer to PAEBI, as well as the miscibility of PI to PAEBI should be investigated for understanding adhesion behavior of the PI/PAEBI/copper joint. Further, the miscibility of precursor

polymer to PAEBI may depend upon its types, PAA and PAE.

Therefore, in the present study, the two types of precursors of BPDA–PDA PI, which are widely used in the micro-electronic industry, were synthesized and then used for studying their miscibilities to PAEBI as well as evaluating the adhesion of PI/PAEBI/copper joint. Their miscibility behaviors and phase diagrams were investigated by light scattering technique. In addition, the effect of miscibility on the adhesion of PI/PAEBI/copper joint was examined by 90°-peel test.

2. Experimental

2.1. Materials

PAEBIs with two different viscosities were supplied from National Starch and Chemical Company (USA): one has an intrinsic viscosity $[\eta]$ of 0.67 dl/g and the other $[\eta] = 0.80$ dl/g. The $[\eta]$ s were measured in *N,N*-dimethylacetamide at 25.0°C using an Ubbelohde suspended level capillary viscometer. BPDA and PDA were purchased from Chriskev Chemical Company (USA). BPDA was purified by recrystallization in acetic anhydride and followed by drying under reduced pressure. PDA was purified by sublimation under reduced pressure. *N*-methyl-2-pyrrolidone (NMP), obtained from Aldrich Chemical Company (USA), was dried with calcium hydride and subsequently distilled under reduced pressure. All the other chemicals used in this study were supplied from Aldrich. In addition, the water used in the present study was deionized and degassed.

2.2. Synthesis of precursor polymers

BPDA–PDA PAA, which is the PAA precursor of BPDA–PDA PI, was prepared in a glove box filled with

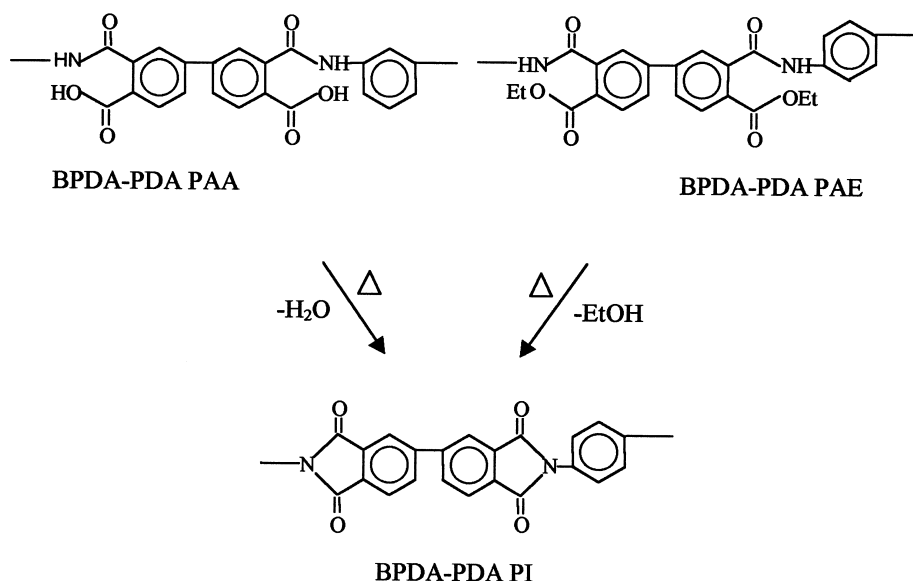


Fig. 2. Chemical structures of precursors (BPDA–PDA PAA and BPDA–PDA PAE) and their thermal imidization schemes.

dry nitrogen gas by slowly adding the equivalent mole of BPDA to the PDA in dry NMP. After the dianhydride addition was completed, the reaction flask was capped tightly and stirring was continued for additional 2 days to make the polymerization mixture completely homogeneous. The solid content of the precursor solution was 10 wt %. The precursor solution was filtered with silver metal membranes of 1.0 μm pore size, tightly sealed, and stored in a refrigerator before use.

BPDA–PDA PAE, which is the PAE precursor of BPDA–PDA PI, was prepared in a glove box filled with dry nitrogen gas by adding the equivalent mole of BPDA diethyl ester diacyl chloride in dried ethyl acetate to the purified PDA in dry NMP. The polymerization was carried out at 0–5°C with vigorous stirring, followed by continuous stirring for an additional 20 h. The precursor polymer solution was precipitated in deionized water under vigorous stirring in a mixer and filtered, followed by washing with methanol several times in order to remove HCl byproduct. Then, the precursor product in powder was dried for 7 days at 50°C in a vacuum oven with 2×10^{-6} Torr in order to remove all the residual solvents. Here, the used BPDA diethyl ester diacyl chloride was prepared via the reaction of BPDA diethyl ester dicarboxylic acid with oxalyl chloride in excess under dry nitrogen gas. The BPDA diethyl ester dicarboxylic acid was prepared by the reaction of BPDA with ethanol. That is, the BPDA was added to ethanol and refluxed for 5–8 h, followed by distillation of excess ethanol under a reduced pressure.

For the synthesized precursors, $[\eta]$ measurements were conducted in NMP at 25.0°C using an Ubbelohde suspended level capillary viscometer as reported previously [12,13]. The measured $[\eta]$ was 0.760 dl/g for the BPDA–PDA PAA and 0.850 dl/g for the BPDA–PDA PAE.

2.3. Cloud point measurement

For the PAEBI ($[\eta] = 0.80$ dl/g)/BPDA–PDA PAA blend system, a series of homogeneous ternary solutions in NMP were prepared by mixing the components at various proportions for 2 days at room temperature, followed by filtering using 1.0 μm Fluoropore filters of the Millipore Company. The solid contents of the ternary solutions were 10 wt %. In a similar manner, a series of homogeneous ternary solutions were prepared for the PAEBI/BPDA–PDA PAE blend system.

For each ternary solution with a known composition, the cloud point due to phase separation was measured using a light scattering apparatus with a specially designed optical slide cell. The light scattering apparatus, which was made in our laboratory, was equipped with a vertical goniometer, a hot-stage, a programmable temperature controller, a photomultiplier detector, and a He–Ne laser (a wavelength of 632.8 nm). This apparatus was controlled by a personal computer. The optical slide cell consisted of a cylindrical cavity which has a flat bottom of 3 mm depth and a diameter of 16 mm. The optical slide cell with a cover slide was weighed before use. The cylindrical cavity was filled with a known amount of the ternary solution and covered with a cover slide. Then, the optical slide cell was moved and inserted into a hot-stage at 80°C. After removal of the cover slide, the scattered light intensity was monitored at a scattering angle (2θ) of 30° as a function of time during isothermal solvent evaporation at 80°C. When a sharp increase in the scattered light intensity due to phase separation was started, the optical slide cell was again covered with the same cover slide as soon as possible and subsequently removed from the hot-stage. Then, the optical slide cell with the cover slide was again weighed, providing the solid content of the ternary solution at the cloud point. This

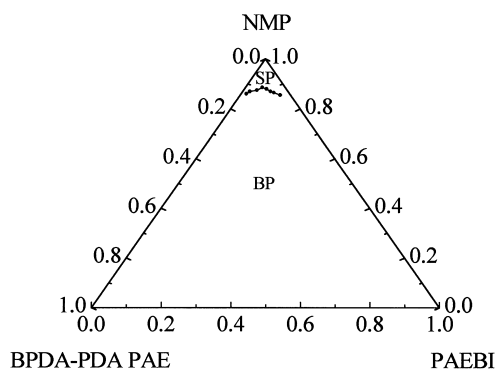


Fig. 3. Ternary phase diagram of PAEBI/BPDA-PDA PAE/NMP mixture obtained by cloud point measurements at 80°C using light scattering technique: SP, single phase; BP, biphasic. PAEBI polymer of $[\eta] = 0.80$ dl/g was used.

cloud point measurement was carried out for all the ternary solutions, allowing the construction of ternary phase diagrams.

2.4. Film preparation and characterization

The homogeneous ternary solutions with known compositions were spin-coated onto the precleaned cover glass slides at 1000 rpm for 20 s, followed by soft-baking on a hot-plate at 80°C for 1 h in air ambient. The soft-baked PAEBI ($[\eta] = 0.80$ dl/g)/precursor films were imidized thermally in nitrogen atmosphere by a three-step protocol: 150°C/30 min, 230°C/30 min, and 380°C/1 h with a ramping rate of 2 K/min (see Fig. 2). The thickness of PAEBI/PI blend films was measured to be 4.2–6.4 μm using a prism coupler which was made in our laboratory.

For both soft-baked and imidized blend films, light scattering measurements were carried out at room temperature in the transmission mode, using the light scattering apparatus described above. Scattered intensity profiles were measured over 5–70° (2θ) where 2θ is the scattering angle. The 2θ scan data were collected with a scan speed of 0.04° (2θ)/s. Light scattering profiles were corrected to the background run.

2.5. Adhesion measurement

PI/PAEBI/copper joint specimens were prepared as follows. PAEBI with $[\eta] = 0.80$ dl/g was dissolved in NMP/cyclohexanone (50/50 in volume) to be a concentration of 1.7 wt % and filtered with a 1 μm Fluoropore filter. In the same manner, another PAEBI solution was prepared from the PAEBI of $[\eta] = 0.67$ dl/g. The PAEBI solutions were spin-coated onto the precleaned copper sheets (3 cm \times 5 cm \times 2 mm in size) at 1100 rpm for 30 s and baked at 200°C for 30 min as described previously in the literature [10]. The thickness of the PAEBI layer is estimated to be ca. 0.2 μm . Here, the used copper sheets were cleaned in chloroform with the aid of an ultrasonicator for 2 h in order to remove the organic materials deposited on the

surface, subsequently dried by blowing nitrogen gas. The copper sheets were treated further in an aqueous sulfuric acid solution (5 wt %) for 5 min to remove the copper oxides formed on the surface and then rinsed with deionized water several times. After the completion of this treatment, immediately the copper sheets were dried shortly with blowing nitrogen gas and quickly followed by the deposition of PAEBI layer.

Precursor solutions were overcoated on the PAEBI coated copper sheets in two different ways, depending on the precursor types. First, a BPPDA-PDA PAE solution (9.6 wt % solid) was spin-coated on the PAEBI coated copper sheet at 1000 rpm for 30 s, followed by the soft-baking at 80°C for 30 min. Then, the precursor solution was again overcoated at 600 rpm for 30 s and subsequently soft-baked at 80°C for 30 min. Finally, the soft-baked precursor layers on the PAEBI coated copper sheet was thermally imidized under a nitrogen atmosphere by the three-step protocol as described above. The thickness of the polyimide layer was measured to be ca. 15 μm using a micro-thickness gauge. Second, a BPDA-PDA PAA solution (9.9 wt % solid) was spin-coated at 1000 rpm for 30 s, followed by soft-baking at 80°C for 30 min and subsequent partial imidization at 230°C for 30 min. Then, the PAE solution was again overcoated at 600 rpm for 30 s and soft-baked at 80°C for 30 min. Subsequently, the whole soft-baked precursor layers on the PAEBI coated copper sheet was thermally imidized under a nitrogen atmosphere by the three-step protocol as described above. The total thickness of the two polyimide layers was ca. 15 μm . Here, the coating condition employed for the PAA precursor solution was found to give a thickness of 2–3 μm for its polyimide film prepared by the three-step imidization protocol, without overcoating of the PAE precursor. Thus, we expect the same thickness for the first polyimide layer prepared from the PAA precursor solution.

For the PI/PAEBI/copper joints prepared, peel tests were performed at room temperature using an Instron mechanical tester (Model 4052) equipped with a 90°-peel fixture. The top polyimide layer with the thin PAEBI layer was diced into a strip of 2.0–5.0 mm width using sharp blades. The width of polyimide layer strips adhered on the copper sheet was precisely measured using a cathetometer of Gaertner Scientific Company. A peeling rate of 5.0 mm/min was employed.

3. Results and discussion

3.1. Miscibility behavior

The miscibility of PAEBI ($[\eta] = 0.80$ dl/g) and PAE precursor was investigated in a mutual solvent, NMP, by cloud point measurement using a light scattering apparatus with a He-Ne laser of 632.8 nm wavelength. For all compositions of the PAEBI/precursor mixture, optically clear

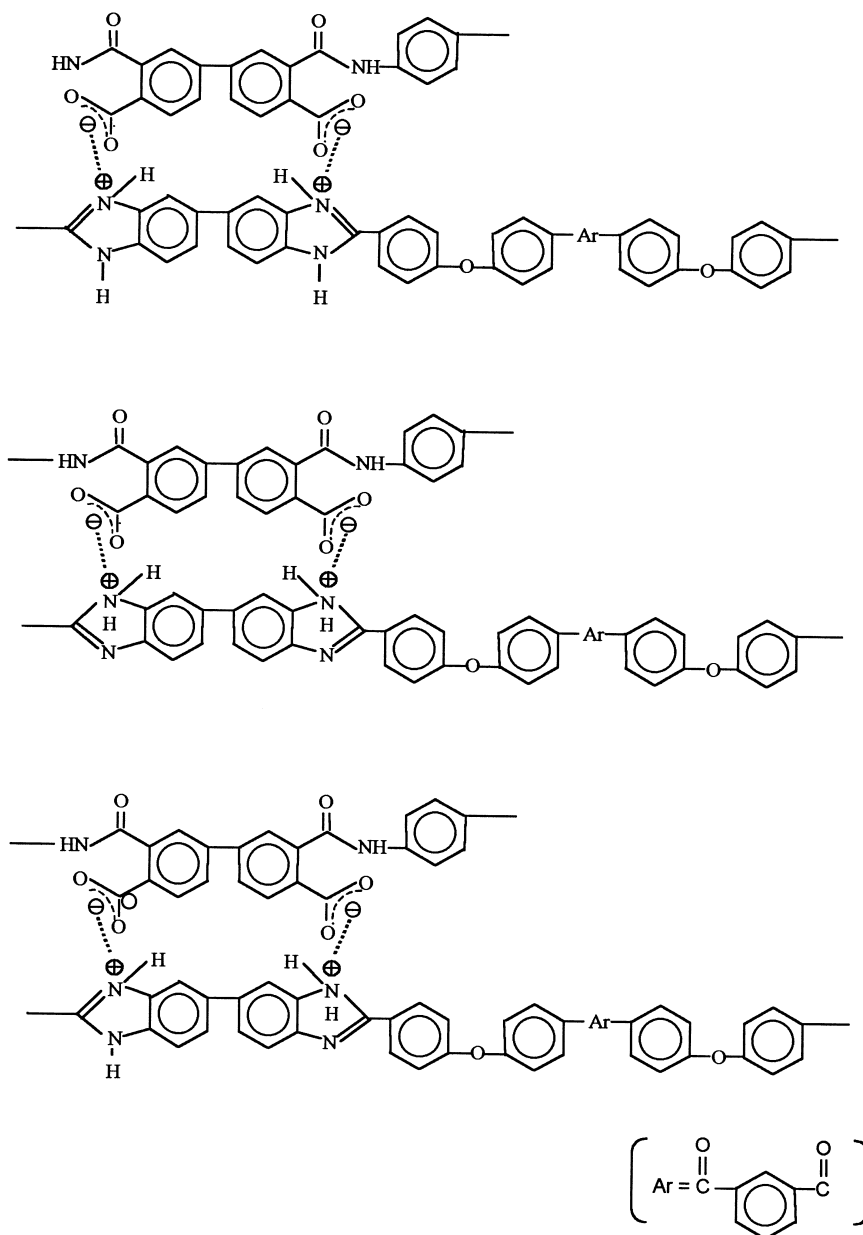


Fig. 4. Proposed interactions between PAEBI and BPDA–PDA PAA via complexation of imidazole rings of PAEBI and carboxylic acid groups of the precursor.

solutions were obtained with a solid content of 10 wt % in NMP. For each ternary solution with a known composition, the cloud point due to phase separation was measured by light scattering technique during the isothermal solvent evaporation at 80°C. At the cloud point, the composition of the ternary solution was determined by measuring weight loss due to the solvent evaporation as described in Section 2. From the compositions at the cloud point, a ternary phase diagram was constructed. The result is shown in Fig. 3; here, the compositions are in units of weight fraction. At the cloud point, the solid content is 11.3–14.5 wt %, depending on the composition of PAEBI and precursor polymer. That is, in the ternary solution the two polymer components are phase-

separated to each other in a solid content higher than 11.3–14.5 wt % which is far before reaching to their own binary mixture. Therefore, it is concluded that the PAEBI is immiscible with the BPDA–PDA PAE precursor. And, their single-phase region even in the ternary solution is relatively very small for the whole composition, compared to the two-phase region.

In addition, the cloud point curve is observed to be slightly asymmetric over the compositions of PAEBI and precursor polymer. The asymmetric cloud point curve might result from a low molecular weight as well as a high solubility of the PAEBI polymer relative to those of the PAE precursor.

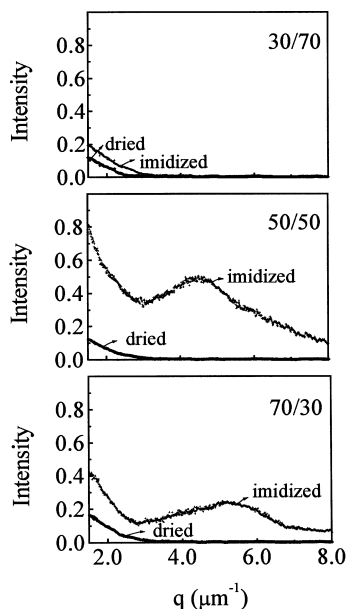


Fig. 5. Light scattering profiles measured from PAEBI/BPDA–PDA PAA blend films before and after imidization, where the denoted numbers are the weight ratios of PAEBI and precursor. The PAEBI polymer of $[\eta] = 0.80$ dl/g was used.

Compared to the PAEBI/BPDA–PDA PAE blend system, the PAEBI/BPDA–PDA PAA blend exhibited a quite different miscibility behavior. Cloud point measurements were performed for their ternary solutions as described above. However, no cloud point was detected for the whole composition. This result indicates that the PAEBI ($[\eta] = 0.80$ dl/g) and PAA precursor are miscible completely over the whole composition range. This miscibility might be driven by a strong intermolecular interaction via the complexation between carboxylic acid groups of the precursor polymer and benzimidazole groups of the PAEBI polymer. The repeat unit of PAEBI polymer has two

benzimidazole rings and each benzimidazole ring consists of two nitrogen atoms in different chemical environments. Therefore, the benzimidazole rings in the repeat unit of PAEBI polymer may involve for the complexation with carboxylic acid groups of the PAA precursor in three different interaction modes as illustrated in Fig. 4.

From this sense, the PAE precursor may interact molecularly with the PAEBI through interactions of the benzimidazole rings of PAEBI with the carbonyls of carboxylate side groups and of amide linkages in the precursor polymer. However, the measured phase diagram suggests that these interactions does not seem to be strong enough to make the PAEBI/BPDA–PDA PAE blend miscible.

3.2. Morphological structure in blends

The homogeneous ternary solutions with a solid content of 10 wt % were spin-cast on the precleaned cover slides, followed by soft-baking at 80°C . For the soft-baked blend films with various compositions, light scattering patterns were measured. These films were imidized at 380°C as described in Section 2. Light scattering patterns were again measured from the imidized blend films. In addition, thicknesses of the blend films were measured using a prism coupler.

For the PAEBI/BPDA–PDA PAA blend system, all the soft-baked films were transparent, regardless of the blend composition. These might result from the miscibility of the two polymer components as discussed in Section 3.1. As some examples are shown in Fig. 5, the scattered light intensity is very low and further angularly independent over the range of $q > 3 \mu\text{m}^{-1}$, where q is the scattering vector magnitude and expressed by $q = (4\pi/\lambda) \sin \theta$ with a wavelength λ of the used light source and a scattering angle 2θ . In contrast, the scattered light intensity is slightly increased with decreasing q in the range of $q < 3 \mu\text{m}^{-1}$. Similar scattering profiles were observed from empty cover slides which were used for casting blend films. Therefore, the scattering

Table 1

Domain sizes measured by light scattering from PAEBI/BPDA–PDA precursor blends before and after thermal imidization^a

PAEBI/precursor (wt/wt)	PAEBI/BPDA–PDA PAA blend			PAEBI/BPDA–PDA PAE blend		
	Soft-baked film ^b Domain size (μm)	Imidized film ^c Domain size (μm)	Film thickness (μm)	Soft-baked film ^b Domain size (μm)	Imidized film ^c Domain size (μm)	Film thickness (μm)
90/10	— ^d	—	5.1	—	—	4.9
80/20	—	—	5.8	0.7	0.8	4.9
70/30	—	1.2	5.5	1.0	1.1	4.2
60/40	—	1.3	6.4	2.5	3.0	4.5
50/50	—	1.4	5.4	≥ 3.6	> 3.6	4.5
40/60	—	0.7	5.5	1.2	1.3	4.5
30/70	—	—	6.0	1.0	1.1	4.5
20/80	—	—	4.3	0.8	1.0	4.7
10/90	—	—	5.8	0.7	0.9	5.1

^a PAEBI polymer of $[\eta] = 0.80$ dl/g was used in the preparation.

^b Film was prepared by spin-casting and subsequent soft-baking at 80°C for 1 h.

^c Imidization was carried out through a three-step protocol: $150^\circ\text{C}/30$ min, $230^\circ\text{C}/30$ min, and $380^\circ\text{C}/1$ h with a ramping rate of 2.0 K/min.

^d Film was optically clear, so that no domain was detected.

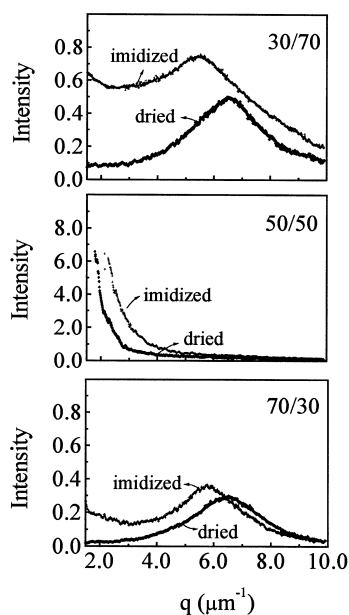


Fig. 6. Light scattering profiles measured from PAEBI/BPDA–PDA PAE blend films before and after imidization, where the denoted numbers are the weight ratios of PAEBI and precursor. The PAEBI polymer of $[\eta] = 0.80 \text{ dl/g}$ was used.

profile at $q < 3 \mu\text{m}^{-1}$ may not come from phase-separated domains in the blend film. This might be attributed to the light source smeared from the main beam.

In contrast to the soft-baked blend films, the 50/50 blend imidized reveals a scattering peak having a maximum intensity at $4.49 \mu\text{m}^{-1} (=q_{\text{max}})$ as shown in Fig. 5. The average size of phase-separated domains is calculated to be $1.4 \mu\text{m}$ from the peak maximum using a relationship of Bragg's d -spacing and q_{max} ; $d = 2\pi/q_{\text{max}}$. Similar scattering patterns were obtained from the 70/30, 60/40, and 40/60 blend films. The estimated domain sizes are listed in Table 1. The average domain size is in the range of $0.7\text{--}1.4 \mu\text{m}$, depending on the compositions. These results suggest that phase separation took place in the miscible PAEBI/BPDA–PDA PAA blend during thermal imidization of the BPDA–PDA precursor component. That is, imidization-induced phase separation occurred in the blend during the thermal imidization, consequently leading to the formation of immiscible PAEBI/PI blends.

However, the other blend films rich with the PAEBI as well as the BPDA–PDA components revealed light scattering profiles similar to those obtained from the soft-baked blend films. That is, these blend films are transparent. For example, the scattering profile of the imidized 30/70 blend film is compared with that of its soft-baked blend film in Fig. 5. The only difference is that the scattered intensity of the imidized blend is slightly higher than that of its soft-baked film over the range of $q < 3 \mu\text{m}^{-1}$. This indicates that the imidized 30/70 blend is miscible. If any phase-separation took place in the imidized blend, it is confined to a domain size smaller than a sub-micrometer.

For the PAEBI/BPDA–PDA PAE blend system which exhibits a ternary phase diagram consisting of single- and two-phase regions, the soft-baked blend films were optically turbid. These films were characterized by light scattering. Some of the measured scattering patterns are presented in Fig. 6. Phase-separated domain sizes were estimated from the scattering profiles, and are summarized in Table 1. Except for the 50/50 and 90/10 blends, all the blends were determined to have phase-separated domains of $0.7\text{--}2.5 \mu\text{m}$, depending upon the compositions. In particular, the 50/50 blend film consisted of large domains of $\geq 3.6 \mu\text{m}$.

These soft-baked blend films were thermally imidized and then characterized by light scattering. In Fig. 6, some of the measured scattering patterns are compared with those obtained from their soft-baked blends before imidization. For the imidized 30/70 blend, the peak maximum in the scattering profile was shifted to the low angle region, compared to that of its soft-baked blend. Similar scattering behaviors were observed for other blend compositions. These results indicate that phase-separation occurred further in the soft-baked PAEBI/BPDA–PDA PAE blends during the thermal imidization, leading to the increase of domain size in the resultant blends.

In addition, the light scattering intensities from the imidized blends are relatively higher than those from their soft-baked blends. This might be attributed to two factors in the following. First, the light scattering intensity is generally proportional to the sixth power of domain size. Thus, the increase of domain size due to the imidization causes an increase in the scattering intensity. Second, the refractive index of BPDA–PDA polyimide is relatively larger than that of its precursor polymer, maybe leading to a relatively high difference between refractive indices of the blend components in the imidized blend than its soft-baked blend. This contributes positively to the light scattering intensity.

Different from the blend compositions mentioned above, the 90/10 blend revealed scattering profiles similar to those obtained from the corresponding PAEBI/BPDA–PDA PAA blend and its imidized blend. That is, the 90/10 blend film was optically transparent before and after the thermal imidization. Therefore, if any phase-separation takes place in this 90/10 blend, its domains should be smaller than a sub-micrometer in a size scale.

3.3. Adhesion properties

In general, it is known that in the 90° -peel test, the adhesion strength is sensitive to the mechanical properties (namely, Young's modulus and tensile strength) of the peeling layer [8,14]. In the case of BPDA–PDA PI, its mechanical properties in the film are dependent primarily on the precursor types [15–17]: the PI film ($10\text{--}20 \mu\text{m}$ thick) obtained from the PAA precursor exhibits 10.2 GPa modulus and 570 MPa tensile strength, whereas the film from the PAE precursor reveals 5.9 GPa modulus and 210 MPa

Table 2

Peel strengths of PI/PAEBI/copper joints prepared from two different precursors of BPDA–PDA polyimide^a

[η] of PAEBI used	Peel strength (J/m ²) of PI/PAEBI/copper joint ^b	
	BPDA–PDA PAA	BPDA–PDA PAE
0.80	441	343
0.67	588	490

^a PI layer was prepared by soft-baking at 80°C for 1 h and subsequent imidization with a three-step protocol: 150°C/30 min, 230°C/30 min, and 380°C/1 h with a ramping rate of 2 K/min.

^b Measured at room temperature by 90°-peel test.

tensile strength. Thus, in the preparation of BPDA–PDA/PAEBI/copper joint specimens, the top PI layer was fabricated in two different ways, depending on the precursor types, as described in detail in Section 2. That is, for the PAE precursor, PAE(thick layer)/PAE(thin layer)/PAEBI/copper sheet was prepared by two times of the serial spin-coating and soft-baking process. Then, the whole PAE layers together were imidized thermally. On the contrary, for the PAA precursor, PAA(thin layer) was coated on the PAEBI/copper sheet, followed by soft-baking and partial imidization. Then, the thick PAE precursor layer was overcoated. The two precursor layers together were imidized. This film formation process allows two things as follows. First, the PAA precursor adhered directly on the PAEBI layer on the copper sheet. Second, an almost uniform PI layer was formed through molecular interdiffusion between the bottom and top precursor layers, so that the top PI layer could not be peeled from the bottom PI layer. The whole PI layer might have mechanical properties similar to those of the layer prepared from the PAE precursor. For 90°-peel test, the top PI thick layer plays as a backing layer together with the bottom PI thin layer.

Peel tests were performed for the PI/PAEBI/copper specimens. The results are listed in Table 2. For the adhesion joints prepared from the PAA precursor, the peel strengths were 441–588 J/m², depending on the [η] values of PAEBI polymers used. The PAEBI polymer with a low [η] value gave a high-peel strength in the adhesion joint. This molecular weight effect is consistent with the results of Lee [18]. However, the peel strengths measured here are relatively lower than that (600–700 J/m²) reported previously by Lee et al. [10]. The difference in the peel strengths may arise from the following two factors. First, the PI layer in the adhesion joint was prepared by the two-layer formation of PAA and PAE precursors rather than the single layer formation of PAA precursor. This two-layer PI might have a relatively lower modulus and tensile strength than the single-layer PI prepared from only PAA precursor. Second, we used PAEBI polymers of [η] = 0.67–0.80 dl/g, whereas Lee et al. employed PAEBI samples of [η] < 0.67 dl/g [10,18]. Therefore, the relatively low peel

strengths in our study may result in part from the relatively weak mechanical properties of the PI peeling layer and from the relatively high molecular weights of the PAEBI polymers used.

For the adhesion joints made from the PAE precursor, the peel strengths were 343–490 J/m². In this case, the PAEBI with a lower [η] value also provided a relatively higher peel strength as observed for the adhesion joints prepared from the PAA precursor.

In comparison, the adhesion joint prepared with the PAE precursor reveals a relatively lower peel strength than one prepared with the PAA precursor. This difference in the adhesion might be attributed to the difference between the miscibilities of PAEBI layer to the BPDA–PDA PAA based PI layer and the BPDA–PDA PAE based PI layer. As described in the earlier sections, the PAA precursor is completely miscible with PAEBI. Thus, when the PAA precursor solution in NMP is overcoated on the PAEBI layer and soft-baked, the NMP solvent may dissolve the thin PAEBI layer partially or completely, possibly allowing the molecular mixing between the overcoated precursor and the PAEBI layer. The molecularly mixed phase formed between the precursor and the PAEBI layer may lead to a strong joint in the PI/PAEBI interface even though phase-separation occurs to generate domain structure in a certain level during the thermal imidization process. In contrast, the PAE precursor is immiscible with PAEBI polymer. In their ternary solution, they are miscible up to 11.3–14.5 wt % solid content, depending on their compositions. Thus, when the PAE precursor solution in NMP is overcoated on the PAEBI layer, the NMP solvent may dissolve the thin PAEBI layer partially or completely, possibly inducing the interdiffusion of the precursor polymer and the PAEBI polymer between the two layers. The interdiffused precursor and PAEBI polymer may be phase-separated with each other because of their inherent immiscibility, leading to a phase-separated domain structure at the interface with a certain depth. The phase-separated domain structure may retain in a certain degree during thermal imidization, consequently not allowing the formation of a sharp interface between the PI and the PAEBI layer. The generated interface contributes positively to the adhesion of the PI/PAEBI interface adhered copper sheet. However, the degree of molecular mixing at the interface might be relatively low, resulting in the relatively low peel strength.

4. Conclusion

PAEBI was miscible completely with the PAA precursor in their ternary solution with NMP and also in the condensed state (that is, soft-baked blend film). This miscibility might result from the strong interaction via the complex formation of imidazole groups in the PAEBI repeat unit with carboxylic acid groups of the precursor repeat unit. However, phase-separation occurred in the soft-baked

blend during thermal imidization, depending on the blend compositions. The imidized blends containing 30–70 wt % PI have phase-separated domains of 0.7–1.4 μm . All the other blend compositions were optically transparent. This indicates that the interaction between the imidazole groups of PAEBI and the imide groups of PI is not enough to make the polymers fully miscible. In addition, BPDA–PDA PI is a semicrystalline polymer, so that its crystallization occurred during thermal imidization may contribute in part to cause phase-separation in the blend with PAEBI.

In contrast, PAEBI and BPDA–PDA PAE formed miscible ternary solution in NMP for a limited concentration region of <11.3–14.5 wt %. They were almost fully immiscible in the condensed state, consequently causing phase-separation during the soft-baking process. This suggests that there is relatively weak interactions of imidazole groups of PAEBI with both the ester and amide linkages in the precursor polymer, leading to phase-separation in the blend. The phase-separation took place further during thermal imidization. The generated domain size was 0.8–3.0 μm , depending on the blend compositions. In particular, the 50/50 blend exhibited to have domains of >3.6 μm . Only the 90/10 blend film was observed to be optically transparent.

In conclusion, morphological structure of the PAEBI/PI blend depends strongly upon the PI precursor type and its miscibility with PAEBI in the ternary solution with a mutual solvent and as well as the molecular demixing occurred possibly during soft-baking and subsequent thermal imidization.

The difference in the miscibilities of PAEBI with the PI precursors was reflected on the adhesion strength of PI/PAEBI/copper joints in which the locus of failure by 90°-peeling is within the PI layer. In the peel test, the PAA precursor, which is miscible with PAEBI, gave a relatively higher peel strength than the PAE precursor which is immiscible partially or completely with PAEBI. In addition, the PAEBI having a relatively low $[\eta]$ value (that is, low molecular weight) provided a higher peel strength in the PI/PAEBI/copper joint than that with a high $[\eta]$ value.

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