Ultra-low-modulus Positive-type Photosensitive Polyimides (4). Improvement of Adhesion Strength with Copper Foil

Junichi Ishii¹, Keisuke Morita² and Masatoshi Hasegawa²

¹*Sony Chemical & Information Device Corporation*

1078 Kamiishikawa, Kanuma, Tochigi, 322-8503, Japan

²*Department of Chemistry, Faculty of Science, Toho University,*

2-2-1 Miyama, Funabashi, Chiba 274-8510

Amide- and triazine-containing diamines were incorporated by copolymerization into a siloxane-containing ultra-low-modulus polyimide (PI) as a novel cover layer material to solve some serious problems in the plating process such as interpenetration of an acidic plating solution into the interface between the S-side of electro-deposited copper foil and the cover layer. Our previous approach, a physical roughness modification of the S-side was effective to inhibit the interpenetration of the plating solution. This result suggests that the Cu/cover layer adhesion strength can be an important factor in the present case. The present work describes our chemical approach to increase the adhesion strength by using some heterocyclic monomers expected as adhesion promoters. The modified siloxane-containing PI possessed significant film toughness in spite of their low inherent viscosities. Unfortunately, the use of the amide- and triazine-containing diamines with minor contents (5–20 mol %) did not enhance the peel strength, however, the initial peel strength was almost maintained at 5 mol% without curling in the copper clad laminates (CCL), although the value significantly decreased at higher contents (10–20 mol%) with a prompt increase in the tensile modulus of the PI films and concomitant CCL curling. The results suggest that the decreased peel strength is closely related to the increased modulus of the PIs. Other properties (thermal and electrical properties, resistance to plating solutions, and photosensitivity etc.) of the modified siloxane-containing PIs will be also discussed in this work.

Keywords: ultra-low-modulus polyimides, soluble polyimides, positive-type photosensitive polyimide systems, adhesion strength with copper foil, FPC cover layers

1. Introduction

Flexible printed circuit board (FPC), which is fabricated by patterned etching of copper layer in copper clad laminates (CCL) and subsequent protection of the printed circuits with a cover layer, is a very important component in microelectronic devices such as cellular phones and mobile personal computers. Recent trends of the target properties in FPCs are lower stiffness and

resistance to repeated bending stress. FPCs possessing lower stiffness (lower spring-back property) are desirable for the assembly processes with bending of FPCs at a lower curvature radius in very narrower spaces of portable electronic devices such as cellular phones and digital cameras. The simplest approach to reduce the stiffness of FPCs is to design thinner FPCs, namely, to decrease the thickness of the cover films and CCL

(copper foils and base polyimide films). One of the conventional cover films consists of adhesive-coated commercially available aromatic polyimide (PI) films. The feature of this type of the cover films is considerably high resistance to repeated bending, excellent Cu-adhesion strength and resistant to Ni/Au-plating processes for the wiring- and the solder bonding. However, an intrinsically high modulus of aromatic PI cover films and the presence of the relatively thick adhesion layers ($> 15\mu\text{m}$) are disadvantageous for improving the a spring-back property of FPCs. Adhesive-coated PI cover films also possess no photo-patterning functionality, as a result, this system requires some complicated processes for high density circuits.

Epoxy-acrylate formulations (so-called photo-solder resists) are also known as another conventional cover layer materials possessing excellent negative-type photo-patternability. However, this type of cover layers has a serious drawback, very poor bending resistance.

On the other hand, ultra-low-modulus siloxane-containing photosensitive polyimide systems (PSPI) can be a promising candidate of a novel cover layer material since it can provide an extremely reduced spring-back property in addition to its excellent microfabrication ability. We have developed an ultra-low-modulus PSPI system by combining an alkali-soluble siloxane-containing PI system with diazonaphthoquinone (DNQ) as a photosensitizer [1]. This PSPI system can be directly formed on the printed circuits without adhesive layers by simple casting process of the PSPI solutions. The CCL obtained really showed no curling owing to the extremely low modulus ($< 0.2\text{GPa}$) of the PSPI and excellent non-flammability. However, we found a serious problem to be solved, a trend of interpenetration of the acidic solution during the Ni/Au plating process into the interface between the S-side of electro-deposited copper foil and the cover layer. This trouble probably comes from insufficient adhesion at the interface and a sort of Cu/cover lay wettability mismatching [2]. The simplest approach against this problem is to improve the adhesion strength at the interface. For this purpose, the use of some low-molecular weight additives may be effective. However, additives, which can migrate in the resins, sometimes become a trigger of some serious troubles such as deterioration of electric insulation properties.

Our final goal is to prevent completely the

above-mentioned problem sometimes occurring in the plating process. For this purpose, our attempts in the present work is to improve the adhesion strength of our original ultra-low-modulus PSPI by partially using some copolymerizable monomers which are expected to have some adhesion-promoting ability. Other properties of the modified PSPIs are also discussed in this work.

2. Experimental Section

2.1. Monomer Synthesis

(a) Amide-containing diamine

N,N'-bis(3-aminophenyl)isophthalamide (**2**) (amide-containing diamine) was prepared according to the reaction scheme shown in Fig.1. The detailed procedure is as follows: in a 300 mL four-necked flask, m-nitroaniline (5.53g: 40.0mmol) was dissolved in 22 mL of dried tetrahydrofuran (THF) at room temperature, then the flask was double cap-sealed. To this solution, isophthaloyl dichloride (4.06g: 20.0mmol) dissolved in a mixed solvent consisting of THF (16mL) and pyridine (9.7mL) as an acid acceptor was gradually added by with a syringe at 0°C . After several hours, the reaction mixture was diluted (final solute content: 20 wt%), then stirred at room temperature for 24h. The precipitation was collected by filtration, washed with THF and a large amount of water to remove pyridine/HCl salt, then vacuum-dried at 120°C for 12h. The overall yield of the light-yellow crude product was 77%. The product was confirmed to be dinitro compound (**1**) by $^1\text{H-NMR}$ and FT-IR spectroscopy.

The reduction of the dinitro compound (**1**) was carried out as follows: in a 300mL four-necked flask, (**1**) (3.00g: 7.39mmol) was dissolved in 45 mL N,N-dimethylformamide (DMF) at room temperature, then Pd/C (0.10g) was added as a catalyst. The reaction mixture was stirred at 100°C for 5 h in a hydrogen atmosphere. After Pd/C was removed by filtration, the filtrate was concentrated by evaporation. The crude product was collected by repetitive fractional precipitation of the oily product into a large amount of water, then purified by recrystallization from DMF/water (1/3; v/v), and finally vacuum-dried at 120°C for 12h. The overall yield of the light-brown product was 93%. The product was confirmed to be (**2**) from $^1\text{H-NMR}$ and FT-IR spectra. mp:

240°C. $^1\text{H-NMR}$ (400MHz, DMSO-d_6) $\delta(\text{ppm})$: 10.11(s, 2H), 8.43(s, 1H), 8.07(d, 2H), 7.65(t, 1H), 7.12(s, 2H), 6.98(t, 2H), 6.88(d, 2H), 6.32(d, 2H), 5.13(s, 4H). FT-IRv KBr max (in cm^{-1}): 3298, 1655, 1543.

Fig.1 Synthetic pathway of amide-containing diamine.

(b) Triazine-containing diamine

2,4-bis(aminoanilino)-6-anilino-s-triazine(**4**)(triazine-containing diamine) was prepared according to the procedure described in the literature [3]. The reaction scheme is shown in Fig.2. In a 300mL four-necked flask, cyanuric chloride (3.79g: 20.5mmol) was dissolved in 20mL of benzene at room temperature. To this solution, aniline (3.82g: 41.1mmol) dissolved in benzene (100mL) was gradually added at 0°C and stirred for 4h, followed by stirring at room temperature for 12h. After the precipitate (aniline/HCl salt) as a by-product was removed by filtration, the filtrate (benzene solution) was washed with a HCl aqueous solution to remove residual aniline and the salt, then washed with a Na_2CO_3 aqueous solution and water, dried over magnesium sulfate, and finally the solvent was evaporated. The crude product (**3**) obtained was purified by recrystallization from benzene/cyclohexane (6/1, v/v), then vacuum-dried at 60°C for 12h. The overall yield of the light-yellow product was 56%. The product was confirmed to be (**3**) from $^1\text{H-NMR}$ and FT-IR spectra.

Triazine-containing diamine (**4**) was synthesized as follows: in a 300mL four-necked flask, a large excess of p-phenylenediamine (8.75g: 40.5mmol) was dissolved in 1,4-dioxane (20mL) at room temperature in the presence of Na_2CO_3 (0.53g: 5.0mmol). To this solution, (**3**) (1.15g: 5.01mmol) dissolved in 1,4-dioxane (100mL) was gradually added. The reaction mixture was refluxed at 100°C

for 4h. The crude product was collected by repetitive fractional precipitation of the solution into a large amount of water at 0°C. The crude solid product was washed with hot toluene, and finally vacuum-dried at 100°C for 12h. The overall yield of the light-red product was 72%. The product was confirmed to be (**4**) by $^1\text{H-NMR}$, FT-IR, LC-MS spectroscopy; mp 222°C. $^1\text{H-NMR}$ (400MHz, DMSO), $\delta(\text{ppm})$: 8.95(s, 2H), 8.63(s, 1H), 7.78(d, 2H), 6.93(m, 7H), 6.50(t, 1H), 4.79(d, 2H). FT-IRv KBr max (in cm^{-1}): 3416. LC-MS: 385.1(M+H).

Fig.2 Synthetic pathway of triazine-containing diamine.

2.2. Polymerization of ultra-low-modulus polyimides

The ultra-low-modulus PIs were polymerized according to the reaction scheme shown in Fig.3. A typical polymerization procedure using triazine-containing diamine as follows: in a 100mL four-necked flask equipped with a condenser and a Dean-Stark trap, a specially designed siloxane diamine (15.04g: 10.96mmol) was dissolved in 10g of γ -butyrolactone (GBL) in a nitrogen atmosphere. To this solution, 7.23g (20.1mmol) of 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA, purity: 99.7%) powder was added in one portion. The reaction mixture was stirred at room temperature for 2 h, and heated at 185°C for 2h in the presence of 5g toluene as an azeotropic reagent, then cooled to room temperature. To the homogeneous solution of anhydride-terminated oligo-imide, 1.96g (6.96 mmol) of bis(3-amino-4-hydroxyphenyl)sulfone (BS-DA, purity: 99.5%), 0.77g (2.00mmol) of the triazine-containing diamine (**4**), and 15g of GBL were added, then stirred at room temperature for 2 h, and finally heated at 185°C for 2 h to ensure complete imidization. The combination of the present two-step polymerization procedure and the choice of an adequate composition/molecular

weight of siloxane-diamine was a key point for obtaining homogeneous PI solutions.

Polymerization using the amide-containing diamine was also carried out in a similar manner.

Fig.3 One-pot polycondensation scheme of siloxane-containing ultra-low-modulus PIs.

2.3. Evaluation of Adhesion strength

Peel test of the present CCL specimens was so difficult to perform because of the considerable softness of the present cover layer materials that our initial approach for evaluation of the adhesion strength was a cross-cut taping test which gives just a very qualitative result. In the present work, we tried to evaluate the adhesion strength by means of the peel test using a mechanical stretching machine. Our CCL specimens prepared by a sophisticated technique made possible its measurement.

The specimens for the peel test were prepared as follows: PI solution was coated on an electro-deposited copper foil (S-side), then dried at 100°C for 10min in an air oven, followed by annealing at 200°C for 1h in a nitrogen atmosphere. After the sample specimens were cut out from the central area of the CCL, a glass cloth-epoxy resin molding plate was attached onto the PSPI surface of the CCL specimens through an epoxy-type adhesive. Finally, the copper foil

with patterned masking tapes was etched by immersing it in a FeCl₃ aqueous solution bath to form 3 mm-wide CCL specimens.

The peel test was conducted on a mechanical testing machine (Toyo Baldwin; Tensilon UTM-II) at a cross head speed of 8 mm/min. The geometry of the 180° peel testing is schematically depicted in Fig.4. It is empirically known that the present testing mode provides comparable results to those of the 90° peel test.

Fig.4 Schematic diagram of the 180° peel test.

2.4. Other Measurements

The coefficient of thermal expansion (CTE) and the glass transition temperature (T_g) of PI specimens (5mm wide, 20mm long, 10–20μm thick) were measured on a thermal mechanical analyzer (Bruker-AXS, TMA 4010) at a heating rate of 5°C/min with a constant load of 0.5g/μm film thickness for the CTE measurements and a sinusoidal load (0.1 Hz) for the T_g measurements in a nitrogen flow. For the CTE measurements, the data were collected from the second heating run after the first run up to 120°C to eliminate absorbed water.

Mechanical properties (tensile modulus and elongation at break (ε_b)) of PI films (20 mm wide, 40 mm long, 10–12μm thick) were measured using a mechanical testing machine (Toyo Baldwin; Tensilon UTM-II) at a cross head speed of 8 mm/min. Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of PI films at a heating rate of 10°C/min in a nitrogen and an air atmosphere. The 5% weight loss temperatures were determined from TGA.

The reduced viscosities (η_{red}) of PIs were determined at 30°C in GBL at a concentration of 0.5wt% using an Ostwald viscometer.

3. Results and Discussion

3.1. Polymerization and Characterization

Ultra-low-modulus polyimides were prepared from diamine components (amide- or triazine-containing diamine, siloxane diamine, and BS-DA) with tetracarboxylic dianhydride component (DSDA) through the reaction scheme as shown in Fig.3. At the first step, the anhydride-terminated oligo-imide containing the flexible siloxane block was formed as confirmed from its FT-IR spectrum; no trace of the amide C=O stretching bands (amide-I at 1650 cm^{-1} and the amide-II band at 1560 cm^{-1}) was observed in addition to the presence of the dicarboxylic acid anhydride C=O stretching band at 1861 cm^{-1} . The 1861 cm^{-1} band of the oligo-imide completely disappeared by the reaction with the diamine components (BS-DA and amide-/triazine-containing diamines) instead, the imide C=O stretching bands at 1778 and 1725 cm^{-1} and the phenolic OH stretching band originating from BS-DA appeared at 3370 cm^{-1} . No trace of the amide C=O stretching band was observed, indicating complete imidization during the second step.

All the PI samples (amide-/triazine- containing diamine content: 0-20 mol%) were highly soluble in a 3wt%-NaOH aqueous solution owing to the presence of the phenolic OH groups, thereby the DNQ-containing PSPI films provided good positive-tone pattern with L&S = 200/200 μm .

The siloxane-containing PIs possessed significant film toughness in spite of their low reduced viscosities ($\eta_{\text{red}} = 0.2\text{--}0.3 \text{ dL/g}$), probably owing to a major fraction of the considerably flexible siloxane block in the structures.

3.2. Adhesion Strength

The original siloxane-containing PSPI without the amide-/triazine-containing diamines showed about a peel strength of 0.7 kgf/cm with the copper S-side, which was lower than our temporal target (1.0 kgf/cm). On the other hand, the value with the M-side was 1.23kgf/cm, suggesting that the surface roughness of Cu foil plays a great role for the PI/Cu adhesion.

The amide- and triazine-containing diamines were used for copolymerization with an

expectation of drastic improvement of the adhesive strength on the basis of strong interaction between the Cu surface and the polar groups of the amide and triazine units [4]. But unfortunately, the use of these polar diamines caused no appreciable increase in the peel strength in the range of 5–20 mol%. However, it should be noted that at 5–10mol%, the peel strength was almost maintained, as shown in Fig.5. The modified PSPI at 5 mol% can be promising for solving the above-mentioned problem in the plating process. The examination is in progress.

Fig.5 also shows the change in the tensile modulus of the PIs. One notices that the increase in the polar diamine content also caused significant increases in tensile modulus. The results are probably due to the decreased siloxane content in the structures as a result of the partial use of these polar diamines.

The results in Fig.5 lead to a hypothesis; the decreased peel strength for the modified PSPIs results from the increased tensile strength, qualitatively speaking, which lowers wettability of the cover layer on the Cu surface.

Alternative approach which can intensify the PSPI/copper interactions without increasing the modulus is required for the present purpose.

Fig.5 Peel strength and tensile modulus as a function of amide-containing diamine (circle) or triazine-containing diamine (square) content in PI diamine monomers. (Open mark is tensile modulus, closed mark is peel strength).

3.3. Properties of PI films

The properties of the PSPI films without DNQ are listed in Tables 1 and 2. The original PSPI films (polar diamine content: 0 mol%) showed a relatively low T_g at 128°C (determined by TMA method), however, no serious problems were observed in the solder-reflowing process at 250–260°C). The increase in the polar diamine content caused an abrupt increase in T_g (up to

ca. 200°C at 20 mol%), changing parallel to the tensile modulus as listed in Tables 1 and 2. The results reflect the increased average chain stiffness.

Table 1. Reduced viscosities and film properties of amide-containing diamine based PI.

Diamine unit			η_{red} (dl/g)	Tg (°C)	CTE (ppm/K)
Amide	Siloxane	BS-DA			
0mol%	65mol%	35mol%	0.252	128	1070
5mol%	60mol%	35mol%	0.203	138	847
10mol%	55mol%	35mol%	0.298	178	218
20mol%	45mol%	35mol%	0.255	197	99.7

Td ⁵ (air) (°C)	ϵ_b (%)	Tensile modulus (GPa)	Peel Strength (kgf/cm)
365	207	0.074	0.73
375	148	0.126	0.67
394	128	0.225	0.60
390	64.3	0.594	0.10

Table 2 Reduced viscosities and film properties of triazine-containing diamine based PI.

Diamine unit			η_{red} (dl/g)	Tg (°C)	CTE (ppm/K)
Triazine	Siloxane	BS-DA			
0mol%	65mol%	35mol%	0.252	128	1070
5mol%	60mol%	35mol%	0.288	138	758
10mol%	55mol%	35mol%	0.237	163	191
20mol%	45mol%	35mol%	0.248	200	109

Td ⁵ (air) (°C)	ϵ_b (%)	Tensile modulus (GPa)	Peel Strength (kgf/cm)
365	207	0.074	0.73
389	126	0.247	0.63
386	59	0.289	0.67
394	30	0.709	0.43

One of the most important properties of CCL is flatness of the laminates. Curling of the PI/copper laminates is caused by thermal stress arising during the solution-casting/drying processes for the formation of cover films. The extent of thermal stress ($\Delta\sigma$) is expressed as a definite integral from a drying temperature (T_{dry}) to room temperature (T_r) as Eq. (I):

$$\Delta\sigma = \int [E_f(1-\nu_f)](\alpha_s - \alpha_f)dT \quad (I)$$

where E_f and ν_f are Young's modulus and Poisson's ratio for the cover films, respectively. α_s and α_f are the in-plane CTE of the substrate (copper foil in the present case) and the cover film, respectively [5,6]. Accordingly, thermal stress can be suppressed by reducing Young's modulus of the cover film materials or the CTE mismatch ($\alpha_s - \alpha_f$) [1,7].

At lower polar diamine contents (0–10 mol%), where the tensile modulus ranges 0.074–0.289GPa, curling of the PSPI/copper laminates was completely suppressed, although curling took place above 10 mol%. This can be interpreted as the result that the contribution of the low modulus overcame that of the CTE mismatch. Thus, a critical modulus required for cover lay materials in CCL can be estimated as 0.2–0.3GPa.

The increase in the polar diamine content also caused a decrease in the elongation at break (ϵ_b), but sufficient film toughness is still maintained as shown in Tables 1 and 2.

4. Conclusion

The partial use of amide-/triazine-containing diamines caused a gradual decrease in the peel strength, but it was almost maintained at a low content (5 mol%). The results suggest that the decreased peel strength is closely related to the increased modulus of the PSPIs. Curling of CCL was completely restricted at lower polar diamine contents (< 10 mol %). The results suggest that a critical modulus required for cover lay materials in CCL can be estimated as 0.2–0.3GPa.

References

1. Ishii, J., Sunaga, T., Nomura, M. and Kanaya, H., *J. Photopolym. Sci. Technol.*, **21**, No.1 (2008), 107.
2. Furukawa, N., Yuasa, M., Omori, H. and Yamada, Y., *J. Adhesion*, **59**(1996),281.
3. E.Butuc, *J.Polym.Sci., Polym.Chem.Ed.*, **22**(1984), 503.
4. I. S. Chung., C. E. Park, M. Ree and S. Y. Kim, *Chem. Mater.* **13**(2001), 2801.
5. Jwo-Huei Jou and Lih-Jiuan Chen, *Appl. Phys. Lett.*, **59**(1) (1991), 46.
6. Furukawa, N., Yamada, Y. and Kimura, Y., *High Perform. Polym.*, **8**(1996), 617.
7. Ishii, J. and Akamatsu, T., *High Perform. Polym.*, **21**(2009), 123.