Organo-soluble Polyimides and Their Applications to Photosensitive Cover Layer Materials in Flexible Printed Circuit Boards

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Two types of photosensitive polyimides (PSPIs) were developed as novel cover layer materials for FPC applications in this work. One of them, **PSPI-1** was highly soluble in common organic solvents such as NMP in spite of its stiff backbone structure. The **PSPI-1** film formed by simple solution-casting exhibited a low CTE of 19–24 ppm/K in addition to a high T_g at 292°C, high thermal stability, low water absorption (0.3%), comparatively good transparency, and sufficient film flexibility. On the other hand, another system, **PSPI-2** displayed an extremely low modulus. Both PSPI systems completely inhibited curling of the PSPI/copper laminates. These PSPI systems also possessed fine positive-tone patterning ability, reliable insulation property, and the highest level of non-flammability(UL-94: V-0 or VTM-0). The results revealed that the present PSPI systems are promising candidates as novel cover layer materials.

Keywords: Organo-soluble polyimides, Low CTE, Low Modulus, Positive-type Photosensitive Polyimides, Flexible Printed Circuit Boards (FPC), Cover Layers

1. Introduction

Flexible printed circuit board (FPC), which is fabricated by copper-patterning of copper-clad laminates (CCL) and subsequent protection with a cover layer (CL), 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 low stiffness are convenient to assemble in narrower spaces of portable electronic devices such as personal digital assistants and cellular phones. The design of cover layers as protection films for printed circuits also influence strongly the target properties of FPCs.

Two types of commercially available cover layers are known: adhesive-coated conventional polyimide films and epoxy-acrylate thermosetting resins (called photo-solder resist). The adhesive-coated PI cover films usually have a high modulus (stiffness) and no photo-patterning

functionality, although this type of cover film is considerably resistant to repeated bending. However, the high-modulus PI cover films possess a disadvantage for an unfavorable spring-back property in assembly processes with bending at a lower curvature radius in very narrower spaces.

Photosensitive epoxy-acrylate / inorganic fillers composite materials are also used as cover layers more suitable for fine pitch processes. However, this type of cover layers has a serious problem that the cured resins are quite brittle against bending stresses. Simple approaches to reduce the spring-back property of FPCs are to use thinner PI cover films and to remove the adhesive layers coated on the PI cover films, namely, to use adhesive-free PI cover layers. However, it is not so easy to develop such photosensitive PI cover layer materials since the following combined properties are demanded for this application: (1) solution-processability, (2) film toughness, (3) solubility in alkaline solutions, (4) film

transparency, (5) sufficient adhesion [1], and (6) a low CTE close to that of copper foil as a conductive layer or a considerably lower modulus [2,3,4]. In this work, we developed novel photosensitive PI cover layer materials which can be directly formed on the printed circuits by simple casting process of the PI solutions and display a low CTE or a very low modulus.

2. Experimental

2.1. Synthesis of NMP-soluble Low-CTE Polyimides (PI-1).

Figure 1 shows a reaction scheme of the one-pot polycondensation of tetracarboxylic dianhydrides with diamines and the structures of polyimides studied. A typical procedure is as follows: in a 500 mL four-necked separable flask equipped with a Dean-Stark trap, 4.89 g (13.2 mmol) of 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (**BisApAf**, purity: 99.00 %) and 16.97 g (52.9 mmol) of 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (**TFMB**, purity: 99.76 %) were completely dissolved in 261 g of NMP in a nitrogen atmosphere. To this solution, mixed powder of 3,4,3',4'-biphenyltetracarboxylic dianhydride (**BPDA**, purity: 99.82 %) 9.84 g (33.4 mmol) and pyromellitic dianhydride (**PMDA**, purity 99.80 %) 7.30 g (33.4 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 1 h to form homogeneous solution, and then heated at 80°C for 2 h. The PAA solution was heated at 185°C for 5 h in the presence of 15 mL toluene as an azeotropic reagent.

Fig.1 One-pot polycondensation of low-CTE polyimides in NMP.

2.2. Synthesis of Siloxane-containing Low-modulus Polyimide (PI-2).

Siloxane-containing low-modulus polyimides were prepared according to a reaction scheme shown in **Figure 2**. In a 20 L pilot plant equipped with a condenser and a trap system, siloxane diamine (4372.7 g : 3.24 mol) was dissolved in 6300 g of triethyleneglycoldimethyl ether (**TriGL**) in a nitrogen atmosphere. To this solution, 1994.5 g (5.54mol) of 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (**DSDA**, purity: 99.60 %) powder was added in one portion. The reaction mixture was stirred at room temperature for 2 h, then heated at 185°C for 2 h in the presence of 1100 g toluene as an azeotropic reagent. The reaction allowed the formation of a homogeneous solution of anhydride-terminated oligo-imide 632.8g (2.25mol) of bis(3-amino-4-hydroxyphenyl)sulfone (**BSDA**, purity 99.70 %) and 700 g of γ -butyrolactone (GBL) was added to this solution at room temperature. The reaction mixture was stirred at room temperature for 2 h, and then heated at 185°C for 2 h.

Fig.2 One-pot polycondensation of siloxane-containing low-modulus polyimide in TriGL/GBL.

2.3. Evaluation of Photosensitivity.

Diazonaphthoquinone (DNQ, NT-200 or 4NT-300) was purchased from Toyo Gosei Co. Ltd. and used without further purification. DNQ and additives were added into each solution of **PI-1** and **PI-2** and dissolved by stirring at room temperature for 24–72 h. This solution was coated on an electrodeposited copper foil and dried at 80–100°C for 10 min. The resultant 10–20 μm thick photosensitive PI (PSPI) films were

irradiated on an i-line stepper (Harison-Toshiba Lighting Corp., TOSCURE 752) with different doses using a step tablet film (Steffe-21). After development, the film thickness was measured by a contact stylus profiler (KLA-Tencor Corp., P-15). The uv-irradiated samples were developed in a 3 wt% sodium hydroxide aqueous solution at 40°C, then rinsed in water at 40°C.

2.4. Measurements.

Infrared absorption spectra of PSPI thin films (2 μm thick) formed on a silicon oxide-free Si wafer by casting of PSPI solution at 100 °C were measured on a Jasco FT/IR-460 plus spectrometer.

Ultraviolet-visible absorption spectra of PSPI films (10 μm thick) formed on a quartz substrate by casting of the PI solution at 100°C were measured on a Jasco V-560 spectrometer.

The coefficient of thermal expansion (CTE) of PSPI specimens (4 mm wide, 20 mm long, 10–12 μm thick) was measured on a thermal mechanical analyzer (SEIKO Instruments Inc., TMA/SS6100) at a heating rate of 10°C/min with a load of 49 mN in a nitrogen flow. In this case, the data were collected from the second heating run after the first run up to 100°C to eliminate absorbed water.

Mechanical properties (tensile modulus; E) of PSPI films (10 mm wide, 100 mm long, 10–12 μm thick) were measured using a mechanical testing machine (T.S.E Co., Ltd., Auto com AC-50) at a cross head speed of 5 mm/min.

Thermo gravimetric analyses of PSPI films were carried out on a TG/DTA6200 (SEIKO Instruments Inc.) at a heating rate of 10°C/min in a nitrogen flow.

The electric insulation property was evaluated by a combination of a LCR meter (Advantest, R8340A Ultra High Resistance Meter) and a comb-type electrode test element group (TEG) composed of copper. In this case, PSPI solutions were coated onto a TEG, and dried at 100°C for 10 min, then heated at 200°C for 30 min in a nitrogen flow to form a cover film (10 μm thick). The electric resistance was monitored as a function of time under an applied voltage of 500 V.

The extent of water absorption ($W_A\%$) was determined from the relation: $(W - W_0) / W_0 \times 100$, where W_0 is the weight of PSPI films vacuum-dried at 100°C for 12 h, and W denotes the weight of PSPI films immersed in water at 25°C for 24 h and subsequently wiped with a cotton paper.

Non-flammability of PSPI films was also

evaluated by UL-94 V-0 or VTM-0 standard test. In this case, the PSPI solutions were coated on both sides of a 25 μm thick commercial PI film (Ube Industries, Ltd., UPILEX-25S) and dried at 100 °C for 20 min, then baked at 200 °C for 30 min in a nitrogen flow. The thickness of the each PSPI layer was about 10 μm .

For a curling test, the PSPI solutions was coated on a rectangular-shaped electrodeposited copper foil (20 $\times$ 15 cm) then dried at 100°C for 10 min in an air oven, followed by annealing at 200°C for 30 min in a nitrogen atmosphere. A sample specimen (10 $\times$ 10 cm) was taken from the central area of the laminate. The extent of curling was estimated from the average height (h mm) of the four corners from the horizontal when the copper layer side of the curled sample was placed on a flat plate.

3. Results and Discussion

3.1. FT-IR characterization of PI-1.

The solutions of **PI-1** remained homogeneous during prolonged storage at room temperature in contrast to our first prediction that the partial use of PMDA must be disadvantageous for homogeneous polymerization and PI solution stability. This unusual result observed in **PI-1** is probably related to a random chain sequence. The lower molecular weights of **PI-1** as a secondary factor can be also responsible for its unexpectedly excellent solution stability as suggested from the fact that $\eta_{\text{red}} = 1.35\text{--}2.05$ dL/g for **PI-1**.

A trace of unimidized amide groups in the **PI-1** sample after imidization in solution was checked from the changes in the FT-IR spectra as a function of post-cure temperature in solid state[5]. **Figure 3** shows that the amide C=O stretching band (amide-I in polyamic acid; PAA) around 1650 cm^{-1} decreased gradually with the increase in post-cure temperature from 200 to 280°C. A comparison with the spectrum of the neat solvent (NMP), which possesses only an absorption peak around 1650 cm^{-1} , suggests that the residual NMP in the PI cast film probably contribute largely to the significant decrease in the 1650 cm^{-1} band due to the increase in post-cure temperature, although complete (100 %) imidization is not always guaranteed for the **PI-1** sample just after solution imidization. As discussed later, the present **PI-1** sample can be used for practical FPC applications without any serious problems.

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Fig.3 IR spectrum of NMP (neat liquid) and change in IR spectra of **PI-1** thin film with an increase in post-cure temperature: (1) 200°C for 1 h, (2) (1) + 230°C for 1 h, (3) (2) + 250°C for 1 h, (4) (3) + 280°C for 1 h.

3.2. FT-IR characterization of **PI-2**.

TriGL as a solvent for polycondensation of **PI-2** is more useful for the subsequent coating process than NMP since more hydrophilic NMP tends to cause precipitation of the PI in the coating process owing to moisture absorption. However in many cases, TriGL has another problem: its poorer dissolution ability for PIs. In fact, a random copolymer with the same chemical composition as **PI-2** was not always highly soluble in TriGL. Then we attempted to control the chain sequence according to the procedure shown in **Figure 2**, and successfully obtained highly soluble **PI-2** in TriGL from the reaction of the anhydride-terminated siloxane-containing oligo-imide with the sulfone-containing bis(*o*-aminophenol).

Figure 4a shows the IR spectrum of the oligo-imide. No trace of amide C=O stretching bands (amide-I around 1650 cm⁻¹ and amide-II band around 1560 cm⁻¹) was observed in the spectrum in addition to the presence of the dianhydride C=O stretching band at 1861 cm⁻¹, indicating the formation of the oligo-imide depicted in **Figure 2**. In the IR spectrum of **PI-2** in **Figure 4b**, the characteristic dianhydride band at 1861 cm⁻¹ completely disappeared, and the phenolic OH stretching band appeared. The results support the formation of **PI-2**.

Fig.4 IR spectra of anhydride-terminated oligo-imide (a) and **PI-2** (b).

3.3. Photosensitivity of **PSPI-1** and **PSPI-2**.

In general, the transparency of matrix polymers in photosensitive formulations is a very important factor from the viewpoints of obtaining higher sensitivity. The 10 μm thick **PI-1** film itself (DNQ-free) showed a sufficiently high transmittance, of 83.6 % at 436 nm (g-line of high-pressure mercury lamp) and 54.4 % at 405 nm (h-line) although it was poorly transparent at 365 nm (i-line) as shown in the transmission spectra in **Figure 5**. On the other hand, DNQ-free **PI-2** film (10 μm thick) showed more excellent transparency than **PI-1** film, namely, *T* = 88.8% at 436nm, 79.1% at 405nm, and 59.4% at 365nm. In general, wholly aromatic PI films are strongly colored on the basis of the intra- and intermolecular charge-transfer (CT) interactions [6] as illustrated from the significantly red-shifted transmission curve of a typical wholly aromatic commercial PI film (UPILEX-S, 25 μm thick) with no transparency even at 435 nm as shown in **Figure 5**. The results also emphasize that **PI-1** possesses a relatively high transparency among wholly aromatic PI systems. This can be explained in terms of partially disturbed intramolecular CT interaction by the presence of the electron-withdrawing trifluoromethyl groups in the diamine components. On the other hand, the much higher i-line transparency of **PI-2** results from strongly inhibited intramolecular CT interaction by the incorporation of the non-conjugated siloxane units into the main chains.

Fig.5 UV-visible absorption spectrum of DNQ in NMP at a concentration of 4×10^{-5} M, the transmission spectra of PI-1, PI-2, and UPILEX-25S films, and spectral energy distribution for the major lines from a super high-pressure mercury lamp.

DNQ acts as a dissolution inhibitor against an alkaline aqueous solution because of its originally hydrophobic structure. However, it can be photochemically converted to keten via the Wolff rearrangement, then finally to alkali-soluble indencarboxylic acid by a reaction with water. Therefore, DNQ has been applied to alkali-developable positive-type photoresist systems by combining with originally alkali-soluble polymers such as phenolic resins [7,8]. In the present work, we evaluated photosensitivity of **PI-1/DNQ (PSPI-1)** and **PI-2/DNQ (PSPI-2)** systems. **Figure 6** exhibits the sensitivity curves for the **PSPI-1** and **PSPI-2** films. The sensitivity determined from the doses, where the PSPI film was completely dissolved (the normalized thickness became zero), was 238 mJcm^{-2} for the **PSPI-1** system ($10 \mu\text{m}$ thick) on the development for 150sec. However, the use of a thicker **PSPI-1** film ($20 \mu\text{m}$ thick) disturbed to evaluate the sensitivity for its too low dissolution rate. On the other hand, the $20 \mu\text{m}$ thick **PSPI-2** film enabled us to determine the sensitivity and showed a relatively good sensitivity value of 475 mJcm^{-2} on the development for only 30sec. These results are attributed to a combined effect of much higher transparency of PI-2 itself as a matrix polymer and its adequate solubility in the developer which originates from the presence of the phenolic OH groups.

Fig.6 Photosensitivity curves for different photosensitive PI systems: (1) $10 \mu\text{m}$ thick **PSPI-1** film developed by a 3wt% NaOH aqueous solution at 40°C for 150sec and (2) $20 \mu\text{m}$ thick **PSPI-2** film developed by the same developer at 40°C for 30 sec.

3.4. Properties of PSPI films.

One of the most important properties required for cover layer materials in FPC applications is to suppress curling 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. (1):

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

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 [2,3]. Accordingly, thermal stress can be suppressed by reducing the CTE mismatch ($\alpha_s - \alpha_f$). When the **PSPI-1** film as a cover layer was formed on a copper foil through the solution-casting process, almost no curling was observed owing to a negligibly small difference in the CTE values between the copper foil (18–20 ppm/K) and the **PSPI-1** film (19–23 ppm/K). It should be noted that the use of **PSPI-2** also caused no curling in spite of its extremely higher CTE values (471–3540 ppm/K). This can be interpreted from the significantly suppressed thermal stress based on its considerably low modulus (E).

Thermal properties of these PSPIs were also evaluated in this work. The **PSPI-1** film possessed a high T_g at 292°C and good thermal stability (5% weight loss temperature in a nitrogen atmosphere (T_d^5) exceeding 350°C), whereas the **PSPI-2** film

showed a low T_g at 121°C. Nonetheless, the cover layer composed of **PSPI-2** passed the solder-reflowing test operated at 260°C. This result suggests that **PSPI-2** causes no serious problems such as an adhesion trouble based on rapid water evaporation-induced foaming during the solder-reflowing process.

Table 1. Film properties of **PSPI-1** and **PSPI-2**.

PSPI	T_g (°C)	CTE (ppm/K)	*Curling (mm)	E (GPa)	T_d^5 (°C)
1	292	19.1 ^(a) 23.9 ^(b)	-1.8	2.57	355
2	121	471 ^(c) 3540 ^(d)	3.2	0.28	354

*Average heights of the four corners in PSPI/copper laminates from the horizontal: “-” means that the corners in the laminates curled toward the copper foil side. The CTE values were averaged in the temperature ranges: a)100–150°C, b)150–200°C, c)60–80°C, d)160–180°C.

3.5. Properties of PSPI-covered CCL .

We finally evaluated other properties required for FPC applications, i.e., electrical resistance and non-flammability. As listed in **Table 2**, **PSPI-1** and **PSPI-2** displayed excellent electrical resistance exceeding 10^{13} – $10^{15}\Omega$, suggesting no serious problems such as ionic migration induced by corrosion in spite of the presence of the phenolic OH groups in the structures. This is basically attributed to the considerably low degrees of water absorption ($W_A = 0.3\%$ for **PSPI-1** and 0.45% for **PSPI-2**).

Non-flammability is also a very important property for practical FPC applications. Conventional photosensitive cover layer materials consisting of epoxy/acrylate resins usually include halogen- and phosphorus-containing fire retardants. However, halogen-containing flame retardants are not environmentally friendly as regulated by the restrictions on the use of certain Hazardous Substances (RoHS) in EU. Phosphate ester flame retardants often cause serious degradation of an insulation property as often induced by hydrolysis of the phosphates. On the other hand, our PSPIs as cover layer materials achieved the highest level of non-flammability (UL-94, V-0 or VTM-0) without the addition of any flame retardants as listed in **Table 2**.

Table 2. Insulation property and non-flammability of **PSPI-1** and **PSPI-2**.

PSPI	Insulation resistance (Ω)	Non -flammability
1	3.83×10^{13}	UL-94, V-0
2	1.00×10^{15}	UL-94, VTM-0

4. Conclusion

We developed two types of PSPIs as cover layer materials for FPCs. **PSPI-1** was highly soluble in common organic solvents such as NMP in spite of its stiff backbone structure. The PSPI-1 film formed by solution-casting exhibited a low CTE in addition to a high T_g , high thermal stability, low water absorption, comparatively good transparency, and sufficient film flexibility. On the other hand, **PSPI-2** displayed an extremely low modulus. Furthermore, Both PSPI systems also possessed fine positive-tone patterning ability, excellent insulation property, and the highest level of non-flammability. The results revealed that the present PSPI systems are promising candidates as novel cover layer materials.

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