

Ultra-low-modulus Polyimide (3). Applications to Screen-printable Cover Layer Materials

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Novel non-photosensitive polyimides were prepared from 3,4'-oxydiphthalic anhydride (a-ODPA) with a siloxane-containing diamine and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) at a very high solid content of 60 wt% for applications to screen-printable FPC cover layer materials. The random copolyimide showed an extremely low tensile modulus in addition to very high film toughness, thereby curling of FPC could be completely suppressed. The sequence-controlled copolyimide with the same chemical composition displayed a further decreased tensile modulus, which can be explained from a sea-island phase-separated morphology controlled by the siloxane block size. The siloxane-containing copolyimide solutions containing an additive showed good screen-printability without sacrificing other target properties.

Keywords: Ultra-low Modulus Polyimides / Morphology-controlled Siloxane-containing Polyimides / Cover Layer Materials for FPC / Screen-printing

1. Introduction

Flexible printed circuit board (FPC), which is fabricated by patterned etching of copper layer in copper clad laminates 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. Lower-stiffness FPCs 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, the copper foils, and the dielectric films. The conventional cover layer material is the adhesive (epoxy resin/NBR)-coated commercially available polyimide (PI) film. The feature of this type of cover film is considerably high resistance to repeated bending, strong adhesion with the smooth surface (S-side) of copper foil, and resistance to the subsequent Ni/Au-plating processes for the wiring- and solder bonding. However, a high modulus of conventional PI cover film and the presence of the relatively thick adhesive layer ($> 15\mu\text{m}$) are disadvantageous from the viewpoints of the FPC "spring-back" property.

Epoxy resin-acrylate formulations (photo-solder resists) are also known as another conventional cover layer material possessing excellent negative-type photo-patternability, which can be developed with a 1% Na_2CO_3 aqueous solution at 40°C. However, this type of cover layer has a serious drawback, that is, very poor resistance to repeated bending stress.

On the other hand, we have so far proposed a positive-type photosensitive siloxane-containing PI system as a promising candidate of novel cover layer materials [1,2]. The fundamental features of this system are: (1) owing to its considerably high solubility in common organic solvents such as γ -butyrolactone (GBL), the cover layer can be directly formed onto the smooth surface of printed circuits without any adhesives via the conventional solution casting process using the PI varnish without subsequent thermal imidization process at elevated temperatures, (2) the cover layer possesses relatively good adhesion with the S-side of copper foil with a relatively high peel strength of 0.73

kgf/cm, (3) the cover layer in which a photosensitizer (diazonaphthoquinone, DNQ) acting as a dissolution inhibitor are dispersed can be developed after uv-exposure with a 3% NaOH aqueous solution at 40°C because of the presence of the phenolic OH groups in the structure, and (4) the FPC covered by the siloxane-containing PI maintains complete flatness owing to its extremely low modulus (< 0.2 GPa). The actually used composite material consists of the siloxane-containing PI as the primary component and minor fractions of some thermosetting polymers and some additives. The composite material also achieved the highest level of non-flammability (UL-94, VTM-0 for the laminated sample with a conventional PI film, Upilex-S), excellent electrical insulation properties retained even after standing of the covered FPC at a high temperature and a high humidity for a prolonged time, and significantly improved resistance to repeated bending compared with the conventional epoxy resin / acrylate photo-solder resist materials. However, there was a serious problem in the present siloxane-containing PI composite system; it was difficult to develop with the conventional Na₂CO₃ solution, thereby the standard development lines can not be used.

An alternative possible approach is to apply the screen-printing technique using a similar but non-photosensitive ultra-low-modulus PI system. A considerable cost-merit can be expected by a shift to non-photosensitive systems since the FPC fabrication processes are drastically simplified. This idea comes from the following situation: in the current cover layer systems, high-resolution photo-patternability is not always necessary for the formation of uncovered area (hole) with a diameter of ~ several hundreds μm. The important factors for screen-printing are: (1) ultimately high solid contents of the PI varnish in less hygroscopic solvents such as GBL and triglyme (common amide solvents such as N,N-dimethylacetamide and N-methyl-2-pyrrolidone are not applicable for the screen-printing) and (2) a thixotropic character of the PI varnish[3].

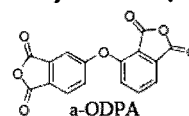
In this paper, we propose novel screen-printable ultra-low-modulus PI systems. The present work also describes the effects of a polymerization procedure with combination of copolymerization and blend techniques on the morphology and the mechanical properties of the cover layer.

2. Experimental Section

2.1. Choice of monomers

The choice of the monomers is one of the key strategies for achieving the target properties mentioned above. The molecular structures of the monomers used in this work are shown in Fig.1. In the present work, a flexible ether-containing tetracarboxylic dianhydride with a significantly bent structure, *i.e.*, 3,4'-oxydiphthalic anhydride (a-ODPA, Shanghai Research Institute of Synthetic Resins) was chosen with expectation of the formation of highly tough PI film in addition to the formation of homogeneous PI varnish with an extremely high solid content (> 50 wt%). The well-designed siloxane-containing diamine used here (Fig.1, n : m = 70 : 30, the average molecular weight = 1340) is reported in our previous papers [1,2]. 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) was also used as a comonomer to improve the film tractability since the homo PI derived from a-ODPA with the siloxane-containing diamine was too sticky. In this case, BAPP is probably more desirable than a common flexible diamine, 4,4'-oxydianiline, from the viewpoints of the solubility of the resultant PI in GBL.

Tetracarboxylic dianhydride



Diamines

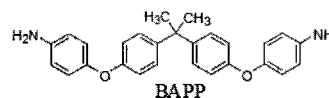
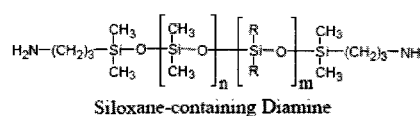


Fig.1 Structures of monomers used in this work.

2.2. Preparation of siloxane-containing PIs

(a) Random copolymerization

Our previous studies revealed that the tensile modulus of the cover layer materials must be lower than 0.3 GPa to avoid curling of the FPC. For this purpose, the copolymer composition was established at a fixed siloxane-containing diamine content of 66.6 mol% in the total diamine components. Random copolymerization was first carried out as follows: in a 100 mL four-necked separable flask equipped with a condenser, a nitrogen inlet, and a Dean-Stark trap, the siloxane-containing diamine (20 mmol) and BAPP (10 mmol) was dissolved in GBL (27 g) at 120°C in a nitrogen atmosphere. After cooling to room temperature, a-ODPA (30 mmol) powder was added to the diamine solution in one portion. The reaction mixture was stirred at room temperature for 1 h and successively heated at 180°C for 1 h in the presence of 5 g toluene as an azeotropic reagent to ensure complete imidization. This procedure allowed the formation of a PI varnish with a very high solid content of 60 wt%.

(b) Sequence-controlled copolymerization

Siloxane-containing copolyimides possessing non-random chain sequences were prepared by reactions between amine-terminated and anhydride-terminated oligoimides: a-ODPA powder (17 mmol) was added to a GBL solution of siloxane-containing diamine (Si-Da, 20 mmol), then the reaction mixture was refluxed at 180°C for 1 h in the presence of toluene to form an amine-terminated oligoimide (A-solution). In a separate flask, an anhydride-terminated oligoimide (B-solution) was also prepared from a-ODPA (13 mmol) and BAPP (10 mmol) in the same manner. A-solution was mixed with B-solution, then refluxed to form a sequence-controlled copolyimide (in this paper, we call it "block copolymer-1" although the chain sequence differs from common block copolymers) in GBL at an extremely high solid content of 60 wt%. Different block sizes of siloxane-containing copolyimides were also prepared by changing the monomer feed ratio at each step of the oligomer synthesis as listed in Table 1.

Table 1 The feed ratios of the monomers for block copolymer preparation.

Code	A-solution		B-solution	
	a-ODPA (mmol)	Si-Da (mmol)	a-ODPA (mmol)	BAPP (mmol)
Block copolymer-1	17	20	13	10
Block copolymer-2	15	20	15	10
Block copolymer-3	12	20	18	10

(c) Blend of the siloxane-containing homo PI with homo PI derived from a-ODPA with BAPP

The siloxane-containing homo PI and a-ODPA/BAPP homo PI were separately polymerized in GBL as described above. These PI solutions obtained were vigorously mixed at the same mol ratio (Si-Da/BAPP = 20/10) as the copolymers by a mechanical homogenizer.

2.3. Measurements

The number- and weight-averaged molecular weights and their distributions of the siloxane-containing copolyimides (0.5 wt% in THF) were estimated by gel permeation chromatography (Shodex GPC system-21) equipped with a RI detector and multiply connected columns (KF-G, KF-606, KF-605, KF-604, KF-601, and KF-600D) at 40°C at a flow rate of 1 mL/min on the basis of standard polystyrenes.

The storage- (E') and the loss modulus (E'') of the PI specimens (30 mm long, 10 mm wide, and typically 50 μ m thick) were measured in a temperature range of -100 to 200°C at a heating rate of 5°C/min with a frequency of 10 Hz to determine glass transition temperatures (T_g) from the peak temperatures in the E'' curve by the dynamic mechanical analysis (DMA) on TA Instruments,

DMA-Q800.

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of fully cured PI films at a heating rate of 10°C/min in nitrogen and air. Thermal stability of fully cured PI films was estimated from the 5 % weight loss temperatures (T_d^5).

Tensile modulus (E), the elongation at break (ϵ_b), and tensile strength (σ_b) of the PI specimens (30 mm long, 3 mm wide, and typically 50 μ m thick) were measured on a stretching testing machine (Toyo Baldwin, A&D at present, Tensilon UTM-II) with a crosshead speed of 8 mm/min.

3. Results and Discussion

3.1. Solution homogeneity

The mechanical blending between the homo PI systems in GBL led to a very turbid fluid solution, then it macroscopically phase-separated to an upper and a lower clear layer after standing for a prolonged time, indicating that it is an essentially immiscible combination. On the other hand, the solution of the as-polymerized random copolymer remained homogeneous during prolonged storage at room temperature without any precipitation and gelation. A pronounced block size effect on the solution homogeneity was observed: block copolymer-1 and 2 provided turbid solutions, whereas a completely homogeneous solution was obtained for block copolymer-3 system as well as for the random copolymer.

3.2. Characterization of siloxane-containing copolyimides

The FT-IR and $^1\text{H-NMR}$ spectra (in DMSO-d_6) of the copolyimides indicated that thermal imidization in the solutions was completed. **Fig.2** shows the GPC curves of the siloxane-containing copolyimides. A small peak is commonly observed regardless of the block size at a retention time of 21.5 min. The GPC measurements of the siloxane-containing diamine monomer itself and the FT-IR analysis of this fraction revealed that the small GPC peak corresponding to a molecular weight of ca. 500 comes from some non-functionalized siloxane components originally contained in the monomer. The GPC curves of these block copolymers (#1–3) were almost overlaid with a usual unimodal shape as well as in the corresponding random copolyimide system. The unimodal GPC curves suggest that the “chain-extension” reactions were indeed allowed between the amine-terminated and the anhydride-terminated oligomers, although the 60 wt% solutions were turbid for block copolymer-1 and 2. The data of M_n , M_w , and M_w/M_n are summarized in **Table 2**.

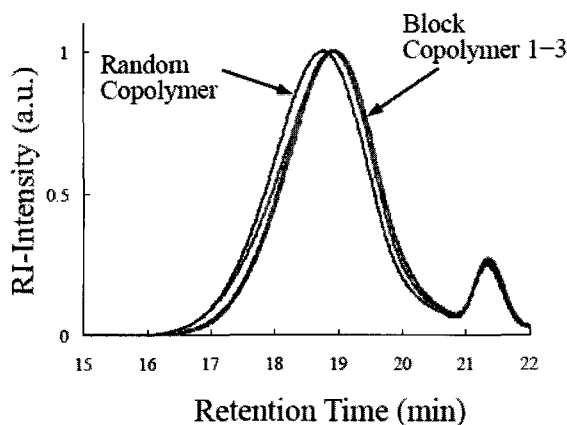


Fig.2 GPC charts of siloxane-containing copolyimides.

Table 2 Molecular weights and its distributions of siloxane-containing copolyimides.

Code	η_{red} (dL/g)	M_n	M_w	M_w/M_n
Block copolymer-1	----	11000	28100	2.56
Block copolymer-2	----	10400	26800	2.58
Block copolymer-3	0.167	11000	31100	2.82
Random copolymer	0.264	12200	33900	2.82

3.3. Film Properties

Block copolymer-1 film was very sticky. The relative surface tackness decreased in to following order: block copolymer-1 > 2 > 3 > random copolymer, which is probably related to the morphologies as discussed later.

Fig.3 displays the DMA curves of block copolymer-3 and the random copolymer. Below -30°C , these films possessed almost a constant E' of ~ 2 GPa common to glassy polymers. The results indicate that the molecular motion of the siloxane segments is practically frozen below -30°C . The copolyimide films showed a single glass transition as the peak temperature of the E' curves at a comparable temperature ($\sim 0^{\circ}\text{C}$). Thus, almost no influence of the chain sequence on the T_g 's was observed. In contrast, one notices a large difference of the E' values above room temperature; the block copolymer-3 exhibited a much lower E' values than the corresponding random copolymer with the same composition. This probably arises from different morphologies as discussed later.

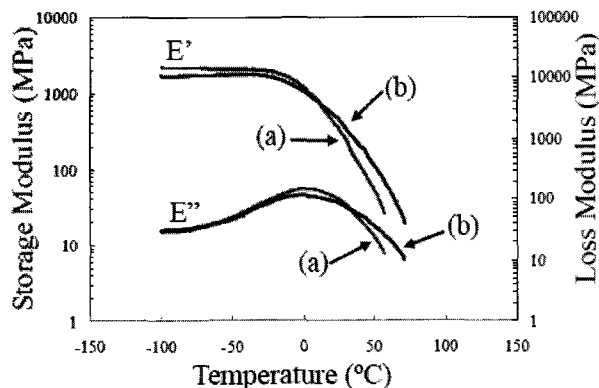


Fig.3 DMA curves of block copolymer-3 (a) and random copolymer (b).

Table 3 summarizes the basic film properties of block copolymer-3 and the random copolymer. The T_g 's determined from an inflection point in the TMA curves where the specimen length abruptly increased were approximately at 50°C for both samples. These systems possessed excellent film toughness ($\alpha_b > 250\%$) and relatively high thermal stability as illustrated from the T_d^5 values exceeding 400°C even in an air atmosphere. The random copolyimide film showed an ultra-low tensile modulus of 0.06 GPa. However, it should be noted that block copolymer-3 possessed a further decreased tensile modulus (0.015 GPa) in spite of the same copolymer composition.

Code	T_g ($^{\circ}\text{C}$) (by DMA)	T_g ($^{\circ}\text{C}$) (by TMA)	E (GPa)	α_b (av) (%)	α_b (MPa)	T_d^5 (in N_2) ($^{\circ}\text{C}$)	T_d^5 (in air) ($^{\circ}\text{C}$)
Block copolymer-3	1.9	48	0.015	253	7.0	419	412
Random copolymer	-1.1	50	0.060	370	4.0	435	434

Table 3 Film properties of siloxane-containing copolyimide systems.

In order to investigate the mechanism, the cross sections of the siloxane-containing copolyimide films were observed by a metallurgical microscope (Olympus, Metal Microscope-BX51). As shown in Fig.4(a), a typical sea-island structure are observed for block copolymer-2 system, where the spherical domains consisting of the BAPP-based hard segments are dispersed in the continuous phase consisting of the siloxane-based soft segments. On the other hand, in Fig.4(b), the block copolymer-3 layer seems to be homogeneous system as well as the random copolymer system. Our hypothesis is that the block copolymer-3 forms a metallurgical microscope-undetectable much finer sea-island structure in contrast to the random copolymer system. The higher relative surface tackness for the block copolymer systems than for the random copolymer is probably attributed to the presence of the siloxane-rich continuous "sea" phases.

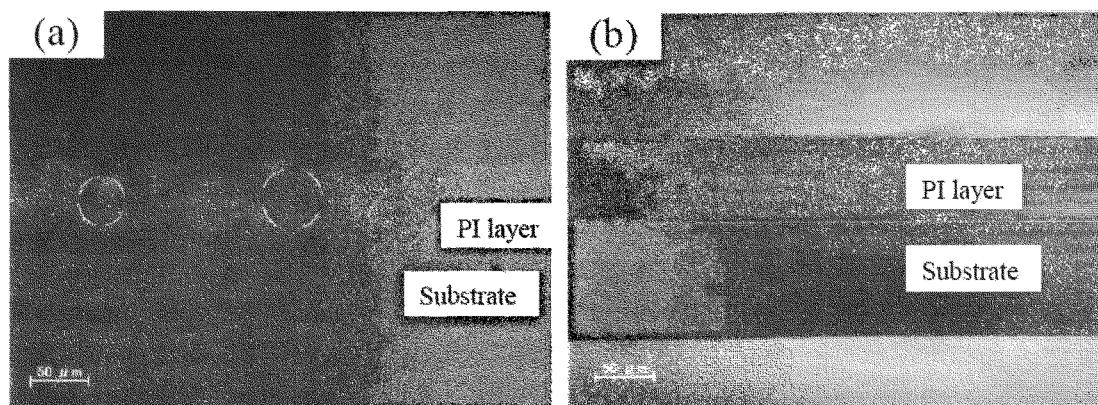


Fig.4 The morphologies of the film cross sections observed by metallurgical microscope photographs: (a) block copolymer-2 and (b) block copolymer-3.

3.4. Screen-printability

We first attempted screen-printing of the present siloxane-containing copolyimide varnishes without any additives onto a copper foil through a screen mask with a total thickness of 135 μm (Murakami Co., SUS 150-60). However, the screen-printability for fine pattern formation was not always sufficient although the solid contents were extremely high (60 wt%). Then a thixotropy modifier (Nippon Aerosil Co., Aerosil-RY200) was added to the copolyimide varnishes at a minor content of 10 phr. **Fig. 5** displays a screen-printed pattern (20 μm thick) with a line and space of 600/400 μm, which was formed by drying at 100°C for 10 min after the printing process. As shown in this optical microscopic photograph, practically sufficient screen-printability was obtained by this approach without sacrificing other target properties.

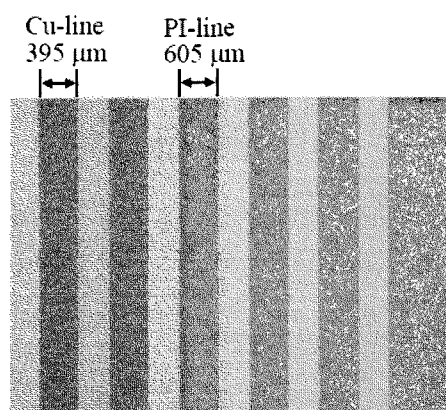


Fig.5 A screen-printed test pattern using the GBL solution of block copolymer-3 and additive.

4. Conclusions

The siloxane-containing random copolyimide prepared from a-ODPA with siloxane-containing diamine and BAPP at 60 wt% showed an extremely low E , thereby curling of FPC was suppressed. The sequence control caused a further decreased E , which can be explained from a sea-island phase-separated morphology. The addition of a thixotropy modifier improved screen-printability without sacrificing other target properties.

References

- (1) J. Ishii, T. Sunaga, M. Nomura, H. Kanaya, *J. Photopolym. Sci. Technol.*, **21**, 107 (2008).
- (2) J. Ishii, K. Morita, M. Hasegawa, *J. Photopolym. Sci. Technol.*, **22**, 417 (2009).
- (3) M. Hasegawa, K. Morita, J. Ishii, *J. Photopolym. Sci. Technol.*, **23**, 495 (2010).