Solution-processable Low-CTE Polyimides (5). Applications to Cover Layer Materials in Flexible Printed Circuit Boards

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Abstract: This work proposes practically useful novel coating-type cover layer materials. A copolyimide (PI) system derived from pyromellitic dianhydride (PMDA, 50 mol%), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA, 50 mol%) with 2,2′-bis(trifluoromethyl)benzidine (TFMB) showed a low coefficient of thermal expansion (CTE) upon thermal imidization. However, this system was not compatible to the chemical imidization process because of gelation. A structural modification of this copolymer by 2-trifluoromethyl-4,4′-diaminodiphenyl ether (3FODA) improved the solubility, as a result, allowed chemical imidization in a homogeneous state and the formation of a stable PI solution from *N*-methyl-2-pyrrolidone (NMP). The NMP-cast PI film of the copolyimide with 3FODA = 25 mol% displayed excellent combined properties; a low CTE (20.7 ppm K^{-1}), a very high T_g (311 °C), and a common level of tensile properties [modulus (E) = 3.2 GPa and the elongation at break (ε_b^{max}) = 5.1%]. The structural modification of PMDA(50);s-BPDA(50)/TFMB copolymer by the ether-linked fluorinated diamine (3FODA) was an effective way to obtain almost satisfying target properties except for a high level of ε_b. A mechanism was proposed for explaining why the effect of the CF_3-substituted ether-linked diamine on the toughness improvement was not so prominent. An alternative approach using some CF_3-free ether-linked monomers enabled us to drastically enhance the film toughness (ε_b^{max} > 50%) while maintaining low CTE characteristics and good solution-processability. Thus, some of the PI systems can be promising candidates as novel coating-type cover layer materials.

Keywords: Polyimide, Low coefficient of thermal expansion (CTE), Toughness, Solution processability, Flexible printed circuit board, Cover layer

1. Introduction

Aromatic polyimides (PIs) have been applied as dielectric layers in various electric/electronic components such as flexible printed circuit boards (FPC) for their distinctive features, i.e., outstanding heat resistance, electric insulation reliability based on an extremely high purity (practically no ionic/metallic contaminations), good mechanical properties, and simple manufacturing processes **[1−6]**. In FPCs, PIs are primary used as dielectric substrates (12–50 μm thick) on which printed circuits are formed. Recently, the dielectric substrates (called “base films”) are needed to possess high dimensional stability against both of heating/cooling cycles and water/moisture absorption in the FPC fabrication processes. For this purpose, we have so far proposed a molecular design for simultaneously controlling the coefficients of thermal expansion (CTE) and the humidity expansion (CHE) while keeping the excellent properties inherent to conventional PIs **[7−9]**. In the conventional FPCs, PIs are also used as protective films (cover layers) for the printed circuits. In this case, the printed circuits are covered by thermo-compressing the protective films (12–50 μm thick) pre-coated with a thermo-setting adhesive layer (15–35 μm thick) on the single face. More recently, a problem is pointed out in the conventional FPCs; i.e., a spring-back property arising when they are mounted in narrow

spaces after three-dimensionally folded at a low curvature radius. The intensive restoring forces against bending can be responsible for a decrease in the reliability of electric connection with other electronic components.

One of the effective strategies for reducing the spring-back property is to replace the conventional (laminate-type) protective films by the coating-type ones, thereby the "stiffness" (consequently, the restoring forces) of the FPCs can be minimized by a decrease in the total FPC thickness. If stable PI solutions are available, adhesive-free protective layers could be directly formed on the printed circuits via simple solution casting (coating and drying) by means of a screen-printing technique without the subsequent thermal imidization process. However, as long as common aromatic PI systems are used as the coating materials, significant curing of the FPCs is unavoidable. To solve this problem, we have studied coating-type ultra-low modulus cover layer materials **[10−12]**. However, this system is inferior to the conventional laminate-type cover films in the circuit break down resistance against repeated bending, although the former is sufficiently resistant to single bending. This probably results from the too low modulus of the cover layer itself, thereby the conductive layers suffer the stress concentration. The present work proposes novel coating-type overcoat materials for solving such crucial problems (curling and insufficient bending stress resistance).

2. Experimental

PI precursors, poly(amic acid)s (PAAs) were prepared by polyaddition of tetracarboxylic dianhydrides and diamines as shown in **Figure 1**. A typical procedure for random copolymerization is as follows: 2,2′-bis(trifluoromethyl)benzidine (TFMB, 2.25 mmol) and 2-trifluoromethyl-4,4′-diaminodiphenyl ether (3FODA, 0.75 mmol) was dissolved in anhydrous *N*-methyl-2-pyrrolidone (NMP). The mixed powder of pyromellitic dianhydride (PMDA, 1.5 mmol) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA, 1.5 mmol) was slowly added to this solution with continuous stirring. The reaction was started at an initial total solute content of 40 wt% (final solute content; 31.9 wt%). The reaction mixture was stirred at room temperature typically for 72 h to form a viscous/homogeneous PAA solution.

PAAs were converted to PIs by different methods (thermal and chemical imidization) as shown in **Figure 1**. Chemical imidization was carried out as follows: a mixture of acetic anhydride (Ac_2O) and pyridine (7/3, v/v) was slowly added with vigorous stirring at room temperature into a PAA solution adequately diluted with NMP (5–10 wt%) at a fixed molar ratio of $[Ac_2O]/[COOH]_{PAA} = 5$, and stirred for 24 h at room temperature in a sealed flask. After the reaction, the solutions were adequately diluted with the same solvent, and very slowly poured into a large quantity of methanol as a poor solvent. The fibrous precipitate formed was repeatedly washed with methanol, collected by filtration, and dried at 80 °C in vacuum for 12 h. The dried precipitate was re-dissolved in a fresh anhydrous solvent (NMP). The homogeneous PI solutions were coated on a glass substrate and dried typically at 80 °C for 1.5 h in an air convection oven, and successively heated typically at 250 °C for 1 h in vacuum on the substrate. After peeling them off from the substrate, the PI films (typically 20 μm thick) were annealed typically at 250–300 °C for 1 h in vacuum to remove residual stress. The drying/annealing conditions were finely adjusted to obtain better quality of PI films. The samples prepared via chemical imidization are denoted as "C" in this work.

PI films were also prepared via the conventional two-step process (PAA film formation and successive thermal imidization); PAA solutions were coated on a glass substrate, and dried at 80 °C for 1.5 h in an air-convection oven. The PAA films formed were heated typically at 250 °C/1 h + 350 °C/1

h in vacuum to transform into PI films (typically 20 μm thick). After peeling them off from the substrate, the PI films (typically 20 μm thick) were annealed at established temperatures (250–300 °C) for 1 h in vacuum to remove residual stress. The thermal conditions were finely adjusted to obtain better quality of PI films. The samples prepared via thermal imidization are denoted as "T".

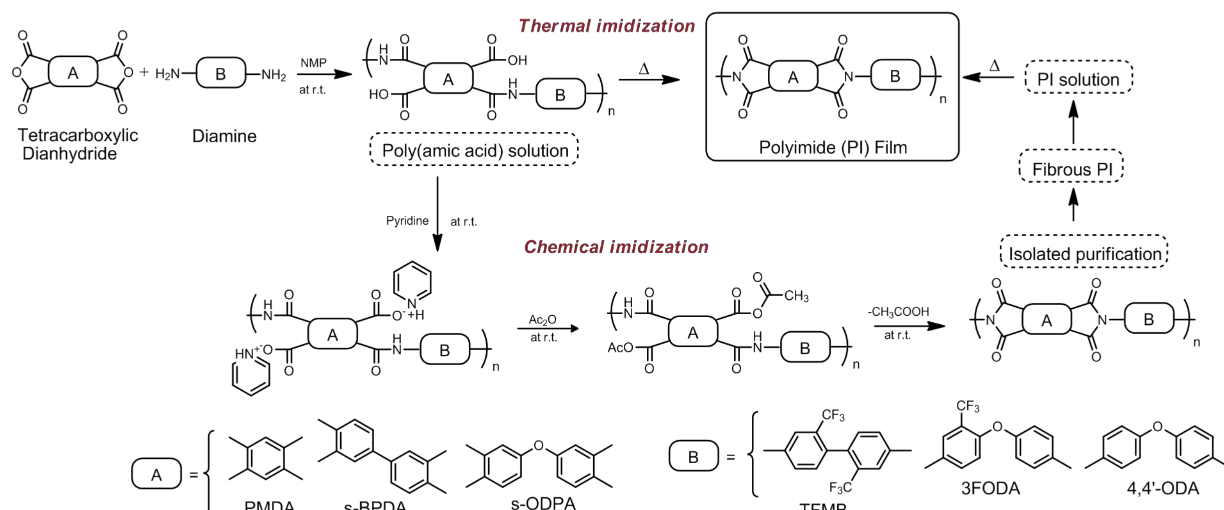

Figure 1 Reaction schemes for polyaddition and imidization of poly(amic acid)s and structures of monomers used.

3. Results and Discussion

3.1. Solubility and Low-CTE characteristics

As mentioned above, the adhesive-free PI cover layers are formed by coating the PI solutions on the printed circuits or the etched area (the exposed face of low-CTE base film). For simplification, we consider here two types of the laminates, i.e., PI/copper foil and PI/low-CTE base film. In this case, curling occurs by thermal stress ($\Delta\sigma$), which is expressed as a definite integral from a drying temperature (T_{dry}) to room temperature (T_{rt}) as Eq. (1) **[13–15]**:

$$\Delta\sigma = \int_{T_{\mathrm{dry}}}^{T_{\mathrm{rt}}} E_{\mathrm{f}}(1-\nu_{\mathrm{f}})^{-1}(\alpha_{\mathrm{s}}-\alpha_{\mathrm{f}})\mathrm{d}T \qquad (1)$$

where E_{f} and ν_{f} are the modulus and the Poisson′s ratio for the cover films, respectively. α_{s} and α_{f} are the CTEs along the X–Y direction for the substrates (copper foils or low-CTE PI base films in the present case) and the cover layers, respectively. The base films usually have a low CTE close to that of copper foil (18–20 ppm K^{-1}). According to equation (1), curling is avoidable by significantly decreasing either the cover layer moduli or the CTE mismatch ($\alpha_{\mathrm{s}} - \alpha_{\mathrm{f}}$) between the cover layers and the substrates. Indeed, the application of the ultralow-modulus PIs containing a siloxane block as the cover layers was an effective way to cancel the curling problem **[10]**. However, this approach was disadvantageous in terms of the bending resistance as mentioned above. Thus, in the present work, we decided to take the strategy toward minimizing the CTE mismatch by lowering the CTE of the cover layer materials themselves, because the molecular design for this purpose also brings about an increase in the modulus of the cover layer, which is also favorable for improving the bending resistance.

Therefore, the aim of the present work is to obtain practically useful solution-processable (screen-printable) PI systems, which can induce low CTE characteristics by simple solution casting. The key parameter for achieving this purpose is chemical imidization process compatibility; complete chemical imidization is disturbed by gelation unless the imidized forms were highly soluble. However,

the molecular designs toward low CTE generation usually prevent chemical imidization in a homogeneous state. For example, the PMDA/TFMB system, which produces a very low CTE (–4.7 ppm K^{-1}) upon thermal imidization **[16,17]**, suffers gelation in the chemical imidization process, as well as s-BPDA/TFMB (CTE = 33.8 ppm K^{-1} for the thermally imidized film) **[16,18]**. Gelation was also inevitable in the PMDA(50);s-BPDA(50)/TFMB copolymer system **[10]**. On the other hand, the PMDA(50);s-BPDA(50)/TFMB copolymer systems modified using the ether-linked CF_3-substituted diamine (3FODA) allowed chemical imidization in a homogeneous state over the wide diamine compositions.

The PMDA(50);s-BPDA(50)/TFMB;3FODA copolymers (C) were soluble in less hygroscopic solvents such as triglyme (TriGL), γ-butyrolactone (GBL), and cyclopentanone (CPN) at room temperature. However, it was difficult to form stable solutions using these non-amide solvents with high solid contents enough for solution casting. Therefore, the PI films were prepared from the NMP solutions (5–18 wt%). **Table 1** summarizes the film properties of PMDA(50);s-BPDA(50)/TFMB;3FODA. It should be noted that a low CTE of 20.7 ppm K^{-1} was achieved at an adequate 3FODA content (25 mol%), although the film toughness was insufficient (ε_b^{max} = 5.1%). Thus, the partial use of 3FODA did not cause a significant CTE increase. This predominance is likely attributed to unexpectedly restricted internal rotation by a steric hindrance effect arising from the *ortho*-substituted CF_3 group (**Figure 2**). This situation would be profitable for withstanding orientational relaxation. An increase in the 3FODA content was distinctly effective to improve the film toughness as listed in **Table 1**. Unfortunately, a significant increase in the CTE was inevitable at higher 3FODA contents (≥ 75 mol%), thus indicating the difficultness of achieving low CTE and good toughness (high ε_b) at the same time.

Table 1 Properties of PMDA(50);s-BPDA(50)/TFMB modified with CF_3-substituted ether-linked diamine (3FODA).

System No.	3FODA (mol%)	η_{red} (dL g^{-1})	Imidization method	Solubility in NMP [b] (wt%)	T_g (°C)	T_d^5 (N_2) (°C)	CTE (ppm K^{-1})	$\varepsilon_{b\ ave/max}$ (%)	E (GPa)
1	0	0.92 [a]	T	---	363	515	12.8	7.4/11.9	4.4
2	25	0.81 [a] 0.94 [b]	C	18.0	311	509	20.7	3.4 / 5.1	3.2
3	50	0.61 [a] 1.09 [b]	C	18.0	297	547	24.9	6.6 / 9.3	3.4
4	75	0.46 [a] 1.24 [b]	C	18.0	294	541	32.5	8.6 / 13.1	2.9
5	100	0.68 [a] 1.08 [b]	C	5.0	287	505	38.4	15.9 / 32.2	2.5

[a] Data for PAA solutions after polymerization. [b] Data for chemically imidized powder samples.

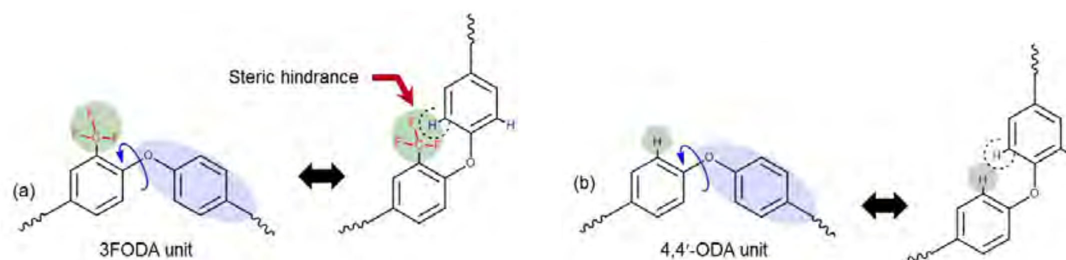

Figure 2 Predicted rotational motions with different barriers for (a) 3FODA and (b) 4,4′-ODA units.

3.2. Attempts of toughness improvement

In the PMDA(50);s-BPDA(50)/TFMB(75);3FODA(25) system, the replacement of PMDA by 4,4′-oxydiphthalic anhydride (s-ODPA) can be expected to improve the PI film toughness. However, in fact, this approach was less effective as listed in **Table 2**, although the low CTE property did not significantly deteriorate unexpectedly. To dramatically improve the film toughness, we used a CF_3-free ether-linked diamine; i.e., 4,4′-ODA instead of 3FODA. The NMP-cast film for s-ODPA(50);s-BPDA(50)/TFMB(75);4,4′-ODA(25) system (C) achieved a significantly enhanced toughness (ε_b^{max} > 50%). Surprisingly, this approach swept away our initial concern; i.e., undesirable property deterioration (significant CTE increase and T_g decrease) accompanied by the simultaneous use of flexible ether-containing 4,4′-ODA and s-ODPA as shown in **Table 2**. The 4,4′-ODA-modified copolyimide system was suitable for the chemical imidization process. However, it was difficult to form a stable PI solution with a high solid content from less hygroscopic solvents such as TriGL and GBL. This is attributed to a decrease in the CF_3 content by using 4,4′-ODA. For all the samples examined in this work, a CTE–toughness (ε_b^{max}) relationship was plotted in **Figure 3**, where the target properties are temporally established as CTE ≤ 20 ppm K^{-1} and $\varepsilon_b \geq 20\%$. Even if the CTE values of PIs developed in this work were much lower than that of copper foils (18–20 ppm K^{-1}), such PIs would be acceptable because too low CTE values can be simply adjusted to ~ 20 ppm K^{-1} by copolymerization with various ether-linked diamines at proper contents. Our previous work illustrated that there is a good linear relationship for a series of poly(ester imide)s, where the film toughness decreases with decreasing CTE **[9]**. Although no distinct linear relationship was observed in **Figure 3**, the results represent that it is not easy to simultaneously accomplish low CTE and high ε_b as indicated from the fact that there are scarcely data points near the target area. Nonetheless, the data for our copolyimide system (#7) was positioned near the target area. Thus we obtained a promising candidate of coating-type cover layer materials.

Table 2 Properties of s-BPDA(50);s-ODPA(50)/TFMB modified with ether-linked diamines (3FODA and 4,4′-ODA) via "C".

System No.	Modifier (mol%)	η_{red} (dL g^{-1})	Solubility in NMP [b] (wt%)	T_g (°C)	T_d^5 (N_2) (°C)	CTE (ppm K^{-1})	$\varepsilon_{b\ ave/max}$ (%)	E (GPa)
6	3FODA (25)	1.15 [a] 1.29 [b]	10.0	243	524	27.7	8.5 / 11.0	3.6
7	4,4′-ODA (25)	1.58 [a] 1.77 [b]	10.0	272 [c]	526 [c]	25.8 [c]	29.7 / 51.6 [c]	3.4 [c]

[a] Data for PAA solutions after polymerization. [b] Data for chemically imidized powder samples.
[c] Thermal condition is 150 °C/0.5h + 200 °C/0.5h + 250 °C/1h

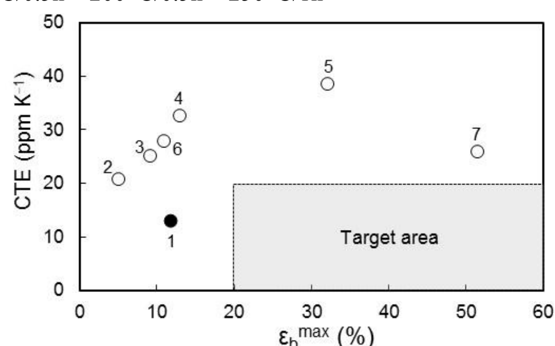

Figure 3 CTE−ε_b diagram for PI films prepared by different methods: (○) chemical and (●) thermal imidization. The numbers inserted refer to system numbers listed in Tables 1 and 2.

4. Conclusions

Novel practically useful coating-type cover layer materials were developed in this work. The PMDA(50);s-BPDA(50)/TFMB system was modified with ether-linked fluorinated diamine (3FODA). At 3FODA = 25 mol%, the NMP-cast film displayed the lowest CTE (20.7 ppm K^{-1}) among the PIs examined in this work. Thus, the structural modifications of PMDA(50);s-BPDA(50)/TFMB with 3FODA were an effective way to obtain almost satisfying target properties except for a high level of ε_b. A mechanism was proposed for explaining why the effect of the CF_3-substituted ether-linked diamine on the toughness improvement was not so prominent. The approach simultaneously using s-ODPA and 4,4′-ODA with adequate contents enabled us to drastically enhance the film toughness ($\varepsilon_b^{max} > 50\%$) while maintaining low CTE characteristics and good solution-processability. Thus, some of the PI systems can be promising candidates as novel coating-type cover layer materials.

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