

Synthesis and Property Measurements of Polyimides with Substituted Pyromellitic Dianhydride for Flexible Printed Circuits Applications

J. K. Choi, T. H. Yoon

Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Buk-gu, Gwangju 500-712, Korea

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ABSTRACT: Pyromellitic dianhydride-based dianhydrides with bulky substituents, such as 1-phenyl pyromellitic dianhydride and 1-(4'-trifluoromethylphenyl)pyromellitic dianhydride, were combined with bis(3-aminophenyl)phenylphosphine oxide and 4,4'-phenylene diamine to prepare polyimides with low coefficient of thermal expansion (~ 17 ppm/ $^{\circ}\text{C}$) and good adhesion (>100 g/mm). The polyimides were synthesized via a conventional two-step process: preparation of poly(amic-acid) followed by solution imidization with *o*-dichlorobenzene. The molecular weights of the poly-

imides were controlled to 25,000 g/mol via off-stoichiometry and the synthesized polyimides were characterized by Fourier transform infrared, nuclear magnetic resonance, differential scanning calorimetry, and thermogravimetric analysis. Their intrinsic viscosity and solubility were also measured, while adhesive property was measured via T-peel test samples of Cu/polyimide. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 736–741, 2010

Key words: polyimides; synthesis; adhesion; FPC; CTE

INTRODUCTION

With the electronic devices becoming smaller and lighter, there has been an increasing demand for flexible printed circuits (FPCs) to replace heavy composite-based printed circuit boards (PCBs). FPCs are, in general, made from Cu foil and polymeric films, requiring polymers utilized to have low coefficient of thermal expansion (CTE) and good adhesion, in addition to high glass transition temperature (T_g), good thermal stability, and low water absorption.^{1,2} Considering these requirements, aromatic polyimides are promising candidates due to their excellent thermal, mechanical, and electrical properties, high thermal and oxidative stabilities, good chemical resistance, and high dimensional stability.^{3,4}

Early FPCs were prepared by the adhesive bonding of polyimide film to Cu foil with adhesives such as acrylics, polyesters, phenolics, epoxies, and polyimides,^{1,2} called three-layer FPCs. However, due to the poor thermal stability of most adhesives, adhesive failure at the Cu/polyimide interface was often observed, especially at high temperatures. Conse-

quently, nonadhesive techniques such as direct casting of polyimide solution on Cu foil, and sputtering and plating of Cu on polyimide films, have been introduced, which are called two-layer FPCs. For both approaches, low CTE of polyimides is necessary, which has led to considerable research efforts being focused on lowering the CTE of polyimides by utilizing rigid-rod-type monomers,^{5–7} resulting in polyimides with CTE of 17 ppm/ $^{\circ}\text{C}$ or lower.

The other requirement for the sputtering/plating process is good adhesion of Cu to polyimide films. Consequently, surface modification of polyimide films by plasma etching,⁸ graft polymerization after ultraviolet radiation,⁹ low energy atomic beam,¹⁰ and plasma source ion implantation¹¹ have been investigated. In comparison, good adhesion as well as good solubility of polyimides are needed for the direct casting method. Most polyimides, however, are insoluble in polar solvents and thus poly(amic-acids) have been utilized, resulting in large volume shrinkage on thermal imidization, which in turn leads to large residual stress.¹² However, this problem has been solved by solution imidization carried out in the temperature range of 180–190 $^{\circ}\text{C}$ in the presence of azeotroping agent,¹³ resulting in soluble thermoplastic polyimides. In addition, structural modification of polyimides by incorporating imidazole,¹⁴ pyridine,¹⁵ or phosphine oxide groups^{16,17} has also been attempted to enhance the adhesive property.

Recently, there have been attempts to prepare soluble polyimides from rigid-rod-type dianhydrides

Correspondence to: T. H. Yoon (thyoon@gist.ac.kr).

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and diamine monomers with adhesion promoting functional groups via solution imidization, but they provided slightly inferior properties for FPC applications.^{18,19} In this study, therefore, it was attempted to prepare polyimides from pyromellitic dianhydride (PMDA)-based dianhydrides, a diamine with phosphine oxide moiety and 4,4'-phenylene diamine (*p*PDA). The polyimides were synthesized via a conventional two-step synthesis; preparation of poly(amic-acid), followed by solution imidization. They were characterized by Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), gel permeation chromatography, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and solubility measurements. The adhesive properties of new polyimides prepared were evaluated by the modified peel test samples of Cu/polyimide instead of Cu/polyimide/Cu samples which may exhibit poor thermal flow of the polyimide adhesive during the bonding process.

MATERIALS AND METHODS

Materials

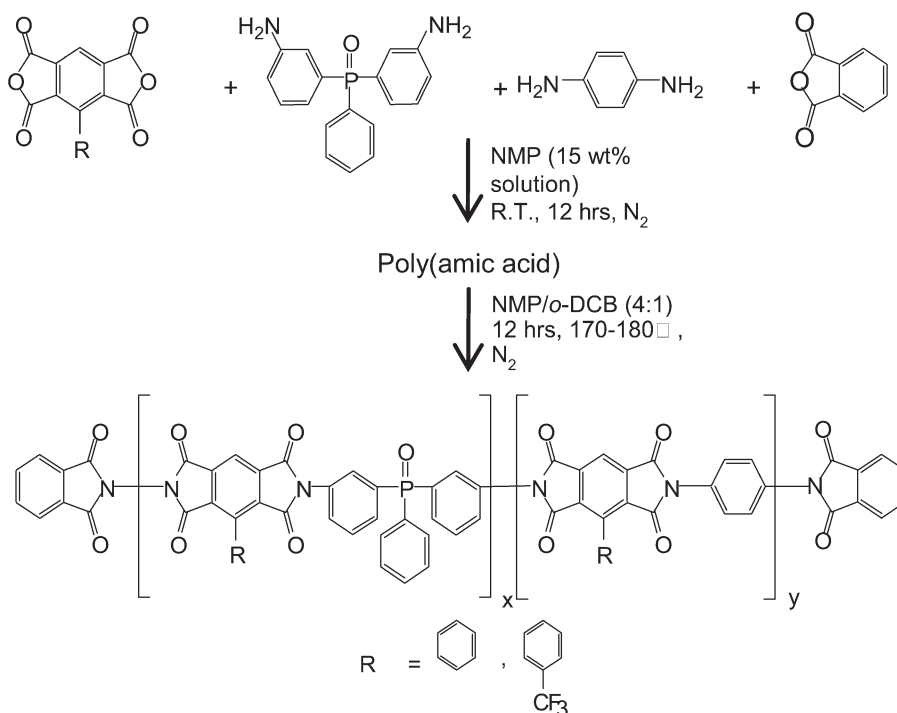
Monomers including 1-phenyl pyromellitic dianhydride (PPMDA) and 1-(4'-trifluoromethylphenyl)pyromellitic dianhydride (3FPPMDA)¹⁸ and bis(3-aminophenyl)phenylphosphine oxide (*m*DAPPO)¹⁶ were synthesized as reported previously, while *p*PDA and phthalic anhydride (PA) were purchased

from Aldrich (St. Louis, MO) and utilized after purification by recrystallization in ethanol and sublimation, respectively. Solvents such as 1-methyl-2-pyrrolidinone (NMP) and *o*-dichlorobenzene (*o*-DCB) were purified by distillation. Cr-silane-coated Cu foil from Sigma-Aldrich Inc. (0.018-mm thick) used in the adhesion study was supplied by LS Cable (Gyeonggi-do, Korea).

Synthesis and characterization of polyimides

The polyimides were prepared from dianhydrides, such as PPMDA and 3FPPMDA, and a diamine (*m*DAPPO) via a conventional two-step process: preparation of poly(amic-acid), followed by solution imidization with *o*-DCB (Scheme 1). In addition, *p*PDA was also utilized in combination with *p*PDA to lower the CTE further. The polyimides were designed to have a molecular weight of 25,000 g/mol by off-stoichiometry and nonreactive end-groups by reacting with phthalic anhydride.

Polymerization was carried out in a three-necked round-bottom flask equipped with a mechanical stirrer, drying tube, nitrogen inlet, and thermometer, and the reaction is described here for the polyimide of PPMDA-*m*DAPPO/*p*PDA (60/40). After flame drying under N₂ flow, the flask was charged with 1.8499 g (6 mmol) *m*DAPPO and 0.4326 g (4 mmol) *p*PDA, followed by the addition of 30 mL dried 1-methyl-2-pyrrolidinone at room temperature (RT). Upon complete dissolution of the diamines, 2.8855 g (9.81 mmol) of PPMDA and 0.0562 g (0.39 mmol) of



Scheme 1 Synthetic scheme of PPMDA and 3FPPMDA-based polyimides.

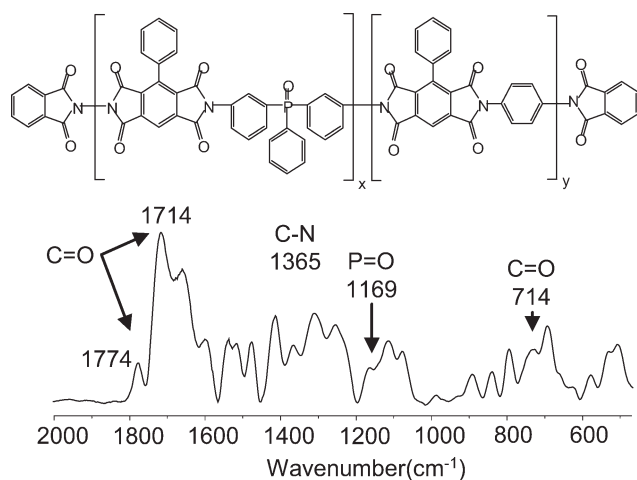


Figure 1 FTIR spectrum of PPMDA-*m*DAPPO/*p*PDA (60/40) polyimide.

PA were added. The mixture was reacted overnight to provide a poly(amic-acid) solution.

Solution imidization of poly(amic-acid) solution was carried out at 170–180°C for 12 h under N₂ flow in the presence of *o*-dichlorobenzene (20 v/v) as an azeotroping agent. Finally, the reaction mixture was precipitated into a water-methanol (1 : 1) mixture, filtered and dried in a vacuum oven, and then subjected to characterization. All other polyimides were prepared in the same manner. The polyimides were characterized by FTIR (Shimadzu, FTIR 8400S) by using KBr pellets, but NMR could not be performed due to the insolubility of polyimides in dimethyl-*d*₆ sulfide or chloroform-*d*.

The solubility of polyimides was evaluated by immersing the polymer film (5 mm × 5 mm) into solvents such as NMP, DMAc, CHCl₃, TCE, THF, acetone, and toluene at RT for 24 h at the polymer concentration of ~ 10 wt %. Solution viscosity was measured with a Cannon-Ubbelohde viscometer at 25°C in NMP. *T*_g values were measured by DSC (TA-2910) at 10°C/min while the thermal stability was evaluated by TGA (TA-2950) in air at 10°C/min. The CTE was measured by TMA (TMA-Q400) in the 50–250°C range from the 2nd heat after heating to 300°C at 5°C/min in air.

Adhesive property of polyimides

In this study, the peel test samples of Cu/polyimide, instead of ASTM D-903 T-peel test samples (Cu/polyimide/Cu), were utilized given that poor flow of polyimide adhesives was observed in the previous study due to the high *T*_g of polyimides.¹⁹ The Cu/polyimide samples were prepared by brush coating the polyimide solution (15 wt % in NMP) on Cu foil and drying at ~ 100°C for 15 min. The process was repeated until the coating thickness reached 0.04 mm, because the polyimide layer has to be thick enough to minimize plastic deformation during testing.

The samples were then dried for 1 h both at 200 and 250°C and for an additional 30 min at 300°C under nitrogen flow to prevent the oxidation of Cu foil. Finally, the polyimide-coated Cu foil was cut into 2 mm × 150 mm and its adhesive strength measured via a T-peel test at RT with Instron 5567 at a cross-head speed of 25.4 mm/min. The peel strength was measured from the middle of the sample with data from the initial 30 mm and the last 30 mm discarded, and at least four samples were tested. Scanning electron microscopy (SEM; JSM-5800) was utilized to investigate the failure mode at 15 kV and the samples were coated with gold to minimize the charging problem.

RESULTS AND DISCUSSION

Synthesis and characterization of polyimides

The polyimides prepared from rigid-rod-type dianhydrides such as PPMDA and 3FPPMDA and diamines such as *m*DAPPO and *p*PDA were characterized by FTIR. In the FTIR spectrum, the polyimide from PPMDA-*m*DAPPO/*p*PDA (60/40) exhibited imide carbonyl peaks at 1774 cm⁻¹ (symmetric stretching), 1714 cm⁻¹ (asymmetric stretching), and 714 cm⁻¹ (C=O bending), as shown in Figure 1. In addition, C–N stretching absorption (1365 cm⁻¹) and P=O stretching absorption (1169 cm⁻¹) appeared, but the amide-carbonyl (C=O) peak at 1650 cm⁻¹ was not observed, indicating successful polyimide synthesis.¹⁸

The polyimides of PPMDA-*m*DAPPO/*p*PDA, as well as the PPMDA-*m*DAPPO polyimides, were soluble only in NMP and DMAc, indicating that the

TABLE I
Solubility of PPMDA and 3FPPMDA-Based Polyimides

	<i>m</i> DAPPO/ <i>p</i> PDA	NMP	DMAc	CHCl ₃	TCE	THF	Tolu
PPMDA	100/0	S	S	I	I	I	I
	70/30	S	S	I	I	I	I
	60/40	S	S	I	I	I	I
3FPPMDA	100/0	S	S	S	S	S	P
	50/50	S	S	S	P	I	I
	40/60	S	S	S	P	I	I

Polyimide films at RT for 24 h (10 wt %). S, soluble; P, partially soluble; I, insoluble.

TABLE II
Characteristics of PPMDA and
3FPPMDA-based Polyimides

	<i>m</i> DAPPO/ <i>p</i> PDA	$[\eta]$ (dL/g) ^a	T_g (°C) ^b	T_g (°C) ^c	T_d (°C) ^d	Residue (wt %) ^e
PPMDA	100/0	0.25	320	325	522	29
	70/30	0.23	338	342	515	17
	60/40	0.22	342	345	517	12
3FPPMDA	100/0	0.26	315	321	522	15
	50/50	0.24	327	331	515	6
	40/60	0.26	333	340	515	2

^a At 25°C in NMP.

^b By DSC, 2nd heat, 10°C/min.

^c By TMA, 1st heat, 5°C/min.

^d By TGA, 5 wt % loss, 10°C/min in air.

^e By TGA at 800°C, 10°C/min.

addition of very rigid *p*PDA did not lower the solubility of polyimides (Table I). Good solubility, despite their rigid backbone structure, can be attributed to the phosphine oxide moiety and the non-coplanar characteristics of *m*DAPPO.¹⁷ In comparison, 3FPPMDA-*m*DAPPO polyimide was soluble in NMP, DMAc, and CHCl₃, while 3FPPMDA-*m*DAPPO/*p*PDA exhibited slightly poorer solubility, being soluble only in NMP and DMAc. Because all polyimides were soluble in NMP, intrinsic viscosities were measured in NMP with Cannon-Ubbelohde viscometer at 25°C, which resulted in values in the range of 0.22–0.26 dL/g (Table II), demonstrating well-controlled molecular weight, given the target molecular weight of 25,000 g/mol.

The polyimides from PPMDA and 3FPPMDA exhibited high T_g above 300°C (Fig. 2), which increased as *p*PDA increased, resulting in T_g of 342 and 333°C with PPMDA-*m*DAPPO/*p*PDA(60/40) and 3FPPMDA-*m*DAPPO/*p*PDA(40/60) (Table II), respectively. These polyimides also exhibited excellent thermal sta-

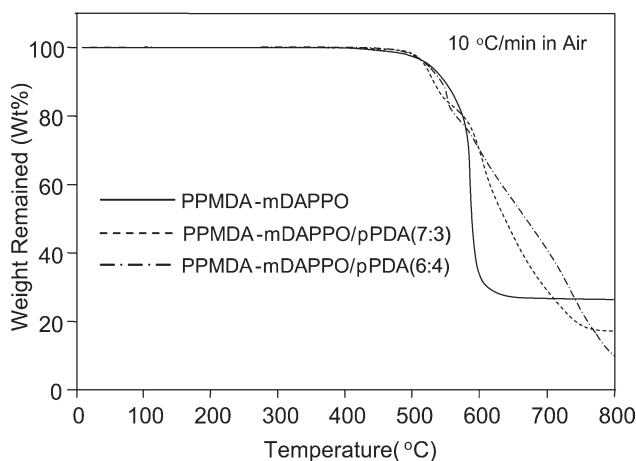


Figure 2 DSC thermogram of PPMDA-*m*DAPPO/*p*PDA polyimides.

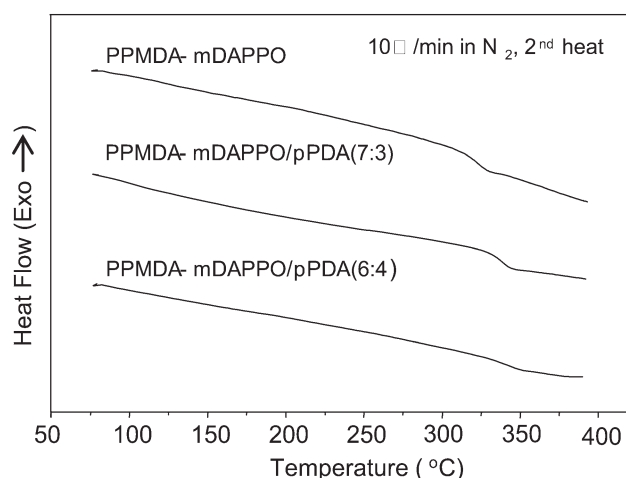


Figure 3 TGA thermogram of PPMDA-*m*DAPPO/*p*PDA polyimides.

bility in air, exhibiting 5% weight loss at temperatures 500°C or higher at 10°C/min (Fig. 3), and it was noted that the addition of *p*PDA slightly reduced the thermal stability in air.

The CTE decreased as the *p*PDA increased, as shown in Table III. The PPMDA-*m*DAPPO polyimide provided a CTE of 24.8 ppm/°C, which decreased to 19.5 and 17.6 ppm/°C at 30 and 40% *p*PDA, respectively. As expected, the 3FPPMDA-*m*DAPPO polyimide exhibited a slightly higher CTE value of 29.4 ppm/°C, compared to the PPMDA-*m*DAPPO polyimide, and the value decreased to 19.1 and 17.2 ppm/°C at 50 and 60% *p*PDA, respectively. Among the polyimides prepared, the polyimides of PPMDA-*m*DAPPO/*p*PDA (60/40) and 3FPPMDA-*m*DAPPO/*p*PDA (40/60) exhibited low enough CTE (~17 ppm/°C) for FPC applications, along with high T_g (>300°C), excellent thermal stability (>500°C), and good solubility (NMP and DMAc).

Adhesive properties of polyimides

The adhesive properties of polyimides were evaluated by using the Cu/polyimide peel test samples. As shown in Table III, the PPMDA-*m*DAPPO and 3FPPMDA-*m*DAPPO polyimides exhibited high peel

TABLE III
Peel Strength and CTE of PPMDA and
3FPPMDA-Based Polyimides

	<i>m</i> DAPPO/ <i>p</i> PDA	CTE ($\mu\text{m}/^\circ\text{C}$)	Peel strength (g/mm)
PPMDA	100/0	24.8	130.1 ± 8
	70/30	19.5	117.5 ± 9
	60/40	17.6	111.3 ± 7
3FPPMDA	100/0	29.4	121.2 ± 8
	50/50	19.1	109.7 ± 11
	40/60	17.2	104.1 ± 9

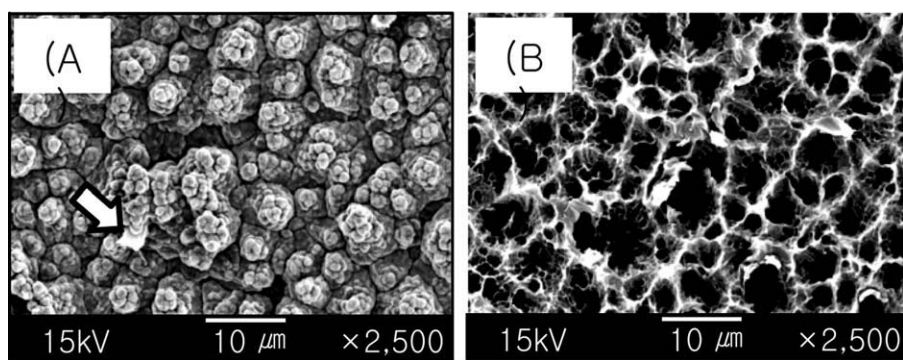


Figure 4 SEM micrographs of failure surface of PPMDA-*m*DAPPO/*p*PDA (60/40) polyimide (A) Cu foil side, (B) polyimide side.

strength of 130 and 121 g/mm, respectively, demonstrating the positive effect of adhesion promoting phosphine oxide moiety in *m*DAPPO, as well as the negative effect of fluorine moiety in 3FPPMDA.¹⁷ It was also noted that the peel strength of PPMDA-*m*DAPPO polyimide decreased to 117 and 111 g/mm at 30 and 40% *p*PDA incorporation, respectively, while that of 3FPPMDA-*m*DAPPO polyimide decreased to 109 and 104 g/mm at 50 and 60% *p*PDA, respectively. Decreased peel strength with *p*PDA incorporation can be attributed to the increased chain rigidity of polyimides.

Compared with the previous study, which reported peel strength of 94 and 91 g/mm with PPMDA-*m*DAPPO and 3FPPMDA-*m*DAPPO polyimides,¹⁹ much higher peel strength was observed in this study (130 and 121 g/mm). This difference can be explained by the different sample geometry: Cu/polyimide samples in this study compared to the Cu/polyimide/Cu samples in the previous study. The Cu/polyimide/Cu samples were prepared by the thermal lamination of polyimide-coated Cu foils and thus poor flow of polyimide adhesives was expected due to their high T_g . This was evidenced by the cohesive failure, which appeared as thick polyimide adhesive layers left on both sides of the Cu foil.

In this study, however, all samples exhibited a clean fracture surface of the Cu layer similar to that of the as-received Cu foil, with the exception of some small pieces of polyimide adhesives remaining [arrow in Fig. 4(A)], whereas the polyimide side showed a sponge-like morphology resembling the Cu foil [Fig. 4(B)]. Therefore, it can be said that the failure occurred at or near the Cu/polyimide interface, although the exact failure mode still has to be clarified by surface analysis techniques.

CONCLUSIONS

1. Soluble polyimides with high T_g (>300°C) and excellent thermal stability in air (>500°C) were

successfully synthesized from rigid-backbone dianhydrides with bulky side groups and diamines, along with adhesion promoting phosphine oxide groups, via the two-step process: preparation of poly(amic-acid) followed by solution imidization.

2. Synthesized polyimides exhibited a CTE of 24.8 (PPMDA-*m*DAPPO) and 29.4 ppm/°C (3FPPMDA-*m*DAPPO), which decreased to 17.6 [PPMDA-*m*DAPPO/*p*PDA(60/40)] and 17.2 ppm/°C [3FPPMDA-*m*DAPPO/*p*PDA(40/60)] with *p*PDA incorporation.
3. The polyimides of PPMDA-*m*DAPPO and 3FPPMDA-*m*DAPPO exhibited excellent peel strengths of 130 and 121 g/mm, respectively, but they decreased to 111 g/mm with PPMDA-*m*DAPPO/*p*PDA (60/40) and 104 g/mm with 3FPPMDA-*m*DAPPO/*p*PDA (40/60).
4. SEM analysis showed a clean Cu side with small pieces of the adhesive remaining, while the polyimide side exhibited a sponge-like morphology, indicating that the failure may have occurred at or near the Cu/polyimide interface.

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