Synthesis and characterization of polyimides for FPC applications

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Introduction

As the microelectronic devices became smaller and lighter, flexible printed circuit boards (FPC) have received great attention ever before. Among the materials for FPC, polyimides are the promising candidate due to their excellent thermal, mechanical and electrical properties, high dimensional stability, and good chemical resistance [1]. In FPC, polyimides have to have CTE of 17ppm since that of Cu is 17ppm and excellent adhesive property (>80g/mm), besides high Tg (>300°C), good thermal stability (>500°C), low water absorption and good solubility [2-3]. Consequently, research has been focusing on the preparation of novel polyimides with low CTE and good adhesion without sacrificing good thermal properties as well as solubility.

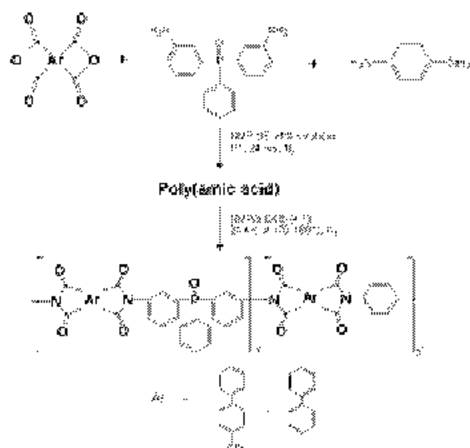
In order to lower CTE, one has to increase rigidity of polyimide backbone by utilizing rigid-rod type monomers. But these monomers would decrease solubility and processability [4-6], resulting in poor adhesion. Consequently, poly(amic-acid) instead of polyimide has been widely utilized, which is converted to polyimide by thermal imidization, leading to large volume shrinkage and thus large residual stress. Another inheritant drawback of polyimide for FPC is relatively poor adhesion property.

In this study, therefore, we attempted to prepare polyimides from mono-substituted PMDA-based rigid-rod type dianhydrides and diamines such as *m*DAPPO and pPDA, in order to prepare soluble processable polyimides with CTE of 17ppm and good adhesion properties besides excellent thermal, mechanical and good solubility.

Experimental

The monomers such as PPMDA, 3FPPMDA and *m*DAPPO were synthesized as reported previously, while pPDA was purchased from Aldrich and utilized after sublimation. The polyimides were prepared via a conventional two-step process; preparation of poly(amic-acid), followed by solution imidization by refluxing in NMP with *o*-DCB (Scheme 1).

In order to lower CTE of polyimides, pPDA was added by varying the molar ratio of *m*DAPPO/pPDA. The polyimides were designed to have a molecular weight of 25,000g/mol and characterized by FT-IR, NMR, DSC and TGA. In addition, intrinsic viscosity, solubility and coefficient of thermal expansion (CTE) were also measured. Adhesion property was evaluated via peel test with the samples prepared from polyimide coated Cu foils.



Scheme 1. Synthetic scheme of polyimides

Results and Discussion

The polyimides prepared from PPMDA and 3FPPMDA with *m*DAPPO/pPDA were characterized by FT-IR and NMR, demonstrating successful polymer synthesis. These polyimides were only soluble in NMP or DMAc among the solvents tested (Table 1). Despite rigid backbone structure, good solubility can be attributed to phosphine oxide segments and non-coplanar characteristics of *m*DAPPO. The intrinsic viscosities evaluated in NMP were in the range of 0.21-0.26 dl/g, demonstrating successful polymerization considering of the controlled molecular weight of 25,000g/mole.

The polyimide of PPMDA-*m*DAPPO provided Tg of 322°C, which increased as *p*PDA increased, providing Tg of 348°C with 40% *p*PDA. Compared to this, 3FPPMDA-based polyimides showed Tg of 319°C, which increased to 350 and 356°C at 50, 60% *p*PDA, respectively. These polyimides also exhibited excellent thermal stability in air, providing thermal degradation temperature of 500°C or higher in air at 10°C/min.

CTE value of PPMDA-*m*DAPPO based polyimide was 24ppm and decreased to 17.3ppm at 40%pPDA, while 3FPPMDA-*m*DAPPO polyimides provided CTE of 29 and 16.8ppm at 0 and 60%pPDA. As expected, CTE decreased as the *p*PDA increased.

Table 1. Solubility of mono-substitued PMDA-mDAPPO polyimides

	mDAPPO:PDA	NMP	DMAc	$CHCl_3$	TCE	THF	Toluene	Acetone
PPMDA	100:0	S	S	P	P	P	P	I
	70:30	S	S	P	I	I	I	I
	60:40	S	S	I	I	I	I	I
3FPPMDA	100:0	S	S	S	S	S	P	P
	50:50	S	S	S	P	I	I	I
	40:60	S	S	P	P	P	I	I

* Polyimide film at R.T. for 24hrs (10wt%)
* S : Soluble, P: Partially soluble, I : Insoluble

Table 2. Characteristics of mono-substitued PMDA-mDAPPO polyimides.

	mDAPPO :pPDA	[η][a] (dL/g)	T_g (°C)[b]	CTE[c]	T_d (°C)[d]	Residue (wt%)[e]
PPMDA	100:0	0.26	322	24.0	522	32
	70:30	0.21	337	20.9	513	30
	60:40	0.23	348	17.3	514	27
3FPPMDA	100:0	0.25	318	29.0	528	17
	50:50	0.22	350	18.6	520	13
	40:60	0.23	356	16.8	522	12

a. at 25 °C in NMP b. by DSC, 2nd heat 10°C/min
c. by TMA 5°C/min d. by TGA, 5wt% loss, 10°C/min in air
e. by TGA at 800 °C, 10°C/min in air

Conclusions

1. Polyimides of PPMDA-*m*DAPPO/*p*PDA and 3FPPMDA-*m*DAPPO/*p*PDA were successfully synthesized with molecular weight of 25,000 g/mol.
2. The polyimides exhibited high Tg, excellent thermal stability in air and good solubility in NMP and DMAc.
3. The CTE of 17ppm was obtained by adding pPDA of 40% (PPMDA-*m*DAPPO/*p*PDA) and 60% (3FPPMDA-*m*DAPPO/*p*PDA).

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