Adhesion Property of Novel Polyimides with 1-[3′,5′-Bis(trifluoromethyl)phenyl] Pyromellitic Dianhydride

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ABSTRACT: Novel polyimides were synthesized from 1-[3′,5′-bis(trifluoromethyl)phenyl] pyromellitic dianhydride (6FPPMDA) by a conventional two-step process: the preparation of poly(amic acid) followed by solution imidization via refluxing in *p*-chlorophenol. The diamines used for polyimide synthesis included bis(3-aminophenyl)-3,5-bis(trifluoromethyl)phenyl phosphine oxide, bis(3-aminophenyl)-4-trifluoromethylphenyl phosphine oxide, and bis(3-aminophenyl)phenyl phosphine oxide. The synthesized polyimides were designed to have a molecular weight of 20,000 g/mol by off-stoichiometry and were characterized by Fourier transform infrared, NMR, differential scanning calorimetry, and thermogravimetric analysis. In addition, their intrinsic viscosity, solubility, water absorption, and coefficient of thermal expansion (CTE) were also measured. The adhesion properties of the polyimides were evaluated via a T-peel test with bare and silane/Cr-coated Cu foils, and the failure surfaces were investigated with scanning electron microscopy. The 6FPPMDA-based polyimides exhibited high glass-transition temperatures (280–299°C), good thermal stability (>530°C in air), low water absorption (1.46–2.16 wt %), and fairly low CTEs (32–40 ppm/°C), in addition to good adhesion properties (83–88 g/mm) with silane/Cr-coated Cu foils. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1801–1809, 2005

Key words: adhesion; fluoropolymers; polyimides

INTRODUCTION

With microelectronic devices becoming smaller and lighter, better dielectric materials in interlayer dielectrics and flexible circuit boards are needed to minimize electrical power loss and delays in signal transmission.[1] Accordingly, a great deal of research has been carried out on enhanced dielectric polymeric materials. In particular, aromatic polyimides have received much attention because of their excellent thermal, mechanical, and electrical properties, good chemical resistance, and high dimensional stability.[2–6] As the dielectric properties are believed to be critical, considerable research effort has also been expended in improving the dielectric properties of polyimides through methods such as fluorination,[7–9] nanofoam technology,[10–12] adamantane/diamantane monomers,[13,14] and organic–inorganic hybrid composites.[15,16]

The fluorination of polyimides results in a very low dielectric constant of 2.3, along with enhanced solubility and reduced moisture absorption, because of the low polarity of fluorine moieties.[8] However, the fluorination method also has drawbacks, such as poor adhesion, a lowered glass-transition temperature (T_g), and an increased coefficient of thermal expansion (CTE).[7] One approach to improving the adhesion properties of fluorinated polyimides is to add the phosphine oxide moiety, which has been proved to be very effective in enhancing adhesion properties.[17,18] In our previous study, therefore, we attempted to prepare diamine monomers containing fluorine and phosphine oxide moieties, such as bis(3-aminophenyl)-3,5-bis(trifluoromethyl)phenyl phosphine oxide (*m*DA6FPPO)[19] and bis(3-aminophenyl)-4-trifluoromethylphenyl phosphine oxide (*m*DA3FPPO).[20]

Although polyimides prepared from these monomers exhibited good adhesion properties,[21] they had relatively low T_g values (247–260°C) and comparatively high dielectric constants (2.8–2.9 at 1 MHz). This led to the synthesis of new rigid-rod dianhydride monomers, such as disubstituted 3,6-di[3′,5′-bis(trifluoromethyl)phenyl] pyromellitic dianhydride (12FPMDA).[22] The polyimides prepared from 12FPMDA and diamines such as *m*DA6FPPO,[19] *m*DA3FPPO,[20] and bis(3-aminophenyl) phenyl phosphine oxide (*m*DAPPO)[23] exhibited very high T_g's, low dielectric constants, and very good adhesion properties.[24]

For comparison, in this study we attempted to prepare polyimides with a monosubstituted rigid-rod di-

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anhydride monomer, 1-[3′,5′-bis(trifluoromethyl)phenyl] pyromellitic dianhydride (6FPPMDA), in an attempt to lower the T_g values of polyimides and improve their processability. The polyimides were prepared via a conventional two-step process: the preparation of poly(amic acid) in *p*-chlorophenol, followed by solution imidization at the reflux temperature of *p*-chlorophenol in the presence of isoquinoline. In addition, monosubstituted 1-(4′-trifluoromethylphenyl) pyromellitic dianhydride (3FPPMDA) and 1-phenyl pyromellitic dianhydride (PPMDA)[25] were used. The polyimides were designed to have molecular weights of 20,000 g/mol and were characterized by Fourier transform infrared (FTIR), NMR, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermomechanical analyzer (TMA), and thermogravimetric analysis (TGA). In addition, their intrinsic viscosity, water absorption, and CTE were evaluated. The adhesion properties of the synthesized polyimides were evaluated via the T-peel test of samples prepared from bare or silane/Cr-coated Cu foils. The failure surfaces were investigated with scanning electron microscopy (SEM) to elucidate the failure mechanism.

EXPERIMENTAL

Materials

For the synthesis of the polyimides, novel dianhydride monomers, such as 6FPPMDA and 3FPPMDA, were prepared in our laboratory as reported previously,[26] whereas PPMDA was synthesized as reported in the literature.[25] Diamines containing phosphine oxide moieties, fluorine moieties, or both, such as *m*DA6FPPO,[19] *m*DA3FPPO,[20] and *m*DAPPO,[23] were also prepared. The end-capping agent, phthalic anhydride (PA; 99%), acquired from Aldrich (St. Louis, MO), was vacuum-sublimed before use. Tetrachloroethane (TCE) was obtained from Aldrich and used as received, whereas isoquinoline (97%; Aldrich) and *p*-chlorophenol (99.9%; Aldrich) were vacuum-distilled after drying over calcium hydride. For the adhesion study, bare Cu foils (grade III) and silane/Cr-coated Cu foils (grade ITY) with a thickness of approximately 0.02 mm, from Iljin Copper Foil Co. (Seoul, Korea), were used.

Polyimide synthesis

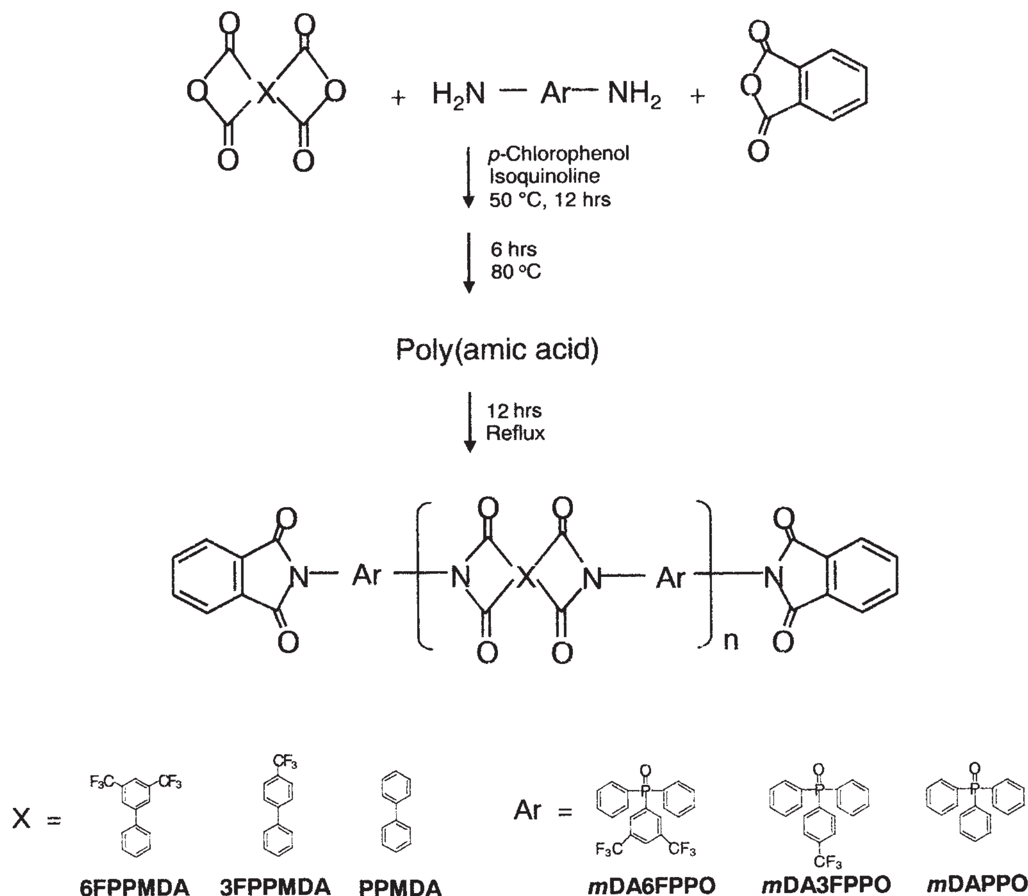
All the polyimides were prepared via a two-step process: the synthesis of poly(amic acid), followed by solution imidization (Scheme 1). The number-average molecular weight (M_n) was controlled to 20,000 g/mol by the addition of excess diamine, and all the polymers were designed to have nonreactive end groups by the addition of PA. Polymerization was carried out in a three-necked, round-bottom flask equipped with a mechanical stirrer, a drying tube, a nitrogen inlet, and a thermometer. After the reaction apparatus was flame-dried under an N_2 flow, the diamine monomer and dried *p*-chlorophenol (solvent) were charged into the flask and heated to 50°C in a silicone oil bath. *p*-Chlorophenol was used as the solvent because it is known to accelerate the acylation reaction of amine to afford high-molecular-weight poly(amic acid).[27]

Upon the complete dissolution of the diamine monomer, PA and isoquinoline (catalyst) were added, and the solid content was controlled to 10 wt %. The reaction mixture was kept at 50°C and allowed to react for 12 h; this was followed by an additional 6 h at 80°C, which resulted in a yellow, viscous poly(amic acid) solution. Imidization was performed at the reflux temperature of *p*-chlorophenol for 12 h. Water that formed during imidization was removed by an N_2 flow, which also removed *p*-chlorophenol; this necessitated the continuous addition of *p*-chlorophenol. Finally, the polyimide solution was cooled to room temperature (RT), precipitated into a water/methanol (1:1) mixture, filtered, and dried in a vacuum oven at 200°C for 24 h.

Characterization of the polyimides

The polyimides prepared were characterized by FTIR (IR-2000, PerkinElmer, Boston, MA) and NMR (JNM-LA300WB, JEOL) with dimethyl-d_6 sulfoxide (DMSO-d_6) or chloroform-*d* ($CDCl_3$). In NMR (JNM-LA300WB; JEOL, Peabody, MA), the chemical shifts of ^1H, ^{31}P, and ^{19}F were calibrated with internal standards of tetramethylsilane [$(CH_3)_4Si$], phosphoric acid (H_3PO_4), and fluorotrichloromethane ($CFCl_3$), respectively. The solution viscosity was measured with a Cannon-Ubbelohde viscometer at 25°C in *N*-methylpyrrolidone (NMP; Fisher, Hampton, NH), and the molecular weights were evaluated by GPC (M77251, Waters, Milford, MA) in tetrahydrofuran (THF) with polystyrene standards. The solubility of the polyimides was evaluated through the immersion of solution-cast polymer films (5 × 5 mm × ca. 0.2 mm) into solvents (10 mL) such as NMP, dimethylacetamide (DMAc), chloroform ($CHCl_3$), TCE, THF, acetone, and toluene at RT for 24 h.

The T_g values were measured by DSC (model 2090, TA Instruments, New Castle, DE) at a heating rate of 10°C/min from the second heating scan, whereas the thermal stability of the polyimides was evaluated by TGA (model 2950, TA Instruments) in air at 10°C/min. CTE was studied by thermomechanical analysis (model 2000, TA Instruments) in the penetration mode with polyimide films at a heating rate of 5°C/min. The water absorption of the polyimides was determined by the measurement of the weight difference before and after the immersion of the polyimide films (5 mm



Scheme 1 Synthetic scheme of the polyimides with 6FPPMDA.

× 5 mm × 0.1 mm) in deionized water at 25°C for 7 days.

Adhesion properties

The adhesion properties of the polyimides were evaluated by a T-peel test (ASTM D 1876-95) with bare (grade III, Iljin Copper Foil Co., Seoul, Korea) or silane/Cr-coated Cu foils (grade ITY, Iljin Copper Foil Co.). Silane/Cr-coated Cu foils (200 mm × 300 mm) were used as received, whereas bare Cu foils were used after etching for 20 min in a solution [60 parts by volume (pbv) of sulfuric acid, 15 pbv of hydrogen peroxide, and 2000 pbv of deionized water] to remove the oxide layer; this was followed by rinsing with deionized water and drying at 100°C for 30 min. The Cu foils were then coated with a polyimide solution (15 wt % in DMAc) and dried at 100°C for 30 min. The coating process was repeated until the thickness of the polyimide layer reached approximately 0.01 mm, and the polyimide-coated Cu foils were dried for 1 h at 150°C, followed by an additional 30 min at 300°C in a vacuum oven.

The T-peel test specimens were prepared via the sandwiching of two polyimide-coated Cu foils according to ASTM D 1876-95. The bonding temperature and bonding time were optimized under a bonding pressure of 10.3 MPa with the 6FPPMDA–*m*DA6FPPO polyimide. The bonding temperature was optimized by the heating of the sample to T_g + 10°C at approximately 7°C/min under contact pressure and then further via heating to T_g + 30, 50, or 70°C under 10.3 MPa (1500 psi). The sample was held for 10, 20, or 30 min and slowly cooled to RT under pressure. All the samples were prepared under optimized bonding conditions. After cooling to RT, the samples were cut into 25.4 mm × 300 mm pieces and were subjected to T-peel tests at RT with an Instron 5567 (Canton, MA) at a crosshead speed of 2.54 cm/min. At least six specimens were tested for each polyimide, and the results were averaged. The failure surfaces were also analyzed by SEM (JSM-5800; JEOL) at 15 kV to elucidate the failure mechanism.

RESULTS AND DISCUSSION

Characterization of the polyimides

Successful polyimide synthesis was demonstrated by FTIR and ^{1}H-NMR. As noted in the FTIR spectrum of

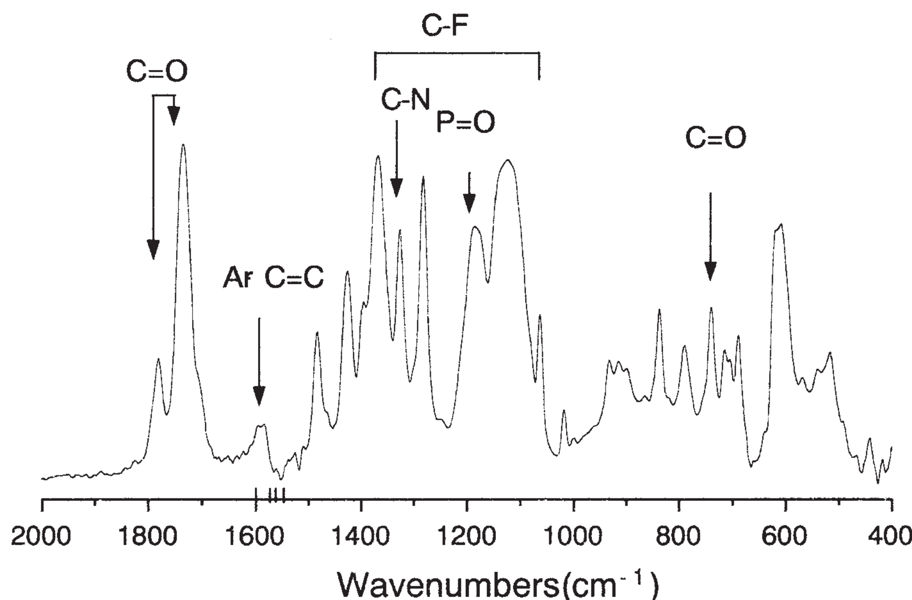


Figure 1 FTIR spectrum of the 6FPPMDA–*m*DA6FPPO polyimide.

the 6FPPMDA–*m*DA6FPPO polyimide, imide C=O stretching absorptions at 1776 and 1733 cm^{-1} (asymmetric and symmetric), imide C=O bending absorption at 742 cm^{-1}, aromatic C=C absorption at 1578 cm^{-1}, and C—N stretching absorption at 1359 cm^{-1} were observed, but no amide–carbonyl peak was found at 1650 cm^{-1}; this suggested complete imidization (Fig. 1). In addition, C—F multiple stretching absorptions at 1376, 1282, 1176, and 1139 cm^{-1}, along with P=O stretching absorption (1180 cm^{-1}), were also found. Similar behavior was observed for all the other polyimides, and this demonstrated successful polyimide synthesis.

In the ^{1}H-NMR spectrum (300 MHz, $CDCl_3$), the 6FPPMDA–*m*DA6FPPO polyimide exhibited four groups of proton peaks besides water and DMSO peaks, as shown in Figure 2. The proton peak appearing far downfield (at 8.478 ppm) was attributable to the proton between the two imide carbonyl groups in the dianhydride unit, which was affected by the strong electron-withdrawing nature of the imide carbonyl groups. The next deshielded protons (at 8.368 and 8.336 ppm) were those at the ortho position to the trifluoromethyl moieties in the diamine (2H, H^8) and dianhydride unit (2H, H^2), followed by the protons between the two trifluoromethyl moieties (2H, H^1, H^9), which appeared at 8.302. The peaks at 8.022 (4H, H^4), 7.977 (2H, H^7), 7.864 (2H, H^6), and 7.831 ppm (2H, H^5) were assigned to the protons from the phenyl moiety in the diamines, with consideration given to the position and distance from the imide, phopshine oxide, and trifluoromethyl moieties.

The 6FPPMDA-based polyimides exhibited high T_g's (280–299°C), which were lower than those of 3FPPMDA (292–318°C) and PPMDA-based polyimides (300–322°C); this demonstrated the negative effect of the CF_3 moiety (Table I). Among the 6FPPMDA-based polyimides, 6FPPMDA–*m*DA6FPPO had a T_g of 280°C, whereas 6FPPMDA–*m*DA3FPPO and 6FPPMDA–*m*DAPPO exhibited T_g's of 290 and 299°C, respectively; this again demonstrated the negative effect of the CF_3 moiety on T_g. A similar trend was observed for the 3FPPMDA- and PPMDA-based polyimides.

The polyimides prepared in this study showed excellent thermal stability in air, showing 5% weight loss at 520°C or higher temperatures. As noted in Table I, the 6FPPMDA-based polyimides exhibited slightly better thermal stability than the 3PPMDA- and PPMDA-based polyimides, possibly because of their higher fluorine content. In addition, the *m*DA6FPPO-based polyimides exhibited slightly better thermal stability than the *m*DA3FPPO- and *m*DAPPO-based polyimides, with the 6FPPMDA–*m*DA6FPPO polyimides exhibiting the best thermal stability; this could be attributed to the highest fluorine content (26%). However, the highest char yield at 800°C was obtained from the PPMDA–*m*DAPPO polyimide (32%), even though it showed the worst thermal stability of the polyimides prepared in this study. Therefore, the high char yield could be attributed to the phosphine oxide moiety.

In the solubility study of the polyimides in NMP, DMAc, TCE, THF, $CHCl_3$, acetone, and toluene, good solubility in all the solvents was observed for the 6FPPMDA-based polyimides, with the exception of 6FPPMDA–*m*DAPPO, which showed partial solubility in toluene (Table II). On the other hand, some 3FPP-

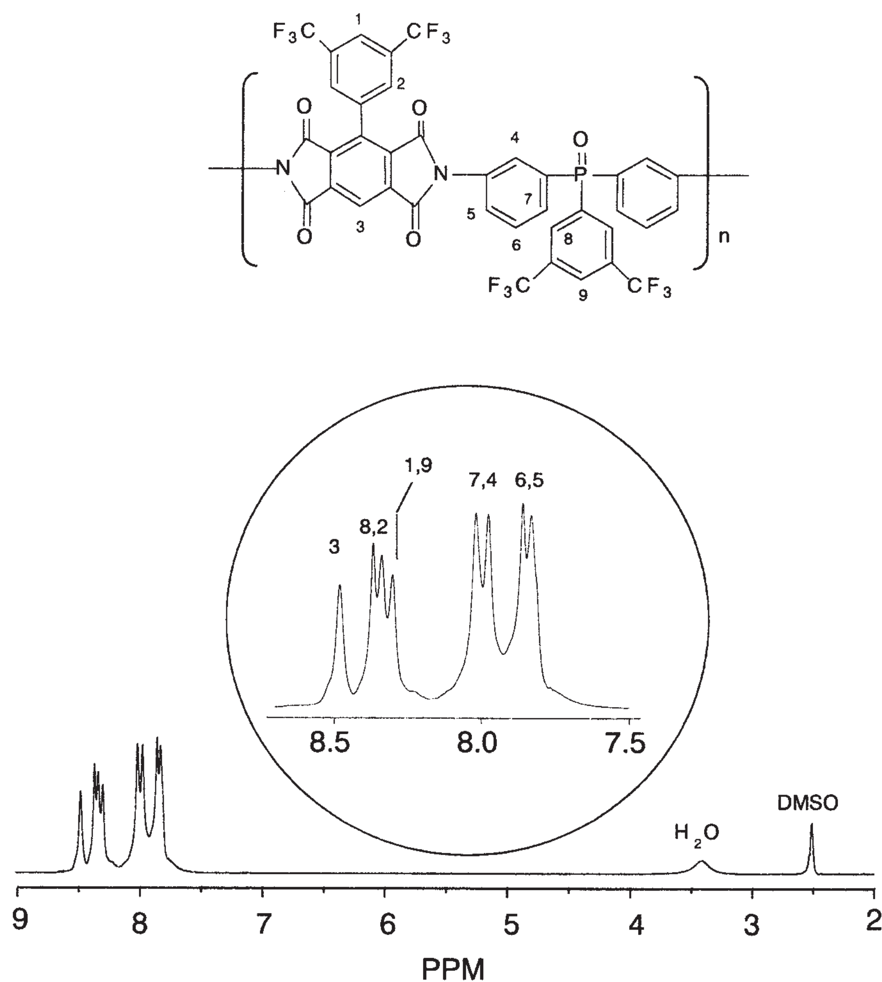


Figure 2 NMR spectrum of the 6FPPMDA–*m*DA6FPPO polyimide.

MDA-based polyimides showed partial solubility in acetone and toluene, whereas the PPMDA-based polyimides exhibited insolubility in toluene and partial solubility in acetone, THF, TCE, and even chloroform; this demonstrated the positive effect of the CF_3 moiety on solubility. Because all the polyimides were soluble

TABLE I
Characteristics of the Polyimides

Anhydride	Diamine	$[\eta]$[a] (dL/g)	M_n[b]	T_g (°C)[c]	T_d (°C)[d]	Residue (wt %)[e]	CTE (ppm/°C)	Water absorption (wt %)
	*m*DA6FPPO	0.27	18,600	280	543	5	40	1.46
6FPPMDA	*m*DA3FPPO	0.27	18,300	290	539	11	36	1.68
	*m*DAPPO	0.26	19,000	299	537	16	32	2.16
	*m*DA6FPPO	0.27	19,100	292	539	10	37	1.76
3FPPMDA	*m*DA3FPPO	0.26	19,000	303	531	15	34	1.91
	*m*DAPPO	0.25	19,200	318	528	17	30	2.32
	*m*DA6FPPO	0.27	18,200	300	532	14	33	2.09
PPMDA	*m*DA3FPPO	0.26	—	311	528	19	31	2.39
	*m*DAPPO	0.26	—	322	522	32	26	3.26

η = intrinsic viscosity in NMP at 25°C; T_d = thermal decomposition temperatures.
[a] At 25°C in NMP.
[b] By GPC.
[c] By DSC, second heating, 10°C/min in N_2.
[d] By TGA, 5 wt % loss, 10°C/min in air.
[e] By TGA at 800°C, 10°C/min in air.

TABLE II
Solubility of the Polyimides

Dianhydride	Diamine	NMP	DMAc	$CHCl_3$	TCE	THF	Acetone	Toluene
	*m*DA6FPPO	S	S	S	S	S	S	S
6FPPMDA	*m*DA3FPPO	S	S	S	S	S	S	S
	*m*DAPPO	S	S	S	S	S	S	P
	*m*DA6FPPO	S	S	S	S	S	S	S
3FPPMDA	*m*DA3FPPO	S	S	S	S	S	P	P
	*m*DAPPO	S	S	S	S	S	P	P
	*m*DA6FPPO	S	S	S	S	S	P	I
PPMDA	*m*DA3FPPO	S	S	S	P	P	P	I
	*m*DAPPO	S	S	P	P	P	P	I

S = soluble; P = partially soluble; I = insoluble.

in NMP, the intrinsic viscosities were evaluated in NMP at 25°C with a Cannon-Ubbelohde viscometer. The measured solution viscosities were 0.25–0.27 dL/g (Table I); this was reasonable in light of the controlled molecular weight of 20,000 g/mol. The M_n values of the polyimides, determined by GPC, were 18,200–19,200 g/mol, indicating the successful synthesis of polyimides with a controlled molecular weight of 20,000 g/mol (Table I). However, the molecular weights of PPMDA–*m*DA3FPPO and PPMDA–*m*DAPPO were not evaluated because of their insolubility in THF.

Property measurements of the polyimides

The polyimides prepared in this study had fairly low CTE values, which increased as the CF_3 moiety was added: 40–32 (6FPPMDA-based), 37–30 (3FPPMDA-based), and 33–26 ppm/°C (PPMDA-based; Table II). The same trend was also observed for the 6FPPMDA-based polyimides: 40 (*m*DA6FPPO), 36 (*m*DA3FPPO), and 32 ppm/°C (*m*DAPPO). This demonstrated the negative effect of the CF_3 moiety on CTE values. The CTE of 6FPPMDA–*m*DA6FPPO (40 ppm/°C) was slightly higher than the value of 31 ppm/°C obtained for the pyromellitic dianhydride–4,4′-oxydianiline polyimide[8] but slightly lower than the value of 49 ppm/°C obtained from the 12FPMDA–*m*DA6FPPO polyimide;[22] this again demonstrated the effect of bulky side groups on CTE values.

As expected, the 6FPPMDA-based polyimides showed very low water absorption (1.46–2.16 wt %) in comparison with the 3FPPMDA-based polyimides (1.76–2.32 wt %) and the PPMDA-based polyimides (2.09–3.26 wt %; Table I). The low water absorption of the 6FPPMDA-based polyimides could be attributed to the hydrophobic nature of the CF_3 moiety. Among the 6FPPMDA-based polyimides, 6FPPMDA–*m*DAPPO exhibited the highest water absorption (2.16 wt %), and it was followed by *m*DA3FPPO with 1.68 wt % and *m*DA6FPPO with 1.46 wt %; this again demonstrated the effect of the CF_3 moiety on water absorption. The same trend was observed for the 6FPPMDA- and PPMDA-based polyimides.

Adhesion properties of the polyimides

The optimized bonding temperature and time with the 6FPPMDA–*m*DA6FPPO polyimide under a bonding pressure of 10.3 MPa were 374°C (T_g + 50°C) and 20 min, respectively (Fig. 3); they were similar to the conditions previously reported for the 12FPMDA–*m*DA6FPPO polyimide.[22] As previously discussed,

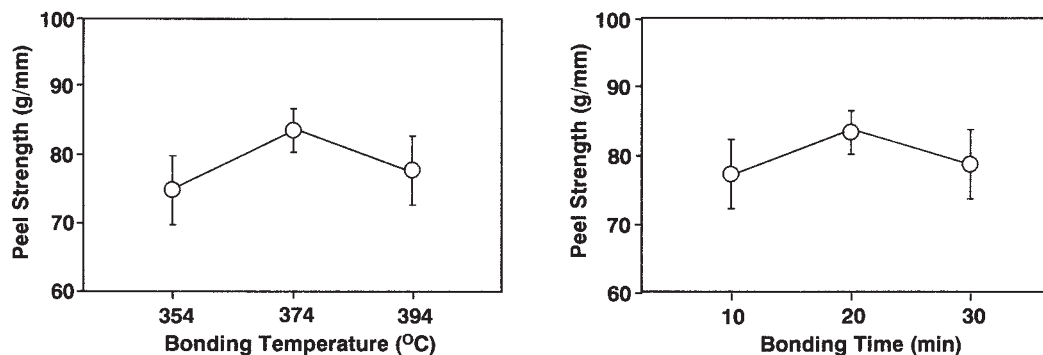


Figure 3 Optimization of the bonding temperature and time with the 6FPPMDA–*m*DA6FPPO polyimide.

354°C (T_g + 30°C) was so low that it provided poor bond consolidation and thus poor adhesion, whereas 394°C (T_g + 70°C) was too high, resulting in oxidation of the Cu foil and possible degradation of polyimide adhesives, which in turn led to lower peel strength than that obtained at 374°C (T_g + 50°C). A similar principle applied to the holding time; 10 min was too short to provide good flow, but 30 min was too long, causing possible oxidation of Cu and degradation of the polyimides.

With silane/Cr-coated Cu foil samples, the 6FPPMDA-based polyimides exhibited high peel strength (88–83 g/mmm), as shown in Figure 4. As expected, these values were slightly lower than the ones obtained from the 3FPPMDA-based (91–86 g/mm) and PPMDA-based polyimides (95–88 g/mm). The lower values were attributed to the negative effect of the fluorine moiety on adhesion, as observed previously.[21] Among the 6FPPMDA-based polyimides, 6FPPMDA–*m*DAPPO had a peel strength of 88 g/mm, which was slightly higher than the values obtained for 6FPPMDA–*m*DA3FPPO (85 g/mm) and 6FPPMDA–*m*DA6FPPO (83 g/mm). This was again explained by the negative effect of fluorine on adhesion. Similar trends were observed for the 3FPPMDA- and PPMDA-based polyimides.

Samples prepared with bare Cu foils exhibited very similar peel strengths: 69–50 g/mm for 6FPPMDA-based polyimides, 71–47 g/mm for the 3FPPMDA-based polyimides, and 70–49 g/mm for the PPMDA-based polyimides (Fig. 5). This trend was different from that observed with the silane/Cr-coated Cu foils and could be explained by the absence of an adhesion-promoting silane/Cr layer. In addition, the peel strength with bare Cu foils was approximately 40–20% lower than that with the silane/Cr-coated Cu foils (Table III), and this again demonstrated the effect of the silane/Cr layer. Among the 6FPPMDA-based polyimides, the 6FPPMDA–*m*DAPPO polyimide showed 69 g/mm, which was much larger than the values of 57 and 50 g/mm obtained from the 6FPPMDA–*m*DA3FPPO and 6FPPMDA–*m*DA6FPPO polyimides, respectively. This difference could be explained by the positive effect of phosphine oxide moieties, which provided strong interaction with bare Cu foils. However, the effect of phosphine oxide was rather small in comparison with the effect of the silane/Cr layer with silane/Cr-coated Cu foils.

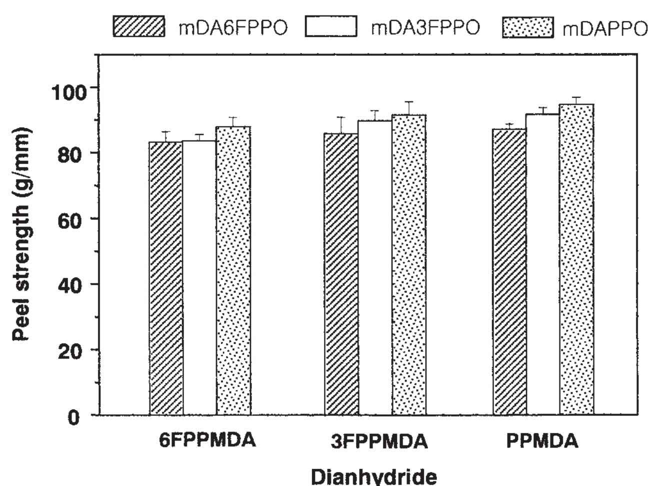


Figure 4 Peel strengths of the polyimides with silane/Cr-coated Cu foils.

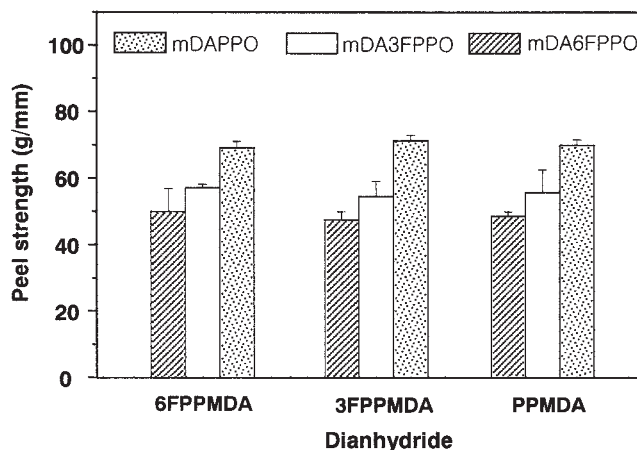


Figure 5 Peel strengths of the polyimides with bare Cu foils.

Failure mode analysis

The as-received silane/Cr-coated Cu foils exhibited small particles with a diameter of 2–5 μm on a seashell-like surface [Fig. 6(A)], whereas the bare Cu foil samples showed a seashell-like surface without small particles. As expected from the high peel strength, the samples with silane/Cr-coated Cu foils had a failure surface fully covered with polyimide (Fig. 6), regardless of the polyimide used, thereby showing a cohesive failure mode. Moreover, polyimide adhesives exhibited elongation, which indicated ductile failure. Small differences in the peel strengths with the silane/Cr-coated Cu foils, regardless of the dianhydrides or diamines used, correlated well with the cohesive failure mode obtained with a thick polyimide adhesive.

However, samples with bare Cu foils all exhibited a mixed-failure mode, regardless of the polyamide used; this was expected from their much lower peel strength compared with that of the silane/Cr-coated Cu foil samples. As expected, the adhesive/cohesive failure area ratio varied with the diamine; it was higher with *m*DAPPO and lower with *m*DA6FPPO, demonstrating the positive effect of phosphine oxide

TABLE III
Peel Strengths and Failure Modes of 6FPPMDA Polyimides

Anhydride	Diamine	F (wt %)	Cr/Silane-coated Cu foil Peel strength (g/mm)[a]	Cr/Silane-coated Cu foil Failure mode	Bare Cu foil Peel strength (g/mm)[a]	Bare Cu foil Failure mode
	*m*DA6FPPO	26	83 ± 3	C	50 ± 3	M
6FPPMDA	*m*DA3FPPO	21	85 ± 2	C	57 ± 1	M
	*m*DAPPO	16	88 ± 3	C	69 ± 2	M
	*m*DA6FPPO	21	86 ± 5	C	47 ± 2	M
3FPPMDA	*m*DA3FPPO	16	90 ± 3	C	54 ± 5	M
	*m*DAPPO	9	91 ± 4	C	71 ± 3	M
	*m*DA6FPPO	16	88 ± 2	C	49 ± 1	M
PPMDA	*m*DA3FPPO	9	92 ± 2	C	56 ± 3	M
	*m*DAPPO	0	95 ± 2	C	70 ± 2	M

C = cohesive failure; M = mixed failure.

or negative effect of fluorine on adhesion. The mixed-failure mode with bare Cu foils, unlike the all-cohesive-failure mode obtained with silane/Cr-coated Cu foils, could be explained by the absence of the adhesion promoter, the silane/Cr layer.

CONCLUSIONS

Polyimides were successfully synthesized from 6FPPMDA in combination with *m*DA6FPPO, *m*DA3FPPO, and *m*DAPPO and had high T_g values (280–299°C), excellent thermal stability (>530°C), fairly low CTEs (32–40 ppm/°C), and very low water absorption (1.46–2.16 wt %).

Although the 6FPPMDA-based polyimides with silane/Cr-coated Cu foils had high peel strength (88–83 g/mm), it was slightly lower than the values obtained with the 3FPPMDA-based polyimides (91–86 g/mm) and PPMDA-based polyimides (95–88 g/mm); this demonstrated the negative effect of fluorine on adhesion.

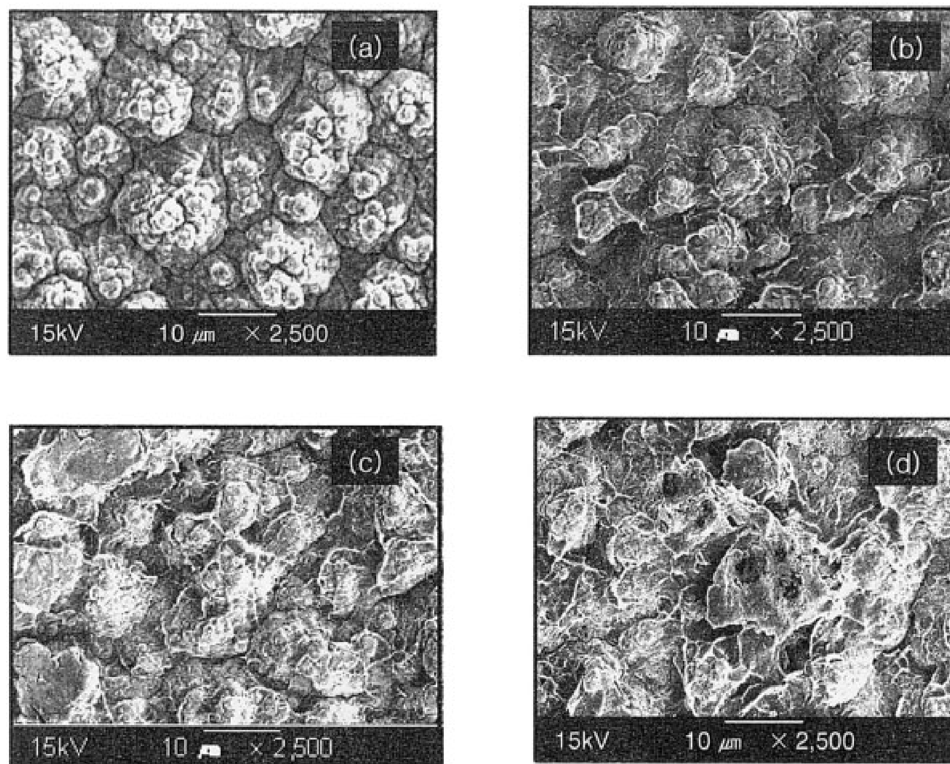


Figure 6 Failure surface of silane/Cr-coated Cu foils: (a) as-received silane/Cr-coated Cu foil, (b) 6FPPMDA–*m*DAPPO, (c) 6FPPMDA–*m*DA3FPPO, and (d) 6FPPMDA–*m*DA6FPPO.

Peel strengths with bare Cu foils were 20−40% lower than those with silane/Cr-coated Cu foils, and this demonstrated the effect of the silane/Cr layer.

Samples with silane/Cr-coated Cu foils showed all-cohesive-failure modes, whereas those with bare Cu foils exhibited mixed-failure modes, which correlated well with the adhesion properties.

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