

# Low Dielectric, Fluorinated Polyimide Copolymers

DIANE M. STOAKLEY,<sup>1</sup> ANNE K. ST. CLAIR,<sup>1,\*</sup> and CATHARINE I. CROALL<sup>2</sup>

<sup>1</sup>NASA Langley Research Center, Hampton, Virginia 23681-0001;

<sup>2</sup>Lockheed Engineering and Science Co., Hampton, Virginia 23666

## SYNOPSIS

Copolymers of fluorinated polyimides and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) have been prepared as films and composite laminates. The addition of BPDA was used as a means to achieve insolubility, making the polymers suitable as aircraft matrix resins. Glass transition temperatures, thermooxidative stabilities, and tensile strengths were increased with increasing BPDA content in the copolymers. Although the addition of BPDA did increase the UV cutoff and decrease the percent transmission slightly, the optical transparency of the polymers was still excellent. Dielectric constants of the polyimide films ranged from 2.6 to 2.9. Astroquartz II laminates made with these resins had dielectric constants of 3.3–3.4. Flexural strengths on unidirectional specimens were in the 1.24–1.41 GPa range and flexural moduli were 41 GPa. © 1994 John Wiley & Sons, Inc.†

## INTRODUCTION

The incorporation of fluorine atoms provides a means of obtaining optical transparency and lowering the dielectric constants of polyimides. Accompanying the improved transparency and lowered dielectric constant, however, is an enhanced solubility in organic solvents.<sup>1,2</sup> Although the increased solubility has proven beneficial for many electronic and space applications where spray-coating the fully imidized polyimide from a low boiling solvent is an advantage, it is undesirable for aircraft applications where exposure to hydraulic fluids and other chemicals is likely to occur. Copolymers of fluorinated polyimides with 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) have been prepared in an effort to achieve a polymer that retains the optical transparency required for many space applications with the insolubility needed for aircraft matrix resins.

## EXPERIMENTAL

### Starting Materials

BPDA was obtained from Mitsui Toatsu Chemicals and Ube Industries, Japan, and was vacuum-

dried at 150°C before use. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was used as received from Hoechst Celanese Corp. 3,5-Diaminobenzotrifluoride (DABTF) was synthesized in-house by hydrogenation of 3,5-dinitrobenzotrifluoride (Aldrich Chemical Co.).<sup>3</sup> 2,2-Bis-(4-hydroxyphenyl)hexafluoropropane (bisphenol AF) was obtained from DuPont and recrystallized from toluene to yield a white crystalline solid (mp 157–159°C). 4-Fluorophthalic anhydride was used as received from Occidental Chemical Corp. (mp 74–76°C). Spray-dried potassium fluoride (99% purity) was used as received from Aldrich Chemical Co. Tetramethylene sulfone (sulfolane) was obtained from Phillips 66 and vacuum-distilled prior to use.

### 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]-hexafluoropropane dianhydride (BFDA)

The synthetic route described in Ref. 4 was used for the in-house preparation of BFDA. Bisphenol AF (33.62 g, 0.10 mol), 4-fluorophthalic anhydride (38.44 g, 0.23 mol), spray-dried potassium fluoride (17.43 g, 0.30 mol), and freshly distilled sulfolane (315 g, 19% w/w) were placed into a 500 mL, three-neck round-bottom flask equipped with mechanical stirrer, nitrogen gas inlet, and reflux condenser. The reaction mixture was heated to 180°C and maintained at this temperature for 3 h. The mixture was

\* To whom correspondence should be addressed.

then cooled slowly, poured onto ice water, and collected. The solid was subsequently washed with deionized water, collected, and stage-dried under vacuum at 215°C to afford a light tan solid (mp 229–231°C, 76% yield).

ANAL: Calcd for  $C_{31}H_{14}O_8F_6$ : C, 59.25%; H, 2.25%; F, 18.14%.

Found: C, 58.94%; H, 2.35%; F, 18.09%.

### Polymers

Polyamic acid resins were prepared in solution containing 20 wt % solids in *N,N*-dimethylacetamide (DMAc) by first dissolving the diamine, DABTF, in DMAc at room temperature. An equimolar amount of a dianhydride or a combination of dianhydrides was then added and the solutions were stirred for 8–24 h. Structures of these monomers are shown in Figure 1. The solutions were cast with a doctor blade onto glass plates to obtain a final film thickness of approximately 0.013 or 0.025 mm (0.5 or 1.0 mil). The polyamic acid films were thermally converted to the corresponding polyimide by heating in a forced air oven for 1 h each at 100, 200, and 300°C.

### Prepreg and Composite Laminates

Polyamic acid resins of 50 : 50 6FDA : BPDA / DABTF and 55 : 45 BFDA : BPDA / DABTF were

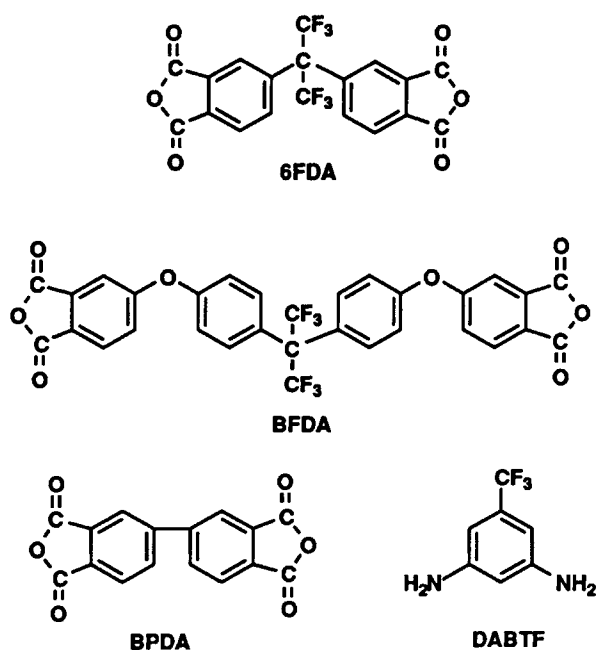


Figure 1 Dianhydride and diamine monomers.

Table I Solubilities of 6FDA : BPDA + DABTF Polyimide Films

6FDA : BPDA Copolymer	Film Solubility in			
	DMAc	CHCl <sub>3</sub>	Diglyme	DMF
6FDA control	S	S	S	S
75 : 25	S	PS	PS	S
60 : 40	S	I	PS	S
55 : 45	S	I	PS	S
50 : 50	PS	I	I	I
25 : 75	PS	I	I	I
BPDA control	I	I	I	I

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

prepared as above at 28 and 20 wt % solids, respectively, in DMAc. These resins were applied to an J.P. Stevens Astroquartz II roving using a Research Tool Corp. drum winder with a drum rotation of 1 rpm and a transverse rate of 16% full speed with minimum applied fiber tension. A die gap of 2.97 × 0.64 mm (0.11 × 0.03 in.) was used for the 6FDA-containing resin and 0.51 × 0.38 mm (0.02 × 0.02 in.) for the lower percent solids BFDA-containing resin. The prepreg was dried until tack-free under infrared heat lamps for 2–3 h. It was then removed from the drum, cut into 0.3 m (1 ft) sections, and B-staged in a forced air oven for 11/2 h at 190°C. Laminates were prepared from the prepreg in 7.6 × 7.6 cm (3 × 3 in.) stainless-steel molds by ramping the press temperature to 350°C with a 1 h hold at that temperature. A pressure of 1.03 MPa (150 psi) was applied at room temperature and held for the entire cycle. Multiply unidirectional laminates were prepared for determination of short beam shear (SBS) strength, flexural properties, and dielectric constant.

### Characterization

The inherent viscosities of the polyamic acids were determined at a concentration of 0.5% in DMAc at 35°C. Apparent glass transition temperatures ( $T_g$ 's) of the films were determined on a DuPont Model 943 thermomechanical analyzer (TMA) at a heating rate of 5°C/min. Thermogravimetric analyses (TGA) were obtained on a Seiko TG-TGA 220 in flowing air (15 cc/min) at a heating rate of 2.5°C/min after an initial 30 min hold at 100°C. Transmission UV-visible (UV-vis) spectra were obtained on 0.013 mm (0.5 mil)-thick films using a Perkin-

**Table II Solubilities of BFDA : BPDA + DABTF Polyimide Films**

BFDA : BPDA Copolymer	Film Solubility in			
	DMAc	CHCl <sub>3</sub>	Diglyme	DMF
BFDA control	S	S	S	S
75 : 25	S	PS	S	S
60 : 40	PS	PS	I	I
55 : 45	I	I	I	I
50 : 50	I	I	I	I
25 : 75	I	I	I	I
BPDA control	I	I	I	I

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

Elmer Lambda 5 UV-vis spectrometer in the reflectance mode with an integrating sphere attachment. Densities were determined on the cured films in a density gradient tube according to ASTM D1505-60T. Dielectric constants were determined using a Hewlett-Packard 8510 automated network analyzer over the frequency range of 8–12 GHz. The polymer films were desiccated overnight prior to measurement. A stack of ten 0.025 mm (1 mil)-thick film specimens were inserted between flanges in an x-band waveguide and tested at 26°C in 25–35% relative humidity to obtain the dielectric constant data. Solubilities of the films were tested at approximately 1% (w/w) in DMAc, chloroform (CHCl<sub>3</sub>), 2-methoxyethyl ether (diglyme), and *N,N*-dimethylformamide (DMF) after 5 days. Coefficient of thermal expansion (CTE) measurements were made on a Seiko 1 TMA 100 using a heating rate of 2°C/min. The CTE values were determined between 70 and 110°C because of the linearity of the region. Tensile properties were determined at room temperature and 200°C on a Model 2000/2 table-top Sintech load frame on film specimens that were 5.1 mm (0.20 in.)

wide. A gauge length of 51 mm (2.0 in.) and a cross-head speed of 5.1 mm/min (0.2 in. min) were used on a minimum of 10 film specimens. Flexural properties were determined at room temperature on five composite laminate specimens on an Instron testing machine in a three-point bending mode according to ASTM D790-71. SBS testing was done at room temperature according to ASTM D2344-76 on 10 specimens.

## RESULTS AND DISCUSSION

Copolymers were prepared combining BPDA with the fluorinated dianhydrides, 6FDA and BFDA, and the fluorinated diamine, DABTF, in an effort to impart insolubility to these polyimides while retaining their low dielectric constants. A variety of dianhydride ratios were used to determine the minimum concentration of BPDA needed to achieve insolubility since the addition of BPDA would also increase the dielectric constant of the resulting polymer. The solubilities in DMAc, CHCl<sub>3</sub>, diglyme, and DMF of the 6FDA : BPDA/DABTF polymers are listed in Table I, and the BFDA : BPDA/DABTF polymers, in Table II. The 50 : 50 6FDA : BPDA ratio contained the minimum amount of BPDA necessary to maintain insolubility. This film was insoluble in CHCl<sub>3</sub>, diglyme, and DMF after 5 days and only partially soluble in DMAc after 5 days. The 55 : 45 BFDA : BPDA/DABTF film was insoluble after 5 days in all four solvents. A further decrease in BPDA content to the 60 : 40 level resulted in partial solubility in DMAc and CHCl<sub>3</sub> after only 4 h.

Selected properties of the 6FDA : BPDA/DABTF polymers are listed in Table III, and the BFDA : BPDA/DABTF polymers, in Table IV. The solution viscosities of the polyamic acids ranged from 0.41 to 0.80 dL/g. Several trends were noted in both series of copolymers. In general, as the concentration

**Table III Properties of 6FDA : BPDA + DABTF Copolymers**

6FDA : BPDA Copolymer	$\eta_{inh}$ (dL/g)	$T_g$ by TMA (°C)	TGA, 10% Wt Loss (°C)	Density (g/cc)
6FDA control	0.65	294	500	1.51
75 : 25	0.41	300	500	—
60 : 40	0.44	305	507	—
55 : 45	0.53	303	508	—
50 : 50	0.50	309	508	1.48
25 : 75	0.60	317	512	—
BPDA control	0.71	325	527	1.45

**Table IV Properties of BFDA : BPDA + DABTF Copolymers**

BFDA : BPDA Copolymer	$\eta_{inh}$ (dL/g)	$T_g$ by TMA (°C)	TGA, 10% Wt Loss (°C)	Density (g/cc)
BFDA control	0.55	232	506	1.46
75 : 25	0.50	246	508	—
60 : 40	0.80	257	508	—
55 : 45	0.69	263	511	1.46
50 : 50	0.73	268	511	—
25 : 75	0.74	288	519	—
BPDA control	0.71	325	527	1.45

of BPDA was increased in the polyimides, the apparent  $T_g$  and the thermooxidative stability increased. Film densities were determined on the polyimide controls and the copolymers that contained the minimum concentration of BPDA required to obtain insolubility. Replacing 50% of the 6FDA monomer with BPDA resulted in a decrease in polymer density from 1.51 to 1.48 g/cc, a result of the reduction in the number of heavy  $CF_3$  groups. The densities of the BFDA and BPDA controls were essentially the same, so no change in density was seen in making the copolymer.

Additional properties of these copolymers are listed in Tables V and VI. Again, certain trends were apparent with the addition of BPDA to the fluorinated polyimides. The CTE and optical transparency generally decreased with increasing BPDA content while the dielectric constant increased slightly. The dielectric constant of both the 50 : 50 6FDA : BPDA and the 55 : 45 BFDA : BPDA films was 2.7. Although this is increased from the 6FDA and BFDA control films, it is a low dielectric constant for a potential aircraft matrix resin. The UV transmission cutoff and percent transmission at 500 nm were determined on 0.013 mm (0.5 mil) films. As seen in Table V, the 6FDA/DABTF control film had excellent optical transparency with a UV cutoff

of 335 nm and 90% transmission at 500 nm. However, the addition of even a small amount of BPDA increased the UV cutoff significantly and decreased the percent transmission slightly. BFDA/DABTF (Table VI) had a UV cutoff of 368 nm and 91% transmission at 500 nm. As expected, the addition of BPDA increased the cutoff and decreased the percent transmission.

Tensile properties were determined at room temperature and 200°C on the controls and the insoluble 50 : 50 6FDA : BPDA/DABTF and 55 : 45 BFDA : BPDA/DABTF copolymers. As shown in Table VII, the 6FDA/DABTF control was too brittle to test and benefited greatly when BPDA was added to make the copolymer. The BFDA : BPDA copolymer also exhibited enhanced tensile properties over those of the BFDA/DABTF control film.

Composite laminates were made from the 50 : 50 6FDA : BPDA/DABTF and 55 : 45 BFDA/BPDA/DABTF copolymer resins on Astroquartz II fiber, which has a dielectric constant of 3.8. The flexural properties, SBS strengths, and dielectric constants are listed in Table VII. The flexural and SBS strengths were slightly higher for the BFDA-containing laminates than for the 6FDA-containing ones, whereas their flexural moduli were the same. The dielectric constants of both copolymer lami-

**Table V Properties of 6FDA : BPDA + DABTF Films**

6FDA : BPDA Copolymer	CTE (ppm/°C)	Dielectric Constant at 10 GHz	% Transmission at 500 nm	UV Cutoff (nm)
6FDA control	46	2.5	90	335
75 : 25	44	2.6	89	367
60 : 40	46	2.6	89	369
55 : 45	43	2.7	89	372
50 : 50	43	2.7	89	374
25 : 75	41	2.9	88	377
BPDA control	40	2.9	88	379

**Table VI Properties of BFDA : BPDA + DABTF Films**

BFDA : BPDA Copolymer	CTE (ppm/°C)	Dielectric Constant at 10 GHz	% Transmission at 500 nm	UV Cutoff (nm)
6FDA control	52	2.6	91	368
75 : 25	51	2.7	90	368
60 : 40	49	2.7	91	369
55 : 45	47	2.7	88	365
50 : 50	48	2.7	90	375
25 : 75	45	2.8	89	379
BPDA control	40	2.9	88	379

**Table VII Mechanical Properties of Copolyimide Films and Composites**

Polymer	Polyimide Films				Astroquartz II/Polyimide Composites			
	Tensile Strength (MPa)		Tensile Modulus (GPa)		Flexural Strength (GPa)	Flexural Modulus (GPa)	Short Beam Shear (SBS) (MPa)	Dielectric Constant at 10 GHz
	RT	200°C	RT	200°C				
6FDA/DABTF	a	a	a	a				
50 : 50 6FDA : BPDA/DABTF	106	71	3.1	2.4	1.24	41.5	54.5	3.3
BPDA/DABTF	139	80	3.5	2.7				
55 : 45 BFDA : BPDA/DABTF	109	57	2.9	2.0	1.41	41.0	61.4	3.4
BFDA/DABTF	100	47	2.7	2.0				

\* Too brittle to test.

nates were low, 3.3 and 3.4, with the combination of the Astroquartz fibers and low dielectric resins.

## CONCLUSIONS

Copolymers of fluorinated polyimides and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) have been prepared as films and composite laminates. The replacement of 45% or more of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) or 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (BFDA) with BPDA has resulted in copolyimides that are insoluble in common organic solvents. In addition, increases in  $T_g$  and thermooxidative stability and improvements in mechanical properties are obtained with increasing BPDA content. Several of these copolymers exhibited a desirable combination of properties that included low dielectric constants, insolubility, optical transparency, and thermal stability.

The authors gratefully thank Robert M. Ely for his contributions to polymer film synthesis and characterization, Burt R. Emerson for technical assistance in the CTE and dielectric measurements, and Ricky E. Smith and John J. Snoha for composite fabrication.

## REFERENCES

1. A. K. St. Clair, T. L. St. Clair, and W. P. Winfree, *Proceed. Am. Chem. Soc. Div. Polym. Mater. Sci. Eng.*, **59**, 28 (1988).
2. A. K. St. Clair, T. L. St. Clair, and W. S. Slemp, in *Recent Advances in Polyimides: Synthesis, Characterization and Applications*, W. Weber and M. Gupta, Eds., Plenum Press, New York, 1987, pp. 16-37.
3. M. K. Gerber, J. R. Pratt, A. K. St. Clair, and T. L. St. Clair, *Polym. Prepr.*, **31**(1), 340 (1990).
4. W. T. Schwartz, Jr., *High Perform. Polym.*, **2**(2), 189 (1990).

Received July 7, 1993

Accepted August 6, 1993