

Dimensionally Stable Polyimide Copolymers for Microelectronics Applications

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ABSTRACT: Polyimides are finding increased applications in microelectronics due to their high thermal stability, good chemical resistance, good adhesion, low moisture absorption, good mechanical properties, and low coefficient of thermal expansion (CTE). Four series of random copolyimides were synthesized and characterized for potential application as encapsulants, stress-relief layers, and interlevel dielectrics. Several candidates exhibited good combinations of physical and mechanical properties with inherent viscosities from 1.21 to 1.42 dL/g, T_g 's ranging from 251 to 277°C, 10% weight loss temperatures between 503 and 527°C, and CTEs ranging from 33 to 39 ppm/°C. Mechanical properties at room temperature for the best candidates included tensile strengths of 17.8–21.3 ksi, moduli between 388 and 506 ksi, and elongations of 11–43%. Moisture absorption for these copolyimides ranged between 0.85 and 1.38 wt %. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2383–2393, 1998

Key words: polyimide copolymers; dimensionally stable; microelectronics applications

INTRODUCTION

Polyimides are finding increased applications in microelectronics due to their high thermal stability, good chemical resistance, good adhesion, low dielectric constant, low moisture absorption, good mechanical properties, and low coefficient of thermal expansion (CTE).^{1–3} During fabrication, electronic packages may be repeatedly exposed to thermal cycling. Thermal stresses occur if there is a mismatch in the CTE of the polyimide and the substrate, resulting in peeling, cracking, delamination, bowing, adhesion loss, crazing, and, subsequently, device failure. Therefore, much research has focused on developing new polyimides with lower CTEs that still maintain good overall properties for microelectronics applications.^{4–10}

The goal of this research was to develop copoly-

imides possessing the right combination of physical, mechanical, and electrical properties for application as encapsulants, interlayer dielectrics, and stress-relief layers. Four series of polyimide copolymers were synthesized and characterized.

EXPERIMENTAL

Materials

4,4'-Oxydipthalic anhydride (ODPA) was recrystallized from acetic anhydride/acetic acid (4 : 1) (Occidental Chemical Corp., mp 226–227°C). Hydroquinone diether dianhydride (HQDEA) was used as received from Occidental Chemical Corp. (mp 267–268°C). 1,2-Bis(4-aminoanilino)cyclobutene-3,4-dione (SAPPD) was vacuum-dried at 150°C prior to use (Kwoya Hakko Kogyo Co., mp 287–288°C). *para*-Phenylene diamine (*p*-PDA) was obtained from Fluka, recrystallized from ethanol, and then sublimed (mp 143°C). 3,3',4,4'-Benzophenone tetracarboxylic dianhy-

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dride (BTDA) was obtained from Allco Chemical Corp. and sublimed prior to use (mp 222–223°C). 4,4'-Oxydianiline (4,4'-ODA) was obtained from Wakayama Seika Kogyo Co., Ltd., and sublimed prior to use (mp 186–187°C). 3,4'-Oxydianiline (3,4'-ODA) was obtained from Wakayama Seika Kogyo Co., Ltd., and recrystallized from ethanol/water (mp 80–81°C). *N,N*-Dimethylacetamide (DMAc) was used as received from Fluka. 1-Methyl-2-pyrrolidinone (NMP) was used as received from Aldrich. Chloroform, 2-methoxyethyl ether (diglyme) and *N,N*-dimethylformamide (DMF) were used as received from Aldrich.

Films

The poly(amide acid)s (PAA)s were prepared at a concentration of 8–15% solids (w/w) by the addition of a stoichiometric amount of the dianhydride in powder form to a mechanically stirred solution of the diamine or a combination of diamines in DMAc under a nitrogen atmosphere at room temperature (RT). Polymer solutions were stirred 16–24 h.

The PAA solutions were centrifuged and the decantate cast onto plate glass using a doctor blade and allowed to dry to a tack-free form in a dust-free chamber at RT, continually purged with dry air. The films on the glass were then thermally converted to the polyimide by heating in a forced air oven at 100, 200, and 300°C for 1 h at each temperature. Cooled films were removed from the glass plates by immersion in warm water.

Characterization

Inherent viscosities (η_{inh}) of the PAAs were obtained on 0.5% (w/v) solutions in DMAc at 25°C. Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) using a Seiko DSC Model 210 at a heating rate of 20°C/min. T_g 's were also obtained by thermomechanical analysis (TMA) using a DuPont 9900 computer thermal analyzer at a heating rate of 5°C/min. Dynamic thermogravimetric analyses (TGA) were obtained on a Seiko TGA Model 5200 in flowing air (50 cc/min) at a heating rate of 2.5°C/min after an initial 30 min hold at 100°C. The CTEs were obtained on a Seiko TMA Model 100 at a heating rate of 2°C/min. The CTE values were determined between 70 and 125°C because of the linearity of the curve.

Thin-film tensile properties were measured us-

ing a SINTECH 2000-2 computer integrated testing system, as recommended in ASTM-D882, at ambient temperature and humidity. Values are reported as the average of at least five specimens, along with the range of percent coefficient of variation (% COV) for the sample group. The % COV is calculated by dividing the standard deviation by the arithmetic mean ($\times 100$).¹¹ Pneumatically actuated, 1-in. grips with steel faces were used for clamping the polyimide films. Films were cut with a 0.200-in. Thwing-Albert JDC precision cutter. Specimen thickness was determined to within 0.0001 in. with a Testing Machines, Inc., Model 49-70 electronic micrometer. Thickness measurements were made at every inch over the specimen length and the average was used for the calculations. Crosshead speed was 0.2 in/min; gauge length was 2.0 in.

Solubility of these polyimide films was evaluated in NMP, DMAc, diglyme, DMF, and chloroform at intervals of 3 h, 1 day, 3 days, and 5 days using a 1% solids concentration in a closed vial. Visual identification determined if the polyimides were soluble, partially soluble, or insoluble. Noted in the evaluations were discoloration of the solvent, swelling of the polymer, or other changes in the polymer films.

For moisture absorption determination, the samples were first desiccated by heating them to 120°C in a vacuum oven until their weights became constant. They were submerged in 90°C water until their weights stabilized. The saturation moisture weight percent (w/o) was determined as

$$\begin{aligned} \text{Saturation moisture weight percent } (w/o) \\ = [(w_{ss} - w_{ds})/w_{ds}] \times 100 \end{aligned}$$

where w_{ss} is the saturated sample weight and w_{ds} is the desiccated sample weight.¹² The saturation moisture volume percent (v/o) was then calculated from the measured weight fraction as follows:

$$\begin{aligned} \text{Saturation moisture volume percent } (v/o) \\ = \frac{100\rho(w/o)}{100 + \rho(w/o)} \end{aligned}$$

where ρ is the density of the dry polymer sample relative to the density of water.¹²

Positron lifetimes in the test films were measured using a low-energy positron flux generation scheme in order to obtain free-volume values in

selected polymers.¹³ The positron source holder was thin aluminized Mylar® film. It was sandwiched between two well-annealed polycrystalline, high-purity, tungsten moderator strips. The test films were placed between the source holder and the moderator strips. The films electrically insulated the source holder from the moderator strips. Thermalized positrons diffused out of the moderator when a small negative potential ($-V$) was applied between the source holder and the moderator strips. The positrons were attracted to the source holder and therefore entered and annihilated in the test films. When a positive potential ($+V$) was applied, the outdiffusing positrons were forced back into the moderator strips. The difference in the two spectra from applied positive and negative potentials was entirely due to the positrons annihilating in the test films. The lifetime data were acquired using a 250-microcuries ^{22}Na positron source and a standard fast-fast coincidence measurement system with a time resolution of approximately 225 ps.¹²

RESULTS AND DISCUSSION

Desirable material requirements for the copolymer systems include glass transition temperatures ranging from 250 to 300°C; cure temperatures between 250 and 325°C; resistance to hydrolysis; resistance to adhesion loss after a water boil test at 120°C and 2 ATM; high toughness; electronically pure materials; inherent viscosities [$\eta(\text{inh})$] between 0.9 and 1.2 dL/g or higher if there were no obvious gels; good mechanical properties; insoluble polymers after curing; an insoluble partially imidized poly(amide acid) in strip solvents (i.e., ketones, butyl acetate); and a coefficient of thermal expansion in the range of 30–35 ppm/°C with a maximum allowable value of 50 ppm/°C.

Polymers were synthesized using an equimolar amount of dianhydride and diamine or a combination of diamines. Ratios of diamines employed were 50 : 50, 75 : 25, and 90 : 10. Additional polymers were synthesized using diamine combinations such as 60 : 40 and 80 : 20 to optimize the desired properties once the original combinations were characterized. The polyimides were characterized by inherent viscosities of the poly(amide acid)s, glass transition temperatures, thermogravimetric analysis reported as a temperature at which 10% weight loss occurred, CTE, mean tensile strength, mean tensile modulus, and mean

elongation at break. Once the best candidates for the intended applications were selected from each series, moisture uptake and positron annihilation spectroscopy were performed to determine a weight percent moisture uptake and free-volume fraction. Atomic force microscopy (AFM) was performed on selected candidates to determine the potential planarity of the film. AFM determined the topography of the film surface. Scanning electron microscopy (SEM) was also performed on selected candidates to see if there were any obvious defects or impurities. Four series of polyimide copolymers were synthesized and characterized: (1) HQDEA + 4,4'-ODA : SAPPD, (2) ODPA + 3,4'-ODA : SAPPD, (3) ODPA + 3,4'-ODA : *p*-PDA, and (4) BTDA + 4,4'-ODA : *p*-PDA.¹⁴

Copolymers of HQDEA + 4,4'-ODA : SAPPD

Copolymers were prepared combining HQDEA with 4,4'-ODA and SAPPD; the HQDEA phenoxy units contributed to a lower processing temperature (T_g) and the SAPPD contributed to a lower CTE. Tamai et al. reported on melt-processible polyimides containing HQDEA.¹⁵ Polyimides containing SAPPD were first reported in 1993.^{16,17} The main focus of this work was on linear polyimides containing the cyclobutene-3,4-dione moiety. These polyimides exhibited high glass transition temperatures, adhered tenaciously to glass, and showed excellent resistance to electron radiation exposures. Polyimides prepared with SAPPD possess relatively low CTEs but have somewhat lower thermal stability than that of commercial polyimide film.

Table I shows the inherent viscosities of the PAAs, T_g 's determined by both DSC and TMA, 10% weight loss temperature (TGA), and CTE. The solution viscosities ranged from 0.93 to 2.72 dL/g. The T_g 's by TMA ranged from 231 to 277°C. The homopolymer, HQDEA/SAPPD, outgassed and no T_g could be determined by DSC or TMA techniques. Weight losses of 10% occurred between 407 and 525°C for the polyimide series. CTEs ranged from 35.5 to 42.6 ppm/°C.

In general, several trends were noted in the HQDEA + 4,4'-ODA : SAPPD series. As the concentration of SAPPD increased, the inherent viscosity and apparent T_g increased while the temperature at which 10% weight loss occurred and CTE decreased. The higher T_g 's are the result of the larger, stiffer SAPPD incorporated into the backbone. The more rigid the molecule, the more difficult the mobility becomes and, consequently,

Table I Characterization of HQDEA + 4,4'-ODA : SAPPD Copolymers:

Ar		η_{inh} (dL/g)	T_g by DSC (°C)	T_g by TMA (°C)	10% Weight Loss (°C)	CTE (ppm/°C)
0	100	2.72	ND	ND	407	ND
50	50	2.35	ND	277	470	35.5
60	40	1.45	254	274	474	37.0
70	30	1.03	271	258	496	39.9
75	25	1.42	266	256	503	38.9
90	10	1.18	251	244	516	42.6
100	0	0.93	240	231	525	40.0

ND, not detected due to decomposition or outgassing of the polymer sample.

the greater the temperature required to give the polymer sufficient energy to move in a way appropriate to the rubber state.

The temperature at which 10% weight loss occurred decreased with increasing SAPPD. The thermal instability was believed to be the result of partial degradation or complexing due to the squaric acid moiety. Thermooxidative stabilities should follow the rule that if a dianhydride and a diamine are electron-deficient then the resultant polyimides should exhibit better oxidative resistance than that of other polymers of similar molecular weights. Electron-poor dianhydrides include BTDA, pyromellitic dianhydride (PMDA), ODPa, and 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA).¹⁸ HQDEA is not listed but it is postulated that it is similar to ODPa. SAPPD is not a common diamine but data produced here indicated that its stability is not as good as that of diphenyl ether. This is tentatively attributed to the aliphatic nature in the SAPPD which is not as stable as the *–phenylene–O–phenylene* bond. The size of the moiety will probably result in a larger or smaller free volume, and this may help explain the CTE values. The CTE decreased nearly linearly with increasing amounts of SAPPD due to its rigidity.

The mechanical properties of HQDEA + 4,4'-ODA : SAPPD are shown in Table II. The tensile

strengths ranged from 15.9 to 23.8 ksi with a % COV ranging from 2 to 9%. The tensile moduli ranged from 370 to 670 ksi with a % COV of less than 4% for the specimen group; elongations at break were between 7.8 and 93.1% with a % COV ranging from 11 to 51%. Elongation is strongly dependent on the film quality. Several observations were noted: The tensile strength changed very little with copolymer compositions up to 50% SAPPD. The strengths of the copolymers did not follow the rule of mixtures; and tensile strengths for the copolymers were lower than for both of the homopolymers. The modulus increased only slightly with compositions up to 40% SAPPD. Elongation decreased with increasing amounts of SAPPD and decreasing amounts of 4,4'-ODA. 4,4'-ODA contributed more flexibility to the polymer, resulting in higher elongations.

All films in the HQDEA + 4,4'-ODA : SAPPD series were insoluble in chloroform, DMAc, NMP, and diglyme. Insolubility was a necessary material requirement.

The best candidates from this series based on the material requirements were the 75 : 25 and 60 : 40 copolymers. The T_g 's were 256 and 274°C, respectively. The CTEs were 38.9 and 37.0 ppm/°C, respectively, that is, only slightly higher than the optimum range of 30–35 ppm/°C. No outgassing occurred in these samples.

Table II Mechanical Properties of HQDEA + 4,4'-ODA : SAPPD Copolymers:

Ar

			Mean Tensile Strength (ksi)	Mean Tensile Modulus (ksi)	Mean Elongation (%)
0	100		21.4	670	7.8
50	50		17.6	460	11.3
60	40		17.2	390	11.1
70	30		15.9	390	10.7
75	25		17.8	390	42.7
90	10		16.6	380	42.2
100	0		23.8	370	93.1

The polyimides in this series evaluated for moisture uptake and free-volume fraction were the two homopolymers, HQDEA/SAPPD and HQDEA/4,4'-ODA, and the 75 : 25 copolymer. The moisture uptake by weight (*w/o*) and volume (*v/o*), cell size, free-volume fraction, *f*(%), and inhibition factor are shown in Table III.

The moisture uptake by weight (*w/o*) ranged from 0.83 to 2.36. The moisture uptake of the homopolymer was not greatly affected by the 25 molar percent addition of SAPPD to afford the 75 : 25 copolymer, which was a very desirable polymer characteristic. Moisture uptake by volume (*v/o*) ranged from 1.11 to 3.23.

Positron annihilation spectroscopy data were used to determine the cell size, free-volume fraction, and inhibition factor in the polymer films. Positrons, the anti-particles of electrons carrying a positive charge equal in magnitude to the negative charge carried by an electron, quickly

thermalize when they enter polymeric solids. These thermalized positrons then destroy the molecular electrons. Three possibilities exist when the positron enters the test films: (1) They exist as free positrons, (2) they exist as positronium species (a bound state of electron and positron), and (3) they exist as a trapped positron. The lifetime of each of these can then be used to calculate the cell size (void) and the free-volume fraction. The free-volume fraction is calculated from the mean size and number of cells and is an indication of how much space is available for infiltration of the moisture. If the moisture uptake (*v/o*) is lower than the free-volume fraction, there is a chemical or geometrical factor inhibiting the penetration of the moisture into the polymer, such as polar groups, electronic factors, or geometric influences due to packing of the chains. The inhibition factor is a ratio of the moisture uptake by volume (*v/o*) to the free-vol-

Table III Moisture-uptake and Free-volume Fraction Data for HQDEA + 4,4'-ODA : SAPPD Polymers

Polyimide	Moisture Uptake (<i>w/o</i>)	Moisture Uptake (<i>v/o</i>)	Cell Size (Å ³)	Free Volume Fraction <i>f</i> (%)	Inhibition Factor
HQDEA/4,4'-ODA	0.83	1.11	3.7	3.7	0.30
75 : 25	0.85	1.14	2.2	2.2	0.53
HQDEA/SAPPD	2.36	3.23	4.8	4.8	0.67

ume fraction. Therefore, if the inhibition factor is close to 1.0, the majority of the free volume is being filled by water molecules. Conversely, if the number is closer to 0.0, the penetration of the water is being inhibited.

The cell size is the average size of the microvoid. The cell size does not account for distributions of small or large voids, only a mean value. The cell size ranged from 4 to 22 Å³. The size of the microvoids was quite large for the two homopolymers compared to the 75 : 25 copolymer. The size of the microvoid is drastically reduced in the copolymer compared to the homopolymers.

The free-volume fraction (f %) ranged between 2.2 and 4.2. The free volume was lowest for the 75 : 25 copolymer. The inhibition factors ranged between 0.30 and 0.67. The HQDEA/4,4'-ODA has the lowest inhibition factor. This backbone structure imparted resistance to moisture.

AFM and SEM were used to characterize the HQDEA/4,4'-ODA homopolymer and the 75 : 25 copolymer. AFM indicated that the surface topography of the homopolymer HQDEA/SAPPD had islands (peaks), approximately 15–20 nm in height, in a directional pattern. The 75 : 25 copolymer had an average surface roughness of 15–20 nm with the same oval-shaped islands of 8–10 nm in height. The copolymer was more planar than was the homopolymer. SEM indicated that there was particulate matter on both surfaces of the films. These data indicated that filtering the PAA solutions may be required to obtain uniform surfaces on substrates or electronic-device packages.

Copolymers of ODPA + 3,4'-ODA : SAPPD

Copolymers were prepared combining ODPA with 3,4'-ODA and SAPPD. The polymer designated ODPA/3,4'-ODA is patented under the trademark LaRC™-IA and is a well-characterized polyimide with excellent thermal, chemical, and mechanical properties.¹⁹ However, its T_g is too low and its CTE is too high for the proposed applications. Adding SAPPD to this homopolymer should impart a higher strength, modulus, and T_g , while lowering the CTE.

Table IV shows the characterization of the random ODPA + 3,4'-ODA : SAPPD copolymers. Inherent viscosities ranged from 1.12 to 1.34 dL/g. T_g 's by DSC were not detected for several polymers due to outgassing or decomposition in the polymers containing greater than 25 molar per-

cent of SAPPD. Other T_g 's ranged from 237 to 261°C. The temperature at which 10% weight loss occurred ranged from 422 to 518°C. CTEs ranged from -2 to 39.5 ppm/°C. The homopolymer ODPA/SAPPD had a negative CTE. Larger amounts of SAPPD in the polymer backbone produced lower CTEs. SAPPD imparted dimensional stability but impaired thermooxidative stability. The mechanical properties of the ODPA + 3,4'-ODA : SAPPD polymers are shown in Table V. Tensile strengths ranged from 16.9 to 25.9 ksi with a % COV ranging from 4 to 11%. Moduli ranged from 420 to 870 ksi with a % COV of less than 5%. Elongations ranged from 4.2 to 63.4% with a % COV ranging from 14 to 115%. The general trends noted were that tensile strengths and moduli increased with increasing amounts of SAPPD while the elongation decreased.

Based on the material requirements for the target microelectronics applications, the best candidate from the ODPA + 3,4'-ODA : SAPPD series was the 80 : 20 polyimide. The T_g was 254°C with a 10% weight loss occurring at greater than 500°C. The CTE was low (36.0 ppm/°C) and mechanical properties were good.

AFM indicated a well-distributed surface roughness of approximately 15–20 nm for the ODPA/SAPPD homopolymer. There were no distinct islands (peaks) on the surface as seen with the HQDEA + 4,4'-ODA : SAPPD copolymer candidate. The surface roughness of the 80 : 20 copolymer was lower, approximately 10–15 nm. SEM showed no particulate matter for the ODPA/SAPPD homopolymer and only a very small amount of particulate matter for the copolymer.

Moisture-uptake and free-volume data for the 80 : 20 copolymer and homopolymers are shown in Table VI. The w/o moisture uptake ranged from 0.88 to 3.07. The v/o moisture uptake ranged from 1.20 to 4.23. The cell size ranged from 9 to 17 Å³. The free-volume fraction ranged from 3.5 to 4.4%. The inhibition factor ranged from 0.27 to 0.97. The 80 : 20 copolymer had the lowest moisture uptake and a higher free volume than that of the ODPA/3,4'-ODA. This indicated that there was more space available for the penetration of moisture but the moisture uptake was inhibited by some chemical or geometric factor. The 80 : 20 copolymer had the lowest inhibition factor.

Copolymers of ODPA + 3,4'-ODA : *p*-PDA

A third series of copolymers were prepared by combining ODPA with 3,4'-ODA : *p*-PDA. As at-

Table IV Characterization of ODPA + 3,4'-ODA : SAPPD Copolymers:

Ar							
		η_{inh} (dL/g)	T_g by DSC (°C)	T_g by TMA (°C)	10% Weight Loss (°C)	CTE (ppm/°C)	
0	100	1.12	ND	ND	422	-2 to 6	
50	50	1.14	ND	ND	456	30.8	
75	25	1.19	ND	261	503	34.2	
80	20	1.23	252	254	505	36.0	
90	10	1.30	249	250	518	38.5	
100	0	1.34	238	237	511	39.5	

ND, not detected due to decomposition or outgassing of the polymer sample.

tempted in the previous series via addition of the SAPPD monomer, *p*-PDA was used in this series of copolymers to lower the CTE and raise the T_g of the LaRCTM-IA polymer. Since ODPA/3,4'-ODA possesses excellent chemical, physical, and mechanical properties, lowering the CTE and raising the T_g by altering the polymer backbone slightly would make it a potential candidate for microelectronics applications. Additionally, no outgassing would be expected as seen in the polyimides with SAPPD in the backbone.

Table VII shows the characterization of ODPA + 3,4'-ODA : *p*-PDA copolymers. Inherent viscosities ranged from 0.70 to 1.34 dL/g. The T_g 's by TMA ranged from 237 to 350°C. Temperatures at which 10% weight loss occurred ranged from 511 to 533°C. CTEs ranged from 26.0 to 39.5 ppm/°C.

Several trends were noted: Generally, as the amount of 3,4'-ODA increased, the viscosity increased. As expected, the T_g 's increased as the amount of *p*-PDA increased due to the rigidity of the *p*-PDA versus a more flexible 3,4'-ODA.

Table V Mechanical Properties of ODPA + 3,4'-ODA : SAPPD Copolymers

Ar				
		Mean Tensile Strength (ksi)	Mean Tensile Modulus (ksi)	Mean Elongation (%)
0	100	25.9	870	6.4
50	50	18.8	600	4.2
75	25	18.5	490	9.6
80	20	20.7	460	10.6
90	10	18.6	440	63.4
100	0	16.9	420	28.1

Table VI Moisture-uptake and Free Volume for the ODPA + 3,4'-ODA : SAPPD Copolymers

Polyimide	Moisture Uptake (<i>w/o</i>)	Moisture Uptake (<i>v/o</i>)	Cell Size (Å ³)	Free-volume Fraction <i>f</i> (%)	Inhibition Factor
ODPA/3,4'-ODA	0.96	1.32	13	3.5	0.35
80 : 20	0.88	1.20	17	4.4	0.27
ODPA/SAPPD	3.07	4.23	9	4.4	0.97

Weight loss temperatures were excellent at greater than 500°C and CTEs decreased as the amount of *p*-PDA increased. This was due to the thermal stability and rigidity that *p*-PDA imparted in the polymer backbones. The mechanical properties of ODPA + 3,4'-ODA : *p*-PDA are illustrated in Table VIII. Tensile strengths ranged from 16.9 to 30.0 ksi with a % COV ranging from 2 to 11%. Moduli ranged from 420 to 830 ksi with a % COV of less than 9%. Elongations ranged between 6.5 and 47.8% with a % COV ranging from 17 to 115%.

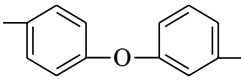
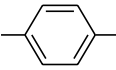
As predicted, tensile strengths and moduli increased with increasing amounts of *p*-PDA due to the rigidity of *p*-PDA. Elongation did not follow a general trend. It was expected that as the *p*-PDA increased the elongation would decrease; however, this was not the case. Elongation is strongly

dependent on the film quality and this could have altered the expected trend.

The best candidate from the ODPA + 3,4'-ODA : *p*-PDA series for the intended microelectronics applications was the 60 : 40 copolymer. The T_g was 255°C, the 10% weight loss temperature was 527°C, the CTE was 33.0 ppm/°C, the tensile strength was greater than 20 ksi, the modulus was greater than 500 ksi, and the elongation was 27%.

Table IX shows the moisture-uptake and free-volume data for the 75 : 25 polyimide and its homopolymers. Although data were evaluated for this polymer prior to the synthesis of the 60 : 40 copolymer, the data should be similar for the 60 : 40 copolymer. The *w/o* moisture uptake was excellent for 75 : 25 copolymer and superior to the two homopolymers which ranged from 0.96 to 1.22.

Table VII Characterization of ODPA + 3,4'-ODA : *p*-PDA Copolymers:

Ar		η_{inh} (dL/g)	T_g by DSC (°C)	T_g by TMA (°C)	10% Weight Loss (°C)	CTE (ppm/°C)
		0.88	ND	350	533	26.0
0	100	1.08	265	301	514	28.7
50	50	0.73	259	256	516	28.1
55	45	1.28	251	255	527	33.0
60	40	0.89	257	249	525	32.6
65	35	0.95	257	247	518	34.4
70	30	1.32	248	245	516	37.3
75	25	0.70	248	243	528	37.9
90	10	1.34	238	237	511	39.5
100	0					

ND, not detected due to decomposition or outgassing of the polymer sample.

Table VIII Mechanical Properties of ODPA + 3,4'-ODA : *p*-PDA Copolymers:

Ar		Mean Tensile Strength (ksi)	Mean Tensile Modulus (ksi)	Mean Elongation (%)
0	100	30.0	830	14.7
50	50	21.5	530	6.5
55	45	21.6	530	21.8
60	40	21.1	510	27.6
65	35	19.3	420	51.6
70	30	15.9	390	10.7
75	25	18.9	370	47.8
90	10	17.9	360	33.1
100	0	16.9	420	28.1

The *v/o* moisture uptake ranged from 1.32 to 1.75. The size of the free volume was relatively small (2.4%) for the 75 : 25 copolymer and its inhibition factor was moderate.

Copolymers of BTDA + 4,4'-ODA : *p*-PDA

The last series of copolymers were synthesized by combining BTDA and 4,4'-ODA : *p*-PDA. Lui and Stoffer²⁰ synthesized and characterized copolyimides based on PMDA and 4,4'-ODA/*p*-PDA.

Characterization data are shown in Table X. Inherent viscosities ranged from 1.21 to 1.49 dL/g. The T_g 's by TMA ranged from 271 to 357°C. Weight loss of 10% occurred between 501 and 527°C. CTEs ranged from 16.6 to 35.4 ppm/°C. The inherent viscosities of the two homopolymers BTDA/*p*-PDA and BTDA/4,4'-ODA were approximately the same. The highest viscosity resulted from the 50 : 50 combination. The T_g 's did not

follow a trend. Similar T_g 's by TMA were observed for the 50 : 50 and 75 : 25 copolymers. Weight loss temperatures did not differ significantly in the series. As the amount of *p*-PDA increased, the CTE decreased. *p*-PDA imparted more dimensional stability than did the 4,4'-ODA since it is more rigid. CTEs of the series were all within the desired range for the intended applications.

The mechanical properties of the BTDA + 4,4'-ODA : *p*-PDA copolymers are shown in Table XI. Tensile strengths ranged from 21.1 to 32.2 ksi with a % COV ranging from 3 to 13%. Moduli ranged from 430 to 790 ksi with a % COV of less than 5%. Elongations ranged from 17.6 to 49.5% with a % COV ranging from 41 to 87%. Tensile strengths and moduli generally increased as the amount of *p*-PDA increased. Elongations, however, decreased as would be expected as a result of the stiffer *p*-PDA versus the flexible ether-containing 4,4'-ODA.

Table IX Moisture-uptake and Free-volume data for the ODPA + 3,4'-ODA : *p*-ODA Copolymers

Polyimide	Moisture Uptake (<i>w/o</i>)	Moisture Uptake (<i>v/o</i>)	Cell Size (Å ³)	Free-volume Fraction <i>f</i> (%)	Inhibition Factor
ODPA/3,4'-ODA	0.96	1.32	16	3.5	0.35
75 : 25	1.05	1.44	4	2.4	0.60
ODPA/ <i>p</i> -PDA	1.22	1.75	3	2.0	0.85

Table X Characterization of BTDA + 4,4'-ODA : *p*-PDA Copolymers:

Ar						
		η_{inh} (dL/g)	T_g by DSC (°C)	T_g by TMA (°C)	10% Weight Loss (°C)	CTE (ppm/°C)
0	100	1.21	ND	341	516	16.6
50	50	1.49	ND	357	501	24.8
60	40	1.28	251	255	527	33.0
75	25	1.38	292	355	512	31.9
90	10	1.21	277	276	519	32.9
100	0	1.22	273	271	516	35.4

ND, not detected due to decomposition or outgassing of the polymer sample.

Based on the material requirements, the best candidate from the BTDA + 4,4'-ODA : *p*-PDA series was the 90 : 10 copolymer. Its inherent viscosity was high (1.21 dL/g). The T_g was 276°C. The copolymer displayed excellent thermooxidative stability and a relatively low CTE of 32.9 ppm/°C. Mechanical properties of this system were also highly suitable for the desired applications.

It should be noted that the moisture uptake of this particular group was higher than that of the previous three series. Moisture-uptake and free-volume data are shown in Table XII. Lower moisture uptake by weight was observed for the BTDA/4,4'-ODA and 90 : 10 copolymers with values of 1.34 and 1.38, respectively, while the homopolymer BTDA/*p*-PDA exhibited a moisture up-

take of 2.12%. Moisture uptake by volume ranged from 1.82 to 2.97. The cell size was quite large for the 90 : 10 copolymer, which indicated that there was free volume available for occupancy by the water molecules; however, their penetration was inhibited by some chemical or structural factor as indicated by the low moisture absorption value and low inhibition factor. The inhibition factors ranged from 0.42 to 1.00. The homopolymer BTDA/*p*-PDA exhibited an inhibition factor of 1.00, which indicated that nearly all the free volume was occupied by the water molecules.

CONCLUSIONS

Four series of polyimide copolymers were synthesized and characterized. In the first two series, the

Table XI Tensile Properties of BTDA + 4,4'-ODA : *p*-PDA Copolymers

Ar				
		Mean Tensile Strength (ksi)	Mean Tensile Modulus (ksi)	Mean Elongation (%)
0	100	32.2	790	27.0
50	50	25.4	590	17.6
60	40	21.1	510	27.6
75	25	23.6	510	33.6
90	10	21.3	470	24.0
100	0	22.3	430	49.5

Table XII Moisture-uptake and Free-volume Data for the BTDA + 4,4'-ODA : *p*-PDA Copolymers

Polymer	Moisture Uptake (<i>w/o</i>)	Moisture Uptake (<i>v/o</i>)	Cell Size (Å ³)	Free-volume Fraction <i>f</i> (%)	Inhibition Factor
BTDA/4,4'-ODA	1.34	1.82	5	3.0	0.58
90 : 10	1.38	1.88	18	3.8	0.42
BTDA/ <i>p</i> -PDA	2.12	2.97	6	2.9	1.00

general trends observed were that the addition of the SAPPD diamine to the polymer backbone decreased the CTEs and increased the mechanical strengths and moduli. The copolymers containing the highest concentrations of SAPPD were observed to have decreased thermooxidative stabilities and outgassing. The third and fourth series of copolymers utilized *p*-PDA to increase the rigidity and significantly lower the CTE of the resultant polyimides. The thermooxidative stabilities and mechanical properties of all *p*-PDA polymers were outstanding. Five polyimide copolymers exhibited the best combinations of physical and mechanical properties useful in the intended microelectronics applications. Candidates from the series incorporating the SAPPD diamine included HQDEA + 75 4,4'-ODA : 25 SAPPD, HQDEA + 60 4,4'-ODA : 40 SAPPD, and ODPA + 80 3,4'-ODA : 20 SAPPD. The best candidates for the intended applications from the series incorporating *p*-PDA included ODPA + 60 3,4'-ODA : 40 *p*-PDA and BTDA + 90 4,4'-ODA : 10 *p*-PDA.

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