The Thermo-Oxidative Stability of Fluorinated Polyimides and Polyimide/Graphite Composites at 371°C

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SYNOPSIS

Increasing demands to decrease engine weight and improve engine performance has led to an investigation to develop polymer composites capable of being used at 371°C and above in 4 atmospheres of air. The results of an investigation to determine the thermo-oxidative stability (TOS) of various fluorinated polyimides, 3F-PDA, 36F-PDA, Avimid-N, AFR700B, and other PMR-type resins and graphite composites containing these polyimides at 371°C in air at 1 and 4 atmospheres are presented. Weight losses due to aging under these conditions are presented as the criteria for measuring the TOS. The data show that 3F-PDA and Avimid-N which have equivalent TOS, exhibit twice the TOS than that of AFR700B and other PMR-type resins. 36F-PDA exhibits even better TOS than 3F-PDA or Avimid-N. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Advanced aircraft such as the Advanced Technical Fighter (ATF) are placing increasing demands on polymeric structural components which are strong, stiff, and light weight at temperatures exceeding 370°C. Very few polymer materials are capable of long-term use at 370°C in air, at 1 atmosphere, and still fewer are capable of operating at 370°C in air at 4 atmospheres, which are operating conditions in the cold section of engines. Some recent studies[1-3] have shown that a newly developed resin system AFR700B may be capable of 371°C use. Other resins such as V-CAP-II-50 and V-CAP-II-75[4,5] and 3,4'-oxydianiline modified PMR-15, known as RP-46[6] also are being investigated for 371°C use.

In this paper, the results of an investigation to determine the thermo-oxidative stability (TOS) of 3F-PDA, 36F-PDA, Avimid-N, AFR700B, and other PMR-type resins and graphite fiber composites containing these resins are described.

EXPERIMENTAL

Monomer and Resin Preparation

Preparation of Monomers

The dimethylester of 5-norbornene-1,2-dicarboxylic acid (NE) was prepared by refluxing a solution of 5-norbornene-1,2,dicarboxylic acid anhydride (NA) (164.2 g, 1 mol) in methanol (10 mol) for 3.0 h. The material on cooling to room temperature crystallized to a white solid. The solid was triturated in a cold solution of ether/n-hexane (50 : 50), filtered, washed with cold ether/n-hexane (50 : 50), air dried, and finally vacuum dried at 60°C overnight. A white crystalline solid, mp 97–98°C in 86% yield was obtained.

The dimethyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDE) and the dimethylester of 4,4'-hexafluoroisopropylidine diphthalic acid dianhydride (6FDME) were prepared by refluxing a solution of the corresponding dianhydride (1 mol) (Allco High Purity 3,3'4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) 322.2 g; Hoechst Electronic grade 4,4'-hexafluoroisopropylidene diphthalic acid dianhydride (6FDA)

444.226 g), in methanol (10 mol) for 1 h. The solution was immediately cooled, and used to prepare the polymerizable monomer reactants (PMR) solution.

Diethyl ester of 4,4'-[2,2,2-trifluoro-1-phenylethylidene]-diphthalic dianhydride (3FDEE) and diethyl ester of 4,4'-(hexafluoro isopropylidene) biphthalic acid anhydride (6FDEE) were prepared as follows: 4,4'-[2,2,2-Trifluoro-1-phenylethylidene] diphthalic dianhydride (3FDA) (10.0 g, 0.0221 mol) or 4,4'-(hexafluoroisopropylidene) biphthalic acid anhydride (6FDA) (9.770 g, 0.0221 mol) was added to a 50-mL round-bottom flask. Absolute ethanol (10 mL, 0.246 mol) was added, and the mixture was brought to reflux. Reflux was stopped after the 3FDA or 6FDA was completely in solution (~ 1 h). The solution was cooled to room temperature, and used to prepare the 3F-PDA and 6F-PDA solutions described below.

Preparation of Resin Solutions

PMR-15 Solution

The mole ratio of NE/BTDE/(4,4'-methylenedianiline) used for PMR-15 resins was 1.000 : 1.0435 : 1.5435. NE (13.285 g, 0.0677 mole) was added to a methanol solution (60 wt %) of BTDE (27.296 g, 0.0766 mol), while stirring at room temperature. We added 4,4'-methylene dianiline (20.460 g, 0.10319 mol) to the ester solution. The PMR-15 solution was used to fabricate G30-500(u) prepreg and resin powder for discs.

PMR-II-30 and PMR-II-50 Solutions

The mole ratio of NE/6FDEE/para-phenylenediamine (p-PDA) used for PMR-II-30 was 1.000 : 2.517 : 3.017. The mole ratio of NE/6FDME/p-PDA used for PMR-II-50 was 1.000 : 4.454 : 4.954. For the PMR-II-30, 6.229 g (0.0317 mol) of NE was used, while for PMR-II-50, 5.615 g (0.0286 mol) was used. PMR-II-30 contained 42.34 g (0.79365 mol) of 6FDME and 10.3 g (0.0952 mol) of p-phenylenediamine. PMR-II-50 contained 65.033 g (0.12794 mol) of 6FDME and 15.328 (0.1417 mol) of p-phenylenediamine. NE was added to a methanol solution (60 wt %) of the dimethylester 4,4'-hexafluoroisopropylidene diphthalic dianhydride (6FDME) while stirring at room temperature to dissolve. The diamine was then added to the ester solution. These solutions were used to make the G30-500 prepreg required for composite fabrication and resin powder for discs.

3F-PDA, 6F-PDA, and 36F-PDA Resin Solutions

The diethyl ester solution was used to prepare a solution of the prepolymer by adding the appropriate quantities of para- and meta-phenylenediamine.

We added para-phenylene diamine (~ 2.00 g, the exact amount depending on the 3FDA/PDA ratio investigated) to a solution of 3FDEE (0.0221 mol) in methanol or 6FDEE (0.0221 mol) in methanol prepared as described above. For the 36F-PDA resin, a 50 : 50 mixture of 3FDEE and 6FDEE was used. It was stirred at room temperature until dissolved. The solution turned from light amber to brown to deep purple. To prepare a solid, the solution was allowed to evaporate at room temperature to a viscous mass. Then it was vacuum treated at 60°C overnight to a powder. To prepare prepreg, the solution was diluted further by the addition of ethanol 19 mL (15.0 g) to give a 30 wt % solution.

Preparation of Resin Powders and Fabrication of Resin Discs

AFR-700B Resin Powder and Fabrication of Resin Discs

This resin was extracted from AFR700B/G30-500 8HS cloth prepreg supplied by Dexter Composites using methanol. Removal of the resin was judged complete when the methanol extract was colorless. The methanol solution of AFR700B resin was allowed to concentrate on a hot plate at 50°C until a dark-purple viscous residue was formed. This was then treated at 70°C for 2 h in vacuum to form a purple foam. The foam was ground into a powder and treated at 110°C for 1.5 h, then 220°C for 1.5 h, and, finally, 260°C for 1.5 h to obtain an imidized prepolymer. Sufficient powder was placed in a 2.54 cm (1 in) or 3.81 cm (1.5 in) diameter mold to obtain a finished, fully dense disc with a thickness of 0.635 cm (0.25 in). The imidized powder was further cured in the mold as follows: the temperature was raised to 200°C at 5°C/min, contact pressure, then application of 4000 psi, with a hold for 10 min, followed by a release of pressure and reapplication. The temperature was raised to 316°C at 2°C/min, 4000 psi, the pressure was released at 316°C, then reapplied, and held for 1 h. After 1 h, pressure was released and reapplied, the temperature was raised to 343°C at 2°C/min, 4000 psi; at 343°C, the pressure was released, reapplied immediately, and held for 2 h at 4000 psi; after 2 h the pressure was released and immediately reapplied (4000 psi), and the temperature was raised to 371°C at 0.7°C/min. At 371°C,

the pressure was released and reapplied immediately, and held at 4000 psi for 2 h. After this time, pressure was released and reapplied, and the temperature was raised to 416°C at 1°F/min. At 416°C, the pressure was released and reapplied, and held at 416°C for 8 h at 4000 psi. After this, the pressure was released and it was allowed to cool to room temperature at 5°F/min.

PMR-II-30 and PMR-II-50 Resin Powder and Resin Discs

The PMR-II resin solutions were allowed to concentrate at room temperature to a viscous oil. The solutions were dried at 60°C in vacuum for 2 h to a solid foam. The foam was ground to a powder and thermally treated as follows: 125°C for 1 h, then 200°C for 1 h, and, finally, 250°C for 1.5 h.

Resin discs were fabricated by placing the imidized powder (~ 5.0 g) in a 1-in diameter mold. The mold was placed in a preheated press, and the temperature was raised to 200°C/at 5°C/min, contact pressure; 4000 psi was applied at 200°C, and held for 10 min; the temperature was raised to 250°C at 2°C/min, 4000 psi, and held for 10 min. The pressure was released and reapplied, then the temperature was raised to 316°C at 2°C/min at 4000 psi, and held 1 h. Pressure was released and reapplied; then the temperature was raised to 343°C at 2°C/min, 4000 psi, and held for 2 h at 340°C; the temperature was raised to 371°C at 1°F/min and 4000 psi, and held for 2 h, at 4000 psi. The pressure was released, and the mold was allowed to cool to room temperature in the free state. The resin disc was removed and post-cured at 371°C for 24 h in the free state.

Avimid-N Resin Powder

An ethanol solution of NR-150B resin (now called Avimid-N) was allowed to concentrate to a viscous solution at 50°C in a hood. The viscous solution was heated in an oven at 60°C for 2 h in vacuum to a solid foam. The foam was ground to a powder and then thermally treated at 125°C for 2 h, then 220°C for 2.0 h and, finally, 275°C for 1 h. The thermally treated resin powder was used to fabricate the resin discs.

3F-PDA, Avimid-N, 6F-PDA, and 36F-PDA Resin Discs

The ethanol solution of 3F or 6F resin was evaporated on a hot plate at 50°C to a viscous solid, then dried at 60°C for 2 h in vacuum. The purple crystalline solid was imidized at 125°C for 2 h, then

220°C for 2 h, and, finally, 275°C for 1.0 h. Approximately 5.0 g were placed in a mold and consolidated at room temperature at 4000 psi. Pressure was released, and the temperature was raised to 250°C at about 3°C/min. At 250°C, pressure (4000 psi) was applied and held for 15 min. The temperature was raised to 280°C at 3°C/min, maintaining 4000 psi. At 280°C, the pressure was released and reapplied. The temperature was then raised to 316°C at 3°C/min and held for 1 h. The pressure was released and reapplied, (4000 psi) and held at temperature for 15 h. The temperature was raised to 370°C at 3°C/min and held at 370°C and 4000 psi for 24 h, then raised to 416°C maintaining 4000 psi, and held 8 h. After this time, pressure was released, and the mold was allowed to cool to RT at 3°C/min in the press.

Fabrication of Composites

3F-PDA, Avimid-N, and 6F-PDA Composites

The G30-500 (e) 8HS weave fabric was cut into 4.5 in × 6.0 in sections. A solution of 3F-PDA or 6F-PDA resin was brush applied to each section to yield a fabric tape containing 40 wt % resin. The impregnated fabric tape or the commercial Avimid-N plies were placed in a mold without the plunger and staged as follows: 60°C for 2 h in vacuum, then at 120°C for 1 h, and 225°C for 2 h, and, finally, at 275°C for 1 h. The plunger was placed in position, the temperature was raised to 280°C at 3°C/min, contact pressure, and held at temperature for 15 min; then pressure (1000 psi) was applied and held for 15 min. The temperature was raised to 316°C at 3°C/min at 1000 psi. At temperature the pressure was released, and then reapplied. The mold was held at 316°C at 1000 psi, for 15 h. The temperature was raised to 370°C at 3°C/min, at 1000 psi, and held under these conditions for 24 h. Pressure was released, and the composite was allowed to cool to room temperature at 3°C/min. The laminates were postcured in argon or nitrogen at 416°C for 8 h in the free state.

PMR-II-30 and PMR-II-50 Composites

Each fiber material was drum-wound in the dry state to a width of 4.5 in. A solution of PMR-15 or PMR-II-30 monomers containing sufficient material to yield a graphite fiber tape containing 40 wt % of PMR monomers, was hand-brushed onto the fiber as it rotated slowly. The solvent was allowed to evaporate at RT. The tape was removed, cut into 10.5-in sections, stacked in a 4.5 in × 11 in mold, and "B" staged at 200°C for 1 h and 250°C for 1.5

h. The mold plunger was placed in position and the mold put into a preheated press (250°C). The temperature was raised to 200°C, pressure was applied (1000 psi), held for 10 min, released, and then the temperature was raised to 250°C at 2°C min and held for 10 min. Pressure was released and reapplied immediately (1000 psi); the temperature was increased to 316°C at 2°C/min at 1000 psi, and held under these conditions for 1 h. For the PMR-II composites, the temperature was raised to 343°C at 2°C min and held for 2 h at 1000 psi, then raised to 371°C at 0.6°C/min, and held for an additional 2 h at 1000 psi. After this time, the pressure was released, and the composites were allowed to cool to RT at 3°C/min. The PMR-15 composite was post-cured at 316°C for 16 h in the free state. A portion of the PMR-15 composite and the PMR-II-30 and PMR-II-50 composites was postcured at 371°C for 24 h in the free state. The nominal thickness of the composites were 0.100 in.

AFR700B/G30-500(e) Composite

The AFR700B/G30-800(e) 8HS weave fabric prepreg was obtained from Dexter Composites. The prepreg was cut into seven 4.5 in × 10.5 in sections. The plies were placed on the female section of the stainless-steel mold. The male section was placed over the plies. The lay-up was heated at 200°C for 1 h, then at 250°C for 2 h. It was placed in a pre-heated press (200°C). The press was programmed for the following cure cycle: (1) the temperature was raised to 200°C at 5°C/min, contact pressure; at 200°C, pressure was applied (1000 psi), and it was held for 10 min, (2) the temperature was raised to 250°C at 2°C/min, at 1000 psi, and it was held for 10 min; then pressure was released and reapplied immediately, (3) temperature was raised to 316°C at 2°C/min, at 1000 psi, and held for 1 h; pressure was released and reapplied immediately, (4) the temperature was raised to 343°C at 2°C/min at 1000 psi, and held for 2 h under these conditions, (5) the temperature was raided to 371°C at 1°F/min, at 1000 psi, and held for 2 h; the pressure was released and reapplied immediately, (6) the temperature was raised to 416°C at 1°F/min, and held for 8 h, at
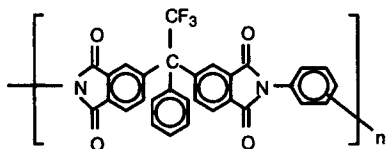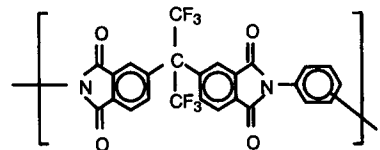

Figure 1   3F polyimide.

Figure 2   Avimid-N.

1000 psi, (7) then the pressure was released and the composite was allowed to cool to RT at 5°C/min.

Resin, Graphite Fiber, and Composite Aging at 371°C

The nominal dimensions of the resin samples which were aged were one-quarter segments of a 2.54-cm (1 in) diameter by 0.645 cm (0.25 in) thick disc. Duplicate samples were run. The nominal dimensions of the flexure specimens which were aged were 0.635 cm wide by 5.59 cm long × 0.254 cm thick. At least six specimens were measured for the 75- and 100-h runs and 12 specimens for the 25.5- and 50-h runs. Duplicate samples (3–4 g) of graphite fiber were aged. Resin, composite, and fiber samples were aged in an autoclave in an air flow of 100 cc/min at 4 atmospheres and 371°C. The temperature of the autoclave was thermally controlled in a Blue M oven, by setting the temperature required to attain 371°C. The temperature of the gas at the autoclave inlet and the temperature of the autoclave internally at the midpoint were recorded continuously during the run. The temperatures were held constant at 371°C within 2°C at both points. Specimens were weighed before and after the aging process to determine weight loss. Samples were also aged at 371°C in this same air circulating Blue M oven by placing the samples on top of the autoclave where the inlet temperature is being monitored.

Composite Composition

The composite composition was determined by the acid digestion method. Composites contained 65–70 vol % fiber, 30–32 vol % resin, and 3–5 vol % void.

Thermal Analysis and Density

Thermomechanical analysis (TMA, Module 943) and differential scanning calorimetry (DSC, Module 912) were performed using a DuPont 9900 Thermal Analyzer to determine the glass transition (T_g) of the polyimide samples. Densities were calculated from the weight and volume measurements of each sample.
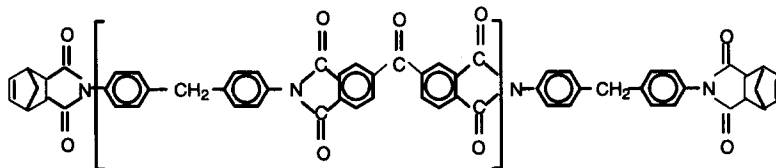
Figure 3 Polyimide PMR-15.

RESULTS AND DISCUSSION

The general structural features of the polyimides investigated are shown in Figures 1 through 5. The fluorinate polyimide (3F-PDA) was reported by Scola in two U.S. Patents[7,8] and later by Alston.[9] Similarities of the 3F-PDA polyimide to the Avimid-N polyimide are shown in Figures 1 and 2. Replacement of one CF_3 unit of the Avimid-N structure with a phenyl group creates a carbon with considerable crowding. This causes the groups attached to the methane-like carbon to bend out of plane creating a pseudo asymmetric carbon. This can lead to unusual polymer properties which have yet to be explored. The reaction sequence to the 3F-PDA polyimide is shown in Figure 6. Monomer and polymer syntheses are described in a recent publication.[10] Thus, the 3F-PDA and 6F-PDA (Avimid-N) polyimides have similar and unique structural features. Except for PMR-15 (Fig. 3), the other polyimides investigated can be considered modifications of the high-temperature polyimide, Avimid-N.

In the modifications, a cross-linkable end group is introduced, thereby controlling the molecular weight of the basic repeat unit chain, and changing this linear unit to a cross-linked polymer, as shown for the nadic end-capped PMR-II polyimide series,[11-13] (Figure 4). This formulation employs a molar ratio of diester/diamine/nadic ester of n : (n + 1) : 2. When n = 5, the theoretical prepolymer molecular weight is 3000, and when n = 8.9, the theoretical prepolymer molecular weight is 5000, designated as PMR-II-30 and PMR-II-50, respectively. The advantage of the nadic end-caps is improved processability and increased glass transition temperature relative to Avimid-N.

A more recent modification[12] of the Avimid-N structure involved introduction of one cross-linkable end group, thereby controlling the molecular weight of the basic repeat unit chain, as shown for the nadic end-capped polyimides AFR700A and AFR-700B (Fig. 5). By controlling the ratio of monomer reactants, polyimides can be produced with nadic and aminophenyl end caps or nadic and anhydride end caps. The molecular weight of the repeat unit and the concentration of end caps is controlled by the moles of monomer utilized in the formulation. The anhydride end capped oligomer employs a diester/
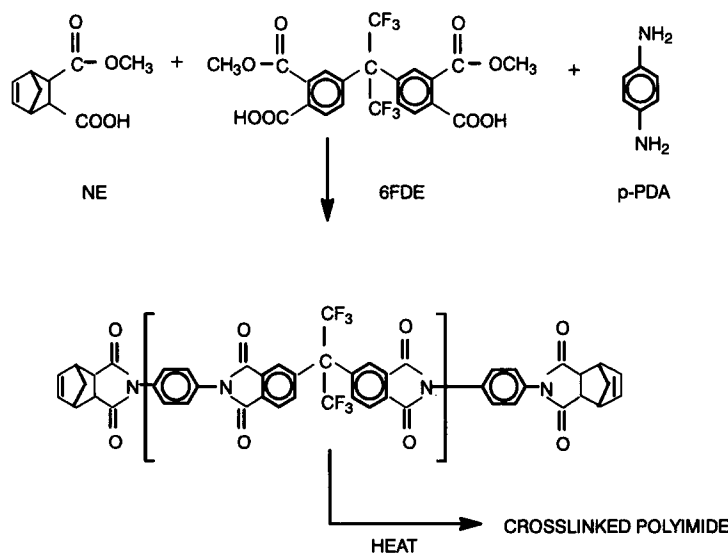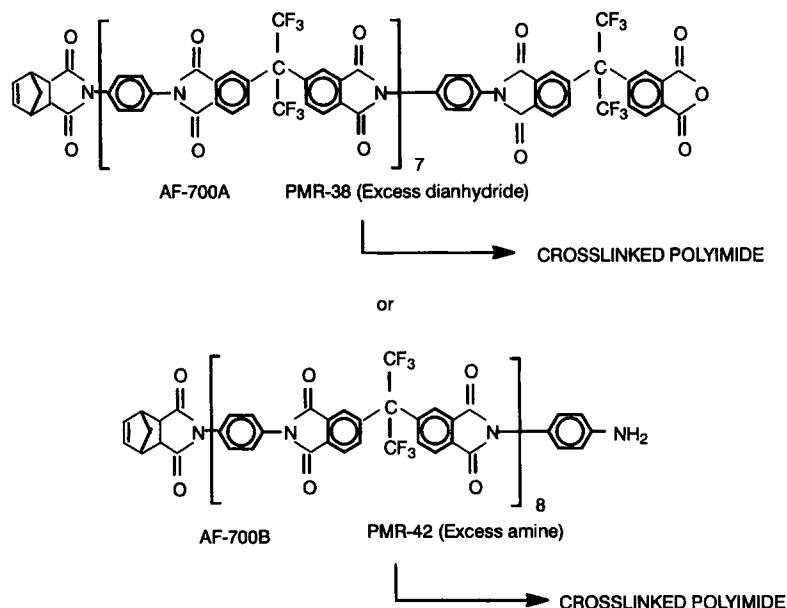

Figure 4 PMR-II polyimide series.

Figure 5   AFR700 polyimides.

diamine/nadic ester mole ratio of $n : n : 1$. For AFR700A, when $n = 7$, the theoretical, formulated oligomer molecular weight is 3800. For the amine end-capped polymer, the mole ratio of diester/diamine/nadic ester (6FDME/p-PDA/NE) used is defined as follows: $n : (n + 1) : 1$. For AFR-700B, when $n = 8$, the theoretical formulated oligomer molecular weight is 4200.

In our studies, to determine the optimum stoichiometric ratio of 3FDA monomer to paraphenylene diamine (3FDA/PDA) required for maximum thermo-oxidative stability, it was found that monomer compositions with excess diamine exhibited poor thermo-oxidative stability.[10] The 3F-PDA

polyimide derived from the optimum composition was used in the present study.

3F-PDA Resin Stability (TOS)

A summary of the thermo-oxidative stability of 3F-PDA at 1 and 4 atmospheres exposure at 371°C relative to Avimid-N, AFR700B, and other PMR-type resins is listed in Tables I and II. For the 1 atmosphere exposure data, it is clear that after 50 h at 371°C, 3F-PDA, Avimid-N and 6F-PDA (our version of Avimid-N) exhibit twice the thermo-oxidative stability of AFR-700B. After 100 h, 3F-PDA, 6F-PDA and Avimid-N exhibit twice the stability
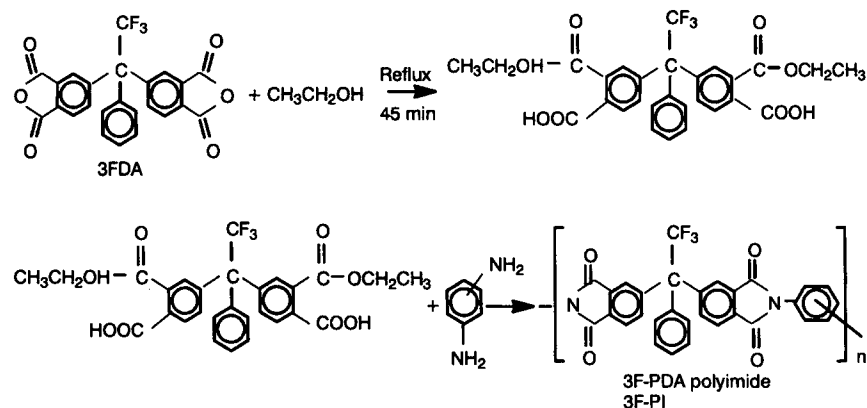
Figure 6   Reaction sequence for 3F polyimides.

Table I   Thermo-Oxidative Stability of Resins Based on Weight Loss[a]

Resin Material	Wt % Loss After			
	25 h	50 h	75 h	100 h
Avimid-N	1.10	1.41	2.86	3.1
6F-PDA	1.15	1.44	2.96	3.3
3F-PDA	1.10	1.45	2.30	3.1
PMR-II-30	2.51	—	—	6.0
PMR-II-50	—	—	—	5.0
PMR-15	5.7	8.3	12.5	17.1
AFR700B	1.57	3.1	4.55	6.4
36F-PDA	0.64	0.96	1.32	1.8

[a] Aged 371°C, 1 atmosphere, air-circulating oven.

as PMR-II-30 and PMR-II-50 and AFR-700B. Resin 36F-PDA is a novel copolymer of 3FDA and 6FDA with paraphenylene diamine. This fluorinated resin exhibited the lowest weight loss after 100 h of exposure than any resin tested.

The weight losses after exposure at 4 atmospheres of air flow (100 cc/min) at 371°C are shown in Table II. After 25 h, 3F-PDA, 6F-PDA, and Avimid-N exhibited a weight loss of about 2.5%, whereas AFR-700B showed a weight loss of 4.28%. UTC's fluorinated polymide 36F-PDA showed the lowest weight loss (1.5%). After 50 h, AFR700B shows a greater weight loss than either PMR-II-30 or PMR-II-50 (8.83% versus 7.55 and 6.6%), and a much greater weight loss than the 3F or 6F polyimides (8.83% versus 5.71%). After 100 h, the 3F-PDA or 6F-PDA polyimides showed a 10.5–12.0% weight loss. Clearly, the 1- and 4-atmosphere data showed that 3F-PDA

Table II   Thermo-Oxidative Stability of Resins Based on Weight Loss[a]

Resin Material	Wt % Loss After				
	10 h	25 h	50 h	75 h	100 h
Avimid-N	1.61	2.30	4.26	6.10	10.5
6F-PDA	1.12	2.54	5.07	7.65	12.2
3F-PDA	1.20	2.66	5.71	8.5	12.1
PMR-II-30	—	4.19	7.55	—	—
PMR-II-50	—	3.41	6.60	—	—
PMR-15	—	6.60	—	—	25.2
AFR-700B	—	4.28	8.83	13.4	18.8
36F-PDA	—	1.57	3.40	6.04	9.1

[a] Aged 371°C, 4 atmospheres, airflow 100 cc/min.

Table III   Density and Glass Transition Temperature of 3F-PDA and Other Resins

Resin System	Tg°C	Density g/cc
3F-PDA	425	1.341
DuPont's Avimid-N	407	1.440
6F-PDA	—	1.440
AFR700B	445	1.419
36F-PDA	406	1.358

and Avimid-N resins are superior to AFR-700B and other PMR-type resins tested.

The superior performance of the 3F-PDA and Avimid-N resins is based on polymer systems consisting of stable monomer building blocks and a composition where the stoichiometry is carefully controlled and optimized for maximum TOS. This is in contrast to the AFR700B and PMR-II resins which consist of stable monomer building blocks and relatively unstable nadic end-caps. AFR-700B also has the added disadvantage of containing excess diamine leading to amine end-capped end groups. In our studies, polyimide compositions, which contain excess diamine, exhibited poorer thermo-oxidative stability, than did compositions with excess dianhydride. In conclusion, the 1- and 4-atmosphere tests show that 3F-PDA and Avimid-N polyimides exhibit twice the thermo-oxidative stability as do AFR700B and other PMR-II-type resins.

Density and Glass Transition Temperatures of 3F-PDA and Other Resins

Table III lists the densities and Tg's of 3F-PDA, Avimid-N, AFR700B and other resins. The densities are what can be expected of resins containing fluorine. The high Tg's are derived from post-cure of the resins at 416°C for 8 h.

Composite Thermo-Oxidative Stability

A limited number of 3F-PDA/graphite fiber composites were fabricated for comparison with AFR700B/, Avimid-N/, PMR-15/, PMR-II-30/, and PMR-II-50/graphite fiber composites.

Weight-loss data for composites aged at 371°C at 1 atmosphere in an air-circulating oven are shown in Table IV. The weight-loss data suggest that the AFR700B resin is equivalent in properties to PMR-II-30 and PMR-II-50, but clearly not superior. To be certain that the effect of resin stability on com-

Table IV   Thermo-Oxidative Stability of Composites Based on Weight Loss[a]

	Wt %[b] Loss After		
Composite System[c]	100 h	200 h	300 h
AFR700B/G30-500(e) 8HS cloth	3.8	11.4	—
Avimid-N/G30-500 8HS cloth	2.7	—	—
PMR-15/G30-500(u) Uni	5.6	14.8	—
PMR-II-30/G30-500(u) Uni	3.1	9.9	—
PMR-II-50/G30-500(u) Uni	3.5	7.0	15.3
Avimid-N/G40-800(u) Uni	0.65	1.35	3.5

[a] Aged 371°C, 1 atmosphere, air-circulating oven.
[b] Based on flexure specimens.
[c] (e) is epoxy sized, (u) is unsized.

posite weight loss is being measured in these tests, and not fiber stability, both components were tested separately.

Fiber stability can have a profound effect on composite weight loss. Fiber weight losses at 371°C, in 1 or 4 atmospheres for G30-500(e) cloth purchased from Dexter, cloth extracted from AFR700/G30-500(e) prepreg, and for G30-500(u) continuous fiber are essentially equivalent (Table V). It is also apparent that G30-500 cloth extracted from Avimid-N/G30-500 prepreg is superior in TOS than the other G30-500(e) fibers. The improved stability of this fiber and composites fabricated from these fibers may be attributed to the Avimid-N size which is reported to be present on the G30-500 fiber used in this prepreg. Therefore, the lower weight loss of Avimid-N/G30-500 8HS cloth composite relative to the AFR700B/G30-500(e) 8HS cloth composite and PMR-II-30 and PMR-II-50/G30-500(u) composites is most likely associated with the greater stability of both components, the resin and the Du Pont sized G30-500 graphite fiber.

Weight-loss data on several composites after exposure at 371°C, 4 atmospheres in flowing air (100 cc/min) are listed in Table VI. Based on weight loss, composites containing the G30-500 graphite fiber and 3F-PDA or Avimid-N resins are clearly more stable than G30-500 graphite composites containing AFR700B, PMR-15, PMR-II-30, or PMR-II-50 resins. Avimid-N composites containing G40-600(u) or G40-800(u) graphite fibers are clearly superior in TOS to composites containing G30-500 graphite fibers. This shows the influence of fibers on composite stability.

CONCLUSIONS

The polyimides 3F-PDA and Avimid-N have superior thermo-oxidative stability over such nadic end-capped polyimides as AFR700B, PMR-II-30, and PMR-II-50, even through, the latter polyimides contain the stable monomer components of the Avimid-N polymer. This has been demonstrated at 371°C at 1 and 4 atmospheres in air for both resin specimens and graphite/polymer composites. Mechanical property characterization of the composites aged under these conditions are presently being in-

Table V   Thermo-Oxidative Stability of Graphite Fibers at 371°C

	Wt % Loss at 371°C After				
	1 Atmosphere (Air-Circulating Oven)	4 Atmospheres, Air Flow 100 cc/min			
Fiber Material[a]	100 h	25 h	50 h	75 h	100 h
G30-500(e) 8HS cloth purchased from Dexter	6.98	6.07	17.7	31.9	50.7
G30-500(e) 8HS cloth from AFR-700B prepreg (Dexter)	6.35	5.34	17.5	31.4	51.2
G30-500(u) continuous fiber	5.91	4.83	14.3	24.9	41.5
G30-500 8HS cloth from DuPont Prepreg	2.94	2.60	8.0	13.5	26.6
G40-600(u) continuous fiber	0.35	—	—	—	0.42
G40-800(u) continuous fiber	1.34	—	—	—	19.9

[a] (e) is epoxy sized, (u) is unsized.

Table VI Thermo-Oxidative Stability (TOS) of Composites Based on Weight Loss[a]

Composite System[c]	Wt %[b] Loss at 371°C After			
	25.5 h	50 h	75 h	100 h
Avimid-N/G40-600(u) Uni	0.85	1.0	—	—
Avimid-N/G40-800(u) Uni	0.60	1.1	—	—
3F-PDA/G30-500(u) Uni	1.7	4.2	—	—
PMR-15/G30-500(u) Uni	4.3	8.8	15.4	23.8
PMR-II-30/G30-500(u) Uni	2.4	6.9	14.2	24.1
PMR-II-50/G30-500(u) Uni	2.0	7.2	15.2	23.7
AFR700B/G30-500(e) 8HS cloth	3.5	10.6	20.7	31.4
Avimid-N/G30-500 8HS cloth	1.6	7.0	11.7	20.9
Avimid-N/G30-500 8HS cloth	3.1	8.6	13.3	21.9

[a] Aged 371°C (700°F), 4 atmosphere in flowing air (100 cc/min).
[b] Based on flexure specimens.
[c] (e) is epoxy sized, (u) is unsized.

vestigated to further define aging effects on composite properties.

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