

REPLACEMENT OF MDA WITH MORE OXIDATIVELY STABLE DIAMINES IN PMR-POLYIMIDES

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Studies were performed to investigate the effect of substituting 4,4'-oxydianiline and 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane for the 4,4'-methylenedianiline in PMR polyimide matrix resin. Graphite fiber reinforced composites were fabricated from unsized Celion 6000 and PMR-polyimide matrix resins having formulated molecular weights in the range of 1500 to 2400. The composite processing characteristics were investigated and the initial room temperature and 316 °C (600 °F) composite mechanical properties were determined. Comparative 316 °C composite weight losses and 316 °C mechanical properties retention after prolonged 316 °C air exposure were also determined.

INTRODUCTION

The development of in situ polymerization of monomeric reactants (PMR) polyimides was first reported by investigators at the NASA Lewis Research Center (ref. 1). They reported that a methanol solution of 2.08 moles of the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), 3.08 moles of 4,4'-methylenedianiline (MDA), and 2 moles of the monomethyl ester of endo-5-norbornene-2,3-dicarboxylic acid (NE) provided a highly processable matrix resin. This resin solution, designated PMR-15, when polymerized in situ on the fiber, provided an optimum balance of desirable composite processing characteristics, composite thermo-oxidative stability, and retention of composite mechanical properties after long-term high-temperature aging. The in situ polymerization from monomeric reactants (PMR) represented a new technology of addition-cured polyimide matrix resins. Today, PMR-15 is commercially available from the major suppliers of prepreg materials and is being used in a wide range of aerospace components (ref. 2). A recent study (ref. 3) concluded that degradation of the MDA monomer is the major contributor to observed weight loss of PMR-15 composites in a 316 °C (600 °F) air environment. The purpose of this study was to determine the effects of replacing the MDA monomer in PMR-15 with two different, more thermo-oxidatively stable diamine monomers, 4,4'-oxydianiline (ODA) and 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA), on composite weight losses and retention of composite high-temperature mechanical properties.

Throughout this paper, interpretative descriptions will refer to more oxidatively stable diamines compared to the less oxidatively stable methylene-containing MDA diamine (used in PMR-15). This is to be understood in the context of meaning addition-cured polyimides containing more oxidatively stable connecting linkages such as those traditionally used in thermo-oxidatively stable condensation polyimides. Examples of these more oxidatively stable connecting linkages are the oxygen linkage (used in all ODA-based condensation polyimides), the carbonyl linkage in BTDE (used in all 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)-based condensation polyimides), and the phenyl trifluoroethane linkage (3F) in 3FDA (similar in structure to the very thermo-oxidatively stable hexafluoroisopropylidene (6F) connecting linkage used in all 6F based condensation polyimides). The 3F

linkage has been shown to be slightly superior thermally to the 6F linkage when compared in polyarylates using thermal gravimetric analysis (TGA) in a nitrogen environment (ref. 4). A slight increase was observed for 3F linkage polyarylate incipient decomposition temperature to 446 from 438 °C for the 6F linkage polyarylate. Similar comparative TGA data (ref. 5) ranked the 3F and 6F connecting linkages as being of the same relative thermal stability. However, neither study (ref. 4 or 5) reported any thermo-oxidative comparisons of the 3F and 6F linkages in an air environment. In contrast, the less oxidatively stable MDA diamine monomer in PMR-15 is to be understood in the context of containing an oxidizable methylene connecting group which kinetically is as much as two orders of magnitude more oxidizable than primary, secondary, and tertiary aliphatic hydrocarbons (ref. 6) such as in the nadimide crosslinker endcaps in PMR-15. Hydrocarbon-containing addition-curing polymers such as PMR-15 are generally considered to be of poorer thermo-oxidative stability than their nonhydrocarbon-containing counterparts, the thermo-oxidatively stable condensation polymers containing connecting linkages such as oxygen, carbonyl, and 6F groups. Thus, based on traditional relative thermal and thermo-oxidative stabilities of connecting linkages and textbook comparative hydrocarbon oxidative reactivities, the predicted order of oxidative stability of the monomeric components within the PMR polyimide polymers in this study would be as follows:

BTDA ~ ODA ~ 3FDA >> Aliphatic Nadic Endcaps >> MDA

EXPERIMENTAL PROCEDURES

Monomer and PMR Solution Preparation

The monomers used in the study are shown in table I. The NE, ODA, and BTDA were obtained as reagent grade chemicals from commercial sources and used in as-received form after verifying the melting points (m.p.). The 3FDA was synthesized by the literature procedure (ref. 7) as shown in row 1 of table II except that the reaction was scaled up five- and tenfold and the 3FDA was purified to a white powder (m.p. 217 to 217.5 °C) in 70 to 79% yields by multiple recrystallizations from chloroform. Table II also shows in row 1 that the purification in reference 7 was done by a chromatographic separation which provided an 88% yield of rose-colored 3FDA (m.p. 201 to 204 °C) in contrast to the improved purification of this study done by recrystallization from chloroform. The BTDE was synthesized by heating at the reflux temperature a suspension of BTDA in a calculated amount of methanol until the BTDA dissolved and then by continued heating for an additional 2 hr to result in a 50 weight percent (wt %) solution of BTDE in methanol. The PMR solutions were prepared at room temperature by adding, all at once to the BTDE solution, the NE, the diamine monomer (MDA, ODA, or 3FDA), and an equivalent weight of methanol to maintain 50 wt % solids. In the ODA and 3FDA formulations, additional methanol and a mixed solvent consisting of methanol and acetonitrile, respectively, were added to provide 35 wt % solids. The use of additional methanol and the mixed solvent were required along with gentle heating to dissolve the ODA and 3FDA in the PMR solution. The monomer combinations, abbreviations, formulated molecular weights, molar ratio value, and alicyclic weight percent of the PMR matrix resins used in this study are shown in table III.

Model Compounds and Instrumental Analysis

Bisnadimide derivatives of MDA, ODA, 3FDA, and 4,4'-diaminobenzophenone (DABP) were prepared by imidization in hot acetic acid followed by addition of acetic anhydride to complete the imidization. The bisnadimide derivatives were isolated in 80 to 90% yields by cooling the acetic acid reaction solution and suction filtration of the precipitated white solids. Recrystallizations were done in acetic acid except for the 3FDA bisnadimide which was recrystallized from acetonitrile. The m.p. of the bisnadimides were: MDA = 255 to 256 °C, ODA = 258 to 260 °C, 3FDA = 245 to 246 °C, and DABP = 320 to 321 °C. Thermal gravimetric analysis (TGA) of the bisnadimide model compounds was done on Perkin Elmer TGS-2, infrared analysis on a Nicolet FT-IR 7199, carbon and hydrogen NMR analysis on a Varian FT-80A, and differential scanning calorimeter (DSC) analysis on a DuPont 990 equipped with a pressure DSC cell. The glass transition temperature (T_g) of the matrix resins was determined at a heating rate of 20 °C (36 °F)/min on a DuPont 942 thermo-mechanical analyzer.

Composite Fabrication

Prepreg tapes were made by drum winding at 4.72 turns/cm (12 turns/in) and impregnating unsized Celion 6000 graphite fiber with the various PMR solutions listed in table III to yield prepregs containing 40 to 41 wt % monomers. (This is calculated to provide cured laminates of 63 wt % fiber when resin flow is about 3%). The prepregs were air dried on the rotating drum at room temperature for 3 to 6 hr and then allowed to stand without rotation overnight. The prepreg tapes were removed from the drum, cut into 7.6 by 20.3 cm (3 by 8 in) plies, and stacked unidirectionally 12 plies thick. The prepreg stack was placed in a pre-forming mold and staged at 204 °C (400 °F) for 1 hr under a pressure of approximately 0.5 kPa (0.067 psi). A typical plystack lost 4 to 6 g of volatiles and weighed 48 to 52 g after staging. Composites were molded by placing the staged prepreg stack into a matched metal die at room temperature. The die was inserted into a 316 °C (600 °F) press. When the die thermocouple read 232 °C (450 °F), a pressure of 3.45 MPa (500 psi) was applied. After the mold reached 316 °C (600 °F), the temperature and pressure were maintained for 2 hr. The mold was then allowed to cool to at least 177 °C (350 °F) before releasing the pressure and disassembling. The weight of the laminate plus flash was typically 0.5 to 1.0 g less than the staged prepreg. The weight of the flash divided by the composite plus flash weight was called the resin flow and ranged from 0.3% for ODAPMR-15 to 7% for 3FDAPMR-15 with a 2 to 4% range for the other composites. The laminates were postcured by heating in air from 24 to 316 °C (75 to 600 °F) over 2 hr, holding at 316 °C for 16 hr, and then slowly cooling to 24 °C. Postcure weight losses were all between 0.3 and 0.6%.

Composite Testing

All laminates were inspected for acceptability by an ultrasonic C-scan technique and then cut into nine 2.5 by 6.7 cm (1 by 2-5/8 in) pieces. Two pieces of each laminate were used to prepare triplicate flexural and interlaminar shear strength (ILSS) test specimens for room temperature and 316 °C (600 °F) tests. All the laminates were then inspected by obtaining photomicrographs of the composite cross sections to assure the composites were void free and of even resin/fiber distribution. Flexural strength tests were performed in accordance with ASTM Test for Flexural Properties of Plastics and Electrical Insulating Materials (D790-71).

Tests were made on a three-point load fixture with fixed span of 5.1 cm (2 in). The thickness of the Celion 6000 composite specimens ranged from 1.93 to 1.98 mm (0.076 to 0.078 in) for 3FDAPMR-15 and ODAPMR-15 to 2.06 to 2.16 mm (0.081 to 0.085 in) for all the other laminates resulting in a span/depth ratio ranging from 26.3 to 23.5, respectively. ILSS tests were performed essentially in accordance with ASTM Tests for Apparent Interlaminar Shear Strength of Parallel Fiber Composites by Short Beam Method (D2344-76) using a constant span/depth ratio of five. The rate of center loading for flexural and ILSS tests was 1.27 mm/min (0.05 in/min). Flexural and ILSS tests were conducted in an environmental heating chamber following a 15-min equilibration time at the test temperature. The mechanical property values reported are averages of three tests at each condition. Fiber content was determined for all laminates before aging by using a H₂SO₄/H₂O₂ digestion procedure. The flexural data were not normalized to a common fiber volume percent because of the small range of the fiber weight percents found by digestion and the insignificant effect of normalization on the raw flexural data (as shown later). The remaining seven 2.5 by 6.7 cm (1 by 2-5/8 in) test coupons were used for long-term isothermal exposure in a 316 °C (600 °F) circulating air oven having an air change rate of 100 cm³/min (6.1 in³/min). Composite weight loss measurements were made throughout the exposure period. Every 300 hr one test coupon was removed for 316 °C mechanical testing as described previously. Thus, the number of specimens for the weight loss measurements decreased sequentially from seven to one. Photomicrographs of the cross sections of aged composites were also obtained to visually investigate the manner in which the composites thermo-oxidatively degraded.

RESULTS AND DISCUSSION

Weight Loss Investigations

The thermal and thermo-oxidative stability of the bisnadimide model compounds of ODA, MDA, 3FDA, and DABP (described in the Model Compounds and Instrumental Analysis section) were investigated by dynamic thermal gravimetric analysis (TGA) in nitrogen and air atmospheres. The TGA curves presented in figure 1 show that the bisnadimide model compounds provided a char yield in nitrogen at 800 °C ranging between 28 and 42% weight retention. The amount of char yield at 800 °C appeared to be proportional to the molecular weight of the diamine. However, the intermediate weight retention plateaus (in the 300 to 500 °C region) in air or nitrogen tended to exhibit an inverse relationship to the molecular weight of the diamine. The MDA bisnadimide, containing the lowest molecular weight diamine, provided an intermediate weight retention plateau in air or nitrogen that was greater than or equal to the weight retentions of the higher molecular weight bisnadimides prepared from the more oxidatively stable diamines, ODA, DABP, and 3FDA. This suggested a greater amount of favorable weight retaining reactions occurred in the MDA bisnadimide compared to the other three bisnadimides.

It should also be noted that the intermediate plateau weight retentions were always greater for all four bisnadimides in air than in nitrogen. This suggests complex weight gaining oxidation reactions occur in all four bisnadimides. Unfortunately, these differences were too inconclusive to use dynamic TGA as a routine technique to screen the bisnadimide binary monomer combinations for decisive conclusions about long-term stability of various connecting groups in matrix resins. For example, even though an oxidation product of MDA would be DABP, the TGA weight retentions in air of the MDA and DABP bisnadimides were not identical. Thus, it would be highly desirable to include DABP (as a higher oxidation state of MDA) along with the three diamines (MDA, 3FDA, and ODA) used in this composite study.

Unfortunately, a small test laminate prepared with BTDE/DABP/NE PMR polyimide at $N = 2.0$ (FMW = 1500) did not exhibit sufficient resin flow to fabricate a comparable quality composite to the other laminates in this study (as listed in table III). Consequently, a DABP PMR-15 laminate was not included in this study even though it represents an oxidation product of PMR-15 and could also be considered as a PMR resin prepared with a diamine containing a more thermo-oxidatively stable connecting linkage such as carbonyl (DABP), oxygen (ODA), or phenyltrifluoroethane (3FDA). In retrospect, the unprocessability of BTDE/DABP/NE is due to the lack of a sufficient melt flow region on a 316 °C (600 °F) processing cycle. This might have been predicted from the approximately 60 °C higher m.p. of the DABP bisnadimide compared to the m.p. of the 3FDA, ODA, and MDA bisnadimides (see the Model Compounds and Instrument Analysis section). Thus, only the processable PMR monomer combinations given in table III were used to prepare graphite fiber composites with the following unsized Celion 6000 fibers: original experimental Celion 6000 of lot number HTA-7-6Y11 (hereafter designated old Celion (OC)), production grade Celion 6000 of lot number HTA-7-1231 (2760 MPa (400 ksi) tensile strength; hereafter designated intermediate Celion (IC)), and improved production Celion 6000 of lot number HTA-7-2531 (3590 MPa (520 ksi) tensile strength; hereafter designated new Celion (NC)).

The weight losses of the Celion 6000/PMR composites after extended 316 °C (600 °F) air exposure are plotted in figure 2. At a common alicyclic weight percent (FMW = 1500) on OC fiber the PMR-15 exhibited a lower weight loss than either ODAPMR-15 or 3FDAPMR-15. A 37.5% reduction in the amount of aliphatic NE (by increasing FMW to 2400) did not reduce the composite weight loss of OC/3FDAPMR-24 below the composite weight loss of OC/PMR-15.

The photomicrographic cross sections shown in figure 3 (and the IC and NC/PMR composites not shown) and the ultrasonic scans of all of the postcured OC, IC, and NC/PMR composites in this study were of comparable quality, thus eliminating void content, or composite processability, as a possible cause of the differing weight loss behavior observed in the OC/MDA, 3FDA, and ODA PMR composite systems and in the IC and NC/PMR composite weight loss comparisons to follow. Figure 2 also shows that the NC/PMR-15 composite provided a lower weight loss than either IC/3FDAPMR-19.5 or NC/3FDAPMR-24; the same trend was observed in comparing PMR-15 to 3FDAPMR-24, both on OC fiber.

It is important to note that all the composites in this study were aged at the same sample size and geometry, at the same time, and in the same 316 °C (600 °C) oven to minimize the effect of oven temperature fluctuations on composite weight loss results. The only exception was the IC/3FDAPMR-19.5, which was aged at a different time. The fact that the IC/3FDAPMR-19.5 and NC/3FDAPMR-24 weight loss measurements were conducted at different times using a different fiber lot and possibly under slightly different temperature conditions could account for the almost identical weight loss behavior exhibited by IC/3FDAPMR-19.5 and NC/3FDAPMR-24. A higher weight loss had been predicted for IC/3FDAPMR-19.5 because it has a higher aliphatic nadimide content than NC/3FDAPMR-24.

The use of two different fibers could also contribute to the similarity in the 3FDAPMR-19.5 and 24 weight losses in figure 2. Composite weight losses are sensitive to fiber type as shown by the comparison of PMR-15 on OC and NC fiber (shown in fig. 2). This suggests that the lower weight loss with NC fiber may result from a lower level of deleterious resin/fiber thermo-oxidative interactions with PMR-15 resin compared to the OC fiber. Differences in thermo-oxidative weight loss of PMR-15 resin on different fibers have been reported previously and discussed as due

to deleterious resin/fiber thermo-oxidative interactions, presumably due to differences in the contaminants of the fiber surfaces (ref. 8).

The OC, IC, and NC fibers used in this study lost 5 to 7% of their weight after 900 hr of air exposure at 316 °C (600 °F). Graphite fiber weight losses after a similar exposure can range from virtually 0% for high-modulus graphite fiber types to virtually 100% for high-strength high-sodium-content graphite fiber types (ref. 8). Therefore, the narrow range of 5 to 7% fiber weight loss in this study indicates the thermo-oxidative stability of the OC, IC, and NC fibers are quite comparable, thus leaving differences in the resin/fiber thermo-oxidative interactions as the probable cause of lower composite weight loss of NC/PMR-15 compared to OC/PMR-15. Thus, the major cause of the observed differences in the composite weight losses shown in figure 2 has to be due to the different diamines used in formulating the PMR matrix resin because variances due to void content, composite processability, sample aging size and geometry, sample aging temperature/time, and fiber thermo-oxidative stability have been eliminated, minimized, or accounted for.

The significantly greater level of weight loss of the ODAPMR-15 and 3FDAPMR-15 composites prepared with the more oxidatively stable diamines, compared to PMR-15 with the oxidizable MDA diamine, seems to be the reverse of what would be predicted based on the general concept that improved thermo-oxidative stability comes from preparing polymers with improved thermally and thermo-oxidatively stable monomers. A similar result was found in previous nadimide cured polymer studies. Neat resins prepared from BTDA/ODA/NE and pyromellitic dianhydride (PMDA)/ODA/NE (ref. 9) and composites fabricated from PMR solutions of BTDE/ODA/NE in N-methyl pyrrolidinone solvent (ref. 1) were of poorer 316 °C (600 °F) thermo-oxidative stability than when MDA was used instead of ODA as the diamine monomer.

In contrast, classical thermo-oxidative stability studies of condensation polyimides have shown that MDA/PMDA (ref. 10) and MDA/BTDA (refs. 10 and 11) provide only comparable or greater weight loss, but never significantly less, than PMDA on BTDA condensation polymers prepared with more oxidatively stable diamines, such as ODA and DABP. However, the level of weight loss reported for MDA condensation polyimides would have been slightly greater had it not been for the weight gaining oxidation reactions of the benzylic methylene connecting linkage oxidizing to a carbonyl linkage and the thermo-oxidative crosslinking reactions of the benzylic methylene linkage as identified in the literature (refs. 10 to 12). In this study of nadimide terminated polyimides the converse result was found: the MDAPMR-polyimide (PMR-15) consistently provided less weight loss than the PMR polyimides containing the more oxidatively stable diamines, ODA and 3FDA. It might be possible to account for the lower weight loss in the same manner as is done in the literature (refs. 10 to 12) for condensation polyimides containing MDA; that is, by oxidation of the benzylic methylene to a carbonyl connecting group and thermo-oxidative benzylic crosslinking reactions. However, these reactions would have to proceed with greater efficiency to provide less weight loss in PMR-15 (compared to ODAPMR-15 and 3FDAPMR-15) than the same benzylic connecting group thermo-oxidative reactions occurring in MDA condensation polyimides. These polyimides provide, at best, only comparable weight loss when compared to oxidatively stable diamines in non-MDA condensation polyimides.

Because the concentration of methylene connecting groups in condensation polyimides is greater than in the nadimide terminated PMR-15 (endcapping dilutes the molar concentration of the "within the chain" species), the same favorable benzylic weight gaining oxidations to a carbonyl connecting group and benzylic thermo-oxidative crosslinking can not kinetically occur to a greater extent in PMR-15 than

in the MDA condensation polyimide. Thus, the lower weight loss of PMR-15 compared to non-MDA PMR resins (ODAPMR-15 and 3FDAPMR-15) is not due solely to the use of the MDA monomer. Instead, the introduction of a second species, the polymerized nadimide endcap in cured PMR-15, in combination with the MDA benzylic linkage must account for a greater efficiency of thermo-oxidative crosslinking reactions such as those between benzylic methylene and polymerized nadimide endcap. This provides an oxidatively crosslinkable polymer exhibiting significantly lower weight loss than polymerized nadimide endcapped polyimides without the benzylic site (ODAPMR-15 and 3FDAPMR-15).

In summary, without both the polymerized nadimide endcap and the benzylic connecting linkage being present simultaneously, the weight loss of condensation or of low molecular weight addition polymers increases. This is the case with MDA condensation polyimides versus oxidatively stable diamine condensation polyimides (refs. 10 to 12) and in this study of PMR-15 versus ODAPMR-15 and 3FDAPMR-15 to 24. Thus, the presence of two easily oxidizable sites (polymerized nadimide and benzylic linkage) in PMR-15 results in a synergistic increase in thermo-oxidative weight retention due to favorable weight gaining oxidations and thermo-oxidative crosslinking reactions of benzylic methylene connecting linkages with polymerized nadimide endcaps.

Elimination of this synergistic effect can be accomplished with comparable weight losses resulting; however, the important point to understand is that the polymers with the synergism will exhibit less weight loss than that predicted, and polymers without the synergism will exhibit weight losses determined solely by the concentration and relative reactivities of the remaining oxidizable species. One example of this is the comparable weight loss observed for NC/3FDAPMR-24 and OC/PMR-15 (fig. 2), obtained by reducing the NE content 37.5% (increase to FMW = 2400) and by reducing the deleterious resin/fiber thermo-oxidative interactions by using NC fiber with the 3FDAPMR-24 resin (without the synergism). Another example (ref. 13) is the identical composite weight loss observed for PMR-II composites (without the synergism effect) and MDA-containing analogous composites (with the synergism), obtained by using a very oxidatively stable diamine monomer without any connecting linkage in PMR-II. In this case the weight loss comparison was done using composite samples that had not been aged together and using a fiber which, at that time period, exhibited deleterious resin/fiber thermo-oxidative interactions. These conditions combine to possibly nullify comparisons of the overall degradation rate of the more easily oxidizable MDA-containing analog and PMR-II. However, if the comparison is done on the same fiber (OC or NC), the PMR-15 composites (with the synergism) exhibited less weight loss than the 3FDAPMR-24 composite (without the synergism). In the PMR-II case (ref. 13) the study would have to be redone either as neat resins or with a fiber that exhibits a reduced level of deleterious resin/fiber thermo-oxidative interactions in order to determine if the weight loss of the MDA analog of PMR-II (with the synergism) would be less than, or only remained equal to, the weight loss of PMR-II (without the synergism).

A more indepth analysis of PMR-15 thermo-oxidative degradation mechanisms (ref. 3) has shown the oxidation of the benzylic connecting linkage to a carbonyl linkage does occur in PMR-15. An infrared analysis using a bulk sampling technique showed the oxidation to be limited (<0.8%). The oxidation to a carbonyl has been more clearly identified (ref. 14) as occurring on the thermo-oxidatively exposed resin surface by infrared analysis using a surface sampling technique; however, the extent of the surface carbonyl formation was not determined. The oxidative crosslinking reaction in PMR-15 has also been observed, but not structurally characterized, by infrared analysis as an oxidation found in the polymerized nadimide

component of PMR-15 (ref. 3). This nadimide thermo-oxidative reaction may be speculated as being the cause of an observed shift in the infrared band pattern related to the nadimide band variations adjacent to a benzylic group that has been oxidized to the carbonyl. This shift was observed in investigations of samples taken from the surface region of oxidatively exposed resin (ref. 14). The net overall effect of the multiple oxidation reactions occurring in PMR-15 (with the synergism) and in ODAPMR-15 or 3FDAPMR-15 or 24 (with the benzylic site for the synergism not present) can be best understood visually. Figure 4 contains photomicrographs of cross sections of composites of ODAPMR-15, PMR-15, 3FDAPMR-15, and 3FDAPMR-24. All the photomicrographs were taken when levels of composite weight loss were comparable or bracketed the weight loss of OC/PMR-15 after 2100 hr of 316 °C (600 °F) air exposure. The pictures in figure 4 show that the synergistic combination of benzylic methylene linkages and polymerized nadimide endcaps in PMR-15 limits the thermo-oxidative behavior to favorable surface oxidation reactions (carbonyl formation) and nadimide-benzylic thermo-oxidative crosslinking (as described above in this interpretation of ref. 14). In contrast, the increased depth of degradative void and crack formation with the PMR resins using more oxidatively stable diamines (without the synergism as in ODAPMR-15 and 3FDAPMR-15 and 24) is the result of unfavorable hydrocarbon thermo-oxidation of the polymerized nadimide crosslinker (being the next most oxidizable species when the benzylic methylene connecting linkage is not present).

Mechanical Property Investigations

The initial room temperature interlaminar shear strength (ILSS) of the seven composites ranged between 108 and 128 MPa (15.6 and 18.5 ksi). The 316 °C (600 °F) ILSS of the seven composites are shown in figure 5 as a function of 316 °C exposure time. The initial 316 °C ILSS ranged from 35 to 63 MPa (5.1 to 9.1 ksi). The initial 316 °C ILSS of composites made with 3FDAPMR-24 exhibited a thermoplastic failure mode which changed to a normal thermoset ILSS failure mode after 300 hr of 316 °C air aging. After 2100 hr of 316 °C air exposure a clear trend was apparent in the ILSS data: the only composites that exhibited excellent retention of 316 °C ILSS were the OC/PMR-15 and NC/PMR-15 composites. The IC/3FDAPMR-19.5 and NC/3FDAPMR-24 composites, which exhibited similar weight loss behavior compared to OC/PMR-15, failed to retain their initial 316 °C (600 °F) ILSS to the extent of the OC/PMR-15 composite. Even the OC/ODAPMR-15 composite which displayed the highest initial 316 °C ILSS fell below the OC/PMR-15 and NC/PMR-15 ILSS after only approximately 700 hr of 316 °C exposure. After 900 hr of 316 °C air exposure, the OC/3FDAPMR-15 composite had formed so much loose surface fiber due to the high rate of weight loss that the test interval was decreased to 150 hr and testing was performed to only 1500 hr of exposure. The OC/ODAPMR-15 had an identical rate of weight loss to OC/3FDAPMR-15 but did not exhibit as much loose surface fiber probably because of the lower fiber weight percent/higher resin weight percent (56.1%/43.9%) of OC/ODAPMR-15 compared to the higher fiber weight percent/lower resin weight percent (70.2%/29.8%) of OC/3FDAPMR-15. Thus, testing was done on the ODAPMR-15 composites for up to 2100 hr of 316 °C exposure. However, both OC/ODAPMR-15 and OC/3FDAPMR-15 composites exhibited a severe decrease in the ILSS after 900 hr of 316 °C air exposure.

The 316 °C (600 °F) flexural strength retention of the composites is shown in figure 6. The initial room temperature flexural strengths were in the range of 1566 to 1973 MPa (227 to 286 ksi). The initial 316 °C flexural strengths ranged from 752 to 1056 MPa (109 to 153 ksi). The flexural data shown have not been normalized to a common fiber weight or volume percent because all the laminates except OC/ODAPMR-15 and OC/3FDAPMR-15 were of very similar fiber weight percents ranging

between 63.9 and 65.7 percent, thus having no visible normalization effect on figure 6. The fiber weight percent for OC/3FDAPMR-15 was 70.2%. Thus, if OC/3FDAPMR-15 was normalized down to a 64% range, it would only further lower by about 10% the curve that was already the lowest of the set of seven curves after long-term exposure. The fiber weight percent for OC/ODAPMR-15 was 56.9%. If it was normalized up to a 64% range, it would only further raise by about 11% the curve that was the highest initially but dropped to the second lowest after long term exposure, hence not causing any changes in the relative position of the curve related to the other six curves in figure 6. Thus, a comparison of these curves shows that after much less than 2100 hr of 316 °C air exposure a similar trend to that seen in the ILSS retention (fig. 5) was again apparent. Only the OC and NC/PMR-15 composites exhibited excellent retention of 316 °C flexural strength; all the composites prepared with PMR monomer combinations using more oxidatively stable diamines exhibited severe decreases in flexural strength after 900 hr of 316 °C exposure. Even the OC/ODAPMR-15 composite, which displayed the highest initial 316 °C (600 °F) flexural strength, fell below the OC/PMR-15 and NC/PMR-15 flexural strengths after only 600 hr of 316 °C air exposure. Also, just as was observed in the ILSS data, the composites IC/3FDAPMR-19.5 and NC/3FDAPMR-24 which had exhibited weight loss behavior similar to that exhibited by OC/PMR-15 failed to display the same high level of flexural strength retention as did the OC/PMR-15 composite. The failure to provide comparable properties at comparable weight losses should not be surprising. PMR polyimide literature cites as an example MDA-containing composites prepared with varying dianhydride monomers (thus all containing the synergism) in which the retention of mechanical properties and extent of composite weight loss were not closely correlated (ref. 1). However, in this study it should be noted that, whether comparisons of mechanical property retention are done on the basis of equal composite weight loss or equal composite exposure time, the retention of ILSS and flexural strength was consistently and significantly better for PMR-15 (containing MDA with the thermo-oxidative synergism) than for PMR composites prepared with resins containing more oxidatively stable diamines (not containing MDA with its synergistic effect).

The flexural moduli of the seven composites are plotted in figure 7. The initial room temperature flexural moduli ranged between 117 300 and 132 480 MPa (17.0 and 19.2 msi). The initial 600 °F flexural moduli ranged from 93 150 to 120 060 MPa (13.5 to 17.4 msi). Unlike the ILSS (fig. 5) and flexural strength (fig. 6) a clear trend is not readily apparent in the retention of 316 °C (600 °F) flexural moduli. However, the flexural moduli after prolonged 316 °C exposure did exhibit the same overall order as the composite weight loss curves in figure 3. Perhaps more important, an examination of the flexural strength load curves uncovered a secondary slope. Recalculation of the flexural moduli with the secondary slopes did again exhibit a trend similar to the trends observed for ILSS and flexural strength retention. Figure 8 shows the retention of secondary moduli of the seven composites during prolonged air exposure. The solid symbols at the 0-, 300-, and 600-hr exposure times are the primary moduli at the exposure time when the primary moduli no longer were the same as the secondary moduli (the resin had started to exhibit a nonelastic response to applied load). The solid symbols at later exposure times (>1500 hr) are the final primary moduli from figure 7. Again the OC and NC/PMR-15 composites exhibited the highest retention of secondary flexural moduli as shown by the least decrease from the initial and final primary moduli values. The PMR-15 composites also took the longest exposure time to exhibit the least decrease in primary moduli to secondary moduli compared to the 3FDA composites which showed a moderate decrease in primary moduli at 0 hr and the ODAPMR-15 which exhibited a large decrease from its 600-hr primary moduli. Just as observed in the ILSS and flexural strength data, even the IC/3FDAPMR-19.5 and NC/3FDAPMR-24 composites which

exhibited similar weight losses when compared to OC/PMR-15 failed to retain their secondary moduli at comparable 316 °C (600 °F) exposure times to the extent the OC/PMR-15 composite retains the 316 °C secondary moduli. Indeed, there exists a large decrease to the secondary moduli at the final exposure times in all the 3FDAPMR composite primary moduli and also in the ODAPMR composite primary moduli compared to OC and NC/PMR-15 composite primary moduli.

Thus, the retention of all three composite 316 °C (600 °F) mechanical properties (ILSS, flexural strength, and flexural modulus) has been shown to be considerably poorer for PMR resin formulations containing the more oxidatively stable ODA and 3FDA compared to PMR-15 containing oxidizable MDA. The poor retention of composite mechanical properties of the OC/ODAPMR-15 and OC/3FDAPMR-15 was not unexpected in view of their greater weight losses compared to PMR-15 (fig. 2). However, when the long-term 316 °C mechanical properties are compared at equal composite weight losses (using later composite exposure times for PMR-15 compared to earlier exposure times for other PMR resins) the retention of mechanical properties of OC/ODAPMR-15 and OC/3FDAPMR-15 was still considerably poorer compared to OC/PMR-15. Reduction in the aliphatic nadimide content and use of the more oxidatively stable 3FDA on NC fiber (NC/3FDAPMR-24) provided a closely comparable rate of weight loss to OC/PMR-15, but even at the identical extended exposure times (and identical weight loss), the long-term retention of NC/3FDAPMR-24 composite mechanical properties was still considerably inferior to the mechanical property retention of OC/PMR-15.

A reason for the inferior mechanical property retention of NC/3FDAPMR-24 may be seen in the photomicrograph cross sections of the ODAPMR-15, 3FDAPMR-15 and 24, and PMR-15 composites shown in figure 4. The photographs were taken after long-term exposure times when composite weight losses were similar or bracketed the weight loss of OC/PMR-15 after 2100 hr of exposure (used as the comparative standard in fig. 4). The ODAPMR-15 and 3FDAPMR-15 and 24 composites show a much greater depth of void and crack formation, due to thermo-oxidative degradation, than PMR-15, thus visually accounting for the reduced level of composite mechanical property retention compared to PMR-15. When the thermo-oxidative reactions (carbonyl formation and thermo-oxidative crosslinking) are confined to the exterior polymer surface by using two easily oxidizable sites in PMR-15 (the synergism of the benzylic methylene of MDA and polymerized nadimide endcap), an undamaged PMR-15 interior results, as shown in figure 4. This would account for the high retention of PMR-15 composite mechanical properties. With the favorable weight gaining benzylic site thermo-oxidation and thermo-oxidative crosslinking of benzylic site with polymerized nadimide endcaps in the PMR-15 surface region (as discussed in the Weight Loss Investigations section), the thermo-oxidatively crosslinked network polymer structure would be maintained to account for the retention of composite mechanical properties of PMR-15.

In contrast, without the favorable synergistic thermo-oxidative reactions, such as occurs in ODAPMR-15 and 3FDAPMR-15 and 24 without the benzylic site of MDA, the thermo-oxidative degradation pathways can only proceed by using the next most easily oxidizable site, the polymerized, aliphatic nadimide crosslinker. The thermo-oxidative degradation rate would then be solely dependent on the reactivity and concentration of the remaining oxidizable species. This nonsynergistic situation provides a thermo-oxidative degradation pathway which would propagate with only limited termination ability (thermo-oxidative crosslinking) leading eventually to a breakdown of crosslink density and molecular weight of the polymerized nadimide structure. The nadimide hydrocarbon thermo-oxidative degradation pathway (in the absence of the benzylic methylene group) would then account for the increased rate of weight loss and inferior retention of mechanical properties, compared to PMR-15.

This is what was observed in this study when doing comparisons where the oxidizable concentration of hydrocarbon endcap was determined by the 1500 to 2400 formulated molecular weight of the PMR resins containing more oxidatively stable diamines.

CONCLUSIONS

Based on the results of this investigation the following may be concluded:

1. The use of 4,4'-methylenedianiline in nadimide-cured PMR-15 matrix resin appears to be essential for obtaining low composite weight loss. The use of more thermo-oxidatively stable diamine monomers such as ODA and 3FDA results in increased composite weight loss of the 1500 to 2400 formulated molecular weight nadimide cured matrix resins in this study.

2. The use of 4,4'-methylenedianiline in nadimide-cured PMR-15 matrix resin also appears to be essential for obtaining high retention of initial composite high-temperature (316 °C) mechanical properties. The use of more thermo-oxidatively stable diamine monomers such as ODA and 3FDA results in a deleterious effect on retention of composite high-temperature (316 °C) mechanical properties of the 1500 to 2400 formulated molecular weight nadimide-cured matrix resins in this study.

3. The lower composite weight loss and higher retention of composite mechanical properties of PMR-15 compared to PMR resins formulated with more oxidatively stable ODA or 3FDA was interpreted to be due to the synergistic combination of two easily oxidizable sites (benzylic methylene of MDA and polymerized nadimide endcap). This interactive site combination confines the thermo-oxidative reactions to favorable weight gaining reactions (such as carbonyl formation) and thermo-oxidative cross-linking in the air exposed surface regions of PMR-15. The synergistic combination reduces the rate of thermo-oxidative degradative weight loss and increases the retention of composite mechanical properties of PMR-15 compared to other nadimide-cured resins without the benzylic methylene group, such as the 1500 to 2400 formulated molecular weight ODAPMR and 3FDAPMR polyimides in this study.

4. The use of new Celion 6000 fiber (NC) might contribute to longer PMR-15 composite 316 °C (600 °F) lifetime than previously obtainable with old Celion (OC) fiber, probably due to a reduced level of deleterious resin/fiber thermo-oxidative interactions with NC than OC fiber.

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TABLE I. - MONOMERS USED IN POLYIMIDE SYNTHESIS

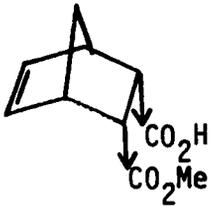
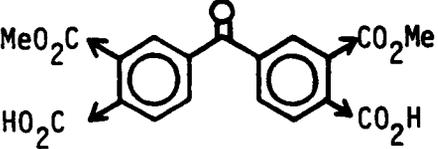
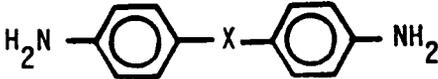
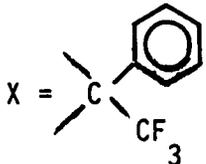
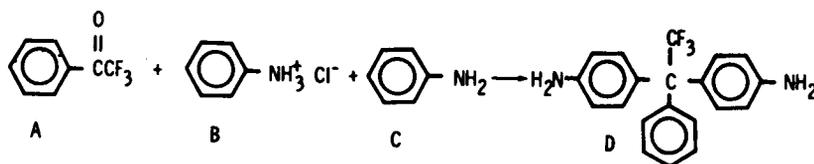
STRUCTURE	NAME	ABBREVIATION
	Monomethyl Ester of Endo-5-Norbornene-2,3-Dicarboxylic Acid	NE
	Dimethyl Ester of 3,3',4,4'-Benzophenonetetracarboxylic Acid	BTDE
 <p>X = -CH₂-</p> <p>X = -O-</p>	4,4'-Methylenedianiline	MDA
	1,1-Bis(4-Aminophenyl)-1-Phenyl-2,2,2-Trifluoroethane	3FDA

TABLE II. - 3FDA MONOMER SYNTHESIS



TIME/TEMP hr/°C	MOLAR RATIO A:B:C	SCALE GRAMS OF A	D, AS SYNTHESIZED			D, AS PURIFIED			
			YIELD, %	MP, °C	COLOR	PROCEDURE	YIELD, %	MP, °C	COLOR
24/REFLUX	1:1.4:7.5	10	-	-	-	SILICA GEL CHROMATOGRAPHY WITH BENZENE, THEN BENZENE/HEPTANE RECRYSTALLIZATION	88*	201-204	ROSE
30/185	1:1.4:7.0	12.5	103.1	191-196	PURPLE		41.0	214-215	LAVENDER
16/185		12.5	103.3	180-190			32.6	213-214	LAVENDER
22/180		12.5	96.2	202-207		MULTIPLE RECRYSTALLIZATIONS FROM CHLOROFORM	78.3	215.5- 216	WHITE
20/160		50	97.4	200-205			78.8	216.5- 217.5	
17/165	1:1.5:2	100	94.9	190-198			69.8	217- 217.5	

* J. ORG. CHEM., 42, 1186 (1977).

TABLE III. - MONOMER STOICHIOMETRY FOR PMR SOLUTIONS

REACTANTS, Molar ratio N/N+1/2	ABBREVIATION	N	FORMULATED MOLECULAR WEIGHT ^a (FMW)	WEIGHT PERCENT ALICYCLIC ^b
BTDE/MDA/NE	PMR-15	2.083	1500	12.27
BTDE/ODA/NE	ODAPMR-15	2.083	1505	12.22
BTDE/3FDA/NE	3FDAPMR-15	1.377	1500	12.27
BTDE/3FDA/NE	3FDAPMR-19.5	2.083	1943	9.44
BTDE/3FDA/NE	3FDAPMR-24	2.808	2400	7.67

^aWhere FMW = N(m.w.BTDE)+(N+1)(m.w.Diamine)+2(m.w.NE)-2(N+1)
(m.w.H₂O+MeOH)

^bWhere percent alicyclic = 100 x 2(m.w.C₇H₈)/FMW

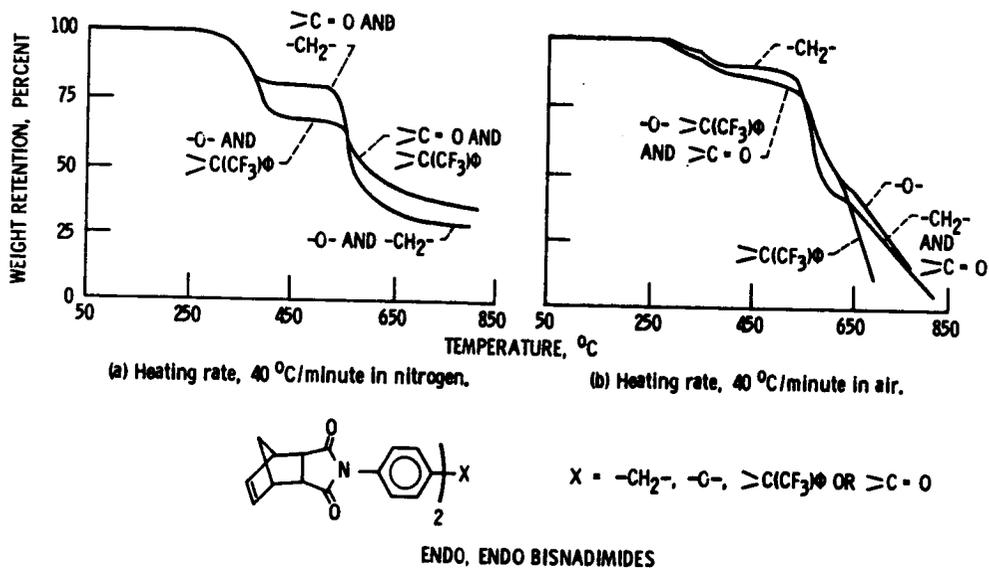


Figure 1. - Model compound thermogravimetric analysis.

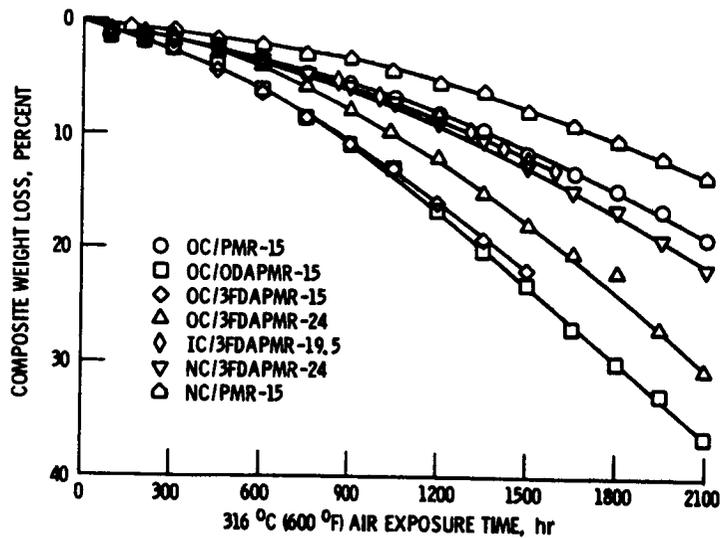
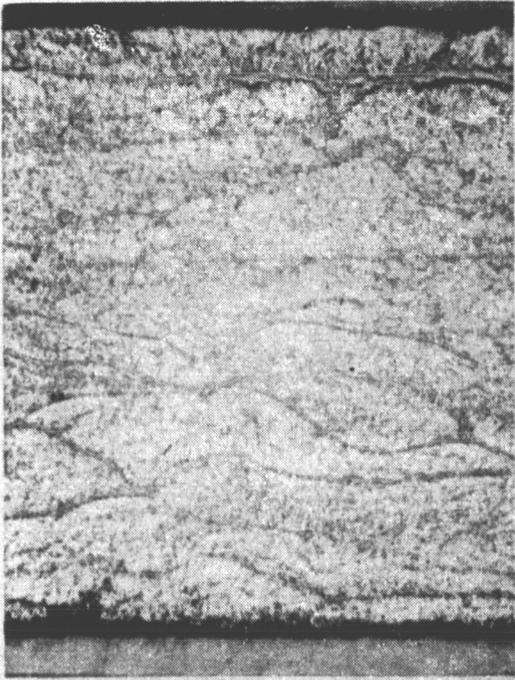
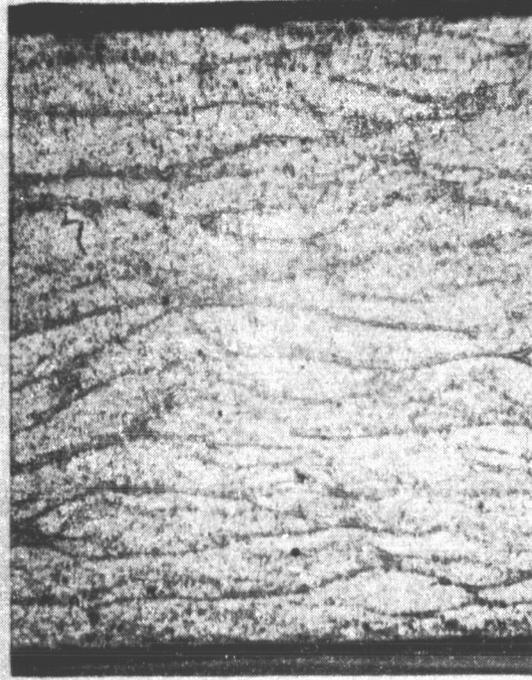


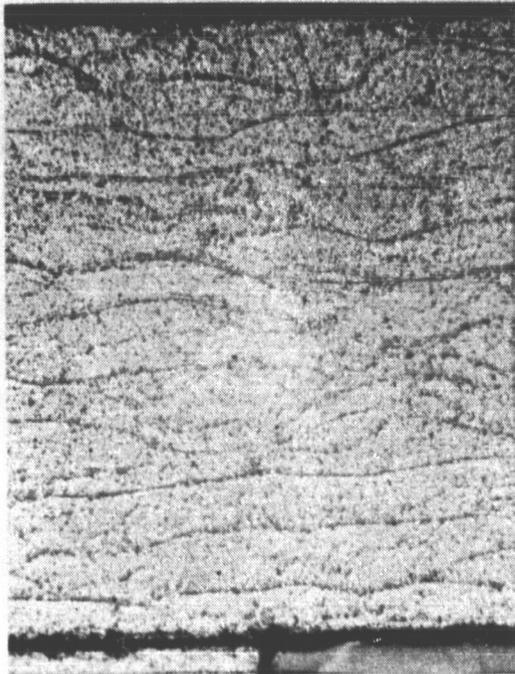
Figure 2. - Composite weight loss of Cellion 6000/PMR polyimide composites as function of 316 °C (600 °F) air exposure time.



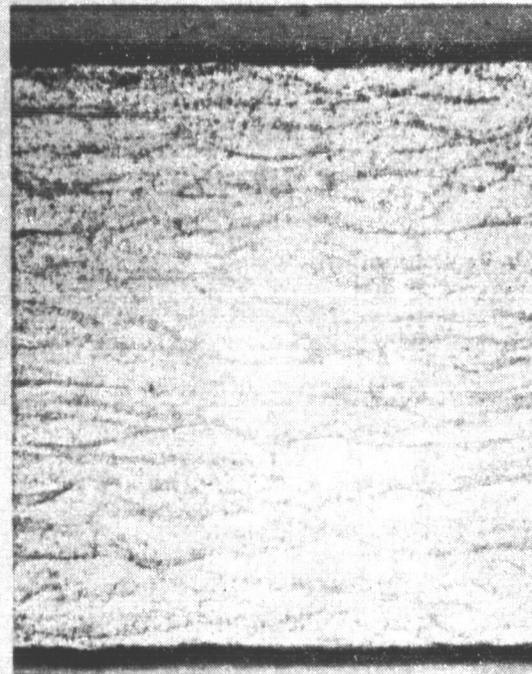
ODAPMR-15



3FDAPMR-24



PMR-15



3FDAPMR-15

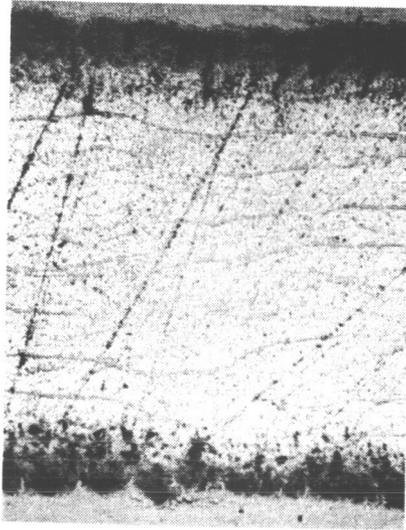
END VIEWS, ALL AT 50X

Figure 3. - Cross sections of original Celion (OC) 6000/PMR-polyimide composites.

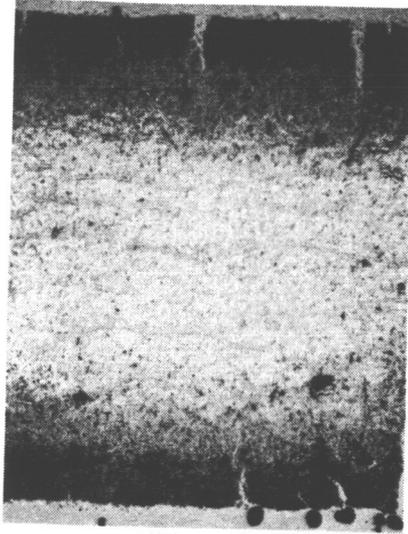
ORIGINAL PAGE IS
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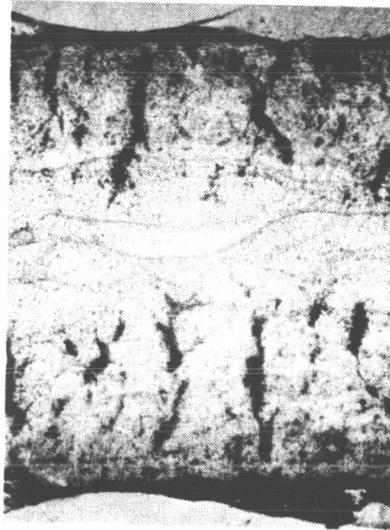
OC/ODAPMR-15
1200 hr/316 °C
16.6% WEIGHT LOSS



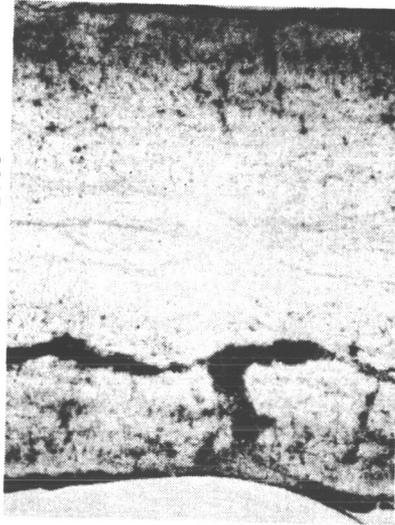
OC/IPMR-15
2100 hr/316 °C
19.0% WEIGHT LOSS



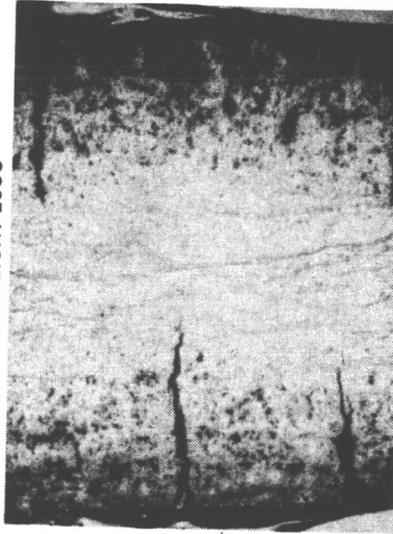
NC/3FDAPMR-24
1800 hr/316 °C
16.5% WEIGHT LOSS



OC/ODAPMR-15
1500 hr/316 °C
22.3% WEIGHT LOSS



OC/3FDAPMR-15
1356 hr/316 °C
18.8% WEIGHT LOSS



NC/3FDAPMR-24
2100 hr/316 °C
21.7% WEIGHT LOSS

ALL ARE 50X END VIEWS, EXPOSED BY CUTTING AFTER INDICATED EXPOSURE TIME, COMPOSITE WEIGHT LOSS INDICATED AT EACH EXPOSURE TIME.

Figure 4. - Physical appearance of Celson 6000/PMR-polyimides at comparable composite weight loss.

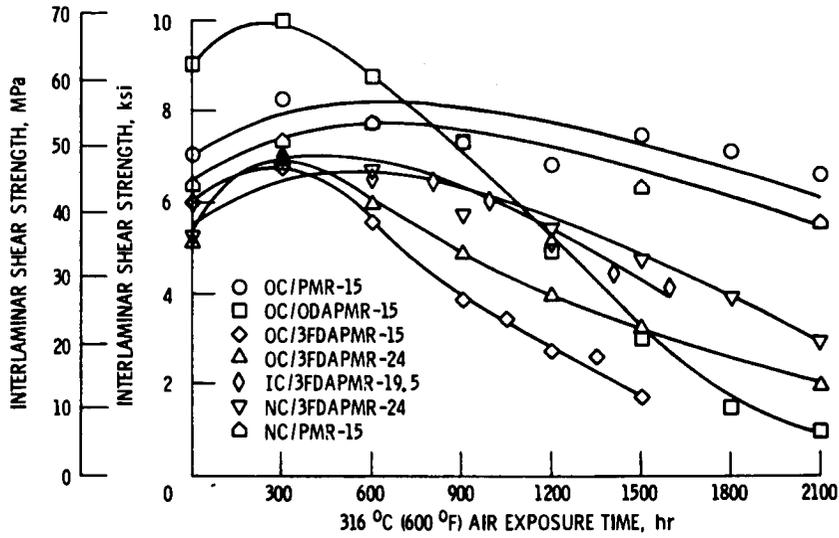


Figure 5. - 316 °C (600 °F) interlaminar shear strength of Celion 6000/PMR polyimide composites as function of 316 °C (600 °F) air exposure time.

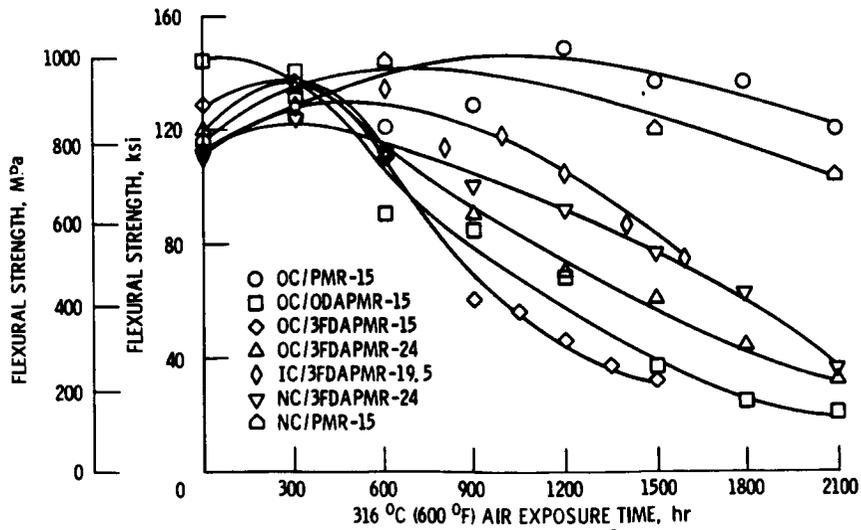


Figure 6. - 316 °C (600 °F) flexural strength of Celion 6000/PMR polyimide composites as function of 316 °C (600 °F) air exposure time.

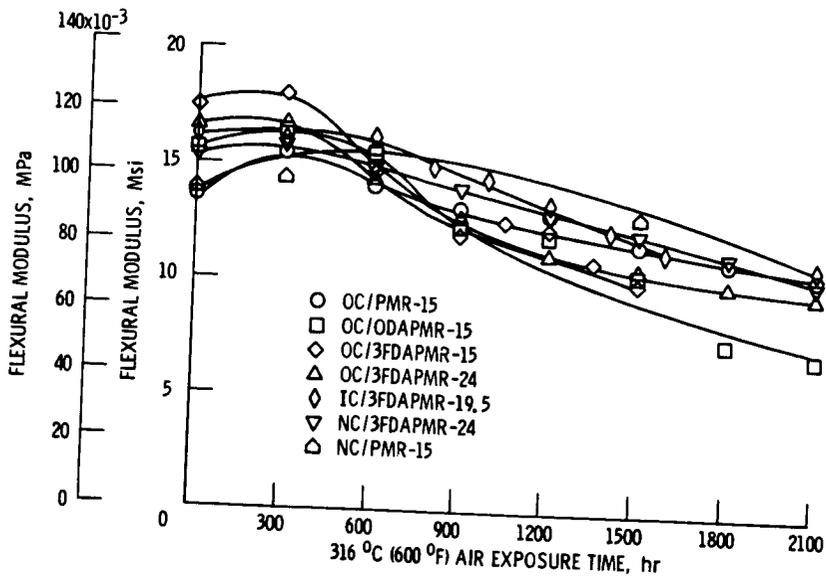


Figure 7. - 316 °C (600 °C) flexural modulus of Celson 6000/PMR polyimide composites as function of 316 °C (600 °F) air exposure time.

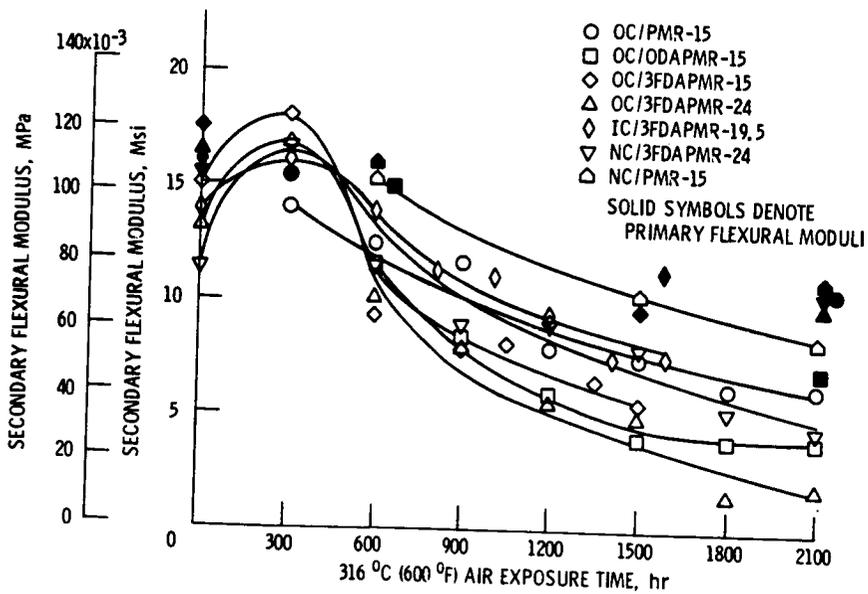


Figure 8. - 316 °C (600 °F) secondary flexural modulus of Celson 6000/PMR polyimide composites as function of 316 °C (600 °F) air exposure time.