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THERMO-OXIDATIVE INTERACTIONS IN PMR  
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IN PMR POLYIMIDE/GRAPHITE COMPOSITES

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Abstract

The amounts of resin weight loss and fiber weight loss in four PMR-polyimide/graphite fiber composites were calculated from the composite weight losses and the fiber/resin ratios of the composites after long term thermo-oxidative aging in 600°F air. The accelerating effect of graphite fiber on resin weight loss, compared to neat resin weight loss, indicated the presence of a deleterious resin/fiber thermo-oxidative interaction, presumably due to fiber impurities. Similarly, the decelerating effect of the protective matrix resin on fiber weight loss, compared to bare fiber weight loss, was also demonstrated. The amount of hydrazine indigestible resin and the amount of loose surface graphite fiber that formed during 600°F exposure of the composites were quantitatively determined. The indigestible residual resin was also qualitatively studied by scanning electron microscopy.

1. INTRODUCTION

The thermo-oxidative stability (TOS) of high temperature resins and composites is most easily assessed using the technique of isothermal-gravimetric analysis (ITGA). However, for composites ITGA fails to separate the observed weight loss into the individual weight loss contributions of the fiber and the resin. In fact, the observed composite weight loss is generally attributed to degradation of the matrix resin. While this may be true for composites containing oxidatively stable fibers such as

glass, this is not true for composites containing graphite fibers. Graphite fibers have been shown to oxidize at temperatures within the use temperature range of high temperature resins (ref. 1).

The purpose of this study was to investigate the thermo-oxidative interaction of graphite fiber type on resin weight loss and the effect of PMR resin type on fiber weight loss in a composite situation. The studies were performed using HTS-1 and Celion 6000 fibers and First and Second Generation PMR polyimide

matrix resins (refs. 2 and 3).

Resin and fiber contents were determined using a hydrazine digestion procedure (ref. 4). Scanning electron microscopic studies were also performed.

## 2. EXPERIMENTAL

### 2.1 MATERIALS AND WEIGHT LOSS DATA

The composites investigated in this study were the mechanical test specimens that had been fabricated, aged and tested as described in the original references. The PMR-13/HTS-1 specimens and weight loss data were from reference 5. The PMR-II/HTS-1 specimens and weight loss data were from reference 2. The PMR-15/Celion 6000 and PMR-II/Celion 6000 specimens and weight loss data were from reference 6. Composite weight loss data at longer exposure times than reported in references 2, 5, and 6 were obtained by continued aging of the previously tested specimens of PMR-13 and PMR-II/HTS-1 and PMR-II/Celion 6000 composites. The 600°F weight loss data of Celion 6000 fiber was from reference 6, and that of HTS-1 from reference 7, both having been the average of triplicate determinations. The 600°F neat resin weight loss data was the average of triplicate and duplicate weight loss determinations during 600°F air exposure of PMR-13 neat resin discs and PMR-II neat resin sheets, respectively.

### 2.2 DIGESTIONS

The previously tested flexural and/or interlaminar shear specimens were digested by treatment in a 15 to 20 fold excess by weight (approximately 75 to 100 fold stoichiometric excess) of an 85% solution of hydrazine hydrate for 4-8 hours at 80-90°C. The resultant fiber mass for gravimetric determination was isolated by suction filtration, washed with 5% aqueous sodium hydroxide, water, 5% aqueous hydrochloric acid, and water, oven dried for a minimum of 24 hours at 110-120°F, cooled to room temperature in a desiccator, and weighed until constant weight was obtained. The fiber/resin ratios for unaged specimens were determined in triplicate, while 600°F aged specimens were single determinations. Single data points that were out of place with other data points in the series of exposure times were checked by hydrazine redigestion of the fiber mass and/or repeating the digestion on another specimen.

### 2.3 RESIN AND FIBER WEIGHT LOSS

The resin and fiber weight loss in an aged composite specimen were calculated from the initial and final fiber/resin ratio and the composite weight loss according to the following equations:

$$C_I = C_F \times 100/100 - C_{WL} \quad (1)$$

where  $C_I$  = Initial composite weight,  
 $C_F$  = Aged composite weight,  
 and  $C_{WL}$  = Percent composite weight loss.

$$F_I = F_{WP,I} \times C_I/100 \quad (2)$$

$$R_I = R_{WP,I} \times C_I/100 = C_I - F_I \quad (3)$$

where  $F_I$  = Fiber weight, initial, by hydrazine digestion,

$R_I$  = Resin weight, initial, by hydrazine digestion,

$F_{WP,I}$  = Fiber weight percent, initial,

and  $R_{WP,I}$  = Resin weight percent, initial =  $100 - F_{WP,I}$ .

$$F_{WL,F} = (F_I - F_F) \times 100/F_I \quad (4)$$

$$R_{WL,R} = (R_I - R_F) \times 100/R_I \quad (5)$$

where  $F_{WL,F}$  = Percent fiber weight loss, based on initial fiber weight,  $F_I$ ,

$R_{WL,R}$  = Percent resin weight loss, based on initial resin weight,  $R_I$ ,

$F_F$  = Fiber weight, final, by hydrazine digestion

and  $R_F$  = Resin weight, final, by hydrazine digestion =  $C_F - F_F$ .

#### 2.4 RESIDUAL RESIN INVESTIGATION

The weighed fiber mass after the hydrazine digestion was treated with 10-20 ml. of concentrated sulfuric acid for 2-4 hours at 80-90°C. The weight loss of the suction filtered, water washed and oven dried fiber mass represents the weight of resin that did not digest with hydrazine. The residual resin was expressed as a

percentage of fiber at 600°F exposure time (as a surface coating function) as follows:

$RR_{FF} = 100(F_F - F_{FS})/F_F$  where  $RR_{FF}$  = percent resin residue based on final fiber weight,  $F_F$ , and  $F_{FS}$  = fiber weight by sulfuric acid digestion. The graphite fibers containing the residual resin were studied with a JEOL JSM-2 scanning electron microscope. The fibers were mounted with a 0° tilt, gold sputtered and photographed with magnifications from 300 to 10,000X.

#### 2.5 LOOSE FIBER DETERMINATION

The amount of loose graphite fiber on the composite surface was determined by weighing the amount of fiber that could be easily removed from the aged composite specimen by gently pulling with the fingers. The percent of loose fiber formed upon 600°F air aging was calculated as follows:

$LF_{FI} = 100 \times LF_R/F_I$  where  $LF_{FI}$  = percent loose surface fiber based on initial fiber weight,  $F_I$ , and  $LF_R$  = weight of loose fiber removed.

When loose fiber contained appreciable amounts of resin (greater than 15 percent),  $LF_R$  was corrected by subtracting the resin weight found in the loose fiber. This correction was made only for loose fiber found on PMR-II composites.

### 3. RESULTS AND DISCUSSION

### 3.1 COMPOSITE WEIGHT LOSS

Figure 1 compares the composite weight loss data of various PMR polyimide/graphite fiber composites exposed in air at 600<sup>o</sup>F reported in references 2, 5, and 6. The curve for the composite exhibiting the fastest weight loss (PMR-13/HTS-1) is characteristic of the thermo-oxidative stability (TOS) results attainable with first generation PMR-13 or 15 addition type polyimide composites using high strength graphite fiber available up to 1976. As can be seen in the figure, the use of second generation PMR-II as a matrix resin with HTS-1 fiber provided almost a three-fold improvement in 600<sup>o</sup>F TOS. Shortly thereafter, the availability of improved high strength graphite fiber containing a lower level of contaminants, primarily sodium ions (ref. 1), allowed the same or slightly improved level of TOS to be attained with PMR-15 as the matrix resin (fig. 1, PMR-15/Celion 6000 curve). The use of the PMR-II matrix resin with the improved graphite fiber provided a small further improvement in the 600<sup>o</sup>F TOS (fig. 1, PMR-II/Celion 6000 curve).

### 3.2 RESIN AND FIBER WEIGHT LOSS

Using the equations in the experimental section, the resin weight loss and fiber weight loss of the four composites were calculated. The calculated resin weight loss

data are shown in Figure 2 as a function of 600<sup>o</sup>F exposure time. PMR-II/HTS-1 weight loss data is shown only for exposure times when significant composite weight loss was observed. Weight loss curves for the two unreinforced matrix resin types are also shown in the figure. By comparing the resin weight losses of the PMR-13 and PMR-II/HTS-1 composites, the three-fold reduction in composite weight loss mentioned earlier can be clearly attributed to the superior TOS of the PMR-II matrix resin. By comparing the resin weight losses of PMR-13/HTS-1 and PMR-15/Celion 6000 composites, the similar three-fold reduction in composite weight loss mentioned earlier can be attributed to a reduced level of resin thermo-oxidative degradation. This can possibly be attributed to a reduced level of resin/fiber thermo-oxidative interaction resulting from the lower level of contaminants in Celion 6000 fiber. The similar resin weight loss of PMR-II on HTS-1 or Celion 6000 fiber in the 1500 to 2100 hour exposure range indicates the TOS of the PMR-II matrix resin is not adversely affected by any graphite fiber impurities.

Comparisons of these resin weight losses to neat resin weight losses clearly shows that HTS-1 fiber causes almost a ten-fold increase in resin weight loss of PMR-13 (53% vs. 6% at 1000 hours). This

is reduced to about a two-fold increase in PMR-15 resin weight loss (11% vs. 6% at 1000 hours) by the use of Celion 6000 fiber. The use of HTS-1 or Celion 6000 with PMR-II failed to show an increase in resin weight loss compared to PMR-II neat resin until about 1400 hours; thereafter a two-fold increase occurred (24 to 26% vs. 13% at 2100 hours). This clearly indicates that for exposure times up to 1400 hours, the PMR-II matrix resin is not susceptible to increased degradation resulting from resin/fiber thermo-oxidative interactions. After 1400 hours, the increased degradation may be due to resin/fiber thermo-oxidative interaction or it may be due to other factors such as an increased surface area to volume ratio of the PMR-II composite.

Figure 3 shows the 600<sup>o</sup>F weight losses of bare HTS-1 and Celion 6000 fibers and the weight losses of these fibers in the presence of a protective resin (expressed on the basis of initial fiber in the composite as  $F_{WL,F}$ ). In all four PMR polyimide composite cases, the fiber weight losses are about an order of magnitude less than the respective bare fiber weight losses. The figure shows that PMR-13 and PMR-II matrix resins were equally effective in preventing thermo-oxidative degradation of the HTS-1 fiber. Similar results were found for PMR-15 and PMR-II with Celion 6000 fiber. Figure 3 also shows

that the weight losses of HTS-1 fiber in composites are three to four times greater than the weight losses of Celion 6000 fiber in composites. This finding is in general agreement with the bare fiber weight loss data; at comparable exposure times the weight loss of HTS-1 was almost an order of magnitude greater than the weight loss of Celion 6000. Celion 6000 exhibits a greater level of TOS, whether TOS is determined in the composite or on bare fiber. The improved TOS of Celion 6000 may be attributed to its lower level of contaminants.

### 3.3 RESIDUAL RESIN

The accurate determination of resin and fiber weight contents requires that the digestion method be capable of completely digesting the resin without digesting any of the fiber. However, further treatment of the fibers from the hydrazine digested aged specimens with concentrated sulfuric acid revealed the presence of a small amount of residual resin material. Scanning electron microscopy studies substantiated this finding. Because the hydrazine digestion procedure is chemically specific for polyimide linkages, the indigestible nature of the residual resin suggests that the molecular structure of the polyimide has been altered during thermo-oxidative aging. The discussion of the formation of this residual resin has been arbitrarily limited to the Celion 6000 composites because only

a limited number of data points for residual resin on HTS-1 fiber were obtained.

Scanning electron photomicrographs (SEM) of the as-received Celion 6000 fiber showed a clean surface but with many lengthwise striations. The as-received fiber after a 40 percent 600<sup>o</sup>F weight loss showed the disappearance of the striations and the appearance of occasional pits in the fiber surface. The pits possibly resulted from impurities in the as-received fiber.

SEM analysis of fibers from hydrazine digested composites showed the presence of residual resin particles which often appeared to grow out of the pits on the fiber surface. This strongly suggests that the residual resin formed in these fiber pits is due to resin/fiber thermo-oxidative interaction.

Figure 4 shows the amount of residual resin (expressed on the percentage basis of fiber in aged PMR-15 and PMR-II/Celion 6000 composites) as a function of 600<sup>o</sup>F exposure time. Both PMR-15 and PMR-II thermo-oxidatively form a resin product on the Celion 6000 fiber that does not digest with hydrazine. As the exposure time increases, PMR-II continues to form more thermo-oxidatively stable residual resin while the PMR-15 residual resin disappears, probably by thermo-oxidative degradation. This competition between the rate of thermo-oxidative formation and degradation of PMR-15

residual resin produced a maximum at about 1800 hours of exposure.

Figure 5 shows the residual resin as a function of 600<sup>o</sup>F fiber weight loss. Because the amount of PMR-15 residual resin is a result of competing formation and degradation rates, the amount of PMR-15 residual resin does not appear to be related to fiber weight loss. The figure does show a linear relationship between PMR-II residual resin formation and Celion 6000 fiber weight change after the fiber begins to lose weight. This relationship may be fortuitous or it may be that residual resin formation and fiber weight loss are related through the amount of contaminants on the fiber. The contaminant level determines the amount of fiber weight loss and, based on SEM analysis, could determine the amount of available sites on the fiber for residual resin formation. Neither PMR matrix resin formed any significant amount of residual resin until a fiber weight loss in the composite, rather than a weight gain, had occurred. These observations, together with the SEM analysis suggests residual resin formation is a fiber controlled function. As such, the formation of residual resin could be considered to be a result of resin/fiber thermo-oxidative interaction, presumably due to contaminants on the fiber surface.



### 3.4 LOOSE SURFACE FIBER FORMATION

During the process of specimen aging for this study a considerable difference was noted in the amount of 600<sup>o</sup>F exposure time a composite specimen could attain before loose surface fiber was observed.

Figure 6 shows the amount of loose surface fiber generated in the four PMR polyimide composites (expressed on the basis of percent of initial fiber weight) as a function of 600<sup>o</sup>F exposure time. Clearly, the first generation PMR-13 and 15 composites generate a greater amount of loose surface fiber at earlier exposure times compared to the second generation PMR-II composites.

A common factor was observed for the initiation of loose surface fibers. Figure 7 shows that when loose surface fibers were first observed, a 2 to 3 percent fiber weight loss had already occurred. This was true for all of the composites in the 0.80 to 0.120 inch thickness range investigated except for the PMR-II/HTS-1 composite which exhibited a fiber weight loss of 5 percent just prior to loose surface fiber formation. However, it needs to be pointed out that the 5 percent fiber weight loss may be somewhat high because it is only an extrapolation from Figure 3. Figure 7 also shows that PMR-13 or PMR-15 composites generate loose surface fiber at a faster rate without exhibiting significant increased fiber weight loss. In contrast,

PMR-II composites undergo fiber weight loss instead of generating significant amounts of loose surface fiber. This major difference in the loose fiber behavior of PMR-13 or 15 vs. PMR-II composites may be regarded as a result of differences in matrix resin TOS and/or resin/fiber thermo-oxidative interactions.

### 4. SUMMARY OF RESULTS AND CONCLUSIONS

Based on this study, the following are the major results and conclusions:

1. During 600<sup>o</sup>F air exposure, comparable levels of fiber weight loss resulted from the use of either first or second generation PMR polyimide matrix resins.
2. PMR-15 type matrix resins were subject to increased weight loss caused by thermo-oxidative interaction with graphite fibers, presumably related to the level of impurities on the fiber. PMR-II matrix resin was considerably less subject to increased weight loss caused by deleterious resin/fiber thermo-oxidative interactions.
3. PMR-15 type matrix resins allowed the formation of significant amounts of loose surface fiber during prolonged 600<sup>o</sup>F thermo-oxidative exposure compared to PMR-II matrix resin.
4. Both PMR matrix resin types formed a hydrazine indigestible residual resin on the graphite

fiber surface as a result of resin/fiber thermo-oxidative interaction, presumably related to impurities on the graphite fiber surface.

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#### 6. BIOGRAPHY

Dr. William B. Alston is presently a Materials Engineer with the Propulsion Laboratory of the U.S. Army Aviation Research and Development Command, assigned to the Polymer Matrix Composites Section of the NASA-Lewis Research Center since 1971. He received his B.S. in Chemistry from the University of Wisconsin, M.S. and Ph.D. in Chemistry from the University of Iowa. His current research is in the areas of polymer synthesis, crosslinking methods, and char formation.

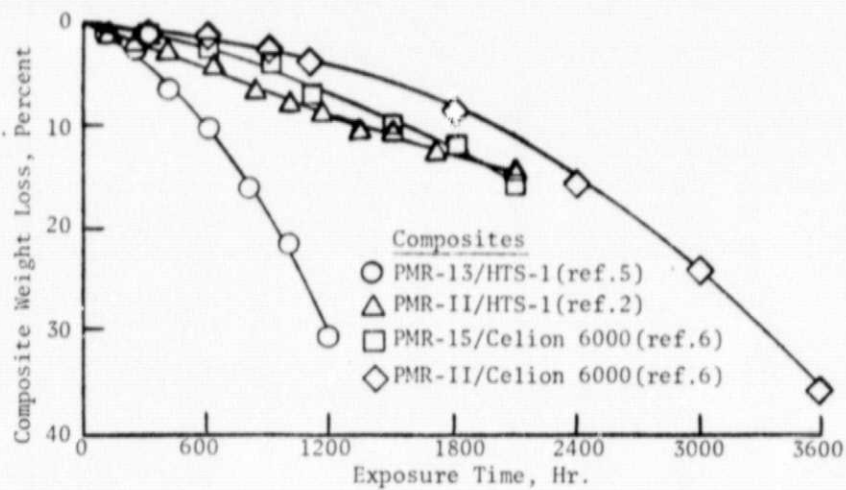


Figure 1.- Comparison of composite weight loss for the PMR polyimide composites as a function of 600°F air exposure time.

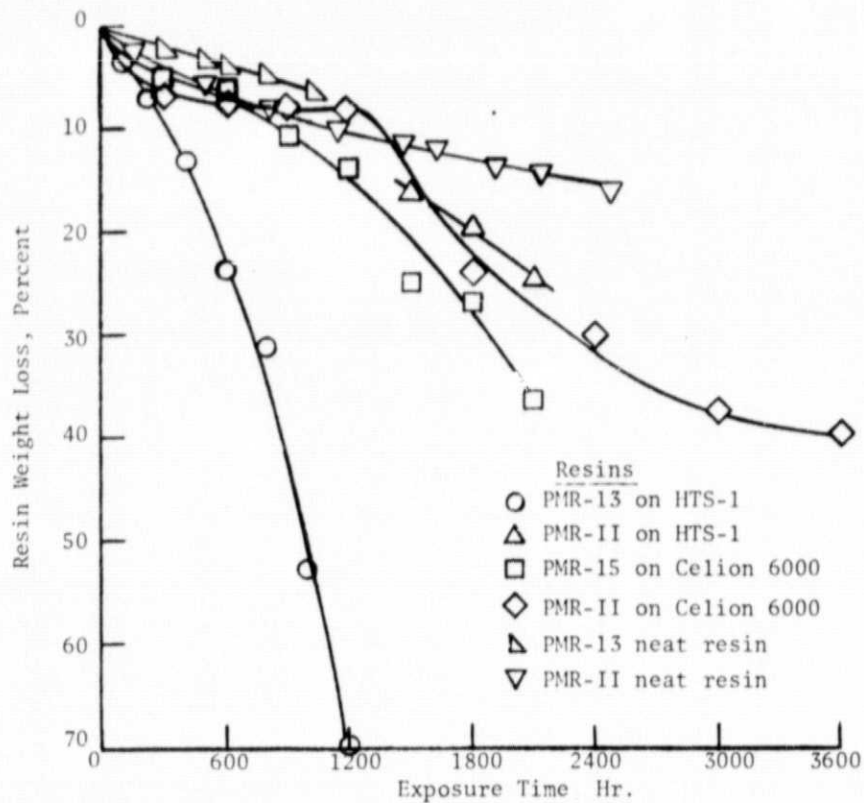


Figure 2.- Comparison of resin weight loss for the PMR polyimide composites and neat resins as a function of 600°F air exposure time.

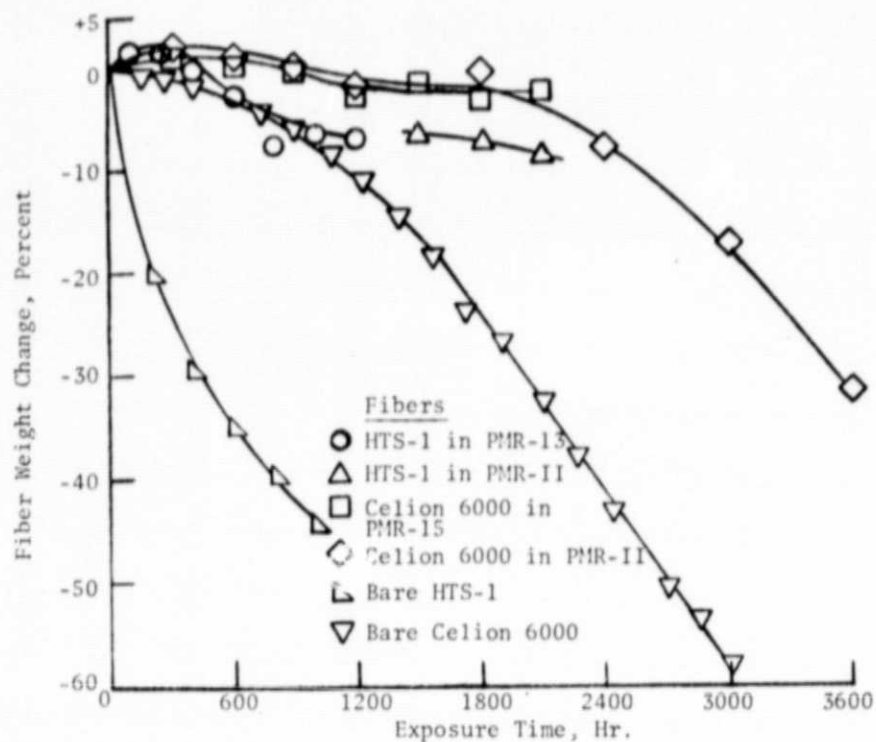


Figure 3.- Comparison of fiber weight change for the PMR polyimide composites and bare fibers as a function of 600°F air exposure time.

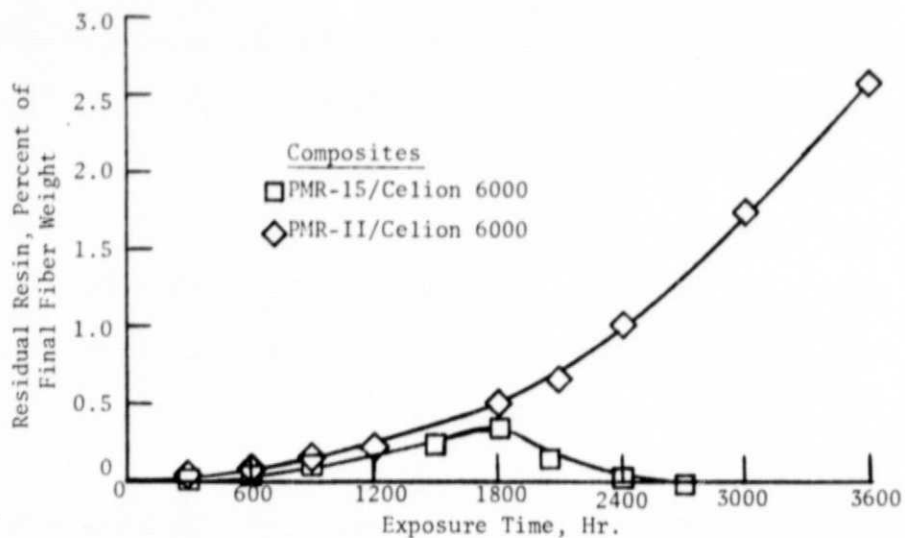


Figure 4.- Comparison of residual resin in PMR polyimide composites as a function of 600°F air exposure time.

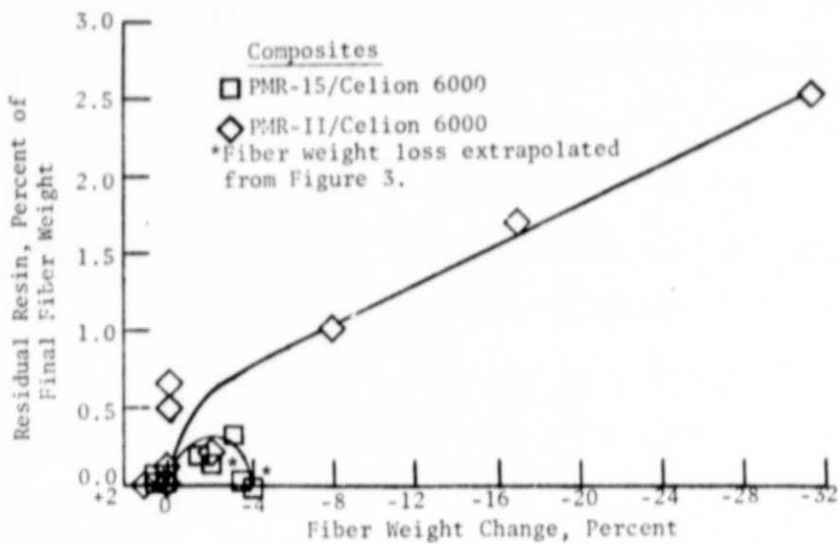


Figure 5.- Comparison of residual resin in PMR polyimide composites as a function of fiber weight change in 600°F air.

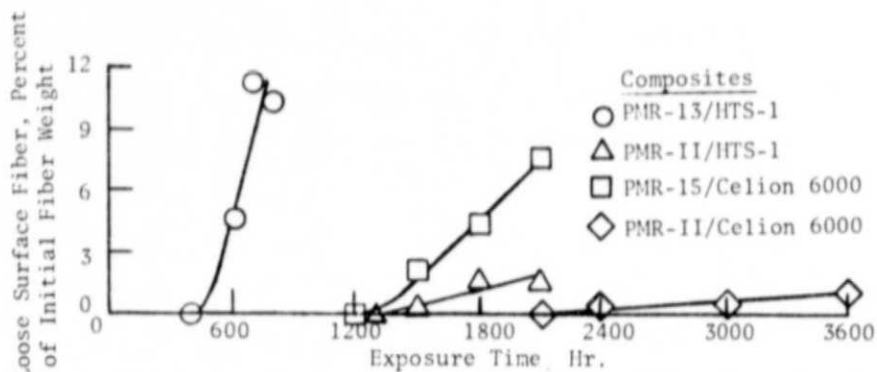


Figure 6.- Comparison of loose surface fiber formation for the PMR polyimide composites as a function of 600°F air exposure time.

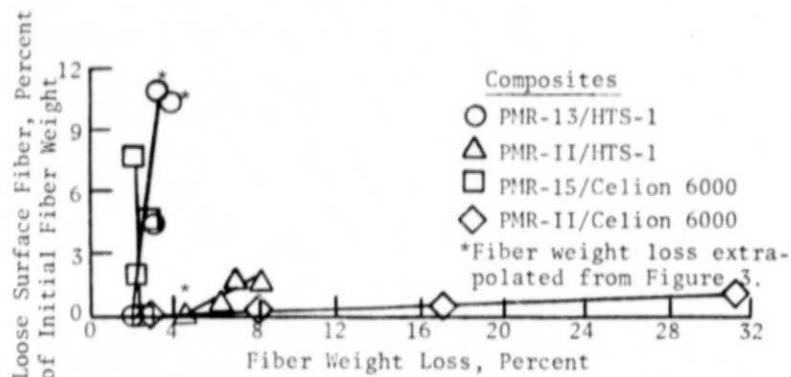


Figure 7.- Comparison of loose surface fiber formation for the PMR polyimide composites as a function of fiber weight loss in 600°F air.