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PMR Polyimide Compositions for Improved Performance at 371 °C

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PMR POLYIMIDE COMPOSITIONS FOR IMPROVED PERFORMANCE AT 371 °C

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SUMMARY

Studies were conducted to identify matrix resins which have potential for use at 371 °C (700 °F). Utilizing PMR methodology, neat resin moldings were prepared with various monomer reactants and screened for thermo-oxidative stability at 371 °C (700 °F) under both ambient and four atmospheres air pressure. The results of the resin screening studies indicate that high molecular weight (HMW) formulated resins of first (PMR-15) (ref. 1) and second (PMR-II) (ref. 2) generation PMR materials exhibit lower levels of weight loss at 371 °C (700 °F) than PMR-15 and PMR-II resins. The resin systems which exhibited the best overall balance of processability, T_g and thermo-oxidative stability at 371 °C were used to prepare unidirectional Celion 6000 and T-40R graphite fiber laminates. Laminates were evaluated for thermo-oxidative stability and 371 °C mechanical properties. Results of the laminate evaluation studies indicate that two of the resin compositions have potential for use in 371 °C applications. The most promising resin composition provided laminates which exhibited no drop in 371 °C mechanical properties and only 11 percent weight loss after 200 hr exposure to 4 atmospheres of air at 371 °C.

INTRODUCTION

The objective of the polymers research being conducted at NASA Lewis Research Center is to develop technology for new generations of organic polymers intended for application in advanced aeropropulsion systems. Studies to improve aircraft engine performance have indicated that advanced designs will dictate higher thrust-to-weight ratios than present day levels. This can be achieved through the use of advanced lightweight composite materials. To meet the requirements for high temperature advanced composites, NASA Lewis developed the PMR polyimides (ref. 1). Today PMR polyimides are the leading matrix resins for high temperature advanced polymer matrix composites and are commercially available from a number of suppliers. The technology for application of these advanced composite materials is developing rapidly. At the present time, PMR materials are being used in a number of composite engine components currently in production or soon to be introduced into production. While current engine applications of PMR materials have resulted in some significant cost and weight savings, their application has been limited to engine sections operating in the 200 to 300 °C (392 to 572 °F) temperature range. Further benefits can be realized by moving composites into the higher temperature regions on engines.

The purpose of this study was to investigate higher molecular weight (HMW) PMR resin formulations and to determine the effect of these formulations on resin and composite physical properties, thermo-oxidative stability, and mechanical properties after exposure in air at 371 °C (700 °F).

EXPERIMENTAL PROCEDURE

Resin Preparation

The monomer reactants used to prepare the resins investigated in this study are shown in table I. All of the monomers except the dimethylesters were purchased from commercial suppliers. The dimethylesters (BTDE and HFDE) were prepared as 50 wt % methanol solutions by refluxing a suspension of the corresponding dianhydride in anhydrous methanol until all solids had dissolved and then for an additional 2 hr.

PMR reactant solutions were prepared at room temperature by dissolving the reactants in anhydrous methanol to form 30 to 50 wt % solids solutions. The stoichiometric ratio of the monomers used for the addition curing resins prepared was as follows: n moles of dimethylester, $n + 1$ moles of diamine, and 2 moles of NE.

Neat resin moldings were prepared by placing solutions containing 15 g of solids into an air circulating oven set at 121 °C (250 °F) until all of the solvent had evaporated and the reactants were partially imidized. The dry material was then crushed and the oven temperature increased to 177 to 204 °C (350 to 400 °F), depending on resin formulated molecular weight (FMW), for 1 hr to complete the imidization to the endcapped prepolymer. The imidized material was then ground into a fine powder. Approximately 4 g of powder was then placed into a 2-in. diameter metal die at room temperature. The die (with thermocouples attached) was placed into a press preheated to 316 to 343 °C (600 to 650 °F). When the temperature of the die reached 260 °C (500 °F), a pressure ranging between 6.9 to 13.8 MPa (1000 to 2000 psi) was applied. Final cure temperature and pressure was dependent on the FMW of the resin. Higher FMW's required higher cure temperatures and pressures. Final cure temperature and pressure was maintained for 2 hr. After curing, the moldings were allowed to cool under pressure to 232 °C. At 121 °C (250 °F) the moldings were removed from the die and postcured in an air circulating oven programmed to heat at 6 °C/min to 260 °C and then 1 °C to 371 °C, followed by a 24-hr hold at 371 °C.

Laminate Fabrication

All laminates were prepared from unidirectional graphite reinforced prepreg tape. The reinforcements used in this study included Celion 6000 and Amoco's T-40R graphite fiber. Prepreg tapes were prepared by brush application of resin solutions onto drum wound unidirectional fiber calculated to yield laminates having 58 vol % fiber after curing. The prepreg was allowed to dry on the drum under quartz lamps to a volatile content of 11 to 12 wt %. The prepreg was then removed from the drum and cut into 7.62- by 20.3-cm (3- by 8-in.) plies and a number of plies stacked unidirectionally into a preform staging tool to yield laminates having a cured thickness of 0.20 to 0.23 cm (0.080 to 0.090 in.). The prepreg stacks were then heated under 0.1 psi of pressure for 60 min at temperatures of 177 to 204 °C (350 to 400 °F). Laminates were then compression molded by placing the staged layup into a flat matched metal die at room temperature and then inserting the die into a press preheated to either 316 °C (600 °F) or 343 °C (650 °F). When the die reached 232 °C (450 °F) a pressure ranging from 3.45 to 17.3 MPa (500 to 2500 psi) was applied. When the die reached the final cure temperature, pres-

sure and temperature were maintained for 2 hr. The laminates were then allowed to cool slowly to 232 °C (450 °F) (~45 min) under pressure and then fast cooled without pressure to room temperature. All laminates were then post-cured according to the same postcure schedule used for neat resin moldings.

371 °C Isothermal Aging

Isothermal weight loss measurements were performed on neat resin and laminates after exposure to air at 371 °C under both 1 and 4 atm of pressure. A forced-air oven was used for 1 atm exposure and the air change rate employed was 100 cc/min. The air change rate for 4 atm exposures was five air changes per hour in a 2.0 liter autoclave chamber.

LAMINATE EVALUATION

Prior to testing all laminates were inspected for porosity using an ultrasonic C-Scan technique.

Flexural and Interlaminar Shear Tests

Flexural strength and interlaminar shear strength (ILSS) tests were performed on specimens ranging in thickness from 0.20 to 0.23 cm (0.080 to 0.090 in.). Flexural strength tests were performed on 0.635- by 7.62-cm (0.25- by 3.0-in.) specimens in accordance with ASTM D-790 at a constant span/depth of 28. ILSS tests were performed on 0.635 cm (0.25 in.) wide specimens in accordance with ASTM D-2344 at a span/depth of 5. Elevated temperature tests were performed in an environmental heating chamber. Property values reported are averages of three to six tests.

RESULTS AND DISCUSSION

Resin Screening Studies

Table I lists the monomer reactants used to prepare the resins investigated. Table II identifies the composition of each of the resins. All of the resins contained NE. The stoichiometric ratio of the reactants used for each of the resins was in the ratio $n/(n+1)/2$, where n = moles of dimethylester, $n+1$ = moles of diamine and 2 = moles of NE. The value of n ranged between 1.67 and 14.5. The formulated molecular weights (FMW) ranged between 1270 and 7500 for the end-capped prepolymers prior to final curing of the resin. The number included in the resin designation corresponds to the FMW of the resin, i.e., 15 = 1500, 30 = 3000. Two of the formulations contained a mixture of diamines and were designated MD. Also shown in table II is the weight percent of NE presented in each of the resin formulations.

Table III lists the percent weight loss for each of the neat resins after exposure to air at 371 °C under both 1 atm and 4 atm of pressure. Also shown are the resin glass transition temperatures (Tg's) after 24 hr and 50 hr exposure to air at 371 °C and 1 atm of pressure.

The 4 atm, 371 °C exposure condition was selected to simulate the condition which composites would experience in an engine zone operating at 371 °C.

The table shows that the 371 °C oxidative stability of both PMR and PMR-II resin formulations improve as the FMW is increased. This is a result of the reduction in aliphatic content due to the Nadic endcap with increasing FMW as shown in table II. However, the data shows that PMR resin FMW's higher than 5000 offer no further improvements in 371 °C oxidative stability. This is probably due to difficulty in processing resins having high FMW's. It can be seen that the PMR-II resins exhibit considerably better thermo-oxidative resistance (TOS) than the other formulations investigated. This is due to the more thermally stable reactants (HFDE, PPDA) used in the PMR-II resins. Note that PMR-II-13 having the highest NE content (25.2 wt %), exhibited comparable weight loss, under both exposure conditions, to that of the higher FMW PMR and MD resins which contained considerably lower NE content. The excellent TOS exhibited by the PMR-II-50 resin was achieved in spite of the presence of blisters which developed during the 24-hr 371 °C postcure prior to the aging study. Blistering might be due to the presence of unreacted material and the low Tg exhibited by the HMW PMR-II-30 resin.

Comparing the Tg's of resins after 50 hr exposure under 1 atm shows that the resins containing BTDE and a mixture of the diamines BDAF and PPDA (MD-60 and MD-64), exhibit significantly higher Tg's than the other formulations. While the NE content of these HMW formulations is ~5 wt %, there appears to be a high degree of oxidative cross-linking taking place as a result of the carbonyl and ether linkages present in BTDE and BDAF, respectively.

Laminate Studies

The resins selected for laminate studies included all the resins listed in table II except MD-64 and PMR-II-50. The reinforcement used to prepare the laminates was unidirectional Celion 6000 graphite fiber.

Figure 1 compares the weight loss of the laminates as a function of exposure time in air at 371 °C and 4 atm of pressure. The figure shows that, as expected, the PMR-II-30 laminate exhibited the lowest 200 hr weight loss (12.5 wt %) while the PMR-15 laminate exhibited the highest weight loss (24 wt %) after only 120 hr of exposure. Laminates prepared from all other resins exhibited comparable weight loss (23 to 24 wt %) after 200 hr exposure.

Figure 2 compares the retention of interlaminar shear strength (ILSS) of the laminates after exposure to 4 atm of air at 371 °C. The figure shows that the laminates prepared from PMR-15 and MD-60 resin, which exhibited the highest resin Tg's, also exhibited the highest initial ILSS when tested at 371 °C. The MD-60 laminate retained 65 percent of its initial ILSS after 200 hr exposure, while the PMR-15 laminate retained only 50 percent of its initial 371 °C ILSS after only 120 hr of exposure. The laminates prepared from PMR-II-13 and PMR-II-30 exhibited the lowest initial 371 °C ILSS, but essentially retained that strength throughout the exposure time.

Figure 3 compares the retention of 371 °C flexural strength for the same laminates exposed under the same conditions discussed above. The figure shows

that the 371 °C flexural strength retention of the laminates are in close agreement with the results shown for 371 °C ILSS retention.

Based on the results of studies shown so far, it can be concluded that the PMR-II-30 resin offers the highest potential for use as a matrix resin for 371 °C composite applications. It must be noted that while the laminates prepared from the MD-60 resin exhibited nearly twice the weight loss shown for the PMR-II-30 laminates during exposure to 371 °C air, the laminates prepared from MD-60 resin exhibited the highest mechanical properties over very nearly the entire 371 °C exposure time. However, MD-60 laminates as well as the laminates prepared from PMR-15, 30, 50 resins exhibited a significant amount of loose surface fiber after 100 hr exposure to 371 °C air at 4 atm, while the PMR-II-30 laminate exhibited no loose surface after 200 hr of exposure. In order to determine any possible effect of the reinforcing fiber on the oxidative weight loss of the laminates, additional laminates were fabricated using Amoco's T-40R graphite fiber which exhibits significantly better oxidative stability during exposure to air at 371 °C and 4 atm pressure than Celion 6000 graphite fiber.

Figure 4 compares the weight loss of laminates prepared from MD-60 and PMR-II-30 resins with both Celion 6000 and T-40R fiber reinforcements during exposure to air at 371 °C and 4 atm of pressure. Also shown are the weight losses of Celion 6000 and T-40R bare fiber exposed to the same conditions for 120 hr. The figure shows that after 200 hr of exposure, the T-40R/MD-60 laminate exhibited 5 percent less weight loss than the Celion 6000/MD-60 laminate. The T-40R/PMR-II-30 laminate exhibited 3 percent less weight loss than the Celion 6000/PMR-II-30 laminate after 200 hr of exposure. The T-40R/MD-60 laminate still exhibited loose surface fiber after 100 hr exposure, but to a lesser degree.

Figure 5 compares the 371 °C flexural strength retention of the laminates compared in figure 4 as a function of exposure time in 371 °C air at 4 atm. It can be seen that the flexural properties of the T-40R/MD-60 were slightly lower than those of the Celion 6000/MD-60 laminate over the entire exposure time. No appreciable differences are apparent for the flexural strength retentions shown for the two laminates prepared from the PMR-II-30 resin. Note that, again, at the end of 200 hr exposure, the MD-60 system seems to be losing strength rapidly, while the PMR-II-30 system curve remains flat.

Based on the results of this study, the following conclusions can be drawn:

1. A PMR-II resin composition has been identified (PMR-II-30) which has potential for use in engine zones operating at temperatures up to 371 °C.
2. The use of higher FMW PMR compositions results in enhanced oxidative stability during exposure to air at 371 °C.
3. Higher FMW PMR compositions require higher cure pressures to yield high quality laminates.

REFERENCES

1. Serafini, T.T., Delvigs, P., and Lightsey, G.R.: Thermally Stable Polyimides from Solutions of Monomeric Reactants, Journal of Applied Polymer Science, Vol. 16, No. 4, Apr. 1972, pp. 905-915.

2. Serafini, T.T., Vannucci, R.D., and Alston, W.B.: Second Generation PMR Polyimides, NASA TM X-71894, 1976.

TABLE I. - MONOMERS USED FOR POLYIMIDE SYNTHESIS

STRUCTURE	NAME	ABBREVIATION
	<p>MONOMETHYL ESTER OF 5-NORBORNENE-2,3- DICARBOXYLIC ACID</p>	NE
	<p>DIMETHYL ESTER OF 3,3',4,4'- BENZOPHENONETETRACARBOXYLIC ACID</p>	BTDE
	<p>DIMETHYL ESTER OF 4,4'- (HEXAFLUOROISOPROPYLIDENE)- BIS(PHTHALIC ACID)</p>	HFDE
	4,4'-METHYLENEDIANILINE	MDA
	P-PHENYLENEDIAMINE	PPDA
	<p>BIS(AMINOPHENOXY) PHENYLHEXAFLUOROPROPANE</p>	BDAF

TABLE II. - COMPOSITIONS OF RESINS INVESTIGATED^a

Resin	Diester	Diamine	n	FMW	wt % NE
PMR-15 (control)	BTDE		2.09	1500	21.8
PMR-30	BTDE		5.2	3000	10.9
PMR-50	BTDE		9.3	5000	6.5
PMR-75	BTDE		14.5	7500	4.4
MD-64	BTDE	BDAF/PPDA	9	6400	5.1
		3:2			
MD-60	BTDE	BDAF/PPDA	9	6000	5.4
		1:1			
PMR-II-13	HFDE	PPDA	1.67	1270	25.2
PMR-II-30	HFDE	PPDA	5	2980	10.9
PMR-II-50	HFDE	PPDA	9	5050	6.5

^aResin stoichiometry: NE/Diester/Diamine
Moles: 2/ n /n + 1

TABLE III. - RESIN WEIGHT LOSS DURING EXPOSURE TO ONE AND FOUR ATMOSPHERES OF AIR AT 371 °C

Resin	Tg °C ^a	Tg °C ^b	Percent weight loss after:	
			300 hr/1 atm	75 hr/4 atm
PMR-15 (control)	370	388	18.0	18.2
PMR-30	365	375	12.0	14.0
PMR-50	363	375	13.0	13.0
PMR-75	358	370	16.5	13.8
MD-64	370	398	16.0	17.0
MD-60	370	403	12.2	14.0
PMR-II-13	368	381	13.0	12.3
PMR-II-30	345	368	8.0	6.4
PMR-II-50	340	355	5.5	5.0

^aAfter 24 hr postcure at 371 °C.

^bAfter 50 hr of exposure, 371 °C, 1 atm.

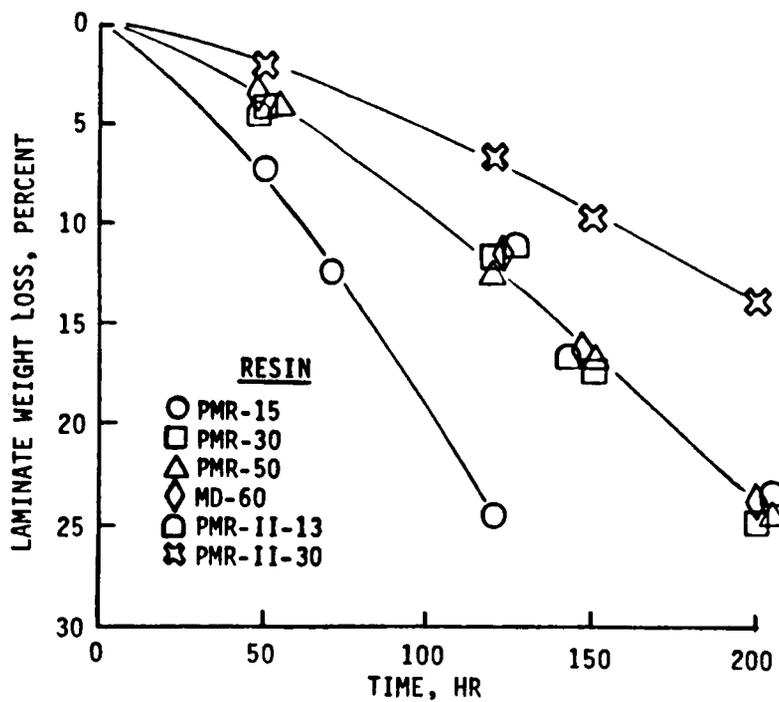


Figure 1.-Weight loss of Celion 6000 graphite/PMR laminates exposed in 4 atm. of air at 371°C.

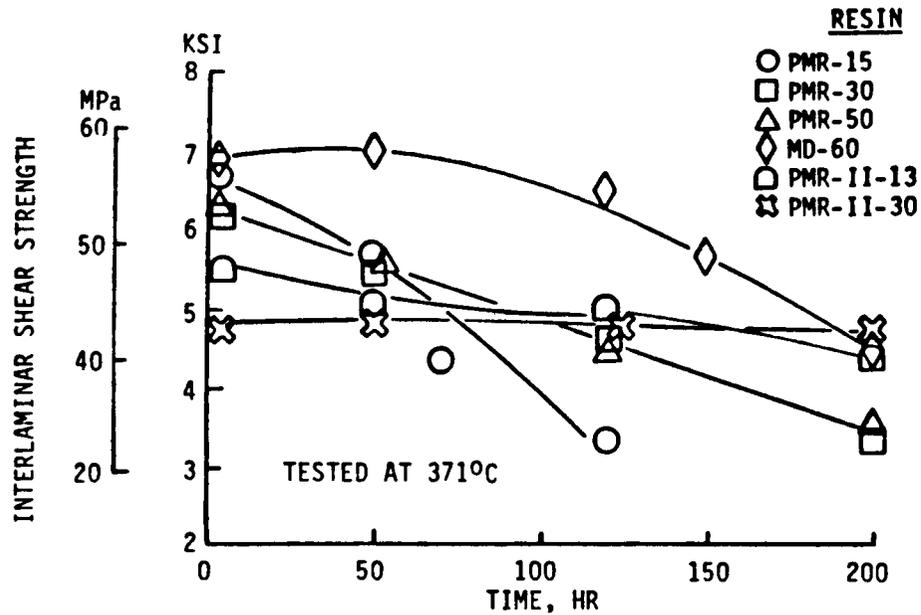


Figure 2.- Interlaminar shear strength of Celion 6000 graphite/PMR laminates after exposure to 4 atm. of air at 371°C

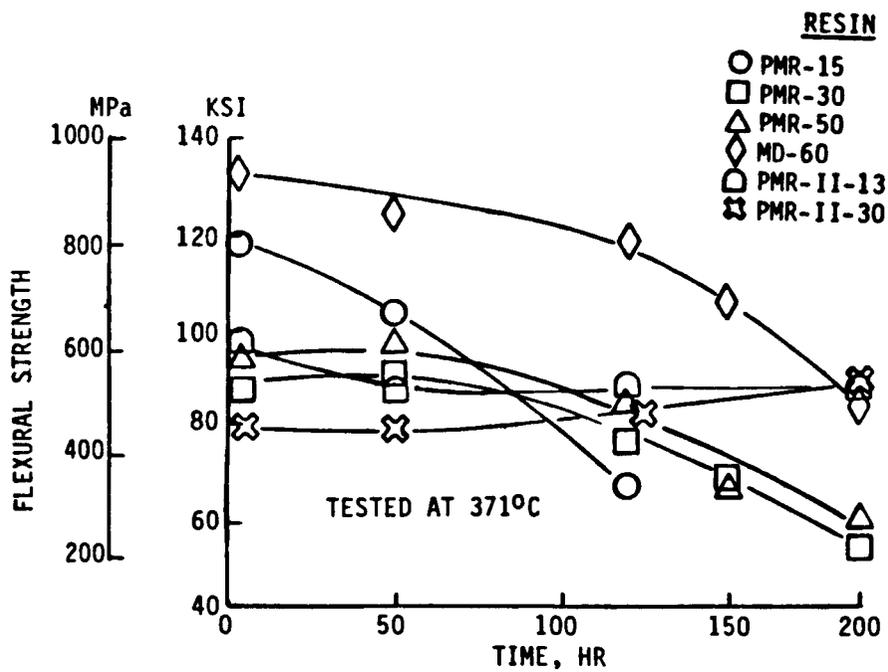


Figure 3.- Flexural strength of Celion 6000 graphite/PMR laminates after exposure to 4 atm. of air at 371°C

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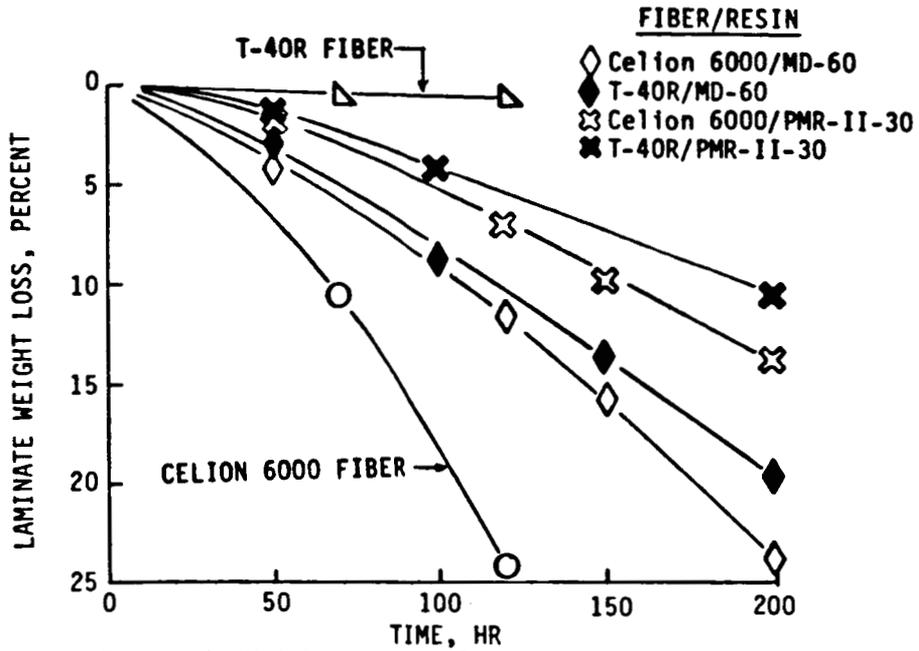


Figure 4.-Weight loss of laminates prepared from Celion 6000 graphite and T-40R graphite fibers, after exposure to 4 atm. of air at 371°C

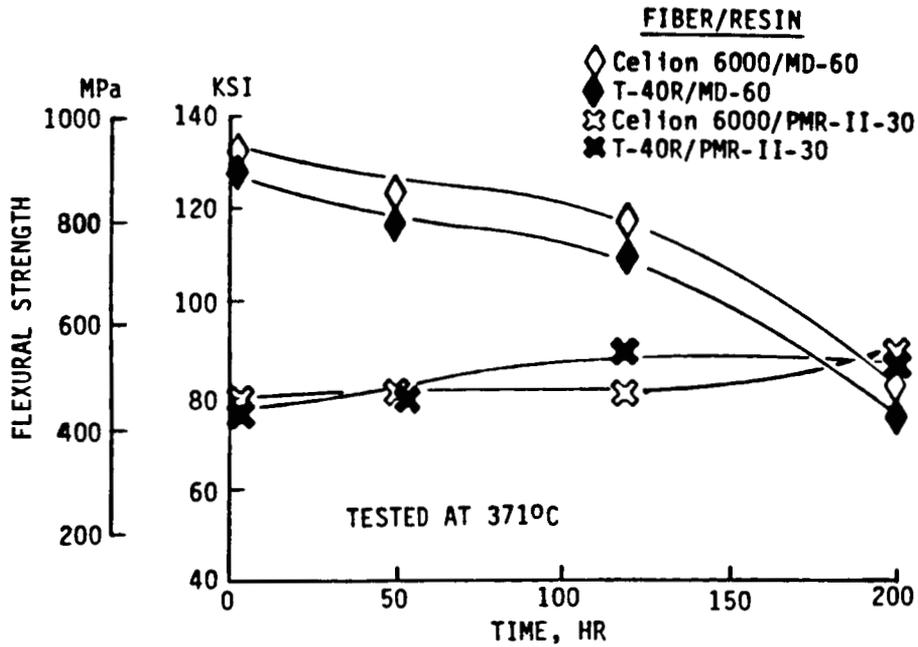


Figure 5.-Comparison of flexural strength retention of laminates prepared from Celion 6000 and T-40R graphite fiber after exposure to 4 atm. of air at 371°C

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