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700 °F Properties of Autoclave Cured PMR-II Composites

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700 °F PROPERTIES OF AUTOCLAVE CURED PMR-II COMPOSITES

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Abstract

Studies were conducted to develop autoclave processing parameters for graphite reinforced PMR-II resin composite materials intended for use in applications at temperatures up to 371° (700°F). The effect of resin composition on autoclaveability was investigated. The effect of various graphite fibers and resin composition on 343°C (650°F) and 371°C (700°F) thermo-oxidative stability and mechanical properties was also investigated.

The results of the processing studies show that PMR-II resin composites can be easily fabricated under autoclave conditions. Autoclaved laminates exposed to 1 atm. of air at 343°C (650°F) and 371°C (700°F) exhibited less than 5% weight loss after 750 hours exposure to 650°F air and 8% weight loss during exposure to 700°F air for 500 hours. After 500 hours exposure, autoclaved laminates exhibited greater than 90% retention of initial 650 and 700°F flexural and interlaminar shear strengths. The effect of resin formulated molecular weight and postcure conditions on laminate glass transition temperature is also discussed.

1. INTRODUCTION

The technology for improving engine performance through the use of advanced, lightweight composite materials is developing rapidly. In order to meet the materials demands, in terms of processability and elevated temperature properties for this advancing technology, investigators at the NASA Lewis Research Center developed the so-called PMR polyimides.(1) The advantages and versatility of the PMR approach have been reviewed.(2)

At the present time two versions of PMR, differing in composition, have been identified. The earlier version has been designated PMR-15, while the later developed second generation material was designated PMR-II.(3) Both the first generation (PMR-15) and second generation (PMR-II) resins are addition curing polyimides employing the same addition curing mechanism. They differ in the dianhydrides and diamines used to prepare the resins.

Today, the first generation material is one of the most widely used matrix resins for advanced composite applications in the 200 to 300°C (392-572°F) temperature range. While the PMR-II resin offered the potential for higher temperature applications,(4) in order to maintain processability comparable to the PMR-15 resin, low molecular weight formulations (LMW) were employed which provided an improved matrix resin, but did not take advantage of the full potential of the second generation materials. A more recent investigation (5) showed that higher molecular weight (HMW) formulations of the PMR-II resin have potential for 371° (700°F) applications. The study showed graphite fiber composites made with a HMW PMR-II formulation exhibited excellent retention of mechanical properties for better than 200 hours of continuous exposure to the highly oxidative environment of 60 psia air at 371°C (700°F). The study also showed that while HMW PMR-II resins exhibit improved high temperature properties, they were more difficult to process and required high pressure compression molding techniques to process high quality laminates. The need for high molding pressures severely limits the application of HMW PMR-II materials. In order to take full advantage of the potential of HMW PMR-II materials, processes more amenable to fabrication of large laminated structures are needed.

The purpose of this study was to investigate parameters for autoclave molding of HMW PMR-II resin laminate materials and to determine the effects of these processing parameters on laminate thermo-oxidative-stability (TOS) and retention of elevated temperature mechanical properties. Laminates were prepared using a simulated autoclave fabrication process at a pressure of 1.38 MPa (200 psi). The effects of processing conditions on laminate resin flow and physical properties are discussed. Laminate TOS and mechanical properties before and after exposure to 343°C (650°F) and 371°C (700°F), are also discussed.

2. EXPERIMENTAL PROCEDURE

2.1 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 hours.

PMR reactant solutions were prepared at room temperature by dissolving the reactants in anhydrous methanol to form 40 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.

2.2 Laminate Preparation

All laminates were prepared from unidirectional graphite reinforced prepreg tape. The reinforcements used in this study included Celion 6000 (C-6) and Amoco's T40R graphite fiber.

Prepreg tapes were prepared by brush application of resin solutions onto drum wound unidirectional fiber calculated to yield laminates having 55 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 were then stacked unidirectionally to yield laminates having a cured thickness of 0.23 to 0.25 cm (0.080 to 0.100 in). Prepreg stacks to be compression molded were placed into a preform tool and heated under 690Pa (0.1 psi) pressure for 60 min at temperatures of 177 to 204°C (350 to 400°F). Laminates were then compression molded by placing the staged lay-up 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 371°C (700°F). When the die reached 232°C (450°F) a pressure ranging from 3.45 to 6.9 MPa (500 to 1000 psi) was applied. When the die reached the final cure temperature, pressure and temperature were maintained for 2 hours. 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.

Autoclave cured laminates were fabricated using the vacuum bagged lay-up shown in figure 1. The laminates were cured in a platen press, using a simulated autoclave process, according to the cure schedule shown in figure 2. After curing the laminates were postcured in an air circulating oven programmed to heat at 20°C/min to 260°C (500°F) and then at 1°C/min to 371°C (700°F) or 385°C (725°F) with two hour holds at 316°C (600°F), 343°C (650°F) and a twenty hour hold at either 371°C (700°F) for the PMR-15 laminates or 385°F (725°F) for the PMR-II laminates.

2.3 Isothermal Aging

Isothermal weight loss measurements were performed on laminates after exposure to air at 343°C (650°F) and 1 atm. of pressure, and after exposure to air at 371°C (700°F) under both 1 atm. and 4 atm. of pressure. The air change rate employed was 100cc/min. for each exposure condition.

2.4 Laminate Evaluation

Prior to testing, all laminates were inspected for porosity using either ultrasonic C-Scan inspection or photo micrographs of laminate cross-sections. Laminate void contents and fiber volumes were determined from density measurements and resin acid digestion.[5]

Flexural and interlaminar shear strength (ILSS) tests were performed on specimens ranging in thickness from 0.23 to 0.25 cm (0.080 to 0.100 in). Flexural tests were performed on 0.635 cm (0.25 in) wide specimens in accordance to ASTM 0-790 at span/depth ratios ranging from 20 to 25. ILSS tests were performed on 0.635 cm 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.

3. RESULTS AND DISCUSSION

3.1 Laminate Processing

Table I lists the reactants used to prepare the PMR-15 and PMR-II matrix resins. PMR-15 matrix resin was the first PMR resin introduced and is prepared from the NE, BTDE and MDA reactants shown in table I. The autoclaveability of PMR-15 is well known and has been widely reported. The more thermally stable PMR-II resins are prepared from the reactants NE, HFDE and PPDA. PMR-15 and earlier PMR-II resins are LMW formulations. These LMW resin formulations undergo very low viscosity melt flow during the early stages of curing. During autoclave fabrication of LMW PMR composite materials, a low vacuum level must be employed until significant resin advancement (imidization) has occurred or excessive bleed will take place and plug up bleeder plies. Compaction is achieved by applying pressure at the temperature which the material undergoes a second melt flow, starting around 232°C

(460°F), followed by the addition cure. For HMW PMR-II formulation, the low viscosity melt does not occur during the imidization cycle. By applying full vacuum (∿ 72 cm-Hg) over the entire cure cycle, a high degree of consolidation occurs during the early stages of resin advancement without excessive bleed. Full consolidation is achieved by applying pressure in steps to the final cure pressure as further resin advancement takes place.

Figures 1 and 2 show the vacuum bag lay-up and cure schedule used for autoclave fabrication of void-free HMW PMR-II. The cure shows that the heating rate was reduced from 3.9°C to 2.8°C (7° to 5°/min.) at 288°C (550°F). Rheometrics studies showed that the minimum viscosity of imidized 3000 FMW PMR-II resin occurs around 292°C (557°F). It is felt that a faster heating rate at this point of the cure should result in increased resin flow. However, press limitation prevented this. Nevertheless, low-bleed high quality unidirectionally reinforced laminates were prepared from FMW 3000 and FMW 5000 PMR-II matrix resins (PMR-II-30 and PMR-II-50, respectively) on both C-6 and T40R graphite fibers.

3.2 Laminate Evaluation

Table II lists the initial physical and mechanical properties of the autoclaved laminates investigated in this study. Listed are the resin and fiber used for each laminate as well as laminate fiber volume, Tg, and flexural and ILSS at each temperature investigated. Also listed are the properties of two compression molded laminates (PMR-15/C-6 and PMR-II-30/T40R) which were used as controls for comparison purposes.

In comparing the mechanical properties of the laminates at each of the test temperatures, it can be seen that both the flexural and ILSS values are higher for all laminates prepared from C-6 fiber, even though the T40R fiber is higher in both tensile strength and modulus.

These results are in agreement with mechanical properties reported for PMR-II laminates in a previous study.(5) Of the two fibers, T40R is significantly higher in thermo-oxidative-stability (TOS). After 200 hours exposure to 4 atm., of air at 371 (700°F), C-6 fiber lost 67 w/o compared to less than 1 w/o for T40R fiber.(5) An earlier study comparing the properties of laminates prepared from graphite fibers reported to have improved TOS showed that there was a relationship between fiber TOS and surface characteristics.(7) The more stable fibers exhibited smoother, less surface irregularities, than the less stable fibers which provided higher laminate mechanical properties.

Figure 3 shows the weight loss characteristics of compression molded PMR-15/C-6 and autoclaved PMR-II laminates, prepared from C-6 and T40R fibers, as a function exposure to 1 atm. of air at 650°F. The figure shows that the laminates prepared from the stable T40R fiber are significantly more resistant to 650°F air oxidation than the laminates prepared from the C-6 fiber. A comparison of the laminates prepared from C-6 fiber shows the PMR-II resins do provide considerable improvement in oxidation resistance over the PMR-15 resin. While the PMR-II/T40R laminates were only exposed to 650°F for 750 hours, the low weight loss (4 w/o) suggests the materials are good candidates for longer term, 650°F applications.

The flexural strength retention of the PMR-15 compression molded and autoclaved molded PMR-II laminates after 650°F air exposure is shown in figure 4. It can be seen that the flexural strength of the PMR-15 and PMR-II-30 laminates increased considerable with exposure time. This was due to the increase in Tg these laminates exhibited during exposure. After 200 hours at 650°F, laminate Tg's increased a minimum of 20°C (38°F) and flexural modulus increased by a minimum of fifty percent, 48 to *83.5 Gpa (7.0 to 12.0* x 10^6 psi) due to additional oxidative crosslinking. The laminates prepared from the C-6 fiber, as expected, exhibited the highest flexural strengths until oxidative degradation became significant at around 600 hours of exposure. The more stable PMR-II/T40R laminates exhibited excellent strength retention throughout the exposure time.

The comparison of 650°F ILSS retention with exposure time is shown in figure 5. As can be seen, the results of the ILSS tests of 650°F exposed PMR-15/C-6 and the autoclaved C-6 and T40R reinforced PMR-II laminates are similar to the results shown in figure 4. Again the better resin/fiber interfacial bonding provided by the C-6 fibers results in higher ILSS properties but lower thermal stability than the T40R reinforced laminates.

Figures 6, 7 and 8 present the results of tests performed on laminates as a function of exposure to 1 atm. of air at 371°C (700°F). Figure 6 shows the weight loss of the compression molded PMR-15/C-6 laminate and the autoclaved PMR-II laminates prepared with both C-6 and T40R fibers. While the 650°F aging results showed little difference between laminate prepared with PMR-II-30 and PMR-II-50, the 700°F air oxidation studies show that the PMR-II-50 resin is the most thermally stable of the resins studied. The PMR-II-50/T40R laminate lost only 8 w/o after 500 hours exposure while the PMR-II-30/T40R laminate lost 10 w/o after 400 hours exposure. The laminates prepared from the C-6 fiber, again, show the highest weight losses. Also, the PMR-15 laminates exhibited loose surface fiber at 100 hours exposure. At 200 hours, the test was ended due to significant amounts of loose surface fiber. After 400 hours of exposure the PMR-II laminates prepared with C-6 fibers did not exhibit loose surface fiber because the fibers were oxidized at the same rate as the resin.

The flexural and ILSS strength retentions after exposure to 1 atm. of air at 700°F is shown in figure 7 and 8 respectively. The differences in mechanical properties between the laminates prepared from the C-6 and T40R fibers become more pronouned at 700°F than was shown for the 650°F mechanical properties discussed above. This, again, can be attributed to the poorer resin/fiber interfacial bonding which exists when the T40R fiber is employed. The increase in Tg for the PMR-II laminates, 30-40°C (54-72°F) after 100 hours at 700°F, provided a more pronounced increase in the flexural and ILSS properties of the laminates prepared from the C-6 fibers. The overall retention of 700°F flexural and ILSS shear strengths is excellent for all the PMR-II laminates throughout the exposure time. The 700°F aging results again, show that the best resin/fiber combination for long term 700°F exposure is the PMR-II-50 resin on T40R fiber.

In order to make a comparison of the quality of autoclaved and compression molded PMR-II laminates, autoclaved PMR-II-30/T40R and PMR-II-50/T40R laminates where compared with a compression molded PMR-II-30/T40R laminate. Figure 8 compares the weight loss of the three laminates during exposure to the highly oxidizing environment of 4 atm. of air at 700°F. The figure shows that the weight loss of the compression molded PMR-II-30 laminate is 2 w/o lower than the autoclaved PMR-II-30 laminate and compares favorably with the laminate prepared from the more stable PMR-II-50 resin. A PMR-II-50 compression molded laminate was not included in this comparison due to blistering problems encountered during post curing of compression molded PMR-II-50 laminates.

Figure 10 compares the flexural strength retention as a function of exposure to 4 atm. of air at 700°F for the laminates discussed above. The figure shows that the flexural strength retention of the autoclaved laminates compared favorably to that shown for the compression molded laminate.

It is apparent from the results shown above that although the HMW PMR-II resins do not exhibit a high degree of tractability, autoclaving procedures have been established which provide fiber reinforced HMW PMR-II laminate equal in quality to those prepared by high compression molding procedures.

4. CONCLUSIONS

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

1. Autoclave procedures have been identified for fabricating high quality graphite fiber reinforced HMW PMR-II resin laminates.
2. Autoclaved HMW PMR-II resin laminates prepared with T40R fiber provided better thermo-oxidative stability at 650 and 700°F than those prepared with C-6 fiber, but exhibited lower mechanical properties.
3. Autoclaved laminates prepared from PMR-II-50 resin and T40R fiber offer the highest potential for extended use at temperatures of 343-371°C (650 - 700°F).

5. REFERENCES

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2. Serafini, T. T.: Processable High Temperature Resistant Polymer Matrix Materials, International Conference on Composite Materials, Vol. 1, E. Scala, ed., pp. 202-220, AIME, New York, 1976.

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6. Jones, R. J.; Vaughn, W. R.; and Burns, E. A.: Thermally Stable Laminating Resins, NASA CR-72984, Feb. 1972.

7. Vannucci, R. D.: Properties of PMR Polyimide Composites made with Improved High Strength Fibers, Proc. of 12th SAMPE Nat. Tech. Cont. October 1980.

TABLE I. - MONOMERS USED FOR POLYMIDE SYNTHESIS

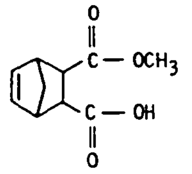
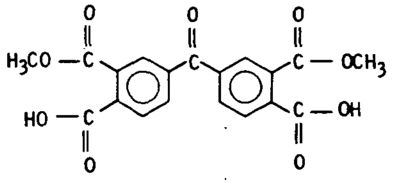
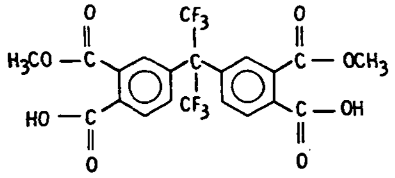
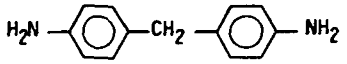
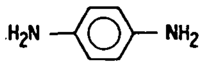
Structures	Name	Abbreviation
	Monomethylester of 5-norbornene-2,3-dicarboxylic acid	NE
	Dimethylester of 3,3'4,4'-benzophenonetetracarboxylic acid	BTDE
	Dimethylester of 4,4'-(hexafluoroisopropylidene)-Bis(phthalic acid)	HFDE
	4,4'-methylenedianiline	MDA
	P-phenylenediamine	PPDA

TABLE II. - INITIAL PROPERTIES OF AUTOCLAVED PMR LAMINATES INVESTIGATED

Resin	Fiber	Tg,[a] °C/°F	Fiber, vol %	Flexural/interlaminar shear strengths		
				RT	343 °C/650 °F	371 °C/700 °F
PMR-15	C-6	[b]378/712	58	1697/109(GPa) 246/15.8(Psi)	580/46(GPa) 84/6.7(Psi)	572/30(GPa) 83/4.3(Psi)
PMR-II-30	C-6	371/700	56	1660/102(MPa) 241/14.8(Psi)	730/40(MPa) 106/5.9(Psi)	503/30(MPa) 73/4.4(Psi)
PMR-II-30	T-40R	385/725	55	1270/60(MPa) 184/8.7(Psi)	558/32(MPa) 81/4.6(Psi)	470/21(MPa) 69/3.1(Psi)
PMR-II-50	C-6	370/698	56	1840/112(MPa) 267/16.2(Psi)	593/46(MPa) 86/6.7(Psi)	324/23(MPa) 47/3.3(Psi)
PMR-II-50	T-40R	366/691	55	1160/66(MPa) 168/9.5(Psi)	517/32(MPa) 75/4.7(Psi)	296/20(MPa) 43/2.9(Psi)

[a] After 24 hours at 385 °C (725 °F).
[b] After 24 hours at 371 °C (700 °F).

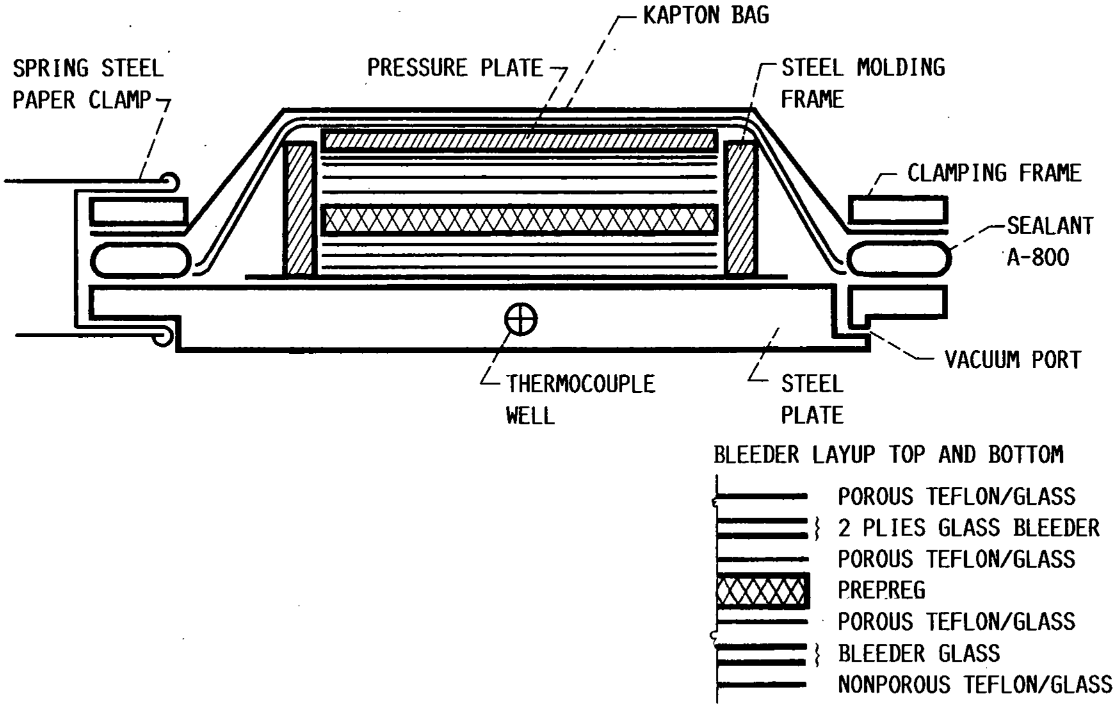


FIGURE 1. - VACUUM BAG SYSTEM USED FOR AUTOCLAVE FABRICATION OF PMR-II COMPOSITES.

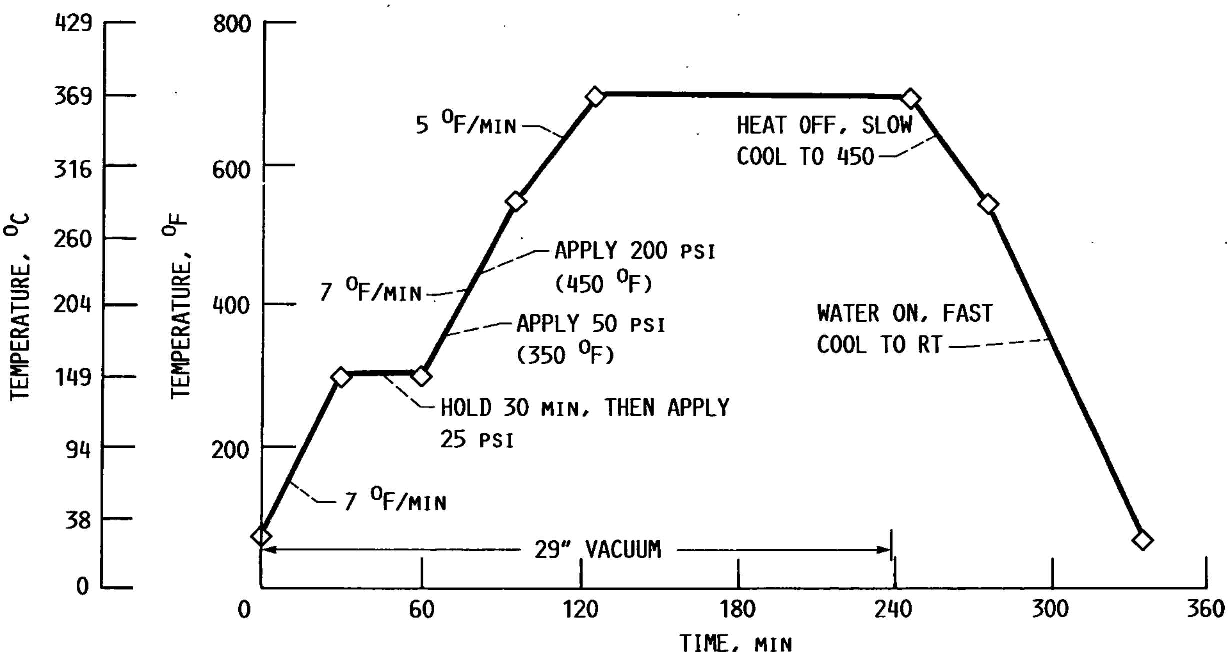


FIGURE 2. - AUTOCLAVE CURE CYCLE FOR GRAPHITE FIBER REINFORCED PMR-II COMPOSITES.

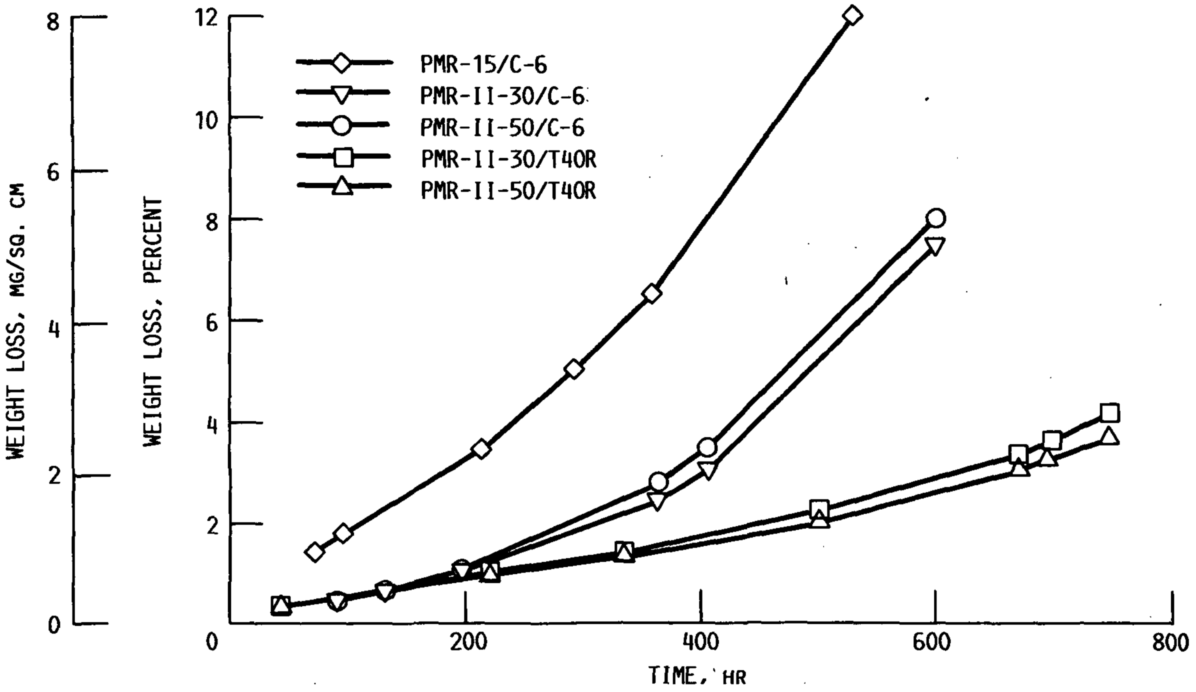


FIGURE 3. - WEIGHT LOSS OF GRAPHITE FIBER REINFORCED PMR LAMINATES AFTER EXPOSURE TO 1 ATM OF AIR AT 343 °C (650 °F).

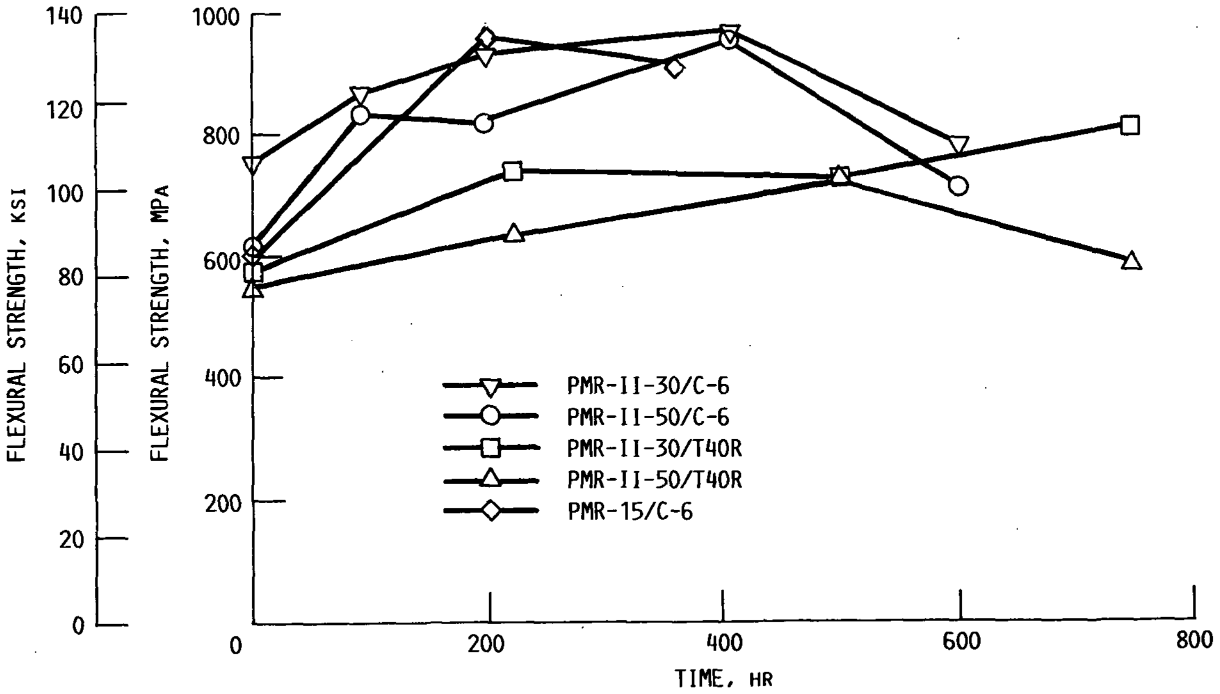


FIGURE 4. - FLEXURAL STRENGTH OF GRAPHITE FIBER REINFORCED PMR LAMINATES AFTER EXPOSURE TO 1 ATM OF AIR AT 343 °C (650 °F). EXPOSED AND TESTED AT 650 °F.

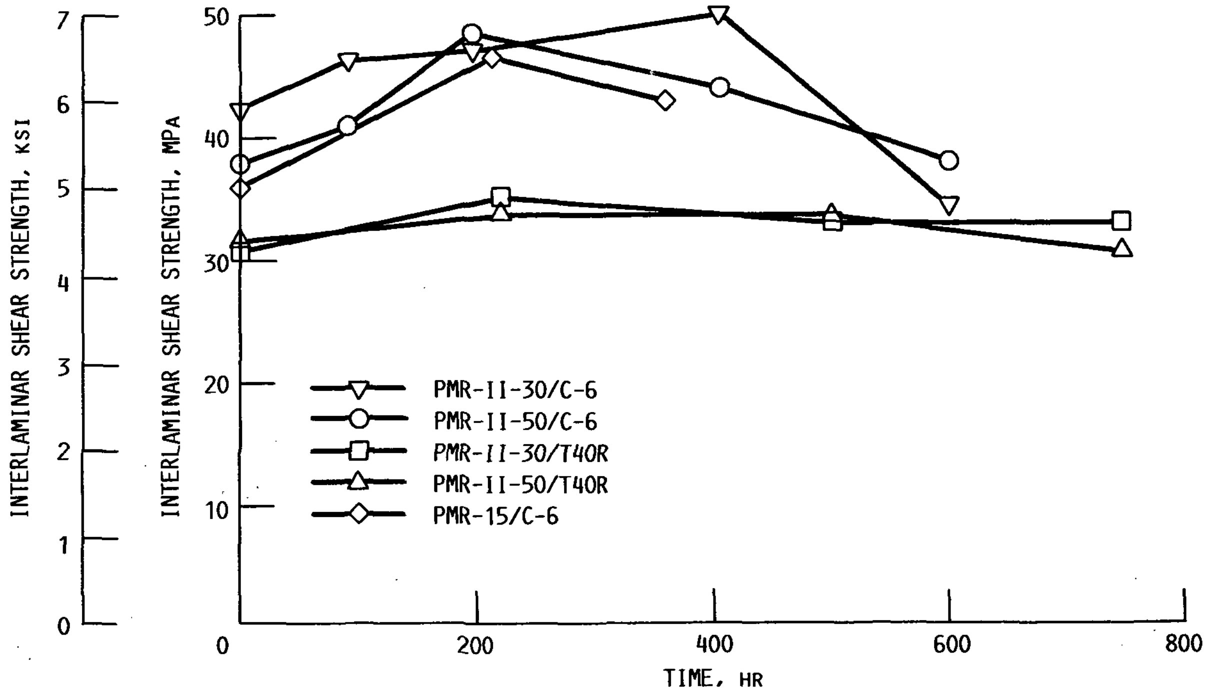


FIGURE 5. - INTERLAMINAR SHEAR STRENGTH OF GRAPHITE FIBER REINFORCED PMR LAMINATES AFTER EXPOSURE TO 1 ATM OF AIR AT 343 °C (650 °F). EXPOSED AND TESTED AT 650 °F.

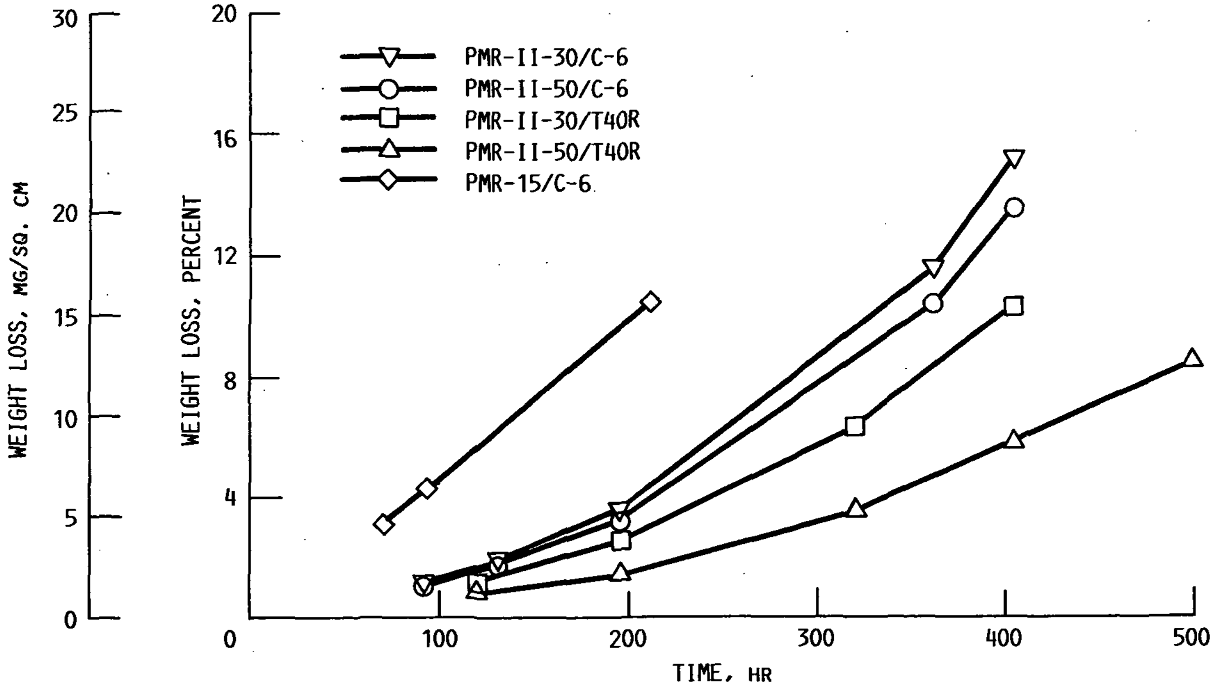


FIGURE 6. - WEIGHT LOSS OF GRAPHITE FIBER REINFORCED PMR LAMINATES AFTER EXPOSURE TO 1 ATM OF AIR AT 371 °C (700 °F).

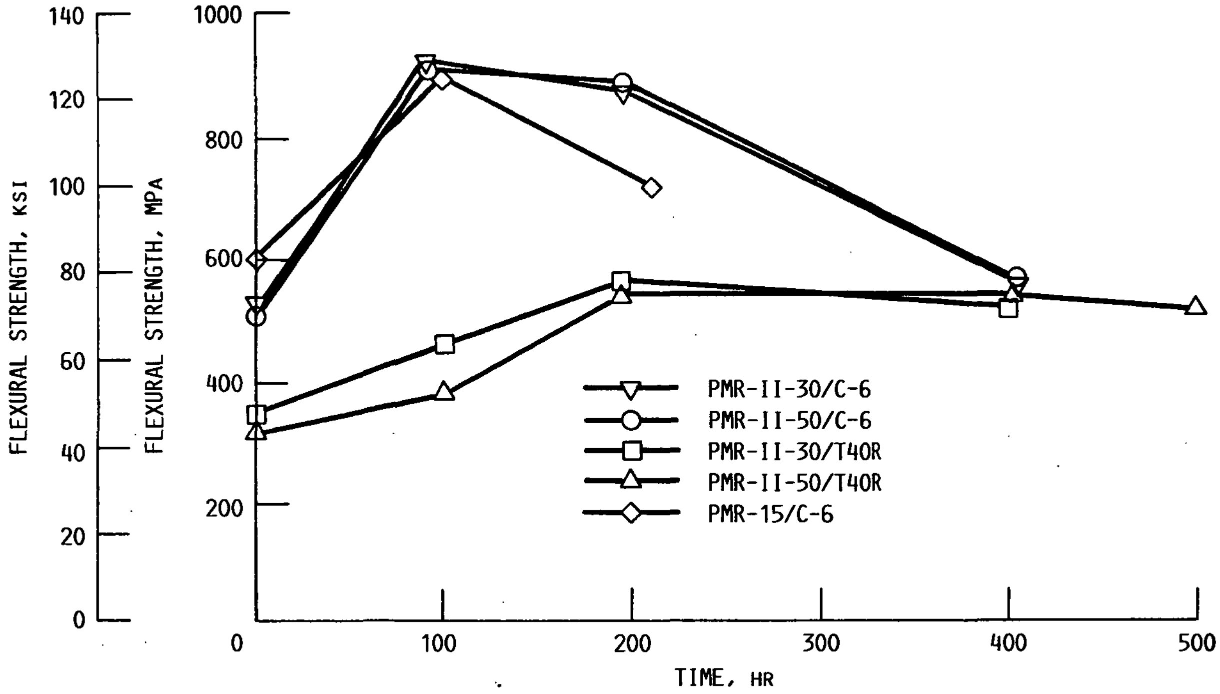


FIGURE 7. - FLEXURAL STRENGTH OF GRAPHITE FIBER REINFORCED PMR LAMINATES AFTER EXPOSURE TO 1 ATM OF AIR AT 371 °C (700 °F). EXPOSED AND TESTED AT 700 °F.

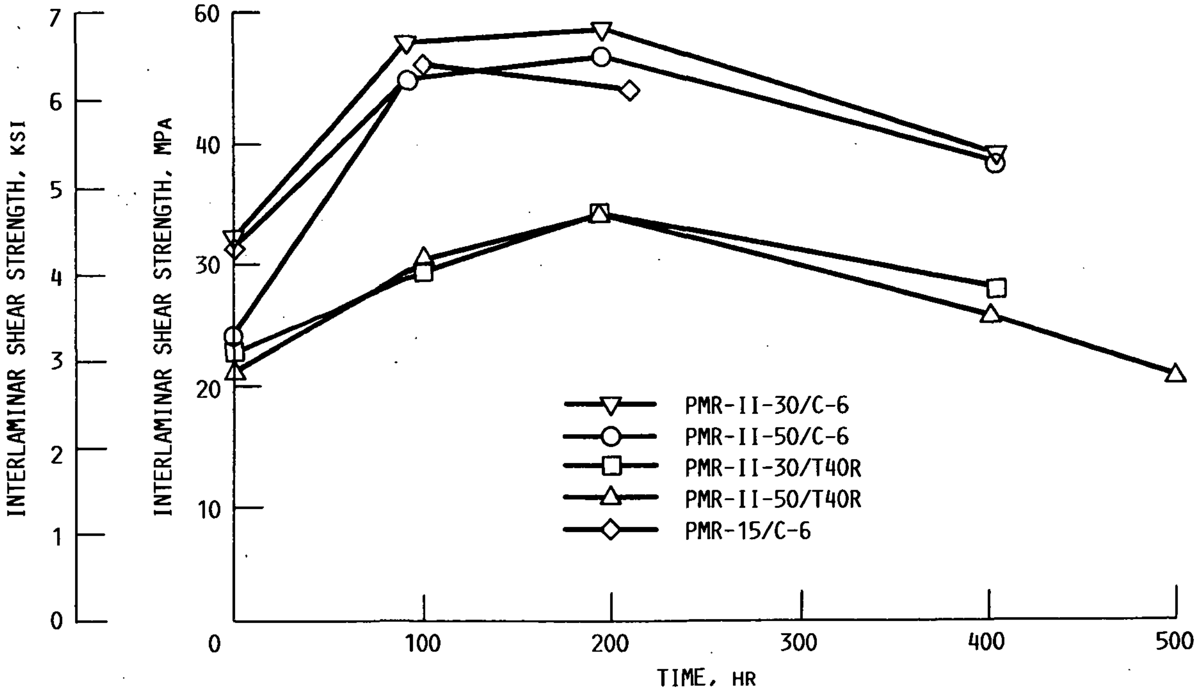


FIGURE 8. - INTERLAMINAR SHEAR STRENGTH OF GRAPHITE FIBER REINFORCING PMR LAMINATES AFTER EXPOSURE TO 1 ATM OF AIR AT 371 °C (700 °F). EXPOSED AND TESTED AT 700 °F.

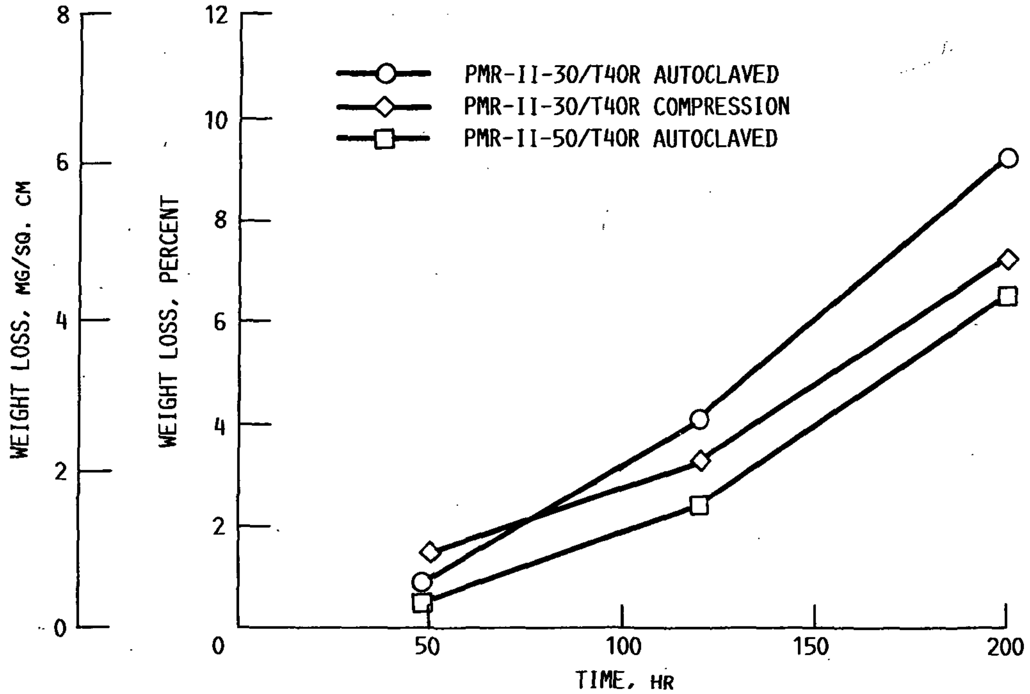


FIGURE 9. - WEIGHT LOSS OF T40 GRAPHITE/PMR-II RESIN LAMINATES AFTER EXPOSURE TO 4 ATM OF AIR AT 371 °C (700 °F).

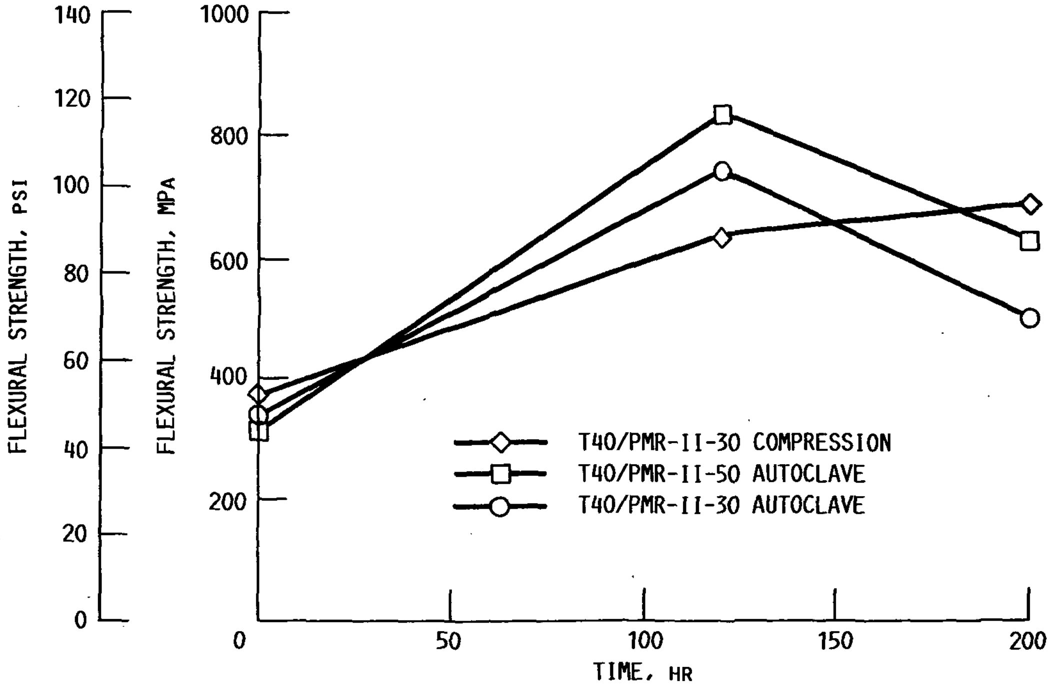


FIGURE 10. - FLEXURAL STRENGTH OF T40 GRAPHITE/PMR-II RESIN LAMINATES AFTER EXPOSURE TO 4 ATM OF AIR AT 371 °C (700 °F). EXPOSED AND TESTED AT 700 °F.

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16. Abstract

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