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EFFECT OF PROCESSING PARAMETERS ON AUTOCLAVED PMR POLYIMIDE COMPOSITES

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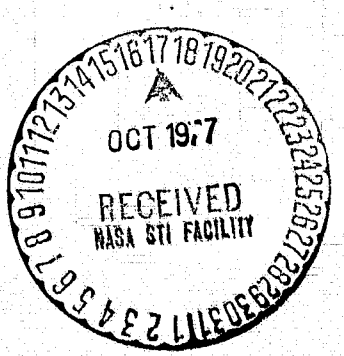

EFFECT OF PROCESSING PARAMETERS ON AUTOCLAVED PMR POLYIMIDE COMPOSITES

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Abstract

A study was conducted to determine the effect of processing parameters on the processability and properties of autoclaved fiber reinforced PMR Polyimide composites. Composites were fabricated from commercially available graphite fabric and glass fabric PMR Polyimide prepreg materials. Process parameters investigated included degree of resin advancement, heating rate, and cure pressure. Composites were inspected for porosity by ultrasonic "C" scan and photomicrographic examination. Processing characteristics for each set of process parameters and the effect of process parameters on composite mechanical properties at room temperature and 600° F are described.

1.0. INTRODUCTION

PMR Polyimide composite materials have been selected or are now being considered for use in making large composite structures which require autoclave processing. When first introduced[1], PMR 15 was considered to be a low flow resin requiring cure pressures in the range of 500 to 1000 psi for fabrication of void free composites. Later studies[2] demonstrated that the resin flow characteristics of PMR Polyimides could easily be varied over a wide range (3 to 20 percent resin flow) by adjusting the stoichiometry of the monomer reactants.

Unpublished results of the preliminary studies conducted at the Lewis Research Center, using a simulated autoclave, indicated that PMR Polyimides could be autoclave processed. These preliminary studies were conducted using vacuum bag lay-up techniques, low heating rates (3° to 5° F/min), and a pressure of 200 psi. A significant finding was that PMR Polyimides exhibit melt flow characteristics in the range of 440° to 495° F prior to undergoing final curing at higher temperatures. These findings were first described[3] at the conference sponsored by the NASA Langley Research Center, held in March 1975, to provide an industry as-

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sessment of graphite-polyimide composite technology. Using autoclave processing parameters based on these findings, a number of large components, such as the inner cowl of the Quiet Clean Short-Haul Experimental Engine (QCSEE) and the augmentor duct for the F-100 engine, are currently being autoclave fabricated using PMR resins.

The purpose of this investigation was to determine the effect of processing parameters on the processability and properties of autoclaved composites made from commercially available graphite fabric and glass fabric reinforced PMR 15 resin prepreg materials.

Flat 6×6 inch laminates were autoclave molded. Parameters investigated included prepreg advancement, heating rate, and cure pressure. The effects of cure parameters on laminate resin flow, void content, room temperature, and 600° F mechanical properties were evaluated.

2.0. EXPERIMENTAL PROCEDURES

2.1 MATERIALS

The PMR Polyimide prepreg materials used in this investigation are listed in Table I. The prepreg materials were obtained from two commercial suppliers of prepreg. Also given in the table are the fiber finishes, the types of solvent and values of the resin solids, and volatile content determined by the vendor and in our laboratory.

2.2 AUTOCLAVE FABRICATION

All prepreg materials were stored at 0° F in plastic bags. Prior to cutting a prepreg material, it was allowed to reach room temperature, debagged, cut into 6×6 inch plies and then stored temporarily in plastic bags at 40° F prior to stacking and fabricating. Material to be staged, or advanced, was then stacked in preforms (graphite fabric - 6 plies, glass fabric - 10 plies). These were staged in an oven for either 3 hours at 250° F or 1 hour at 400° F under an applied pressure of 0.1 psi. The volatile content of PMR 15/T 300 and glass fabric prepreg to be processed without prior staging was controlled to 8.5 to 9.0 and 7.5 to 8.0 weight percent, respectively, by drying in an air circulating oven at 120° F. Three prepreg stacks, representing each of the staging conditions being investigated, were then vacuum bagged according to the schematic shown in figure 1. A vacuum of 15 inches of Hg was applied to the lay-up and maintained until the elevated temperature cure had been completed. This level of vacuum was utilized for all of the cure cycle studies. Heating rates of 4.5° and 9° F per minute and final cure pressures of 50, 100, and 200 psi were employed. Figure 2 shows the variation of vacuum, pressure and temperature for a cure cycle which employed a heating rate of 4.5° F/minute and a final curve pressure of 200 psi. The hold at 480° F was required to permit the selected cure pressure to be applied at 480° F. Pressurization of 50, 100, and 200 psi required times of 4, 10, and 29 minutes, respectively. The time to achieve a pressure of 200 psi was reduced to 22 minutes by resuming heating after a 15-minute hold at 480° F, at which time a pressure of 150 psi had been achieved. Full pressure was achieved 7 minutes after heating was resumed. All laminates were cured under pressure for 1 hour at 600° F. The autoclave heat-

ers, vacuum pump, and air compressor were then turned off and the pressure allowed to decrease during system cool down. Cool down was achieved by first allowing the autoclave to air cool to 450° F and then water cooling to 120° F. The autoclave was then depressurized and the laminates removed. The laminates were post-cured by placing them into an air circulating oven at room temperature, raising the temperature to 600° F at 4°/minute and holding at 600° F for 16 hours. The oven was then allowed to air cool at 4°/minute to 450° F and the laminates removed.

2.3 LAMINATE TESTING

The laminates were inspected for porosity by photomicrographic examination and ultrasonic "C" scan analysis. Laminate void contents were determined by comparing measured laminate densities to calculated densities based on fiber contents of the laminates. Fiber content was determined by digestion of laminate specimens in concentrated sulfuric acid and hydrogen peroxide. Measured laminate densities were determined gravimetrically in distilled water.

Flexural tests were performed using a 3-point fixture with a fixed span of 2 inches. The thicknesses of the laminates ranged from 0.080 to 0.106 inch. The resultant span/depth ratio ranged from 19 to 25. The rate of center loading for flexural testing was 0.05 inch/minute. Interlaminar shear strength tests were conducted at a constant span/depth of 5 and a center loading rate of 0.05 inch/minute. Elevated temperature tests were performed in an environmental heating chamber. For flexural and shear tests the load was applied after a 15-minute soak at temperature.

The properties data presented are averages of three tests at each condition. Fiber content ranged from 53.5 to 63.5 volume percent for graphic fabric laminates and from 52.5 to 64.8 volume percent for glass fabric laminates. For flexural tests all results were normalized to 60 volume percent fiber.

3.0. RESULTS AND DISCUSSION

3.1 PRELIMINARY INVESTIGATION

To determine the feasibility of using slow heating rates, such as those required for autoclave processing, a series of preliminary experiments was conducted at heating rates in the range of 3.0° to 5.0° F/minute and at a cure pressure of 200 psi. These experiments were conducted on prepreg prepared from PMR Polyimides having formulated molecular weights (FMW) of 1000, 1300, and 1500 with Fortafil 4R graphite fiber reinforcement. The prepreg was staged 3 hours at 250° F and then molded in a matched metal die with one of the end plates removed to permit visual observation of the resin flow events which occurred as the temperature was increased from room temperature to 600° F. Full pressure (200 psi) was applied at 400° F.

Melt flow was observed to occur at two different temperatures. As expected, melt flow was observed at 525° F coinciding with the addition crosslinking reaction. Of greater significance was the observation that melt flow also occurred at 440° F for the FMW of 1000 and increased to 460° F for the FMW of 1500 (PMR 15). The relative amount of flow appeared to be inversely proportional to the FMW. More importantly, the unrestricted flow at slow heating rates and low cure pressure was essentially the

same as resin flow reported for PMR composites fabricated under containment in close fitting matched metal dies as fast heating rates and high cure pressure[2]. Maximum resin flow was observed to occur at a temperature which was generally about 20° F above the flow onset temperature.

Several additional experiments were then performed using PMR 15/Fortafil 4R prepreg (staged 3 hr at 250° F), however, in these experiments a Kapton bag was employed and a vacuum of 15 inches of Hg was maintained throughout the cure cycle. The heating rate was 4° F/minute and full cure pressure was applied at the temperature of maximum flow in the first melt flow zone (480° F). The resulting laminates were void free as determined by ultrasonic "C" scan analysis.

These preliminary results served as the basis for the autoclave processing study of the PMR 15 system to be discussed in the following sections.

3.2 PMR 15 PROCESS PARAMETERS

The parameters, and the levels of each parameter are indicated in Table II. In order to determine the effect of resin advancement on resin flow and autoclave cured laminate quality, three staging conditions were selected to yield various degrees of resin flow during cure. The conditions of staging and degree of resin advancement, as measured by the extent of imidization, are listed in table III. Laminates representing the three staging conditions were then autoclave cured at three different cure pressures (50, 100, and 200 psi) and two autoclave heating rates (4.5° and 9.0° F/min) to determine the effect of cure pressure and heating rate on laminate quality.

It was recognized that processing unstaged prepreg material under the same processing conditions chosen for staged material would result in considerably higher resin flow. However, the cure cycle employing unstaged prepreg was of particular interest to determine if high flow and better compaction during staging and cure at a low pressure would result in low void composites. For this reason no attempts were made to restrict flow during staging of layups in the autoclave.

For ethanol based glass fabric prepreg material an excessive amount of flow was observed, therefore a non-porous peel ply was used to restrict flow during laminate fabrication.

In processing unstaged prepreg it was found that the initial volatile content of the prepreg had an important effect on the amount of monomer flow which occurs prior to imidization. Substantial flow was observed under vacuum-bag drying of unstaged PMR 15/T 300 fabric prepreg which had an initial volatile content of 15 weight percent. Drying of this material at room temperature under a vacuum of 15 inches of Hg resulted in saturation of the three glass bleeder plies. Excessive monomer bleed under vacuum at room temperature was not experienced for PMR 15/T 300 prepreg containing 8.5 to 9.0 weight percent volatiles and 37.8 to 39.0 weight percent resin solids. In this investigation all PMR 15/T 300 prepreg which was staged in the autoclave had an initial volatile content of 8.5 to 9.0 weight percent or was dried at 120° F to achieve that level of vola-

tile content. For glass fabric prepreg, the volatile content was controlled to 7.5 to 8.0 weight percent volatiles and 27.5 to 28.2 weight percent resin solids.

3.3 LAMINATE EVALUATION

Figure 3 shows the variation in resin flow during cure as a function of cure pressure for staged and unstaged PMR 15/T 300 graphite fabric laminates at two heating rates, 4.5° F/minute (fig. 3(a)) and 9.0° F/minute (fig. 3(b)). It can be seen that the extent of flow is affected by the degree of staging and also by the cure pressure. By comparing figures 3(a) and (b) it can be seen that doubling the heating rate resulted in increased flow for all of the staged materials except for the fully staged material cured at 50 psi. At the faster heating rate approximately a 150-percent increase in flow was observed for the fully staged material cured at 200 psi. In contrast the partially staged material exhibited about a 70-percent flow increase at the faster heating rate and 200 psi cure pressure. Heating rate did not appear to affect the flow of unstaged material.

The effect of process parameters on void content of PMR 15/T 300 graphite fabric laminates is shown in figures 4(a) and (b). The figures clearly show that cure pressure is the process parameter which had the most pronounced effect on laminate void content, or porosity. Laminates cured at 200 psi pressure exhibited void contents ranging from 0 to 1.5 volume percent (V/o). At 100 psi cure pressure the void contents ranged from 2.8 to 4.5 V/o with the laminates prepared from unstaged prepreg having the lower porosity at both heating rates. Laminates cured at 50 psi from unstaged prepreg also exhibited the lower porosity at both heating rates. The higher quality of these laminates could possibly be attributed to higher compaction during resin advancement in the autoclave. However, it needs to be pointed out that the use of unstaged prepreg could result in excessive resin flow and inferior laminate properties. Therefore, it is desirable to determine the optimum staging parameters for staging of PMR prepreg in the autoclave with uninterrupted cure at 50 and 100 psi pressure.

Figure 5 shows the effect of autoclave processing parameters on the flexural strength of PMR 15/T 300 graphite fabric laminates fabricated at a heating rate of 4.5° F/minute (fig. 5(a)) and at 9.0° F/minute (fig. 5(b)). Flexural strength data are shown in figure 5(a) for composites tested at room temperature and after short-time (15 min) exposure at 600° F. Figure 5(b) shows room temperature data. Room temperature flexural strengths of laminates cured at 100 and 200 psi pressure were not significantly affected by cure pressure or degree of staging at either of the heating rates. Short-time 600° F flexural strengths for laminates cured at the heating rate of 4.5° F/minute exhibited about 70 percent retention of their room temperature flexural strength with the exception of the laminates prepared from partially staged prepreg cured at 200 psi which exhibited a 62-percent retention of its room temperature property. The room temperature flexural strengths shown for laminates cured at 100 and 200 psi pressure compare favorably with flexural strength data for T 300 fabric reinforced resin matrix composites at 60 V/o fiber loading.

By plotting flexural strength as a function of void content (fig. 6) it can be seen that laminate void content had a negligible effect on room temperature and short-time 600° F flexural strength of laminates cured at 100 and 200 psi cure pressure. The effect of void content on flexural properties was more pronounced for laminates cured at 50 psi for which porosity ranged from 8 to 13 V/o.

Figure 7 shows the variation of interlaminar shear strength (ILSS) at room temperature and after short-time 600° F exposure for autoclaved cured PMR 15/T 300 laminates. It can be seen that the ILSS increased significantly as the cure pressure was increased from 50 to 200 psi with laminates fabricated from unstaged material exhibiting the higher ILSS at all three cure pressures. If we return to figure 3(a), we see that laminates cured from unstaged PMR 15/T 300 prepreg exhibited the lowest porosity at all three cure pressures. The plot of ILSS against laminate void content (fig. 8) shows that, as expected, the ILSS decreased with increasing void content[4].

The effects of autoclave process parameters on PMR 15/E-glass and PMR 15/S-glass composite void content and room temperature flexural properties are shown in figures 9 to 12. As previously described (in the experimental section) a non-porous peel ply was used to reduce resin bleed during fabrication of these laminates. In comparing the porosity of S-glass and E-glass laminates (figs. 9 and 10), it can be seen that laminates cured at 200 psi exhibited essentially zero porosity except for S-glass laminates prepared from fully staged prepreg. The E-glass laminates prepared at 50 psi from unstaged and partially staged prepreg and at 100 psi from unstaged prepreg exhibited lower porosity than the S-glass laminates prepared under the same conditions. The void contents of the laminates were about equal for partially staged E- and S-glass prepregs cured at 100 psi and for fully staged E- and S-glass prepregs cured at 50 and 100 psi.

Figures 11 and 12 show the effect of process parameters on the room temperature flexural strength of autoclaved PMR 15/E-glass and PMR 15/S-glass fabric laminates. The results for the E-glass laminates (fig. 11) varied widely making it difficult to establish any trends concerning the effect of process parameters on flexural strength for this material.

Flexural strength data presented in figure 12 show that for S-glass laminates, prepared from any of the prepregs, increasing the cure pressure from 50 to 100 psi led to increased flexural strength properties. A 9-percent increase occurred for laminates prepared from unstaged prepreg, 15 percent for laminates from partially staged prepreg and 32 percent for laminates prepared from completely staged prepreg. An increase in the cure pressure from 100 to 200 psi did not lead to a further increase of flexural strength properties for the laminates prepared from fully or partially staged prepregs. In contrast the flexural strength of the laminate prepared from unstaged material at 200 psi increased by about 8 percent.

These results point out the need for using cure pressures above 50 psi for fabrication of laminates from partially

or fully staged prepreg. It also needs to be pointed out that although the use of higher cure pressures with unstaged prepreg results in higher properties, high flow also occurs which could result in resin starved laminates. This suggests that a cure cycle which includes staging in the autoclave would be highly desirable.

It needs to be recalled that the data points presented in figures 4 to 12 are averages of three determinations. Therefore, the "crossing over" of several of the curves (see, e.g., figs. 4 and 5) might not have been found if a larger number of specimens had been tested.

4.0. SUMMARY OF RESULTS AND CONCLUSIONS

1. The melt flow obtained when processing staged PMR Polyimide prepreg materials at high heating rates and high pressure is also obtained when employing slower heating rates and low pressures which are required for autoclave processing. The flow-onset temperature is a function of PMR Polyimide formulated molecular weight with the maximum flow occurring at approximately 20^{o} F above the flow-onset temperature.

2. Low heating rates (4.5^{o} to 9.0^{o} F/min) and low cure pressures (50 to 200 psi) can be employed to autoclave process PMR Polyimide fiber reinforced materials.

3. Cure pressure has the most pronounced effect on the void content and mechanical properties of autoclaved PMR 15 laminates. A cure pressure of 200 psi provided the best overall laminate properties.

4. The degree of prepreg advancement and also cure pressure have a significant effect on the resin flow characteristics of autoclaved PMR 15 laminates with unstaged prepreg exhibiting the highest resin flow at any cure pressure.

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2. T. T. Serafini and R. D. Vannucci, "Tailor Making High Performance Graphite Fiber Reinforced PMR Polyimides," Proceedings of the 30th Anniversary Technical and Management Conference on Reinforced Plastics - Milestone, The Society of the Plastics Industry, Inc., 1975.

3. "Industry," Technology Assessment of Graphite-Polyimide Composite Materials. NASA CR-132685, June 1975.

4. W. Hand, "Quality Control of Filament Wound Materials for Deep Submergence Vessels," Proceedings of the 20th Anniversary Technical Conference on Reinforced Plastics, The Society of the Plastics Industry, Inc., 1965.

TABLE I. - PMR 15 PREPREG MATERIALS INVESTIGATED

Reinforcement	Supplier	Fiber finish	Solvent	Resin solids, W/o		Volatile content, W/o	
				Supplier	In-house	Supplier	In-house
PMR 15/T 300, 24×24 warp/fill	Fiberite	Epoxy	Methanol	37.7	37.8	8.1	9.0
PMR 15/T 300, 24×24 warp/fill	Ferro	Epoxy	Methanol	35.6	39.0	16.0	15.0
S-6581 glass	Fiberite	A-1100	Ethanol	27.8	28.2	8.2	9.4
E-7781 glass	Fiberite	A-1100	Ethanol	27.3	27.5	10.6	11.0

TABLE II. - AUTOCLAVE PROCESS PARAMETERS INVESTIGATED

Staging, hr/°F	Heating rate, °F/min	Cure pressure, psi		
		50	100	200
None	4.5	×	×	×
	9	×	×	×
3/250	4.5	×	×	×
	9	×	×	×
1/400	4.5	×	×	×
	9	×	×	×

TABLE III. - PREPREG STAGING AND RESIN ADVANCEMENT

Number	Staging	Resin advancement,[1] percent
1	None	0
2	3 hours at 250° F	20 to 30
3	1 hour at 400° F	95 to 100

[1]Based on unpublished results of an in-house infrared study by R. W. Lauver.

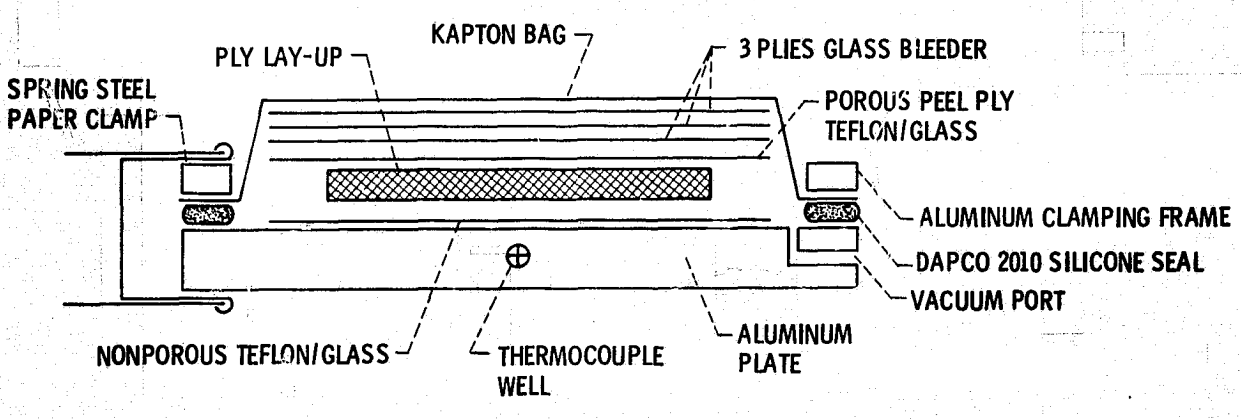


Figure 1. - Vacuum bag system used for autoclave fabrication of fabric reinforced PMR 15 laminates.

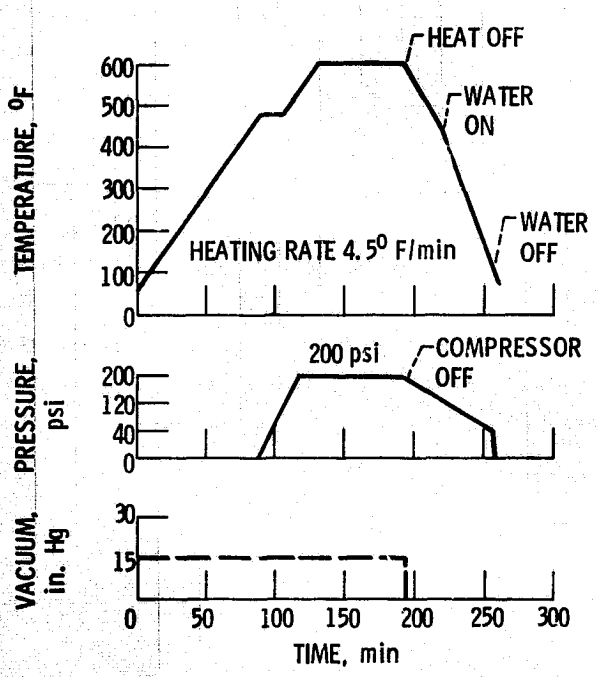
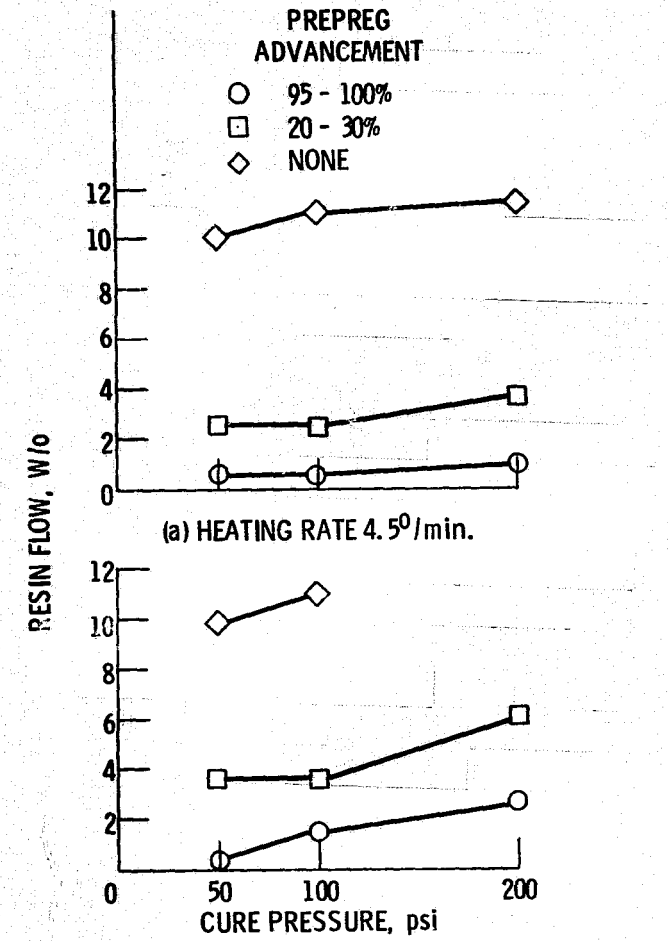


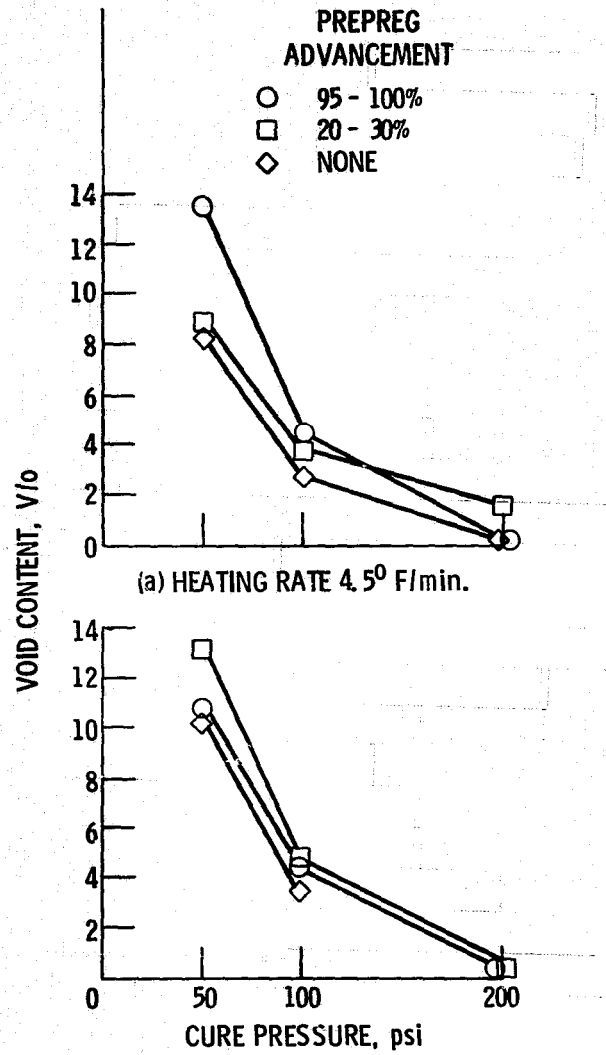
FIGURE 2. - AUTOCLAVE CURE CYCLE FOR PMR-15 FABRIC REINFORCED LAMINATES.



(a) HEATING RATE 4.5^{0}/min.

(b) HEATING RATE 9.0^{0} F/min.

FIGURE 3. - RESIN FLOW DURING CURE FOR AUTOCLAVED PMR 15/T-300 GRAPHITE FABRIC LAMINATES.



(a) HEATING RATE 4.5^{0} F/min.

(b) HEATING RATE 9.0^{0}/min.

FIGURE 4. - VOID CONTENT OF AUTOCLAVED PMR 15/T 300 GRAPHITE FABRIC LAMINATES.

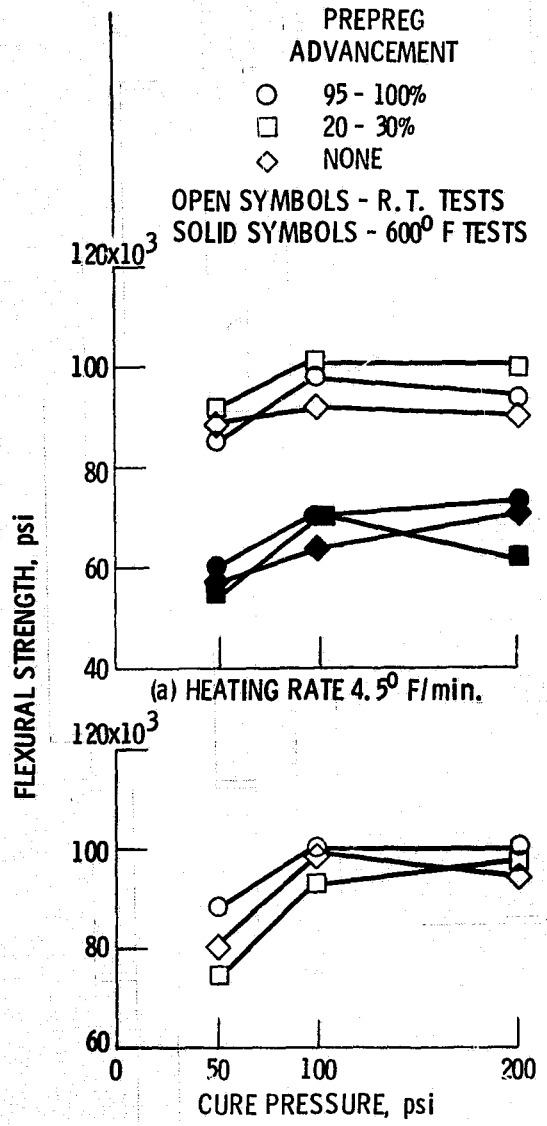


FIGURE 5. - ROOM TEMPERATURE AND SHORT-TIME 600° F FLEXURAL STRENGTH OF AUTOCLAVED PMR 15/T 300 GRAPHITE FABRIC LAMINATES.

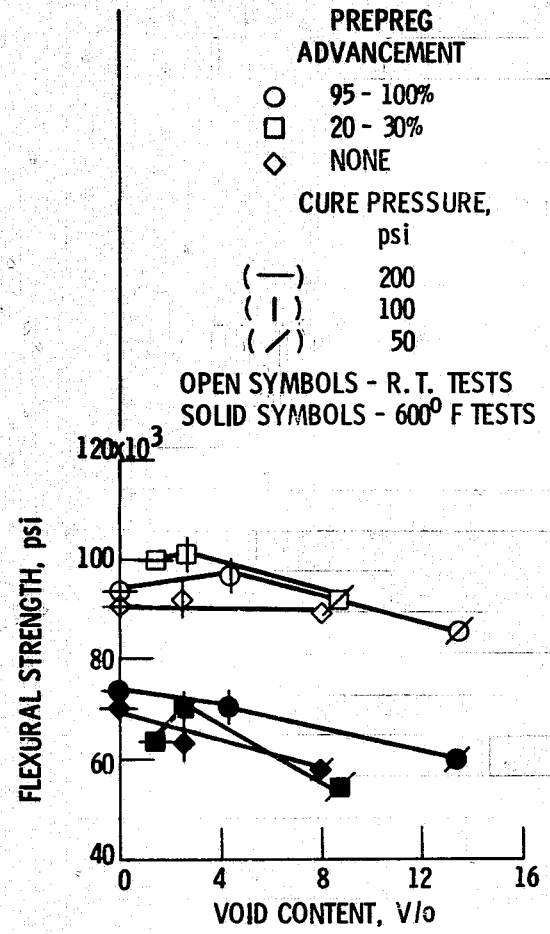


FIGURE 6. - EFFECT OF VOID CONTENT ON FLEXURAL STRENGTH OF PMR 15/T 300 GRAPHITE FABRIC LAMINATES AUTOCLAVED AT 4.5° F/min.

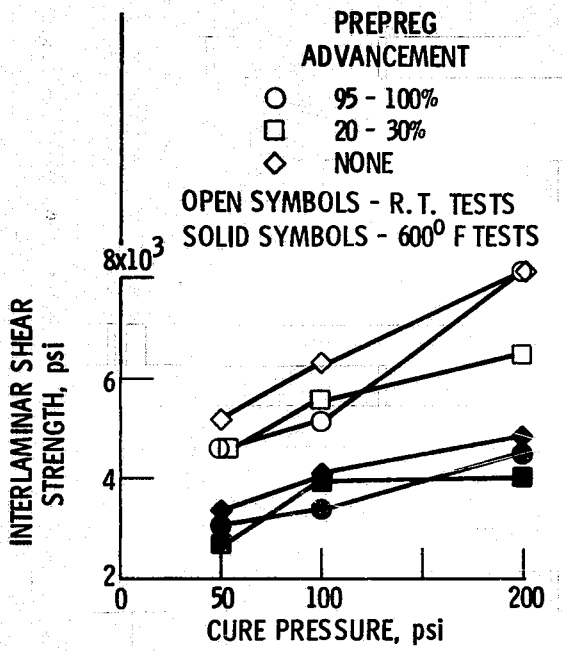


FIGURE 7. - ROOM TEMPERATURE AND SHORT-TIME 600° F INTERLAMINAR SHEAR STRENGTH OF PMR 15/T 300 GRAPHITE FABRIC LAMINATES AUTOCLAVED AT 4.5° F/min.

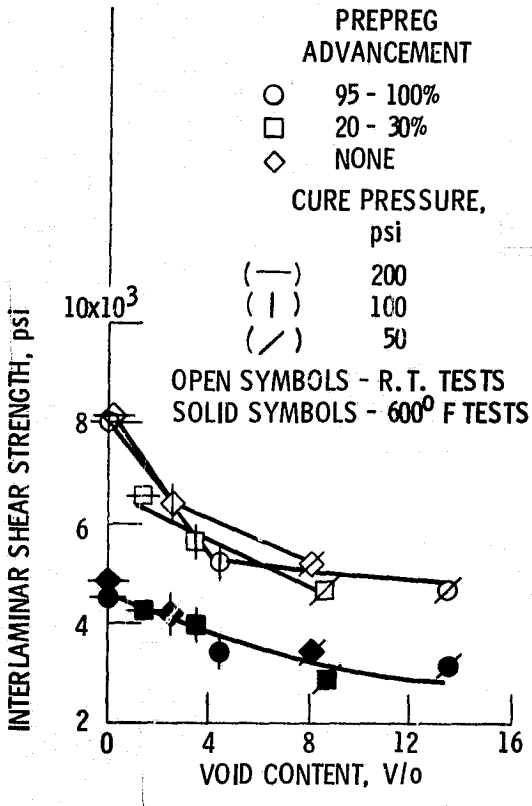


FIGURE 8. - EFFECT OF VOID CONTENT ON INTERLAMINAR SHEAR STRENGTH OF PMR 15/T 300 GRAPHITE FABRIC LAMINATES AUTOCLAVED AT 4.5°F/min.

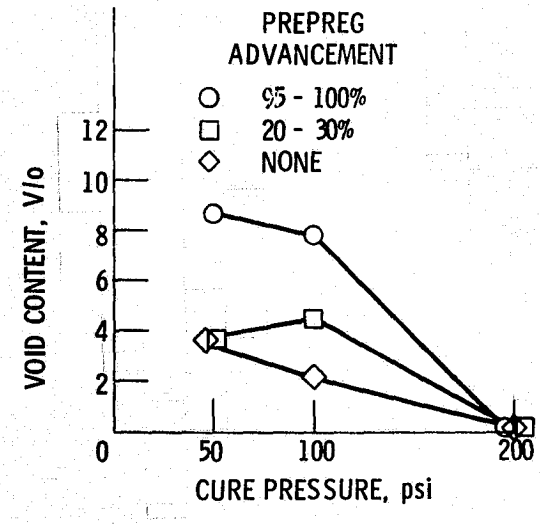


FIGURE 9. - VOID CONTENT OF PMR 15/E-7781 GLASS FABRIC LAMINATES AUTOCLAVED AT 4.5°F/min.

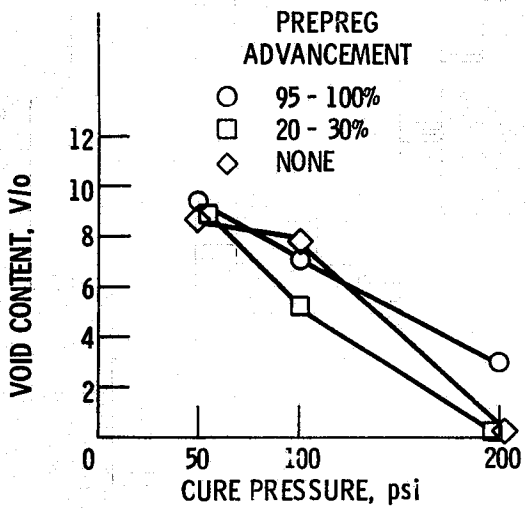


FIGURE 10. - VOID CONTENT OF PMR 15/S-6581 GLASS FABRIC LAMINATES AUTOCLAVED AT 4.5° F/min.

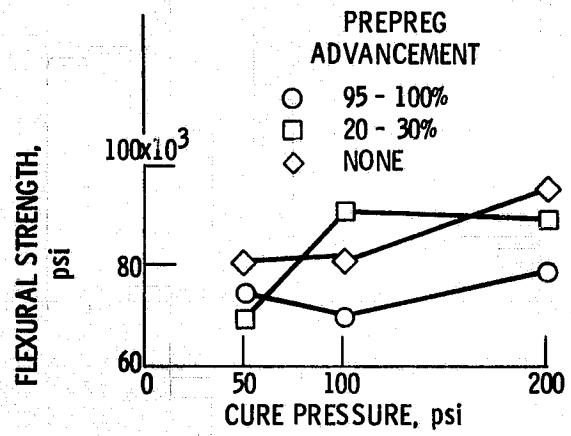


FIGURE 11. - ROOM TEMPERATURE FLEXURAL STRENGTH OF PMR 15/E-7781 GLASS FABRIC LAMINATES AUTOCLAVED AT 4.5° F/min.

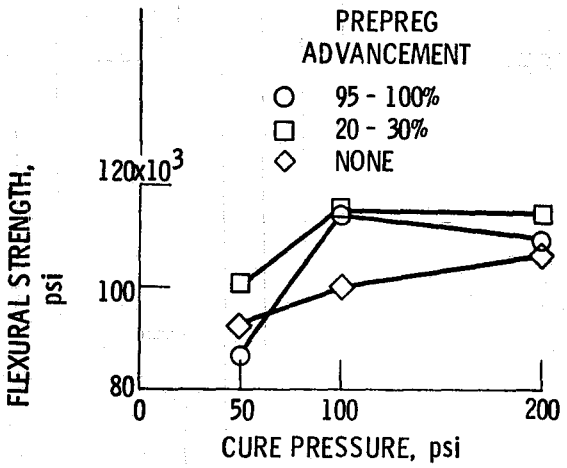


FIGURE 12. - ROOM TEMPERATURE FLEXURAL STRENGTH OF PMR 15/S-6581 GLASS FABRIC LAMINATES AUTOCLAVED AT 4.5° F/min.