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PROPERTIES OF AUTOCLAVED Gr/PI COMPOSITES  
MADE FROM IMPROVED TACK PMR-15 PREPREG

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Autoclave processing studies were conducted, using improved tack PMR-15 prepreg, to determine the effect of tack enhancing PMR resin modifications on composite processability and mechanical properties.

Improved tack graphite fiber reinforced PMR-15 prepregs were prepared and exposed to ambient conditions for various times and then autoclave molded into composites. Composite specimens were prepared and tested for flexural and interlaminar shear strengths at room temperature and 316 °C. The retention of flexural and interlaminar shear strength as a function of exposure in air at 316 °C was also determined.

The results show that the modified PMR resin solutions provide prepreg with improved tack and drape retention characteristics without adversely affecting processability or mechanical properties of autoclave-molded graphite fiber reinforced PMR-15 composites.

INTRODUCTION

Composites made with PMR-15 polyimide are now gaining acceptance as viable engineering materials for high-use-temperature applications. This acceptance is due to both the thermo-oxidative stability of PMR-15 and the ease with which PMR-15 prepreg materials can be processed into composite structures. An important factor contributing to the processability of PMR-15 materials is the volatility of the alcoholic solvents used in preparing prepregging solutions. These low-boiling-point solvents (methanol or ethanol) are easily removed during fabrication, making it possible to obtain void-free or low-void composites. However, the volatility of these solvents does limit the tack and drape retention of PMR-15 prepreg exposed to the ambient. Retention of these two important material handling properties is essential for consistent performance during layup of composite structures, particularly large composite structures which may require long layup times.

In the past, efforts to improve the tack and drape retention of PMR-15 prepreg materials involved the use of reactive diluents (ref. 1) or higher boiling point solvents (ref. 2). The use of reactive diluents provided only slight improvements in tack and drape retention. Higher boiling point solvents, while providing significantly improved tack and drape retention, are difficult to remove during processing and severely affect the processability of PMR-15 materials.

In a more recent study (ref. 3), PMR resin compositions were identified which offer potential for improving the tack and drape retention of PMR prepreg materials without affecting the processability or elevated temperature mechanical properties of compression-molded graphite fiber reinforced PMR-15 composites. This was accomplished by utilizing mixtures of low-boiling alcoholic solvents, which are easily

removed during processing, and modified monomer reactants which do not alter PMR resin cure chemistry.

The purpose of this investigation was to determine the effect of improved tack PMR-15 prepreg on the processability and mechanical properties of graphite fiber reinforced autoclave-molded PMR-15 composites.

## EXPERIMENTAL PROCEDURE

### Prepreg Fabrication and Testing

The monomer reactants used to prepare the resins used in this study are shown in table I. The monomer reactants and PMR-15 prepregging solutions were prepared as described in reference 3. Style 182 fabric woven from epoxy sized T-300 graphite fiber and unsized Celion 6000 unidirectional graphite fiber tows were used as reinforcing materials. Prepreg was prepared by brush application of the PMR solution onto flat 45.7 by 30.5 cm sections of fabric and onto drum wound (4.72 turns/cm) unidirectional tows to yield composites having 58 vol % fiber. Silicone coated paper was used as the peel ply for both prepreg materials.

Prepreg tack was determined on simple lap shear specimens having a length of 12.7 cm, a width of 2.54 cm, and an overlap of 2.54 cm. The test specimens were prepared from prepreg exposed for various times under ambient conditions by removing the peel ply and joining the unexposed side to the exposed side. The force to separate the prepreg was then measured at a loading rate of 12.7 cm/min. All tack values reported are averages of three or more tests. A qualitative assessment of prepreg drape, or deformability, was obtained by supporting a prepreg strip (30.5 by 2.54 cm) at its center and observing the deformation of the prepreg under its own weight.

### Composite Fabrication and Testing

Composites were autoclave molded from both T-300 graphite fabric prepreg and from Celion 6000 graphite fiber tape prepreg. The schematic for vacuum bag layup of the unidirectional tape prepreg is shown in figure 1. The prepreg tapes were cut into 15.2 by 20.3 cm plies, fiber axis parallel to the long direction, and stacked unidirectionally to produce 12-ply composites. The fabric prepreg was cut into 15.2 by 15.2 cm plies and stacked 6 plies thick, with the warp aligned in the zero degree direction. The vacuum bag layup for fabric reinforced prepreg was identical to that shown in figure 1, except that no side containment or pressure plate was employed. The autoclave cure cycle used for fabricating composites from both tape and fabric prepreg materials is shown in figure 2. After curing, all composites were given a free-standing postcure in a forced-air oven by heating at 5 °C/min to 316 °C followed by a 24-hour hold at 316 °C.

Prior to test specimen preparation, all composites were inspected using the ultrasonic C-scan technique. Composite flexural strength tests were performed in accordance with ASTM D-790 at a fixed span of 5.08 cm. Specimen thicknesses ranged from 0.191 to 0.216 cm. The resultant span/depth ratios ranged from 27 to 23.5. Interlaminar shear strength tests were performed essentially in accordance with ASTM D-2344 at a constant span/depth of 5. Elevated temperature tests were conducted on specimens after isothermal exposure in air, for various times, at the

test temperature. Flexural and interlaminar shear strength values reported are averages of three or more tests.

## RESULTS AND DISCUSSION

### Resin Selection

The commercially available PMR polyimide, designated PMR-15, consists of a methanol solution of the monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid (NE), the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), and 4,4'-methylenedianiline (MDA). In a previous study (ref. 3), it was found that the substitution of higher alkyl ester monomers for methyl ester monomers in PMR-15 resins, as well as the use of a mixture of low-boiling-point alcoholic solvents, provided PMR-15 prepreg with improved tack and drape retention.

Table II lists the various modified PMR-15 resin systems investigated in the earlier study (ref. 3). The table lists the alkyl ester monomers and solvent used for each resin system and the designated abbreviation for each resin system.

Table III summarizes the results obtained in the earlier study from the tack and drape tests performed on graphite fiber prepreg made from each of the resin systems listed in table II. The results show that the substitution of a 3:1 methanol/1-propanol (M/P) solvent mixture for methanol in the resin system containing methyl esters (C<sub>1</sub>) extended the prepreg tack retention from 2 to 3 days to 6 to 7 days for T-300 fabric prepreg and to 7 to 8 days for Celion 6000 reinforced tape prepreg. The results also show that the prepregs containing the higher alkyl esters in the mixed solvents exhibited more pronounced improvements in tack and drape retention than the methyl ester mixed solvent system. The best overall tack and drape retention was obtained from prepreg containing propyl ester (C<sub>3</sub>) monomers, even in a solvent mixture of 9:1 M/P.

However, this system exhibited excessive resin flow during imidization. The 1-propanol produced as a by-product during imidization, together with 1-propanol present in the solvent mixture causes a significant reduction in the resin melt viscosity during the early stages of the imidization reaction and results in increased resin flow.

Based on the results from the earlier study (ref. 3), the PMR resin systems selected for study in this investigation included the systems containing C<sub>1</sub> and C<sub>2</sub> esters in solvent mixtures of 3:1 M/P, the control resin system C<sub>1</sub>-M, and two resin systems which were not previously studied, C<sub>1</sub>-4:1 M/P and C<sub>2</sub>-5:1 M/P. In the present study, it was found that these two resin systems, containing a reduced level of 1-propanol, provided prepregs with tack retention comparable to those made using a 3:1 M/P solvent mixture (5 to 6 days versus 6 to 7 days for C<sub>1</sub>-3:1 M/P and 10 days for C<sub>2</sub>-5:1 M/P versus 12 days for C<sub>2</sub>-3:1 M/P using T-300 reinforcement).

### Composite Processing Studies

In the earlier study (ref. 3), it was found that the resin modifications employed to improve prepreg tack did not necessitate altering the parameters previously established for compression molding PMR-15 composites. In this investigation, studies were conducted to establish autoclave cure parameters for the

selected resin systems using T-300 fabric reinforced and unidirectionally reinforced Celion 6000 graphite fiber prepreg materials.

A commonly used autoclave cure cycle for state-of-the-art PMR-15 prepreg material is shown in figure 3. During this study, it was found that the improved tack prepreg exhibited excessive resin flow when using the cure cycle shown in figure 3. As discussed earlier, the 1-propanol added to the carrier solvent significantly reduced the melt viscosity of the resin during the early stages of the imidization reaction. Therefore, to minimize resin flow, initial imidization was conducted at a lower heating rate (0.6 °C/min) and a reduced vacuum level (5 cmHg). When a temperature of 137 °C was reached, sufficient resin advancement had occurred to permit the use of a faster heating rate and increased vacuum level (3 °C/min and 60 cmHg, respectively). The recommended cure cycle for autoclave curing improved tack graphite fiber reinforced PMR-15 prepreg is shown in figure 2. Low-void (1.3 vol %) composites were fabricated from each of the prepreg materials by employing this cure cycle.

### Composite Properties

The mechanical properties of autoclave-molded PMR-15/Celion 6000 composites made from the control resin and the selected modified resin systems are shown in table IV. Also shown in the table are the prepreg storage conditions, prepreg volatile content, and the percent fiber volume for each composite. It can be seen that after 5 days exposure at ambient conditions, the C<sub>2</sub> prepreg containing a 3:1 M/P solvent exhibited a volatile content 1.2 percent higher than that of the C<sub>2</sub> prepreg prepared with a 5:1 M/P solvent. The 3 percent difference in fiber volume between the composites prepared by the C<sub>2</sub>-3:1 M/P and C<sub>2</sub>-5:1 M/P prepreg systems can be attributed to the higher concentration of 1-propanol present in the C<sub>2</sub>-3:1 M/P system. Therefore, a 5:1 M/P solvent mixture is recommended for prepared improved tack prepreg with ethyl esters (C<sub>2</sub>). Furthermore, comparison of the fiber content data shows that by employing the modified autoclave cure cycle shown in figure 3, it was possible to control the resin flow of improved tack prepreg having a volatile content of 12.4 percent or less to yield composites having a fiber volume of close to 63 percent. In order to achieve resin flow comparable to state-of-the-art PMR-15 prepreg material, it is recommended that the volatile of improved tack prepreg not exceed 12.4 percent prior to autoclave molding.

A comparison of the composite mechanical properties data of table IV shows that the room temperature and 316 °C flexural and interlaminar shear strengths of composites prepared from the improved tack prepreg, which had been exposed for 5 days, compare very favorably to the properties of the control composite prepared from freshly made prepreg.

Figures 4 and 5 show the retention of 316 °C composite flexural and interlaminar shear strengths, respectively, as a function of isothermal exposure in air at 316 °C for the autoclave-molded Celion 6000 graphite fiber composites.

Figure 4 shows that the 316 °C flexural strength retention of the composites prepared from the improved tack prepreps is equivalent to the flexural strength retention of the composite prepared from the control prepreg. In figure 5 it can be seen that the 316 °C interlaminar shear strength retention of the composites made from the improved tack prepreps is nearly identical to that exhibited by the composite made from the control prepreg.

The mechanical properties of autoclave-molded PMR-15/T-300 graphite fabric reinforced composites are shown in table V. Data are shown for composites prepared from the control resin and the modified resin systems (C<sub>1</sub>-3:1 M/P, C<sub>1</sub>-4:1 M/P, and C<sub>2</sub>-5:1 M/P) which exhibit resin flow comparable to that of the control resin system during autoclave molding. The data show that the room-temperature and short-term 316 °C flexural and interlaminar shear strengths of the composites prepared from the improved tack prepreg are in close agreement with the flexural and interlaminar shear strengths of the composites made from the control system.

### CONCLUSIONS

Based on the results of this investigation, the following conclusions may be drawn:

1. By employing a modified autoclave cure cycle, it is possible to fabricate high-quality, low-void composites from improved tack graphite fiber reinforced PMR-15 prepreg materials.
2. Autoclave-molded composites fabricated from improved tack graphite fiber reinforced PMR-15 prepreg exhibit mechanical properties which are essentially equivalent to the mechanical properties of composites autoclave molded from state-of-the-art graphite fiber reinforced PMR-15 prepreg.

### REFERENCES

1. T. T. Serafini and P. Delvigs, ICCM/2, Proc. of 1978 Conf. on Composite Materials, B. Norton, ed., AIME, New York, 1978, pp. 1320-1329.
2. R. A. Buyny, NASA CR-165432, Oct. 1981.
3. R. D. Vannucci, Proc. of 1982 Nat. Tech. Conf. of Society of Plastics Engineers, Bal Harbour, FL., pp. 131-133.

Table I.-MONOMERS USED FOR PMR-15 POLYIMIDE SYNTHESIS

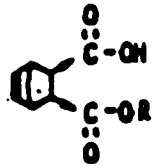

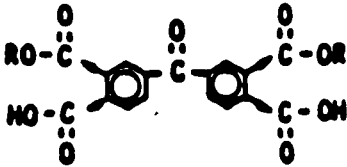
Structure	Name	Abbreviation
	Monoalkyl ester of 5-norbornene-2,3-dicarboxylic acid	NE
	4,4'Methylenedianiline	MDA
 <p>R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub></p>	Dialkyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid	BTDE

TABLE II. - ESTER AND SOLVENT MODIFIED PMR-15 RESIN SYSTEMS<sup>a</sup>

Ester <sup>b</sup>	Solvent <sup>c</sup>	System abbreviation
C <sub>1</sub> (Control)	M	C <sub>1</sub> -M
C <sub>1</sub>	3:1 M/P	C <sub>1</sub> -3:1 M/P
C <sub>2</sub>	E	C <sub>2</sub> -E
C <sub>2</sub>	3:1 M/P	C <sub>2</sub> -3:1 M/P
C <sub>3</sub>	9:1 M/P	C <sub>3</sub> -9:1 M/P
C <sub>3</sub>	3:1 M/P	C <sub>3</sub> -3:1 M/P

<sup>a</sup>Reference 3.

<sup>b</sup>C<sub>1</sub> = methyl, C<sub>2</sub> = ethyl,

C<sub>3</sub> = propyl.

<sup>c</sup>M = methanol, E = ethanol,

P = 1-propanol.

TABLE III. - TACK AND DRAPE  
RETENTION OF MODIFIED  
PMR-15 PREPREG<sup>a</sup>

Prepreg system	Tack limit <sup>b</sup> fabric/tape	Drape limit <sup>b</sup> fabric/tape
C <sub>1</sub> -M	2-3/2-3	2/2
C <sub>1</sub> -3:1 M/P	6-7/7-8	5/6
C <sub>2</sub> -E	3-4/-	2/-
C <sub>2</sub> -3:1 M/P	12/15	7/8
C <sub>3</sub> -9:1 M/P	12/15	12/15
C <sub>3</sub> -3:1 M/P	12/21	12/21

<sup>a</sup>PMR-15/T-300 graphite fabric and  
PMR-15/Celion 6000 graphite fiber tape,  
reference 3.

<sup>b</sup>Days at ambient conditions.

TABLE IV. - MECHANICAL PROPERTIES OF AUTOCLAVE-CURED MODIFIED PMR-15/CELION  
6000 GRAPHITE FIBER COMPOSITES

Prepreg system	Prepreg exposure, days <sup>a</sup>	Prepreg percent volatile content	Composite fiber, vol %	Interlaminar shear strength, MPa		Flexural strength, MPa	
				R.T.	316 °C	R.T.	316 °C
C <sub>1</sub> -M (Control)	1	11.7	62.7	103	44.8	1532	834
C <sub>1</sub> -3:1 M/P	1	13.5	65.0	90	42.7	1632	861
C <sub>1</sub> -3:1 M/P	5	12.4	63.0	100	46.2	1639	841
C <sub>1</sub> -4:1 M/P	5	12.0	63.0	107	41.3	1570	896
C <sub>2</sub> -3:1 M/P	5	13.2	66.0	96	46.1	1612	875
C <sub>2</sub> -5:1 M/P	5	12.0	63.0	106	42.0	1557	875

<sup>a</sup>Days exposed to ambient conditions.

TABLE V. - MECHANICAL PROPERTIES OF AUTOCLAVE-CURED MODIFIED  
PMR-15/T-300 GRAPHITE FABRIC COMPOSITES

Prepreg system	Prepreg exposure, days <sup>a</sup>	Prepreg fiber, vol %	Interlaminar shear strength, MPa		Flexural strength, MPa	
			R.T.	316 °C	R.T.	316 °C
C <sub>1</sub> -M (Control)	3	64.0	50.3	36.5	1337	682
C <sub>1</sub> -3:1 M/P	3	65.5	49.6	35.8	1268	689
C <sub>1</sub> -4:1 M/P	3	64.0	54.1	36.5	1337	709
C <sub>2</sub> -5:1 M/P	3	65.0	54.4	35.8	1280	662

<sup>a</sup>Days at ambient conditions.

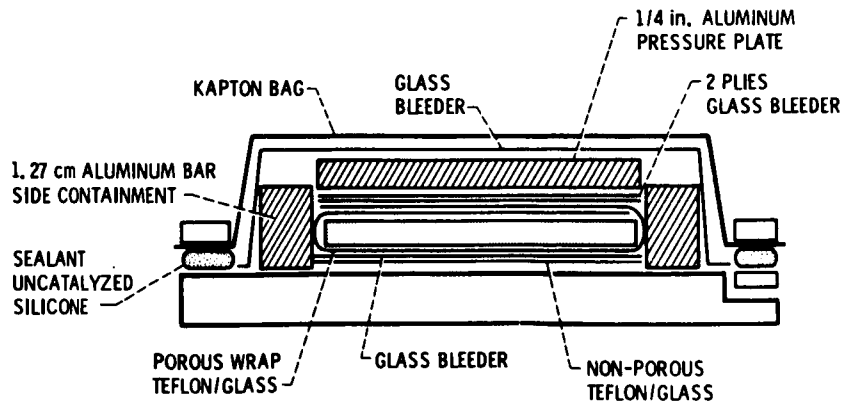


Figure 1. - Vacuum bag layup for unidirectional reinforced PMR-15/Cellon 6000.



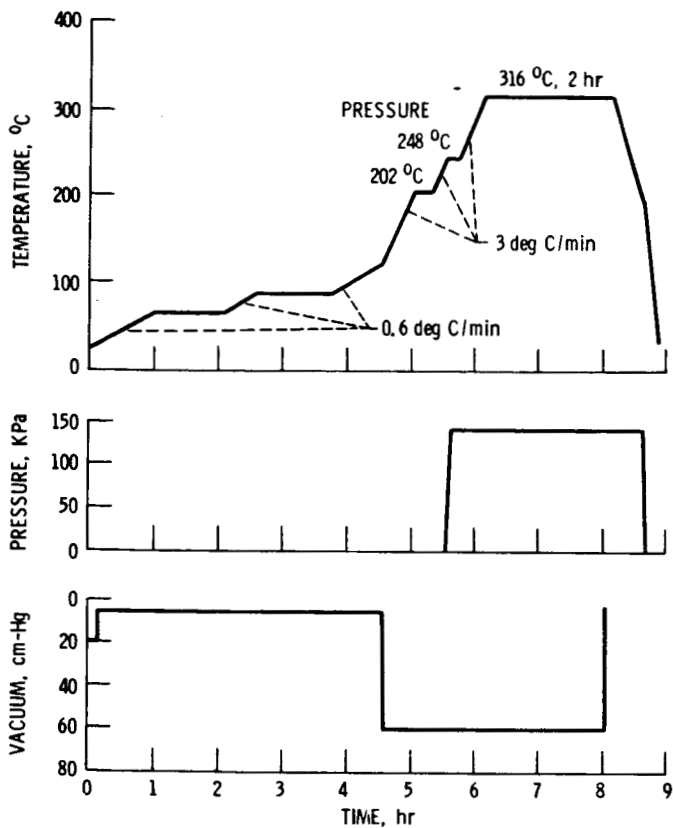


Figure 2. - Autoclave cure cycle for improved tack PMR-15/graphite fiber prepreg.

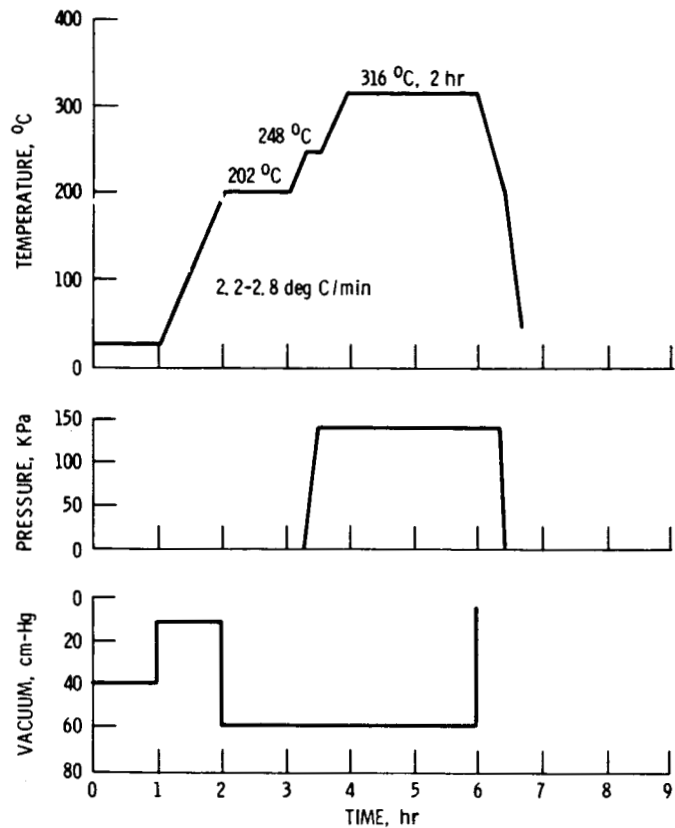


Figure 3. - Typical autoclave cure cycle for PMR-15 materials.

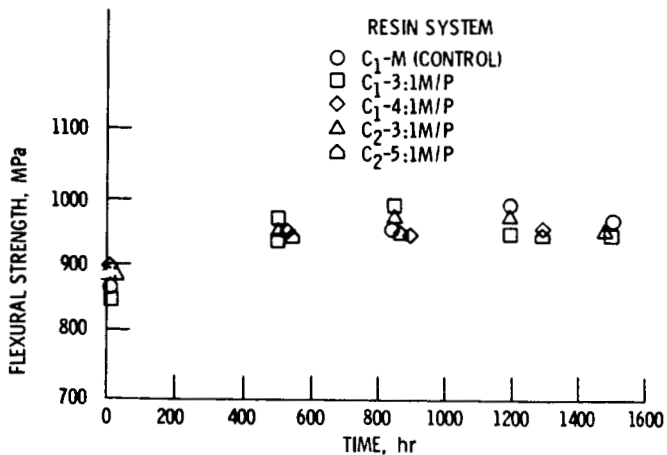


Figure 4. - Flexural strength of autoclave molded modified PMR-15/Celion 6000 graphite fiber composites exposed and tested at 316 °C.

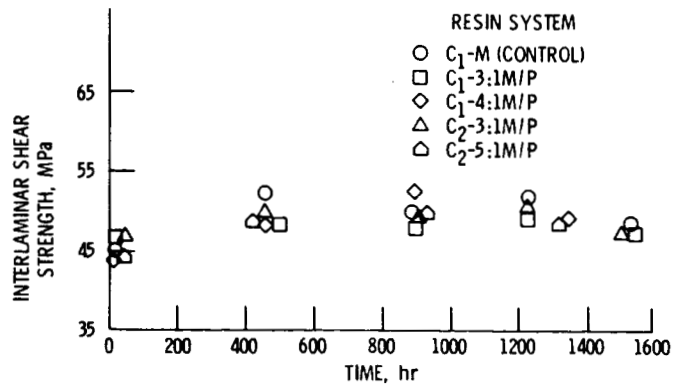


Figure 5. - Interlaminar shear strength of autoclave molded PMR-15/Celion 6000 graphite fiber composites exposed and tested in air at 600 °C.