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PMR-15 Polyimide Modifications for Improved Prepreg Tack

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INTRODUCTION

PMR polyimides were developed at the NASA Lewis Research Center in response to the need for processable, high temperature resistant matrix resins for fiber reinforced composites(1). The advantages and versatility of PMR polyimides have been reviewed (2). At the present time, PMR composite materials are being used or being considered for use in a number of aerospace, aeronautical and commercial applications. Current PMR technology utilizes methanol or ethanol for preparation of PMR impregnating solutions. The volatility of these solvents, which is highly desirable for obtaining void-free composites, limits the tack and drape retention characteristics of prepreg exposed to ambient conditions. The loss of tack and drape can present problems during fabrication of large composite structures which may require prepreg layup times of several days.

Earlier studies aimed at improving the tack and drape retention of PMR materials involved the use of reactive diluents(3) or higher boiling point solvents (4). The use of reactive diluents provided only an additional two days of tack retention. Although the approach of adding a higher boiling point solvent extended tack to about 15 days, significant modification of the established processing procedure was necessary to obtain void-free laminates. Of primary concern in conducting this investigation was the selection of monomer reactants and/or solvents with potential for improving the tack and drape retention of PMR prepreg materials without affecting PMR resin cure chemistry or processability.

The commerically 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). This report describes a study in which higher alkyl ester monomers and mixtures of low boiling alcohol solvents were substituted for the methyl ester monomers and solvent currently used in PMR-15 resin formulation. The purpose of this investigation was to determine the effect of these modifications on the tack and drape retention characteristics of graphite fabric and unidirectional graphite tape prepregs. Composite processability and elevated temperature mechanical properties of composites prepared from the modified resin formulations and unidirectional graphite fibers were also determined.

EXPERIMENTAL PROCEDURE

MATERIALS

The monomer reactants used to prepare the resins used in this study are shown in Table I. The monoalkyl esters were prepared as described in reference 1. The dimethyl and diethyl esters (BTDE) were prepared as 50 and 80 weight percent solutions, respectively, by refluxing a suspension of the dianhydride of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDA) in the corresponding alcohol until all the solids had dissolved and then for an additional two hours. The dipropyl ester of BTDA was prepared as an 80 weight percent solution by heating a stirred suspension of BTDA in 1-propanol to a temperature not exceeding 85° C until all solids had dissolved and then for an additional 2 hours. The IR spectra of all BTDE solutions showed the absence of anhydride bands. The 4,4'-methylenedianiline (MDA) was purchased from a commercial source and used as received.

The monomer stoichiometry for the PMR solutions was 2NE/2.087BTDE/3.087MDA. The solutions were prepared at room temperature by dissolving the monomers in a calculated amount of the carrier solvent to give 50 weight percent solutions.

PREPREG FABRICATION AND TESTING

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 volume percent 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 a 2.54 cm overlap. 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 x 2.54 cm) at its center and observing the deformation of the prepreg under its own weight.

COMPOSITES FABRICATION AND TESTING

All composites were fabricated from prepreg tape made with Celion 6000 graphite fiber tow material. The tapes were cut into 7.62 by 20.3 cm plies and stacked unidirectionally to produce 12 ply composites. The prepreg layups containing propyl ester monomers were staged 30 minutes at 66° C followed by 60 minutes at 204° C. All other prepreg layups were staged 60 minutes at 204° C. The staged layups were then cured by placing them into a cold die, inserting the die into a press at 316° C and applying 3.45 Mpa pressure when the die temperature reached 232° C. After the die temperature reached 316° C, the temperature and pressure were maintained for 90 minutes. After curing the composites were cooled, under full pressure, to 204° C, removed from the die and then given a free standing postcure in air at 316° C for 24 hours.

Composite flexural strength tests were performed in accordance with ASTM D-790 at a fixed span of 5.08 cm on specimens ranging in thickness from 0.203 to 0.216 cm. Interlaminar shear tests were performed 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 strength values reported are averages of three or more tests.

RESULTS AND DISCUSSION

The various NE and BTDE alkyl ester monomers used in the investigation are shown in Table I. Three PMR reactant compositions were studied using methanol, ethanol, or mixtures of methanol and 1-propanol as solvents. In preparing the BTDE dipropyl ester it was found that reaction of BTDA at the reflux temperature of 1-propanol (98° C) resulted in the formation of both dipropyl and tripropyl esters. The presence of triesters in PMR-15 resins has been shown to present processing problems, particularly if their presence is unknown(5). Triester free solutions of the dipropyl ester were prepared by not exceeding a temperature of 85° C during esterification.

Table II lists the various PMR-15 resin systems investigated. The table lists the alkyl ester monomers and solvent used for each resin system and the designated abbreviation for each resin system.

Figure 1 shows the tack retention charcteristics, as a function of exposure to ambient conditions, for prepreg prepared from T-300 graphite fabric and the resin systems listed in Table II. It can be seen that prepreg made from the C_3-3:1 M/P and C_3-9:1 M/P resin systems exhibited the highest degree of tack retention. The figure also shows that the substitution of a 3:1 M/P solvent mixture for methanol in the resin containing methyl esters extended the prepreg tack retention from 2-3 days to 6-7 days. Substitution of a 3:1 M/P solvent for ethanol in the resin containing ethyl esters extended prepreg tack from 3-4 days to greater than 12 days. It should be pointed out that the resins containing ethyl esters were prepared from ethyl esters containing a low concentration of ethanol. Accordingly, the C_2-3:1 M/P resin system contains a small amount (less than 5 percent) of ethanol. However, the ethanol present is not considered to have exerted a significant effect on the tack and drape characteristics of prepreg made with the C_2-3:1 M/P resin system. Therefore, its presence is not noted in the resin system abbreviation scheme.

The lower initial tack values exhibited by prepreg made with the resin systems containing the 3:1 M/P solvent mixture are due to the presence of 1-propanol which exerts a stronger plasticizing effect than methanol and lowers the viscosity of the resins. However, after short-time exposure (~2 days), and continued volatilization of 1-propanol, the resin viscosity increases resulting in increased levels of tack.

Figure 2 shows the variation of tack retention , as a function of exposure to ambient conditions, for prepreg tapes prepared from Celion 6000 unidirectional graphite fiber and all of the resin systems listed in Table I except the C_2-E resin system. It can be seen that, except for the higher overall tack values, the tack retention characteristics of the tape prepregs are similar to those exhibited for the fabric prepreg made from the corresponding resin systems. The higher tack values result from the more uniform surface and unidirectional fiber alignment of the tape prepreg.

Table III summarizes the results of the tack and drape tests performed on the graphite fiber prepreg made from each of the resin systems. It can be seen that all of the prepregs exhibit drape retention comparable to the corresponding tack retention, except for the prepreg made from the C_2-3:1 M/P resin system, which exhibited drape retention times of 7 and 8 days and tack retention times of 12 and 15 days.

From the results shown in Table III, the following conclusions can be made: (1) the use of the resin systems containing a 3:1 or 9:1 methanol/1-propanol solvent mixture provided prepreg with improved tack and drape retention, and (2) substitution of higher alkyl ester monomers for methyl ester monomers provides improved tack and drape retention.

Based on the results of the tack and drape tests, the resin systems employing the mixed carrier solvents (C_1-3:1 M/P, C_2-3:1 M/P, C_3-9:1 M/P and C_3-3:1 M/P) were selected for composite processing studies. Composites were also fabricated with the control resin system. Celion 6000 unidirectional graphite fiber tows were used as the reinforcing material.

Prepreg made with the control, C_1-3:1 M/P and C_2-3:1 M/P resins were imidized using established PMR-15 imidization conditions (60 min at 204° C). The prepreg made from resin systems containing propyl ester monomers (C_3:9:1 M/P and C_3-3:1 M/P) exhibited increased resin flow during imidization under the same conditions. Apparently the 1-propanol by-product produced during imidization, together with the 1-propanol originally present in the carrier solvent, significantly reduces the resin melt-viscosity during the early stages of the imidization reaction and results in increased resin flow. A 30 minute hold at 66° C prior to the established imidization condition (60 min at 204° C) was found to be adequate for controlling resin flow of the C_3-9:1 M/P resin system. However, under the same conditions the C_3-3:1 M/P still exhibited excessive resin flow. Because of the resin flow control problem exhibited by the C_3-3:1 M/P system, the C_1-3:1 M/P, C_2-3:1 M/P, C_3-9:1 M/P and the control resin systems were selected for composite mechanical property studies.

The mechanical properties of as-fabricated PMR-15/Celion graphite fiber composites made with the selected resins systems are listed in Table IV. Shown are room temperature and 316° C interlaminar shear and flexural strengths of composites made from freshly prepared prepreg, from prepreg exposed 15 days at ambient conditions, and from prepreg stored in sealed bags at -18° C for 15 and 30 days. It can be seen that all of the modified resin prepregs, regardless of exposure conditions, yielded composites with mechanical properties which compare favorably to the mechanical properties of the composite made from the control resin system. It should be pointed out that all of the composites listed in Table IV were processed under identical cure conditions except for the slight modification (30 minute hold at 66° C prior to imidization) used for the composites made from the C_3-9:1 M/P resin system. All of the composites exhibited the same degree of resin flow during the final cure and were void-free as determined by ultrasonic C-scan analysis.

Figures 3 and 4 show the retention of 316° C composite flexural and interlaminar shear strengths, respectively, as a function of isothermal exposure in air at 316°C. Figure 3 shows that the 316° C flexural strength retention of each of the composites made from the modified PMR-15 prepreg is identical to the flexural strength retention of the composite made from the control resin system. As can be seen in Figure 4, similiar results were obtained for the retention of 316°C interlaminar shear strength.

The results of this study indicate that the C_1-3:1 M/P, C_2-3:1 M/P and C_3-9:1 M/P resins systems provide improved tack and drape retention without adversely affecting the mechanical properties or processability of compression molded PMR-15 composites. The resin system containing the propyl ester is considered to be the least desirable system because of the possible formation of tripropyl esters during the esterification of BTDA with 1-propanol at reflux temperatures. Therefore, the preferred PMR-15 resin systems are those prepared using either methyl ester or ethyl ester monomers in a 3:1 solvent mixture of methanol and 1-propanol.

CONCLUSIONS

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

1. The substitution of higher alkyl ester monomers for methyl ester monomers in PMR-15 resins as well as the use of a solvent containing 25 percent or 10 percent 1-propanol in methanol provides PMR-15 prepreg with improved tack and drape retention.

2. PMR-15 resins prepared with methyl ester or ethyl ester monomers and a 3:1 methanol/1-propanol solvent mixture provided PMR-15 prepreg with improved tack and drape retention without sacrificing processability or composite mechanical properties.

3. Although the use of propyl esters in PMR-15 resins provide prepreg with excellent tack and drape retention, alternate processing methods are required to minimize resin flow during imidization.

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4. R. A. Buyny, NASA CR-165432, Oct. 1981.

5. P. Delvigs, R.D. Vannucci, and T. T. Serafini; Amer. Chem. Soc. Polymer Reprints, Vol. 22, No. 2, pp. 226-228, Aug. 1981.

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

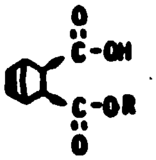
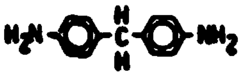
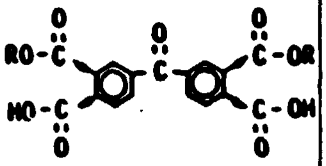
Structure	Name	Abbreviation
	Monoalkyl ester of 5-norbornene-2,3-dicarboxylic acid	NE
	4,4'Methylenedianiline	MDA
 R=CH_3,C_2H_5,C_3H_7	Dialkyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid	BTDE

Table II.-ESTER AND SOLVENT MODIFIED PMR-15 RESIN SYSTEMS

Ester(a)	Solvent(b)	System Abbreviation
C_1(Control)	M	C_1-M
C_1	3:1 M/P	C_1-3:1 M/P
C_2	E	C_2-E
C_2	3:1 M/P	C_2-3:1 M/P
C_3	9:1 M/P	C_3-9:1 M/P
C_3	3:1 M/P	C_3-3:1 M/P

(a)C_1=methyl,C_2=ethyl,C_3=propyl
(b)M=methanol,E=ethanol,P=1-propanol

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Table III.-TACK AND DRAPE RETENTION OF MODIFIED PMR-15 PREPREG(a)

Prepreg System	Tack Limit(b) Fabric/Tape	Drape Limit(b) Fabric/Tape
C_1-M	2-3/2-3	2/2
C_1-3:1 M/P	6-7/7-8	5/6
C_2-E	3-4/-	2/-
C_2-3:1 M/P	12/15	7/8
C_3-9:1 M/P	12/ 15	12/ 15
C_3-3:1 M/P	12/ 21	12/ 21

(a)PMR-15/T-300 graphite fabric and PMR-15/Celion 6000 graphite fiber tape
(b)days at ambient conditions

Table IV.-MECHANICAL PROPERTIES OF COMPOSITES MADE WITH MODIFIED PMR-15 RESINS

Prepreg System	Prepreg Storage, days/Temp.	Composite Fiber Vol.%	Interlaminar Shear Strength,MPa		Flexural Strength,MPa(a)	
			R.T.	316°C	R.T.	316°C
C_1-M(Control)	0	58.6	111	50	1660	943
C_1-3:1 M/P	15/R.T.	58.0	110	51	1640	935
C_2-3:1 M/P	"	58.2	110	50	1688	923
C_2-3:1 M/P	30/-18°C	57.9	103	51	1640	978
C_3-9:1 M/P	0	58.9	106	50	1653	909
C_3-9:1 M/P	15/R.T.	58.6	117	47	1674	916
C_3-9:1 M/P	15/-18°C	59.0	106	53	1588	950

(a)Normalized to 58 volume percent fiber

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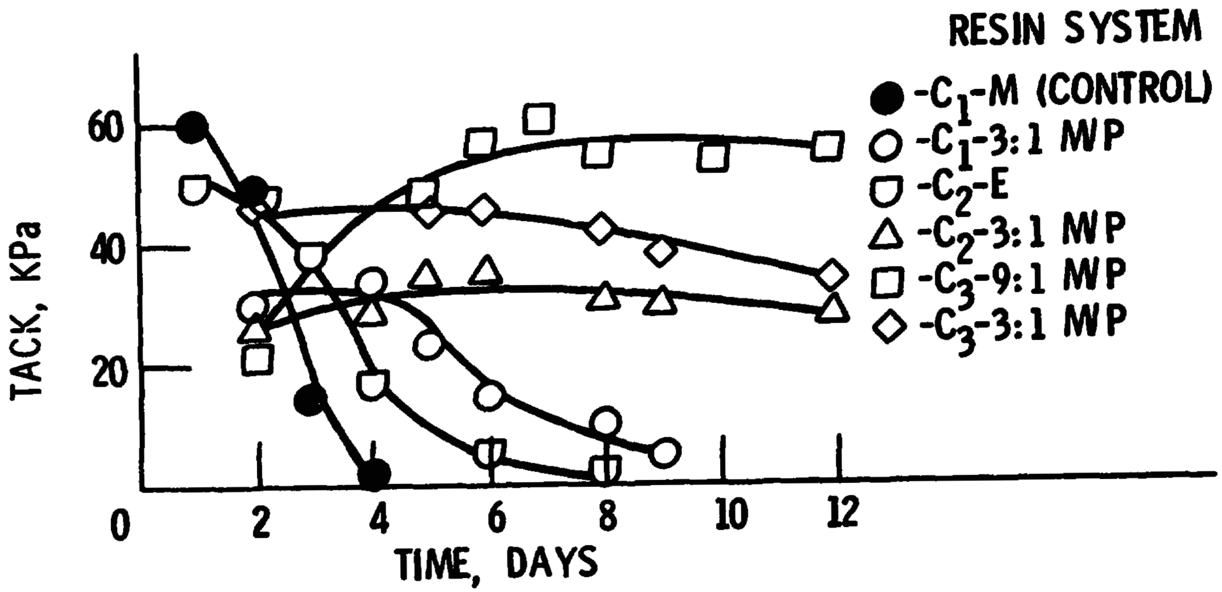

Figure 1. - Tack retention of modified PMR-15/T-300 graphite fabric prepreg after exposure at ambient conditions.

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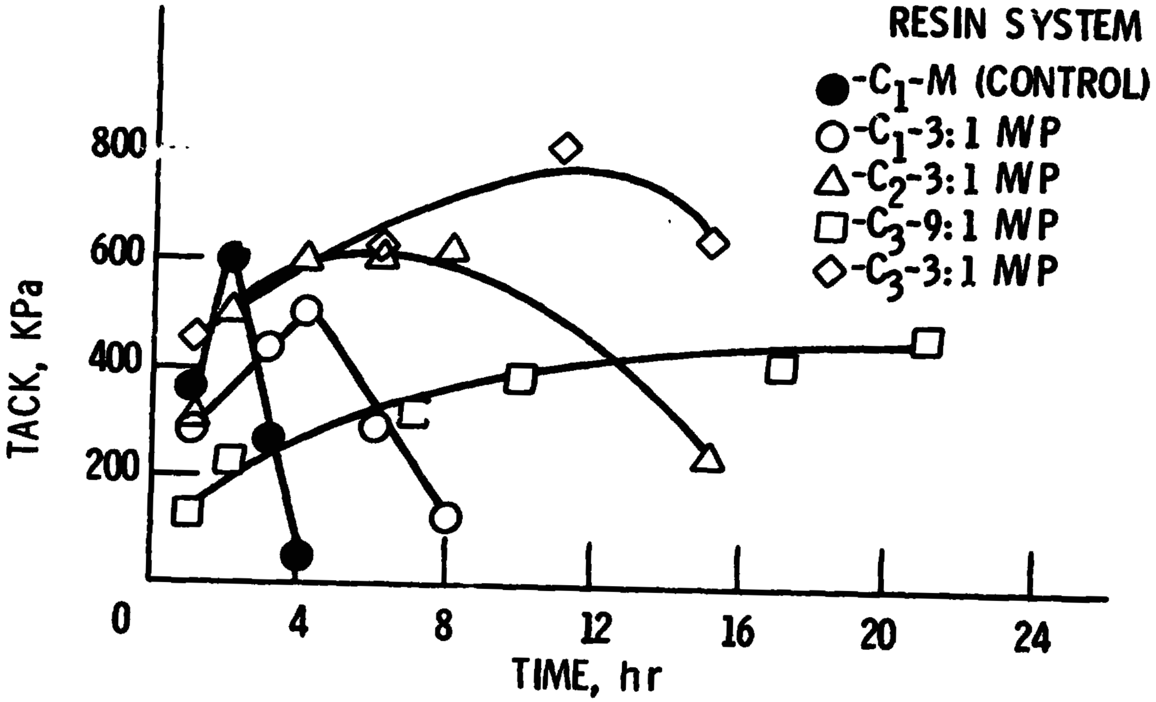

Figure 2. - Tack retention of modified PMR-15 resin/Celion 6000 graphite fiber prepreg after exposure at ambient conditions.

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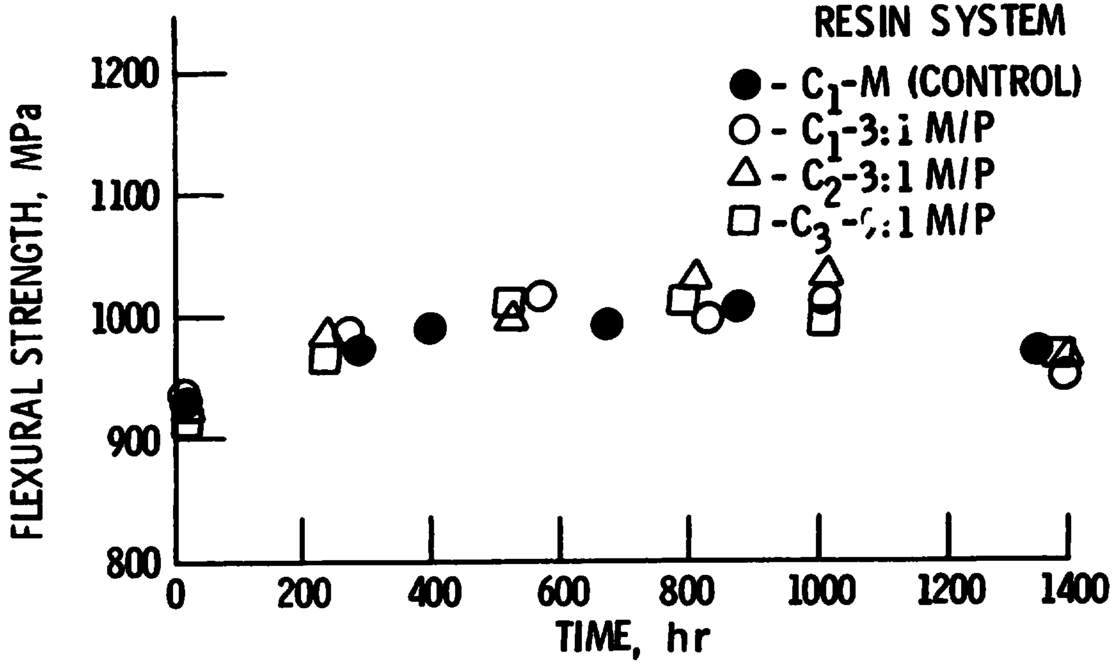

Figure 3. - Flexural strength of modified PMR-15/Celion 6000 graphite fiber composites exposed and tested in air at 316° C.

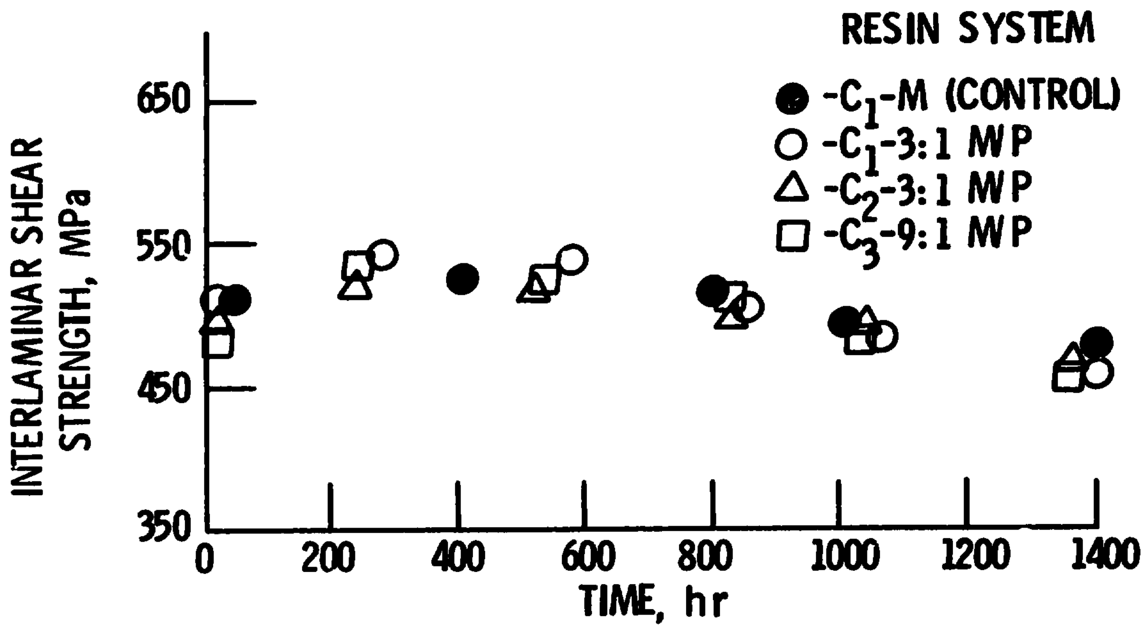

Figure 4. - Interlaminar shear strength of modified PMR-15/Celion 6000 graphite fiber composites exposed and tested in air at 316^0 C.

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