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# **INFLUENCE OF EXCESS DIAMINE ON PROPERTIES OF PMR POLYIMIDE RESINS AND COMPOSITES**

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# INFLUENCE OF EXCESS DIAMINE ON PROPERTIES OF PMR POLYIMIDE RESINS AND COMPOSITES

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## ABSTRACT

PMR polyimide resin is prepared from 4,4'-methylenedianiline (MDA), a diester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) and an ester of 5-norbornene-2,3-dicarboxylic acid (NE) in methanol solution. By varying the stoichiometry of the reactants, the distribution of chain lengths of the imidized material can be altered. Such changes in molecular weight distribution influence the rheological properties, and thus the processability of the resin, as well as the mechanical properties of the composite.

This preliminary study explores the influence of 1-10 percent molar excess MDA on the molecular weight distribution and rheological properties of an imidized PMR system. Molecular weight distribution is characterized by gel permeation chromatography of the imidized molding compound; shear viscosity is related to changes in average molecular weight. The thermo-oxidative stability at 600°F, glass transition temperature, flexural and interlaminar shear properties of PMR polyimide/Celion 6000 graphite fiber composites are compared as a function of the percent excess MDA in the monomer reactant mixture.

## 1. INTRODUCTION

The PMR polyimide resin system developed at NASA Lewis Research Center provides processing versatility for the fabrication of fiber reinforced polyimide components.<sup>(1,2)</sup> A solution of monomer reactants in a low boiling alcohol solvent is used to impregnate the reinforcing fibers. During staging of the impregnated fibers in situ polymerization occurs forming end-capped imide prepolymers. The end-capped prepolymers undergo an addition reaction to form a thermally stable crosslinked structure without the evolution of volatile material.

The chemistry of the PMR system is summarized in Figure 1. The monomethyl ester of 5-norbornene-2,3 dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA) and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) are reacted in a ratio of 2NE: (n + 1) MDA: n BTDE. The stoichiometry of the reactants controls the length of the imide prepolymers. Monofunctional NE groups "end-cap" the prepolymer and serve as cross-linking sites. Variations in stoichiometry have been shown to influence the flow characteristics (processability), and the mechanical properties of PMR polyimide

composite.<sup>(3)</sup>

The PMR-15 system has a formulated molecular weight of 1500 ( $n = 2.087$ ), which optimizes both processability and retention of mechanical properties after long-term exposure to temperatures of 600°F.<sup>(4)</sup> This paper investigates the effects of 1 to 10 mole percent excess MDA on the chemical and physical characteristics of imidized, but not crosslinked PMR-15 molding powder, as characterized by gel permeation chromatography, rheology and Fourier transform infrared spectroscopy. The physical and mechanical properties (glass transition temperature,  $T_g$ , thermo-oxidative stability, flexural strength and modulus and interlaminar shear strength) of composites of these resins with Celion 6000 fiber were also determined.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 MONOMERS

The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were obtained from commercial sources. The dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) was synthesized by refluxing a suspension of 100 gm of BTDA in 140 gm of methanol for 2 hours after the material went into solution (approximately 2 hours and 45 minutes total time) to yield a BTDE solution which was 50 weight percent methanol. The BTDE not used immediately was stored under refrigeration to retard the formation of higher order esters.<sup>(5)</sup> Any refrigerated BTDE was used within 30 days.

### 2.2 MOLDING POWDERS

PMR-15 monomer solutions (50 percent solids) containing a 1 to 10 percent molar excess of MDA were prepared by mixing the monomers NE, MDA and BTDE in anhydrous methanol. The monomeric composition of each solution is given in Table 1. The solutions were heated at 248°F

to reduce the methanol to approximately 25 percent of its original volume, and then heated at 400°F for 1 hour to form the imidized prepolymer. All molding powders were synthesized from a single batch of BTDE and imidized in the same oven at the same time. Molecular weight and rheological characterizations were performed on a single batch of each composition.

### 2.3 COMPOSITE FABRICATION

Unsize Celion 6000 graphite fiber (Celanese lot HTA-7-8112) was wound on a drum at 12 turns per inch. The 50 w/o monomer solutions were applied to the fiber using approximately 65 grams of solution for each 10 ply 3" x 8" laminate (calculated to yield a laminate which is 60 v/o fiber, 40 v/o resin). The prepreg was air dried to reduce the solvent content, removed from the drum, cut into 3" x 8" plies and then stacked (unidirectionally) 10 plies thick in a preforming mold. The stacked prepreg was staged at 400°F for 2 hours. Composites were then molded by placing the staged prepreg into a cold matched metal die which was inserted into a press preheated to 600°F. Contact pressure was applied until the temperature of the die reached 450°F, at which time 500 psi molding pressure was applied. The laminate was held at 600°F and 500 psi for 2 hours. The heater was turned off, and the laminate removed from the press when the press temperature had cooled to 450°F. All composites were then postcured at 600°F for 16 hours.

### 2.4 CHARACTERIZATION OF MOLDING POWDERS

The molecular weight distribution of the imidized molding powders was characterized by gel permeation chromatography (GPC). A small amount (< 1 mg) of sample was dissolved in 200  $\mu$ l of N,N'-dimethylformamide (DMF) and 1800  $\mu$ l of tetrahydrofuran (THF) added. A 20  $\mu$ l sample was injected onto two 100 Å  $\mu$ -spheragel columns and eluted with THF at a flow rate of .5 ml/min. The separation was monitored by UV

detection at 254 nm.

Model compounds of mononadic MDA (N-MDA, the mono-imide of nadic anhydride and 4,4'-methylenedianiline), the bis-nadimide of MDA (N-MDA-N, the  $n = 0$  oligomer) and the 974 molecular weight PMR oligomer (the monodisperse  $n = 1$  oligomer prepared from the reaction of mononadic MDA and BTDE in a ratio of 2N-MDA/1 BTDE) were used as standards for peak identification. Using these standards and making the assumption that the two peaks which eluted just prior to the  $n = 1$  oligomer peak corresponded to the  $n = 3$  and  $n = 2$  oligomers (molecular weights 1942 and 1458, respectively), a linear regression fit of log molecular weight versus retention time was used to construct a calibration curve. The number average ( $\bar{M}_n$ ), weight average ( $\bar{M}_w$ ) molecular weights and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) were determined for each of the imidized prepolymers using Hewlett Packard software package P-2051.

Fourier transform infrared (FTIR) spectra were obtained from KBr pellets of the imidized prepolymers using a commercially available spectrometer. A total of 200 scans were signal averaged for each spectrum.

Rheological behavior of the imidized prepolymers was characterized using a dynamic viscometer. The powder specimens were placed between parallel plates within an environmental chamber. The temperature was raised rapidly to 464°F to melt the sample. Then, the gap was set and the normal force on the plates allowed to return to zero (a total time of 3-4 minutes). The sample was subjected to torsional shear at a constant frequency ( $\omega$ ) of 20 radians/second. The sample chamber was heated at a rate of 7.2°F per minute, the same heating rate employed in compression molding of laminates, over the range 464-590°F. Storage modulus ( $G'$ ), loss modulus ( $G''$ ) and viscosity ( $\eta^*$ ) were determined every 30 seconds over this temperature range, where

$$\eta^* = \frac{G^*}{\omega} \quad \text{poise}$$

$$\text{and } G^* = [(G')^2 + (G'')^2]^{1/2} \text{ dynes/cm}^2.$$

The maximum temperature was set at 590°F and the measurement terminated prior to full cure to facilitate removal of the sample from the instrument.

## 2.5 CHARACTERIZATION OF COMPOSITES

Prior to any testing, all of the composites were examined for defects using an ultrasonic C-scan technique. Only laminates shown to be void-free were used. All test specimens were taken from a single laminate of each composition. Laminates ranged in thickness from 0.072 - 0.080 inches. Flexural specimens, 0.25 inches wide, were tested in three point bending with a fixed span of 2 inches at a center loading rate of 0.05 inch/minute, in accordance with ASTM standard method D790-66. The span to depth ratio for the flexural tests ranged from 25.0 to 27.8. Interlaminar shear strength (ILSS) tests were conducted at a fixed span to depth ratio of 5 to 1 using ASTM standard method D 2344-72. The flexural strength and modulus and ILSS were determined at room temperature and at 600°F for composites that had been subjected to long-term exposure in air at 600°F. The elevated temperature tests were performed in an environmental heating chamber. A forced air convection oven having an air exchange rate of 6.1 in<sup>3</sup>/min was used for the long-term isothermal exposure at 600°F. Flexural specimens were used for the long-term exposures; ILSS specimens for the 600°F tests were machined from the isothermally exposed flexural specimens. Periodic weight measurements were made throughout the exposure time to determine the composite weight loss.

All interlaminar shear results are the average of at least three tests. Flexural tests were conducted in triplicate on the as-fabricated laminates, and in duplicate on isothermally exposed specimens.

The glass transition temperature was determined on composite specimens using a thermomechanical analyzer (TMA) to measure the change in the rate of expansion of the laminate with increasing temperature.

### 3. RESULTS AND DISCUSSION

#### 3.1 RESIN CHARACTERISTICS

Figure 2 shows the molecular weight distribution of the imidized prepolymers containing 0-10 percent molar excess MDA. It can be seen that all of the prepolymers contained small quantities of mononadimide and bisnadimide of MDA materials. It also can be seen that the distribution curves for all of the prepolymers are fairly similar except for the PMR-15 prepolymer which contained a 1 percent molar excess of MDA. Its molecular weight distribution appears to have been slightly narrowed.

The ratio of the weight average molecular weight ( $\bar{M}_w$ ) to the number average weight ( $\bar{M}_n$ ) depends on the breadth of the molecular weight distribution.  $\bar{M}_n$ ,  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  were calculated using an area slice method. The absorbance values at 15 and 36.5 minutes (prior to the elution of the first peak and following the elution of N-MDA) were used to establish a baseline. The area of each "slice" was determined and associated with a molecular weight obtained from the calibration curve. Linearity over the narrow observed range of molecular weights was assumed. No correction was made for differences in extinction coefficients for the various peaks. For this reason, and because the peaks were not completely resolved, the calculated molecular weights must be interpreted as relative, rather than absolute values, and are used here for the purposes of comparing this series of prepolymers.

Since the absorbance did not return to baseline after the 974 molecular weight peak was eluted (Figure 2) calculation of  $\bar{M}_n$  and  $\bar{M}_w$  over all peaks was found to be quite sensitive to choice of baseline,

and weighted toward the lower end of the distribution. The average molecular weights as determined both by integrating over all peaks and by excluding the N-MDA-N and N-MDA peaks from the calculation are listed in Table II. Omission of the two lower molecular peaks does not alter the relative trends observed in the average molecular weight values with varying amounts of molar excess MDA, and at the same time minimizes the problem of defining a baseline. The average molecular weights which omit the N-MDA-N and N-MDA peaks are used in all further discussion.

$\bar{M}_n$  ranged from 1415 to 1616 and  $\bar{M}_w$  varied from 1588 to 1847 with no significant change in polydispersity ( $\bar{M}_w/\bar{M}_n$ ). However, the data presented in Table II indicate that more higher oligomers were formed with addition of excess MDA, with the exception of the 1 mole percent excess stoichiometry. One somewhat speculative explanation for this finding is that a small amount of MDA is consumed in the formation of low molecular weight N-MDA units, resulting in some chains terminated by BTDE groups. (These BTDE end groups would be converted to the anhydride on heating.) As excess MDA is added, the probability of chains terminating in BTDE decreases. Support for this hypothesis for this particular batch of resins come from the small anhydride band observed at  $1840\text{ cm}^{-1}$  in the FTIR spectrum of PMR-15 which diminishes with increasing MDA addition (Figure 3).

Despite the small differences in number average molecular weight among the resins, subtle shifts in distribution were found. Whereas the 1458 molecular weight oligomer ( $n = 2$ ) was the dominant species in PMR-15 and resins with 1 and 3 percent excess MDA, the 1942 molecular weight oligomer ( $n = 3$ ) predominated on addition of 5 and 10 percent excess MDA (Table III). Since the peaks were not completely resolved, overlapping peaks were divided by a perpendicular in integrating the areas. The baseline used for these calculations was determined by extrapolation of the

baseline established prior to elution of the first peak. Therefore, and because no correction to the uv absorbance was made for changes in extinction coefficient with molecular weight, these area percentages must be viewed as relative values.

The observed shifts in molecular weight distribution correlated with changes observed in the  $T_g$  of the laminates. The glass transition temperature has been shown to vary with  $\bar{M}_n$ .<sup>(6)</sup> The variation of  $T_g$  as a function of  $\bar{M}_n$ , as calculated from the GPC analysis of the prepolymer, is shown in Figure 4. It can be seen that the glass transition temperature increased with increased  $\bar{M}_n$ .

Changes in prepolymer molecular weight distribution affect rheological properties, and hence processing characteristics of the matrix resin. Figure 5 shows the variation of storage modulus ( $G'$ ) loss modulus ( $G''$ ) and viscosity ( $\eta^*$ ) over a temperature range of 473-590°F for a PMR-15 (prepolymer) molding powder.  $G'$ ,  $G''$  and  $\eta^*$  showed first a decrease, or thermo-plastic behavior on heating. As the temperature increased, so did the rate of crosslinking of the norbornenyl end groups, and the resin showed a thermosetting behavior. Comparison of the viscosity profiles for the prepolymer series shows that viscosity increased as the molar excess of MDA was increased (Figure 6). In Figure 7 the minima of the viscosity curves are plotted as a function of  $\log \bar{M}_w$  (determined from GPC). The observed increase in viscosity (decrease in flow) corresponds with the increase in molecular weight. It is possible that intermolecular interactions, such as complex formation, would also contribute to the observed viscosity increase.

### 3.2 COMPOSITE PROPERTIES

Despite rheological changes, all of the prepolymer formulations could be compression molded with Celion 6000 graphite fiber into void free laminates using the same fabrication cycle (see Section 2.3). It is not known at this time if the

observed viscosity changes would have an adverse affect on the quality of autoclave processed laminates.

The thermo-oxidative stability of the laminates was evaluated by measuring the weight loss of 2.5 x .25 inch specimens isothermally exposed in air at 600°F for up to 900 hours. Figure 8 illustrates the percentage weight loss of composite samples exposed under those conditions. Composites with 10 percent molar excess MDA showed the largest weight loss. The 1 percent and 3 percent excess MDA laminates also showed more rapid weight loss than did PMR-15, although the curves for PMR-15 and the 5 percent excess MDA containing laminate were found to be nearly identical. Therefore, based on this preliminary study, the thermo-oxidative stability of the resin decreases as the amount of excess MDA is increased. The anomalous behavior of the laminate containing 5 percent excess MDA cannot be explained at this time, but is the subject of further investigation.

The room temperature and 600°F flexural and interlaminar shear strength (ILSS) properties of the as-fabricated laminates are summarized in Table IV. Flexural properties were not normalized for fiber content; however small variation in laminate thicknesses was found, which suggests that the various laminates had similar fiber/resin ratios. Little significant variation of initial room temperature and 600°F mechanical properties was observed within the range of matrix resin compositions investigated.

Larger differences in mechanical properties were seen for composites exposed and tested at 600°F. Flexural strength as a function of exposure time in air at 600°F is shown in Figure 9. The laminate having a 10 percent excess of MDA showed a marked decrease in flexural strength at exposure times greater than 500 hours compared with composites made with lesser amounts of MDA. The other composites all exhibited similar flexural

strengths, although again the behavior of the samples having a matrix containing 5 percent excess of MDA is somewhat anomalous.

The flexural modulus of composites exposed and tested in air at 600°F are shown Figure 10. Again, there was considerable loss in modulus with the 10 percent excess MDA formulation, while the values for the other laminates were within a similar range. However, as noted before, the composite with 5 percent excess MDA did not follow the trend of decreasing modulus with increasing MDA addition observed for the composites made with the matrix resin containing 1, 3 and 10 percent excess MDA.

Figure 11 illustrates the changes in interlaminar shear strength with exposure at elevated temperature. Here once again, the 10 percent excess MDA laminate showed the greatest loss in strength. However, the ILSS remained similar for all the other laminates tested.

#### 4. SUMMARY OF RESULTS

The following results were obtained from a preliminary investigation of the effects of excess MDA on the properties of PMR-15 matrix resin and composites:

(1) Addition of 1-10 mole percent excess MDA to the PMR-15 monomer reactant mixture resulted in minor changes in the molecular weight distribution of the prepolymer.

(2) The viscosity of the molding powder increased with addition of excess MDA.

(3) Using the same fabrication cycle, all of the prepolymer formulations could be compression molded with Celion 6000 graphite fiber into void free composites.

(4) Thermo-oxidative stability at 600°F decreased with addition of 1, 3 and 10 percent molar excess MDA. Addition of 5 percent excess MDA did not result in a similar decrease.

(5) The laminate fabricated with

the 10 mole percent excess MDA formulation exhibited the greatest loss of flexural and interlaminar shear strengths after 900 hours of exposure in air at 600°F.

(6) The subtle variation in molecular weight of the prepolymer appeared to correlate with changes in the glass transition temperature of the composite.

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TABLE I  
PREPOLYMER COMPOSITION

Molar excess MDA, percent	Monomers (moles)		
	NE	MDA	BTDE
0 (PMR-15)	2	3.087	2.087
1	2	3.117	2.087
3	2	3.179	2.087
5	2	3.241	2.087
10	2	3.395	2.087

TABLE II  
MOLECULAR WEIGHT DISTRIBUTION

Molar excess MDA, percent	$\bar{M}_n^*$	$\bar{M}_w^*$	$\bar{M}_w/\bar{M}_n^*$	$\bar{M}_n^{**}$	$\bar{M}_w^{**}$	$\bar{M}_w/\bar{M}_n^{**}$
0 (PMR-15)	1490	1699	1.14	1107	1584	1.43
1	1415	1588	1.12	1052	1470	1.39
3	1540	1763	1.14	1256	1659	1.32
5	1592	1838	1.15	1145	1626	1.42
10	1616	1847	1.14	1339	1761	1.31

\* Calculated from GPC data; N-MDA-N and N-MDA peaks are omitted from the calculation.

\*\* Calculated from GPC data including N-MDA and N-MDA peaks

TABLE III

AREA PERCENT REPRESENTED BY EACH GPC PEAK  
MOLAR EXCESS MDA, PERCENT

M.W.	0	1	3	5	10
>1942	31.92	23.91	40.59	42.01	53.58
1942	21.08	27.56	18.22	22.25	17.82
1458	25.13	28.41	21.83	19.27	15.35
974	21.55	19.09	18.44	15.86	13.12
490	.29	.61	.67	.16	.46
344	-	.37	.21	.44	.21

TABLE IV

MECHANICAL PROPERTIES OF PMR/ CELION 6000 COMPOSITES

Molar excess MDA, percent	Flexural Strength (Ksi)		Flexural Modulus (Msi)		Interlaminar Shear Strength (Ksi)	
	72°F	600°F	72°F	600°F	72°F	600°F
	0 (PMR-15)	243	134	17.00	15.17	15.83
1	230	137	16.27	15.96	16.63	7.61
3	244	142	16.75	16.39	16.81	7.87
5	243	152	17.37	16.70	17.56	7.74
10	234	158	17.32	16.62	16.47	8.04

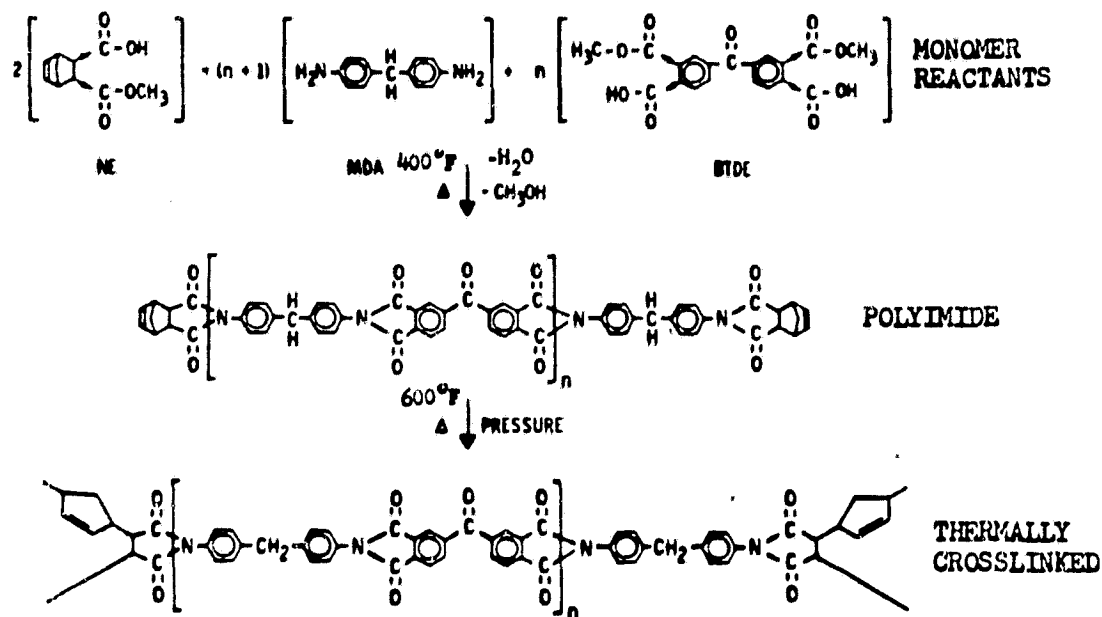


Figure 1. Chemistry of PMR polyimides.

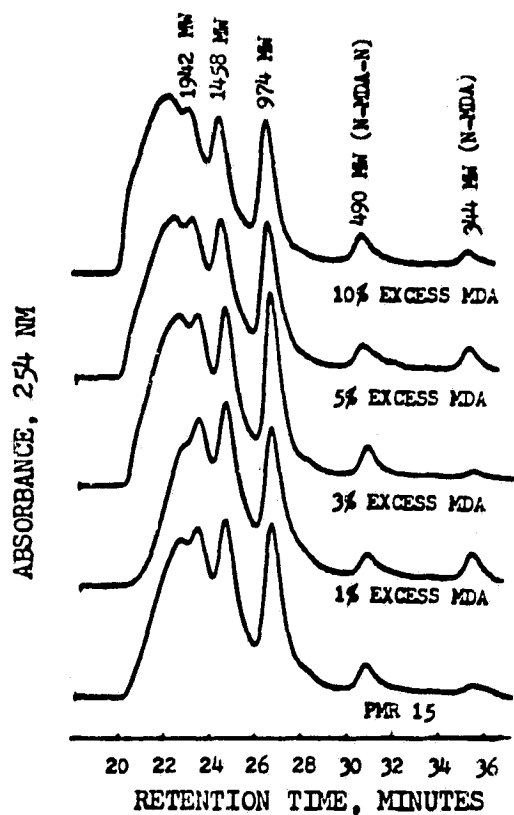


Figure 2. GPC analysis of imidized prepolymers varying in molar excess MDA.

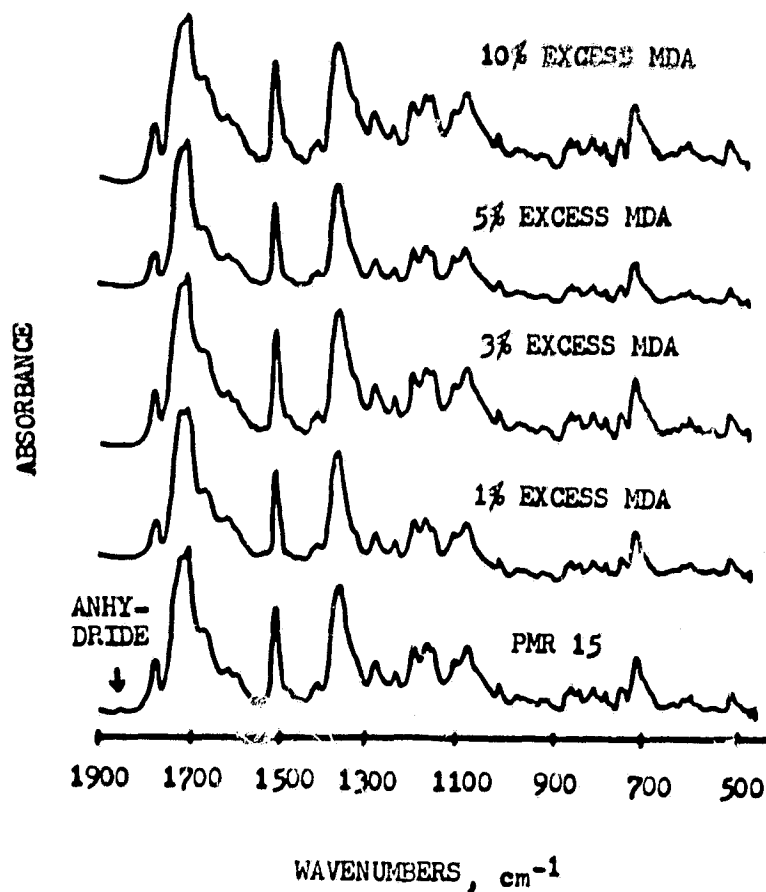


Figure 3. FTIR spectra of imidized prepolymers varying in molar excess MDA.

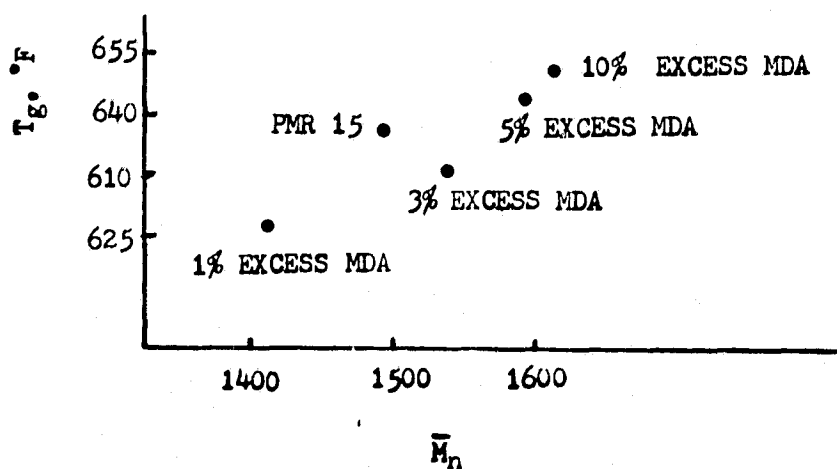


Figure 4. Glass transition temperature of laminates as a function of the number average molecular weight of molding powders of varying molar excess MDA.

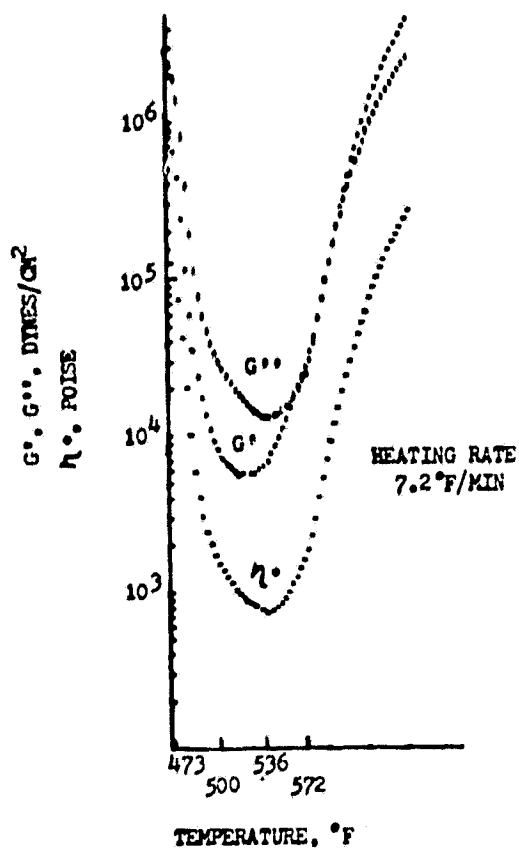


Figure 5. Loss modulus ( $G''$ ), storage modulus ( $G'$ ) and viscosity ( $\eta^*$ ) of PMR-15 molding powder over the temperature range 473-590°F. Temperature held constant at 590°F.

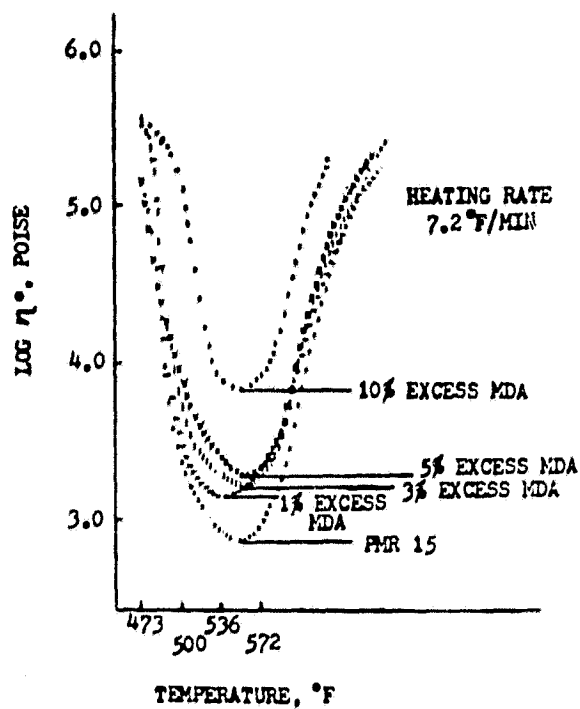


Figure 6. Dynamic viscosity of molding powders over the temperature range 473-590°F. Temperature held constant at 590°F.

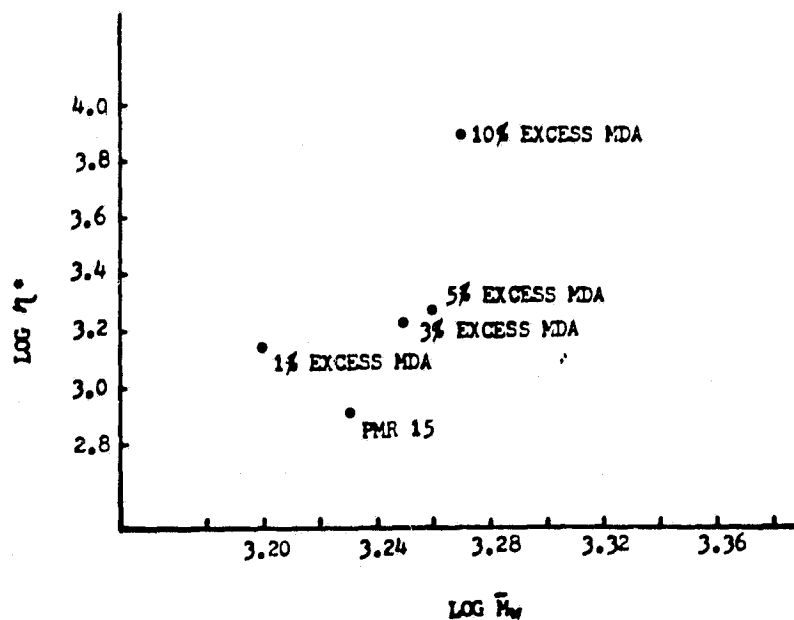


Figure 7. Minimum of  $\log \eta^*$  (from Figure 6) as a function of  $\log \bar{M}_w$  (Table II).

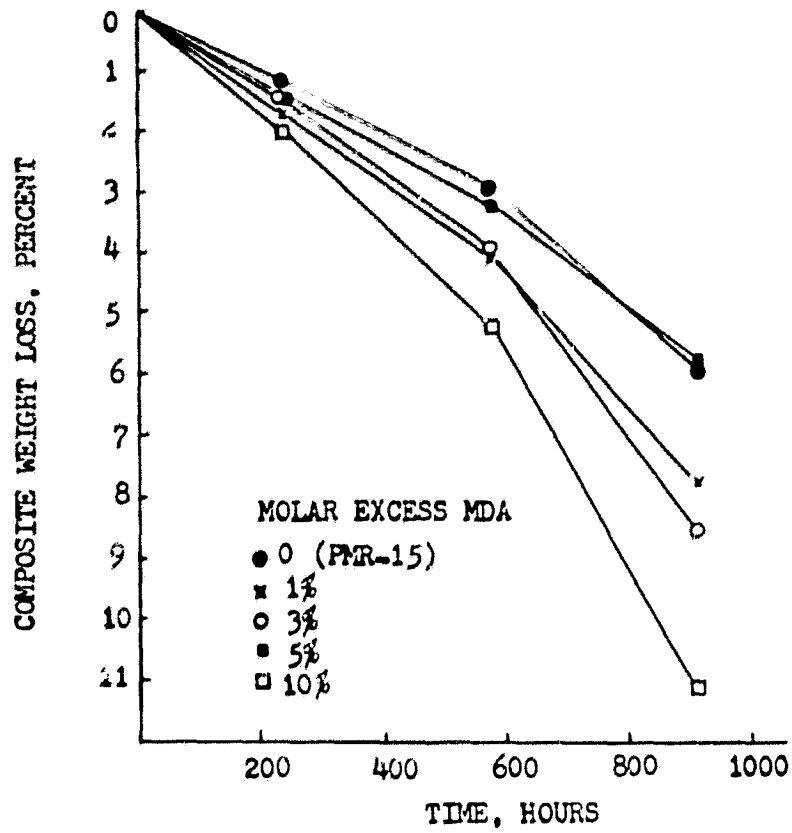


Figure 8. Weight loss of PMR/Celion 6000 composites exposed in air at 600°F as a function of exposure time.

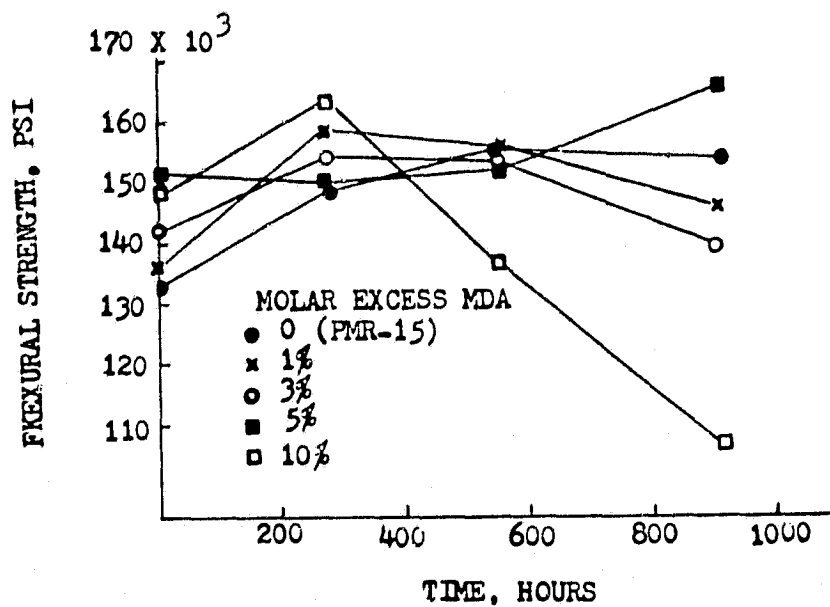


Figure 9. Flexural strength of PMR/Celion 6000 composites exposed and tested in air at 600°F as a function of exposure time.

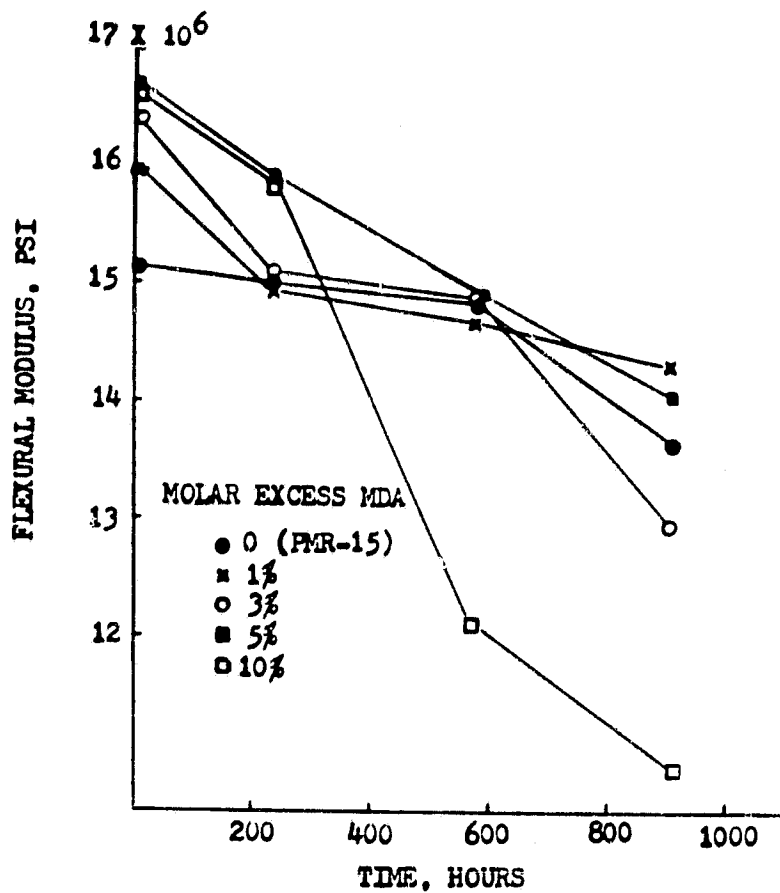


Figure 10. Flexural modulus of PMR/Celion 6000 composites exposed and tested in air at 600°F as a function of exposure time.

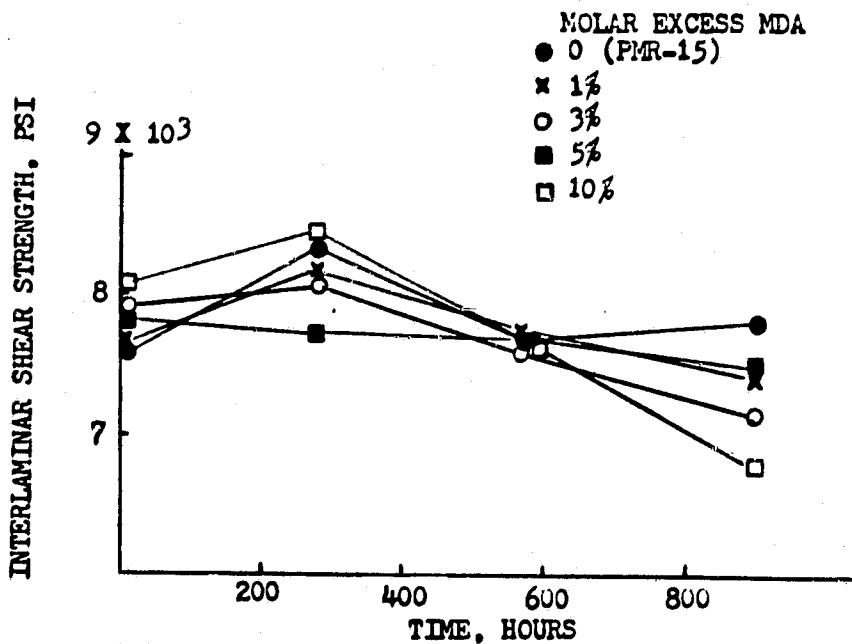


Figure 11. Interlaminar shear strength of PMR/Celion 6000 composites exposed and tested in air at 600°F as a function of exposure time.

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