

# A STUDY ON THERMO-OXIDATIVE STABILITY OF PMR POLYIMIDES

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## ABSTRACT

Two kinds of diamine monomers were used in PMR polyimides instead of the methylenedianiline(MDA). Thermo-oxidative stability and elevated-temperature mechanical properties of graphite fiber reinforced composites were evaluated to be compared with PMR-15 resin.

## 1 INTRODUCTION

The in-situ of polymerization of monomer reactants(PMR) polyimide resins which first developed at the NASA Lewis Research Center<sup>[1]</sup> have been used in aircraft engines for its high temperature mechanical properties and Processability<sup>[2]</sup>. PMR-15 is of the best known PMR polyimide synthesized from three monomers, 4,4' - methylenedianiline(MDA), monomethyl ester of endo-5-norbornene-2,3-dicarboxylic acid(NE), and dimethyl ester of 3,3' - 4,4' - benzo-phenonetetracarboxylic acid(BTDE). PMR-15 has a number of unique performances, including easy processing, good mechanical properties, excellent retention of mechanical properties at elevated temperatures(288 - 316 °C)<sup>[3]</sup>, however, its notable shortcomings are inadequate resin flow for complicated composite structures' fabrication and a suspected carcinogen from the use of MDA<sup>[4]</sup>, so it is severely limited in the applications.

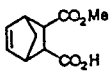
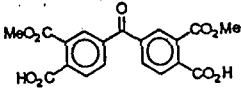
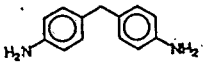
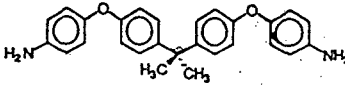
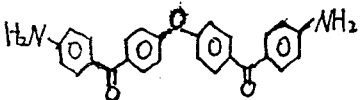
The purpose of this study was to determine the effects of replacing the MDA monomer in PMR-15 with other two aromatic diamine monomers BAPP and BABE on composite high-temperature mechanical properties.

## 2 EXPERIMENTAL

### 2.1 MONOMERS AND PMR SOLUTIONS

The monomers used in this study are shown in table 1. The BTDE was prepared by refluxing a suspension of the corresponding dianhydride in methyl until the BTDE dissolved and then continued heating at the reflux temperature for an additional two hours to result to a 50 wt% methyl solution. The PMR solution was prepared at room temperature by adding the NE and the diamine monomer ( MDA, BAPP, or BABE ) to the BTDE solution to maintain 50 wt% solids. All of the resin formulated molecular weights are 1500.

Table 1- Monomers used for polyimide synthesis

Structure	Name	Abbreviation
	monomethyl ester of endo-5-norbormene-2,3-dicarboxylic acid	NE
	dimethyl ester of 3,3' - 4,4' - benzo-phenonetetracarboxylic acid	BTDE
	4,4' - methylenedianiline	MDA
	2,2' -bis(4-aminophenoxy)propane	BAPP
	4,4' - bis(aminobenzoyl)diphenyl ether	BABE

## 2.2 Composite Fabrication

Prepreg tapes were made by drum winding and impregnating AS4 graphite fiber with PMR solutions calculated to give composites having approximately 60 vol% fiber. The tapes were cut into 26 cm by 18 cm plies and stacked unidirectionally 16 plies thick. The stack was placed into a matched metal die and cured on a hot molding press, figure 1 showed the cure cycle. The postcures were carried out in the air circulating oven at 330 °C for 6 hours.

## 2.3 composite testing

Isothermal exposure of the specimens was performed in air circulating oven. Flexural and interlaminar shear tests were carried out before and after exposure to 260 °C. Flexural strength and modulus tests were performed in accordance with ASTM D-790, interlaminar shear strength tests were performed in accordance with ASTM D-2344. Elevated temperature tests were conducted in an environmental heating chamber following at the test temperature. The value reported mechanical properties are averages of five or more tests at each condition. Composite weight loss measurements were performed after exposure to 260 °C. Prior to specimen preparation, the composites were inspected by ultrasonic C-scan inspection for acceptance. Glass transition temperatures (T<sub>g</sub>) were determined by dynamic mechanical analysis (DMA).

## 3 RESULT AND DISCUSSION

The composite weight loss characteristics after exposure in air at 260 °C are shown in figure 2 (BAPP used in LP-15 and BABE used in LF-15). It is seen that all systems have the similar weight loss for exposure to air at 260 °C beyond 300 hours. After 1000 hours of exposure, LP-15 and LF-15 have higher weight loss (1.1 wt%) than that of PMR-15 (0.9 wt%), and there is still not apparent difference between LP-15, LF-15, and PMR-15. Thus LP-15 and LF-15 have a similar

thermo-oxidative stability to that of PMR-15.

Table 2 showed the Tg and room temperature mechanical properties of LP-15, LF-15, and PMR-15 composites. Both of LP-15 and LF-15 have lower Tg than PMR-15, while LP-15 and LF-15 exhibited the high flexural strength values. The Figure 3, figure 4, and figure 5 showed the interlaminar shear strength, flexural strength and modulus retention characteristics of the composites after exposure and testing in air at 260 °C. The results exhibit that the flexural properties at 260 °C of LF-15 and LP-15 are similar to that of PMR-15. After 1000 hours of exposure to air at 260 °C, all systems have a very high flexural property retention(>90%), Both of LP-15 and LF-15 have higher flexural modulus values than that of PMR-15. LP-15 exhibits lower interlaminar shear strength retention, this can be attributed to its lower Tg, but PMR-15 showed the best interlaminar shear strength retention characteristics.

Table 2. -Tg and mechanical properties at room temperature

	LP-15	LF-15	PMR-15
Tg, °C	318	332	343
flexural strength, MPa	1930	2030	1825
flexural modulus, GPa	134	117	124
interlaminar shear strength, MPa	100	115	99

#### 4 CONCLUSION

1. LP-15 and LF-15 have similar processability, mechanical properties, and thermo-oxidative stability to that of PMR-15 and offer excellent potential as PMR-15 replacements for use at temperatures up to 260 °C.
2. BAPP and BABE have the potentiality of replacing MDA to be used in PMR polyimide composites.

#### REFERENCE

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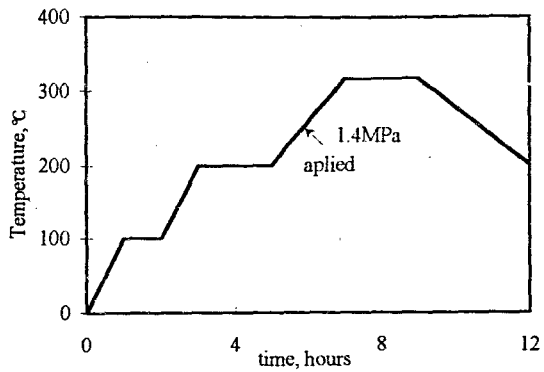


Figure 1. -Cure cycle used for laminate processing

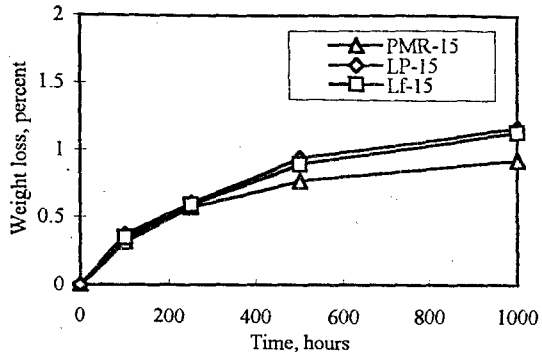


Figure 2.-Weight loss of the composites after exposure to 260°C

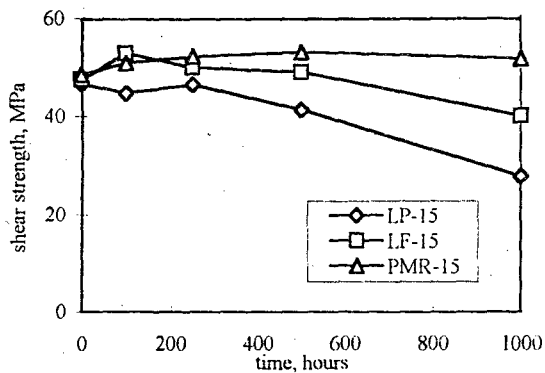


Figure 3.-260°C interlaminar shear strength of the composites after exposure to 260°C

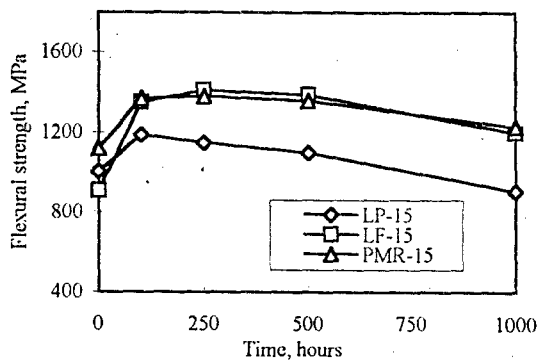


Figure 4.-260°C Flexural strength of the composites after exposure to 260°C

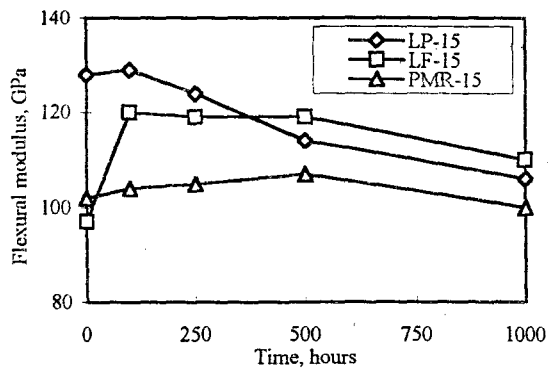


Figure 5.-260°C flexural modulus of the composites after exposure to 260°C