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STATUS REVIEW OF
PMR POLYIMIDES

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STATUS REVIEW OF PMR POLYIMIDES

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INTRODUCTION

Until recently the application of polymer matrix composite materials has been limited to structural components having use-temperature requirements which could be met by epoxy resins. Although high temperature resistant polymer matrix composites provided an opportunity to design structures having nearly a two-fold increase in use-temperature, the chemistry and severe processing requirements of early technology (condensation-type) high temperature polymers made it impractical and difficult to fabricate high quality structural components. In contrast, fiber reinforced epoxy resins can easily be processed using a variety of techniques at relatively low temperatures and pressures.

Studies conducted at the NASA-Lewis Research Center led to the development of a class of polyimides known as PMR (for in situ polymerization of monomer reactants) polyimides (refs. 1-4). In the PMR approach, the reinforcing fibers are impregnated with a solution containing a mixture of monomers dissolved in a low boiling point alkyl alcohol solvent. The monomers are essentially unreactive at room temperature, but react in situ at elevated temperatures to form a thermo-oxidatively stable polyimide matrix. These highly processable addition-type polyimides can be processed by either compression (ref. 5) or autoclave (ref. 6) molding techniques and are now making it possible to realize much of the potential of high temperature polymer matrix composites.

Our research has identified monomer reactant combinations for two PMR polyimides differing in chemical composition. The earliest or "first generation" PMR material is designated PMR-15 and a more recently developed "second generation" material is designated PMR II (ref. 7). Prepreg materials employing PMR-15 are commercially available from the major suppliers of prepreg materials. The development of a modified PMR-15 has been reported (ref. 8).

The purpose of this paper is to review the current status of first and second generation PMR polyimides. The following topics are reviewed: (1) synthesis, (2) processing, and (3) applications.

DISCUSSION

Synthesis and Properties

Condensation type aryl polyimides are generally synthesized by reacting aryl diamines with aromatic dianhydrides, aromatic tetracarboxylic acids or dialkyl esters of aromatic tetracarboxylic acids. The diamine/dianhydride reaction is preferred for preparing polyimide films whereas the latter two reactions are generally preferred for preparing polyimide matrix resins. The solution used to impregnate fiber reinforcement materials is prepared by dissolving the reactants in aprotic high boiling point solvents such as N,N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP). During composites fabrication, volatilization of the solvent and condensation reaction by-products results in high void content composites having inferior mechanical properties and thermo-oxidative stability.

Investigators at the Systems Group of TRW, Inc., working under NASA sponsorship, developed an approach to prepare polyimides by means of an addition reaction (ref. 9). Their approach consisted of synthesizing low molecular weight amide-acid prepolymers whose chain ends were terminated, or end-capped, with norbornenyl groups. Addition polymerization of the norbornenyl groups occurred at elevated temperatures (275-350°C) (527-662°F) without the evolution of volatile materials making it possible to synthesize low void composites. The prepolymer approach, however, did have several shortcomings. These included: (1) the use of DMF, (2) variable solution stability, and (3) less than desirable thermo-oxidative stability at 316°C (600°F).

Another approach was developed in our laboratories for preparing fiber reinforced addition-type polyimides. Our approach eliminated the need for prepolymer synthesis and circumvented most of the shortcomings associated with the use of prepolymers. In our approach a dialkyl ester of an aromatic tetracarboxylic acid, an aromatic diamine and a monoalkyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), are dissolved in a low boiling point alkyl alcohol, such as methanol or ethanol, and the solution is used to impregnate the reinforcing fibers. The number of moles of each monomer reactant is governed by the following ratio:

$$n: (n+1): 2$$

Where n , $(n+1)$ and 2 are the number of moles of the dialkyl ester of the aromatic tetracarboxylic acid, the aromatic diamine and NE, respectively. In situ polymerization of the monomer reactants (PMR) occurs upon heating the impregnated fibers.

In the initial study (ref. 1) which established the feasibility of the PMR approach, it was noted that composites made from monomer solutions containing the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), 4,4'-methylenedianiline (MDA) and NE exhibited a higher level of thermo-oxidative stability than did composites prepared from a monomer solution consisting of the dimethyl ester of pyromellitic acid, MDA and NE. The unexpected observation was confirmed in a subsequent study (ref. 10) and the optimum number of moles of BTDE (n) which provided the best overall balance of processing characteristics and thermo-oxidative stability was found to be 2.087, corresponding to a PMR polyimide having a formulated molecular weight (FMW) of 1500. The FMW is considered to be the average molecular weight of imidized prepolymer that could have been formed if amide-acid prepolymer had been synthesized. The equation for the FMW of a PMR polyimide prepared from n moles of BTDE, $(n+1)$ moles of MDA and 2 moles of NE is:

$$\text{FMW} = n \text{ MW}_{\text{BTDE}} + (n+1) \text{ MW}_{\text{MDA}} + 2 \text{ MW}_{\text{NE}} - 2(n+1) \left[\text{MW}_{\text{H}_2\text{O}} + \text{MW}_{\text{CH}_3\text{OH}} \right]$$

Where MW_{BTDE} , MW_{MDA} , etc., are the molecular weights of the monomer reactants and by-products. It is now common practice to denote the stoichiometry of a PMR resin by dividing the FMW by 100. PMR matrices employing BTDE are referred to as "first generation" materials. The first generation PMR matrix prepared from BTDE, MDA and NE having an FMW of 1500 is widely known as PMR-15. Prepreg materials based on PMR-15 are commercially available from the major prepreg suppliers. The structures of the monomers used in PMR-15 are shown in Table I.

These early studies (refs. 1 & 10) also clearly demonstrated the efficacy and versatility of the PMR approach. By varying the chemical nature of either the dialkyl ester acid or aromatic diamine, or both, and

the monomer reactant stoichiometry, PMR matrices having a broad range of processing characteristics and properties could easily be synthesized. A modified PMR-15, called LARC-160, has been developed by substituting an aromatic polyamine for MDA (ref. 8). Other studies (refs. 11 & 12) have shown that the PMR approach has excellent potential for "tailor making" matrix resins with specific properties. Figure 1 shows the effect of FMW on resin flow for PMR/HTS graphite fiber composites. It can be seen that significantly higher resin flow can be achieved by reducing the FMW. However, as shown in Figure 2, the PMR compositions which exhibit increased resin flow are less thermo-oxidatively stable at 288°C (550°F). The lower resin flow and increased thermo-oxidative stability in going from PMR-10 to PMR-15 clearly show the sensitivity of these properties to imide ring or alicyclic contents. The reduction in resin flow with increased FMW also serves to quantitatively account for the intractable nature of linear high molecular weight condensation polyimides.

Replacement of BTDE with the dimethyl ester of 4,4'-(hexafluoroisopropylidene)-bis(phthalic acid) (HFDE) significantly improved the thermo-oxidative stability of "first generation" PMR resins (ref. 12). However, the initial 316°C (600°F) mechanical properties of HFDE/MDA/NE PMR polyimide composites were considerably lower than the corresponding properties of BTDE/MDA/NE PMR polyimides. Graphite fiber reinforced PMR polyimide composites prepared from a monomer solution consisting of HFDE, p-phenylenediamine and NE at an FMW of 1267 ($n=1.67$) were found to exhibit significantly improved thermo-oxidative stability and retention of mechanical properties at 316°C (600°F) compared to PMR-15 composites (ref. 7). The HFDE-PMR compositions are referred to as "second generation" materials to differentiate them from the "first generation" BTDE-PMR materials. The "second generation" resin consisting of HFDE, PPDA and NE with $n = 1.67$, is known as PMR II. The structure of the monomers used in PMR II are shown in Table II. The interlaminar shear strength of PMR II ($n=1.67$) and PMR-13 (a first generation composition with $n=1.67$) HTS graphite fiber composites are compared in Figure 3. It can be seen that the PMR II composites have at least twice the useful 316°C (600°F) life of the earlier PMR composites. PMR II was compared to PMR-13 because they each contain an identical number of imide rings.

Composites Processing

High pressure (compression) and low pressure (autoclave) molding cycles have been developed for fabrication of PMR composites. Although the thermally induced crosslinking addition cure reaction of the norbornenyl group occurs at temperatures in the range of 275° to 350°C (527° to 662°F), nearly all of the processes developed use a maximum cure temperature of 316°C (600°F). Cure times of 1 to 2 hours followed by a free standing post-cure in air at 316°C (600°F) for 4 to 16 hours, are also normally employed. Compression molding cycles generally employ high rates of heating (5 to 10°C/min) and pressures in the range of 3.45×10^6 to 6.9×10^6 N/m² (500 to 1000 psi). Vacuum bag autoclave processes at low heating rates (2 to 4°C/min) and pressures of 1.38×10^6 N/m² (200 psi) or less have been successfully used to fabricate void-free composites. The successful application of autoclave processing methodology to PMR polyimides results from the presence of a thermal transition, termed "melt-flow", which occurs over a fairly broad temperature range (ref. 6). The lower limit of the melt-flow temperature range depends on a number of factors including the chemical nature and stoichiometry of the monomer reactant mixture, and the prior thermal history of the PMR prepreg. Differential scanning calorimetry studies have shown the presence of four thermal transitions which occur during the overall cure of a PMR polyimide (ref. 13). The first, second and third transitions are endothermic and are related to the following: (1) melting of the monomer reactant mixture below 100°C (212°F), (2) in situ reaction of the monomers at 140°C (284°F), and (3) melting of the norbornenyl terminated prepolymers

in the range of 175° to 250°C (347° to 482°F) referred to as the melt-flow temperature range. The fourth transition, centered near 340°C (644°F) is exothermic and is related to the addition crosslinking reaction. To a large extent the excellent processing characteristics of PMR polyimides can be attributed to the presence of these widely separated and chemically distinct thermal transitions.

Applications

Because of their excellent processing characteristics and commercial availability, PMR-15 polyimide materials have been or are being used in a number of diverse structural components. Some of these components are listed in Table III and a brief description of several is presented. The QCSEE (for Quiet Clean Short Haul Experimental Engine) inner cowl is for an experimental turbofan engine developed for NASA-Lewis by General Electric (ref. 14). The cowl has a maximum diameter of about 90 cm. and is currently undergoing ground-engine tests. The compressor blade skins are for spar-shell blades having a 30 cm. chord and a 150 cm. span. The oil tank bracket was fabricated by TRW, Inc., using a chopped graphite fiber molding compound. The shuttle orbiter aft body flap currently being developed by Boeing is approximately 2 m. wide by 6.5 m. long.

CONCLUDING REMARKS

The in situ polymerization of monomer reactants (PMR) approach is a powerful method for fabricating high performance polymer matrix composites. The PMR approach offers a number of significant advantages to fabricators and users of polyimide/fiber composites. Foremost among these are superior high temperature properties and processing versatility. Because of their excellent processability, high performance and commercial availability, PMR polyimides are becoming accepted as engineering materials for fabrication of high temperature resin/fiber structural components.

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TABLE I
MONOMERS USED FOR PMR 15 POLYIMIDE

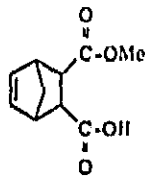
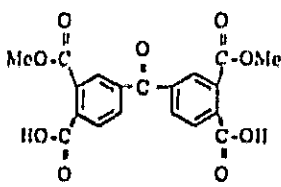
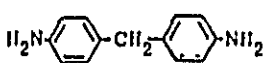
STRUCTURE	NAME	ABBREVIATION
	MONOMETHYL ESTER OF 5-NORBORNENE-2,3-DICARBOXYLIC ACID	NE
	DIMETHYL ESTER OF 3,3',4,4'-BENZOPHENONETETRACARBOXYLIC ACID	BTDE
	4,4'-METHYLENEDIANILINE	MDA

TABLE II
MONOMERS USED FOR SECOND GENERATION PMR POLYIMIDES

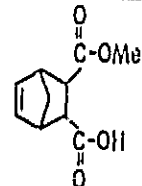
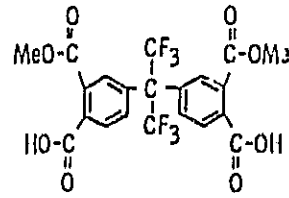
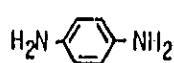
STRUCTURE	NAME	ABBREVIATION
	MONOMETHYL ESTER OF 5-NORBORNENE-2,3-DICARBOXYLIC ACID	NE
	DIMETHYL ESTER OF 4,4'-(HEXAFLUOROISOPROPYLIDENE) - BIS(PHTHALIC ACID)	HFDE
	p-PHENYLENEDIAMINE	PPDA

TABLE III.- APPLICATIONS OF PMR-15 POLYIMIDES

COMPONENT	AGENCY	CONTRACTOR
QCSEE INNER COWL	NASA-LEWIS	GENERAL ELECTRIC
SUPERSONIC WIND TUNNEL, COMPRESSOR BLADE SKINS	AIR-FORCE	HAMILTON-STANDARD
OIL TANK BRACKET FOR F100 ENGINE	NAVY	PRATT & WHITNEY/TRW
SHUTTLE ORBITER AFT BODY FLAP	NASA-LANGLEY	BOEING
AUGMENTOR DUCT OF F100 ENGINE	AIR FORCE	COMPOSITES HORIZONS
FAN BLADES FOR AN ULTRA-HIGH SPEED AXIAL FLOW FAN STAGE	NASA-LEWIS	PRATT & WHITNEY/TRW

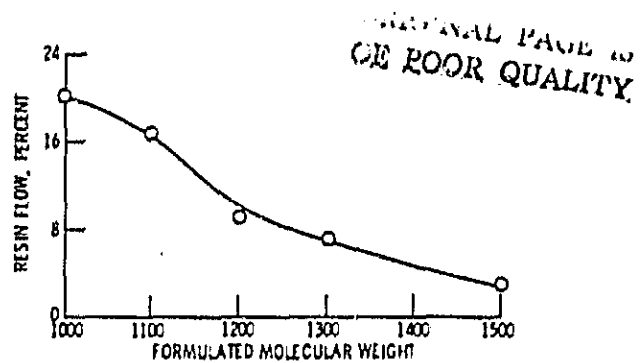


Figure 1 - Percent resin flow for PMR PI/HTS graphite fiber composites

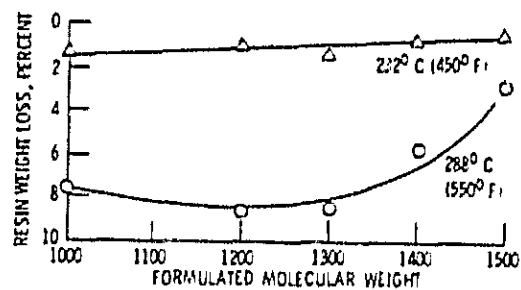


Figure 2 - Percent resin weight loss for PMR PI/HTS graphite fiber composites after 600-hour exposure in air at 232°C (450°F) and 288°C (550°F)

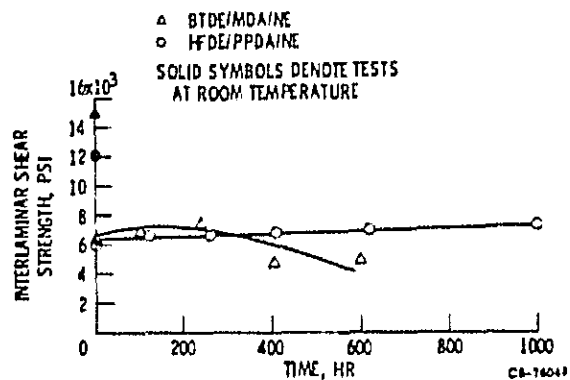


Figure 3 - Interlaminar shear strength of PMR polyimide (n = 1.67) HTS graphite fiber composites exposed and tested at 600°F.