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HIGH-TEMPERATURE POLYMER MATRIX COMPOSITES

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An increasing emphasis on high-performance aircraft and high thrust-to-weight systems has driven the need to develop and use new, lightweight, high-specific-strength materials in aeropropulsion. These newer materials (in particular, composites) must not only offer a weight savings over more conventional materials, but should also be amenable to fabrication into complex shapes and designs, be resistant to the threats of their use environment (thermal and thermal oxidative degradation, corrosion, etc.), have good mechanical properties, and be cost effective.

Current state-of-the-art polymer matrix composites will withstand extended use at temperatures as high as 600 to 650 °F in oxidizing environments. While this may limit their application as aeropropulsion materials, polymer matrix composites can be shaped or molded easily during processing, are corrosion resistant, and can be chemically modified to provide a variety of specific properties, for example, increased toughness, and increased electrical or thermal conductivity (fig. 1). Where appropriate, the use of polymer matrix composites in aeropropulsion and other material applications can offer savings not only in weight, but in production costs as well.

The first polymer matrix composites to find use in aircraft engines were fiberglass/epoxy systems (fig. 2). The earliest uses of polymer matrix composites were in noncritical applications, and were also severely limited by the upper use temperatures of epoxies (250 to 300 °F). Since that time, further research has led to polymer matrix composites with higher and higher use temperatures (e.g., 600 °F for graphite/polyimides). In addition, time has seen the acceptance of these materials move from noncritical to critical structural applications. Current research in the Polymers Branch at the NASA Lewis Research Center is directed at advanced polymers and polymer matrix composites for extended use at 700 °F and beyond.

A major concern in the processing of polymer matrix composites is the production of voids. These voids can arise from a number of sources: the evolution of volatile byproducts during processing, contaminants, degradation, or poor resin flow. Regardless of their origin, voids are not only potential sources for mechanical failure but can also lead to enhanced thermal oxidative degradation in the composite. Therefore, one of the major goals of polymer matrix composite processing is the minimization of void content. One approach to this (fig. 3) involves a two-step cure procedure. Generally, the first step (condensation reaction) of this procedure involves the formation of a low-molecular-weight prepolymer. This first step also produces some quantity of volatile byproducts which escape during this step. The prepolymer formed in this step is endcapped with a group which undergoes a cross-linking reaction at a higher temperature (addition reaction) to form a more thermally

stable polymer network. Unlike the first step, the cross-linking addition reaction proceeds with no formation of byproducts. The result is a highly processable, void-free composite.

In the early 1970's researchers at the NASA Lewis Research Center developed an addition-curing polyimide resin system known as PMR (polymerization of monomer reactants) polyimides (ref. 1). These polyimides (in particular, PMR-15) afford exceptional thermal oxidative stability coupled with good processability by way of a number of conventional techniques. The useful lifetimes of PMR-15 in air (60 psia) are 10 000 hr at 550 °F and 1500 hr at 600 °F (fig. 4).

PMR-15 represents the state of the art in 550 °F matrix resins and has found a wide range of use in both aeropropulsion and nonpropulsion applications. A study prepared by General Electric (ref. 2) under contract to the Navy concluded that the inclusion of graphite/PMR-15 composites in a number of military aircraft engines, such as the F-404, F-110, and F-101, could result in considerable savings in weight and manufacturing costs (fig. 5). As a result of this study and a joint Navy-NASA Lewis funded program, General Electric is currently producing a graphite/PMR-15 duct for their F-404 engine (fig. 6). Originally made out of titanium, this duct was manufactured by forming and machining titanium plates followed by chem-milling to reduce the final weight. The graphite/PMR-15 replacement duct, on the other hand, is autoclave molded in two pieces. In initial tests, the graphite/PMR-15 replacement duct successfully completed over 1000 engine test cycles for a total engine exposure time of 700 hr. Replacement of the original titanium duct by the graphite/PMR-15 duct has resulted in a total weight savings of 7 pounds per engine, as well as in a substantial reduction both in production costs and in the use of titanium.

Offering the combination of good processability and thermal/oxidative stability, PMR-15 is a recognized leader in high-temperature polymer matrix resins. It is one of the most widely used resins for 550 °F applications and is available from a number of suppliers (fig. 7).

Since the development of PMR polyimides, the Polymers Branch at NASA Lewis has responded to industry needs for improvements in these resins, for understanding the mechanisms for their thermal/oxidative degradation (ref. 3), and for developing quality control procedures (ref. 4). (See fig. 8.) For example, modification of the original PMR-15 formulation has produced a toughened polyimide, designated PMR-T (ref. 5), with an increase in failure shear strain and failure impact energy (fig. 9).

One concern that has arisen with graphite/PMR-15 and other polymer matrix composites is that they experience some microcracking during thermal cycling, which can affect mechanical properties. The NASA Lewis Polymers Branch has approached this problem from two angles - one a chemical solution, the other an engineering solution. The use of PMR-T in place of PMR-15 resulted in a 50-percent reduction in the composite transply crack density after 1000 thermal cycles (0 to 450 °F). Use of a random fiber mat finish on a graphite/PMR-15 composite virtually eliminated microcracking during the same thermal cycling test (fig. 10).

A major thrust of the Polymers Branch at Lewis has been in developing PMR polyimides with improved thermal oxidative stability over PMR-15. One such

improvement is PMR-II (ref. 6), a 1977 I-R 100 Award winner. Increased thermal oxidative stability was achieved in this system by substituting more thermally stable monomers into the original PMR-15 formulation. The result is a lower weight loss and better retention of mechanical properties at 600 °F in air than PMR-15 (fig. 11). A higher molecular weight formulation of PMR-II, PMR-II-700, shows promise as a 700 °F resin candidate (ref. 7). This resin experiences only a slight loss of mechanical properties after 200 hr in air (60 psia) at 700 °F and has a weight loss roughly a third of that of PMR-15 under these conditions (fig. 12).

Mechanistic studies have revealed that the end cap is responsible for much of the thermal oxidative instability of PMR polyimides at high temperatures (above 600 °F). The polyimide PMR-II-700 represents one approach to counteracting the deleterious effects of these end caps. By increasing the formulated molecular weight of the polymer, such as is done in PMR-II-700, the overall weight percent of endcap is reduced. The result is improved thermal oxidative stability with some sacrifice in processability (higher molecular weight polymers do not flow as well as their lower molecular weight analogs).

However, it is clear that to achieve higher and higher use temperatures in polymer matrix composites, alternatives to PMR polyimides must be developed. These alternatives may be anything from simply changing to a more thermal, oxidatively stable end cap to developing entirely new polymer systems. A recent effort in the Polymers Branch has been focused on finding new addition-curing polymers which offer improved thermal oxidative stability over PMR polyimides, while at the same time affording good processability. The polyimide MARVIMIDE (ref. 8) is one product of this effort (fig. 13). This linear ladder polyimide combines thermoplastic processing behavior with high softening temperatures (glass transition temperatures (T_g 's) as high as 790 °F) and good thermal oxidative stability. Figure 14 shows a comparison of the short-term weight loss (obtained by thermal gravimetric analysis (TGA)) of samples of MARVIMIDE and PMR-15. The MARVIMIDE has a (131 °F, 55 °C) higher onset of decomposition than the PMR-15. More recently prepared formulations of MARVIMIDE exhibit onsets of decomposition approaching 1150 °F (620 °C). Graphite/MARVIMIDE composites are currently being prepared, and their long-term thermal oxidative behavior is under investigation.

Polymers research at the NASA Lewis Research Center has produced high-temperature, easily processable resin systems, such as PMR-15. In addition, the Polymers Branch has investigated ways to improve the mechanical properties of polymers and the microcracking resistance of polymer matrix composites in response to industry need for new and improved aeropropulsion materials. Current and future research in the Polymers Branch is aimed at advancing the upper use temperature of polymer matrix composites to 700 °F and beyond by developing new resins, by examining the use of fiber reinforcements other than graphite, and by developing coatings for polymer matrix composites to increase their oxidation resistance.

REFERENCES

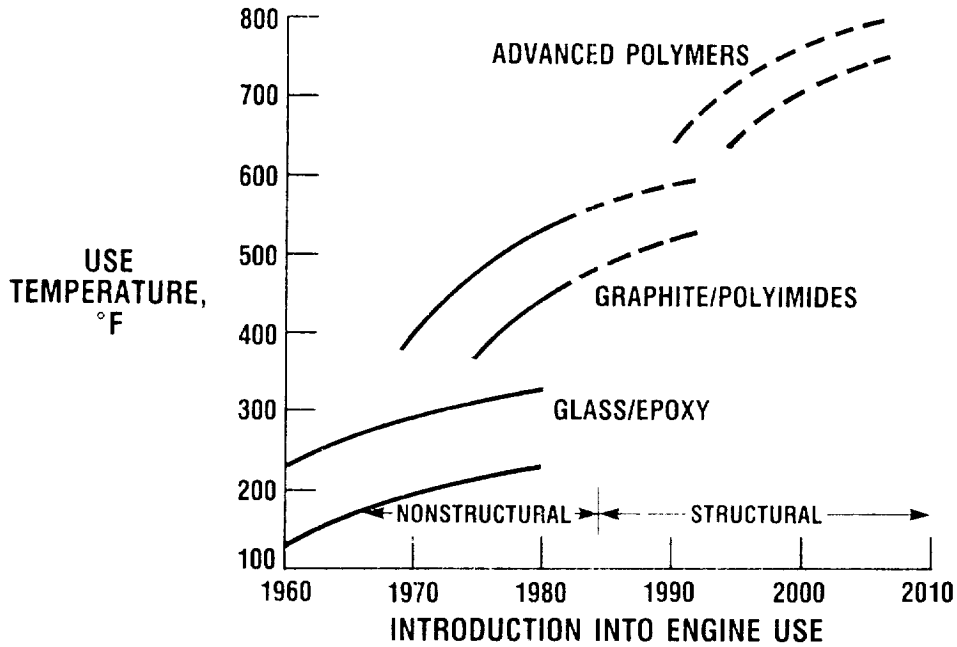
1. Serafini, T.T.; Delvigs, P.; and Lightsey, G.R.: Thermally Stable Polyimides From Solutions of Monomeric Reactants. *J. Appl. Polym. Sci.*, vol. 16, No. 4, Apr. 1972, pp. 905-915.

2. Stotler, C.L.: Development Program for a Graphite/PMR-15 Polyimide Duct for the F404 Engine. The 1980's - Payoff Decade for Advanced Materials, SAMPE, 1980, pp. 176-187.
3. Alston, W.B.: Structure-to-Property Relationships in Addition Cured Polymers. I. Thermooxidative Stability of Norbornenyl-Cured Polyimide Resins. Polym. Prepr., vol. 27, no. 2, Sept. 1986, pp. 410-411.
4. Roberts, G.E.; and Lauver, R.W.: Quantitative Analysis of PMR-15 Polyimide Resin by HPLC. J. Appl. Polym. Sci., vol. 33, no. 8, June 1987, pp. 2893-2913.
5. Vannucci, R.D.; and Bowles, K.J.: Graphite/PMR Polyimide Composites With Improved Toughness. 17th National SAMPE Technical Conference, SAMPE, 1985, pp. 352-363. (NASA TM-87081).
6. Serafini, T.T.; Vannucci, R.D.; and Alston, W.B.: Second Generation PMR Polyimides. NASA TM X-71894, 1976.
7. Vannucci, R.D.: PMR Polyimide Compositions for Improved Performance at 371 °C. Advanced Materials Technology '87, R. Carson et al., eds., SAMPE, 1987, pp. 602-612. (NASA TM-88942).
8. Meador, M.A.B.: Addition Polymers From 1,4,5,8-Tetrahydro-1,4,5,8-diepoxyanthracene and Bis-dienes: Processable Resins for High Temperature Applications. Polym. Prepr., vol. 28, no.2, Aug. 1987, pp. 375-376. (NASA TM-89838).

- CAN BE SHAPED OR FORMED EASILY
- LIGHTWEIGHT
- CORROSION RESISTANT
- CAN BE TAILORED TO SPECIFIC NEEDS

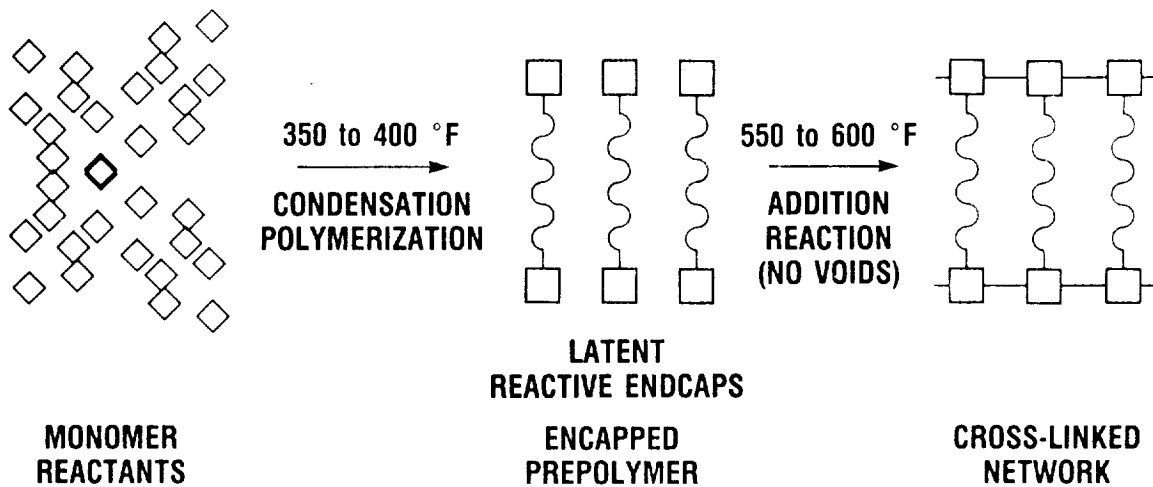
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Figure 1. - Properties of polymer matrix composites.



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Figure 2. - Trends for polymer composites in engines.



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Figure 3. - Reaction scheme for addition polyimides.

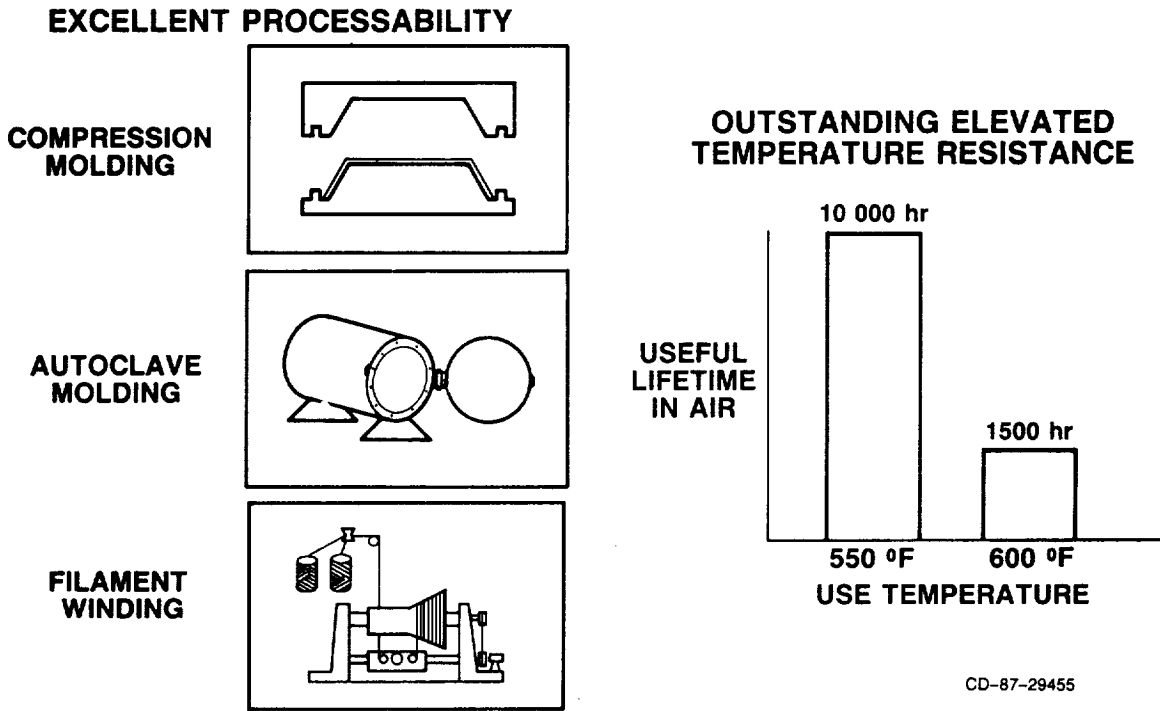


Figure 4. - Lewis-developed PMR-15 polyimide technology.

NAVY MANUFACTURING TECHNOLOGY

F404 Composite Engine Duct Fabrication

Established Mini-Process for the Production of Composite Engine Parts

SAVINGS

- 6 Pounds Fuel
- \$9000 Expense
- 220 Pounds Titanium

APPLICATION

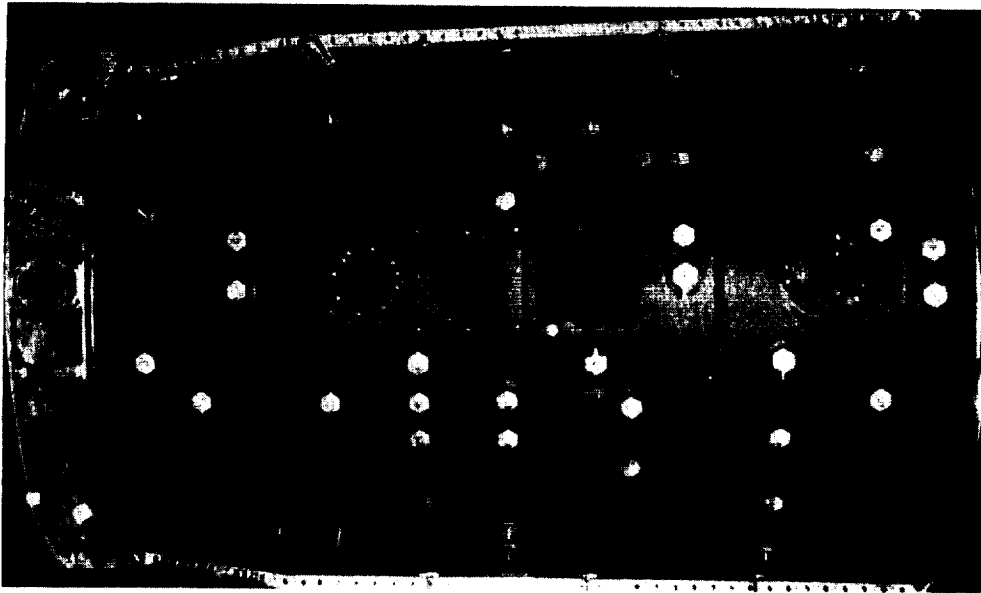
All Military Low By Pass Turbofans

Figure 5. - Navy manufacturing technology.

**WEIGHT
SAVINGS**

7 POUNDS/ENGINE

PRODUCTION QUALITY DUCT



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Figure 6. - Graphite/PMR-15 titanium replacement F-404 duct (Navy/NASA Lewis/GE joint development).

- **PMR RESINS DEVELOPED IN RESPONSE TO NEED FOR A *PROCESSABLE*, HIGH TEMPERATURE MATERIAL**
- **EIGHT *COMMERCIAL* LICENSES FOR PMR RESINS. MAJOR SUPPLIERS: AMERICAN CYANAMID, CIBA-GEIGY, FERRO, FIBERITE, HEXCEL, U.S. POLYMERIC, HYSOL/GRAFIL, TRIBON.**
- **ONE OF THE MOST *WIDELY USED* MATRIX RESINS FOR 550 °F APPLICATIONS.**

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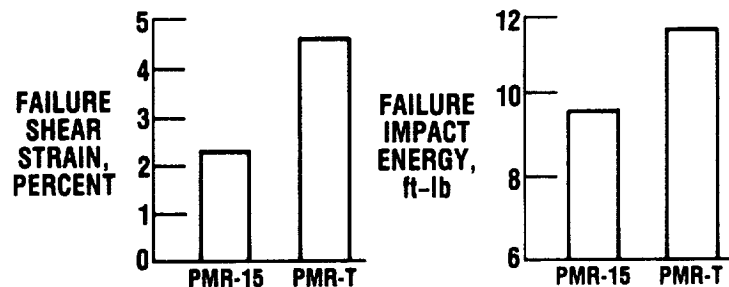
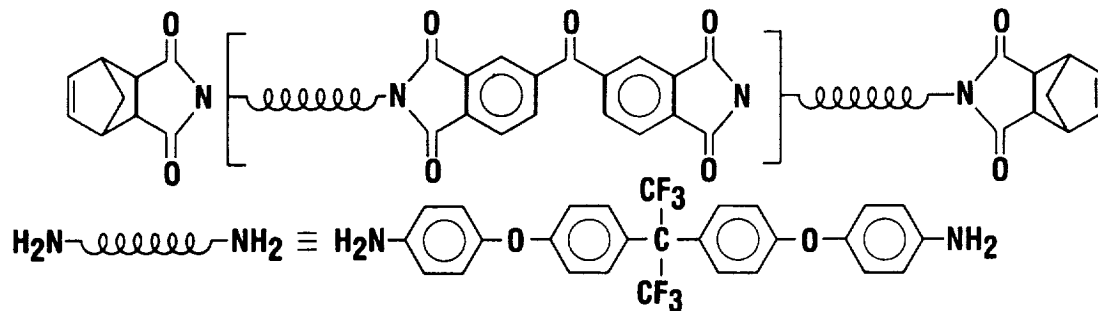
Figure 7. - PMR-15: recognized leader in high-temperature polymer matrix resins.

- IMPROVED TACK/EASIER HANDLING PMR
- LOWER CURE TEMPERATURE MATERIALS
- MECHANISTIC STUDIES
- UNDERSTANDING OF STRUCTURE/PROPERTY RELATIONSHIPS
- DEGRADATION STUDIES
- IMPROVED TOUGHNESS
- IMPROVED THERMAL STABILITY
- QUALITY CONTROL PROCEDURES

THIS WORK HAS LED TO OVER SEVENTY SCIENTIFIC PUBLICATIONS, TWELVE PATENTS AND SEVEN PATENTS PENDING.

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Figure 8. - Lewis Polymers Branch response to industry needs for improvements and further understanding of polyimides.



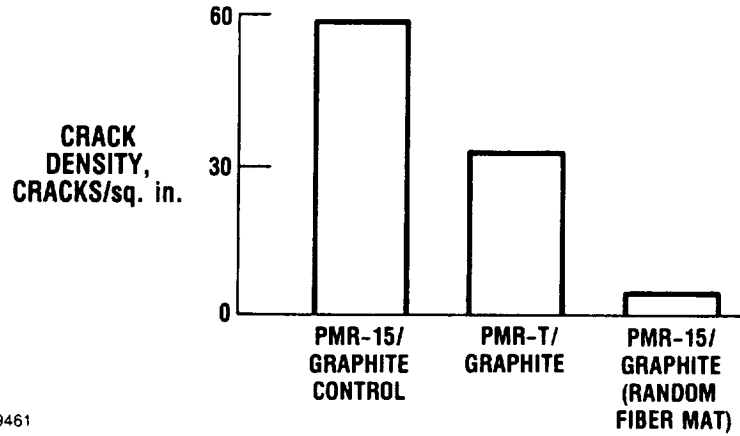
COMPARISON OF COMPOSITE PROPERTIES WHICH AFFECT COMPOSITE TOUGHNESS

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Figure 9. - PMR polyimides with improved toughness.

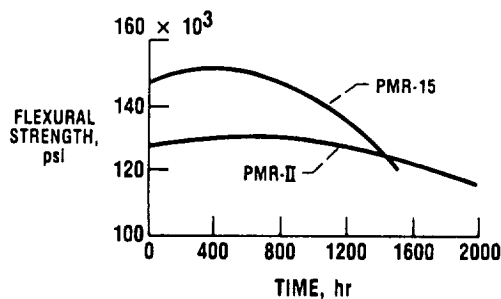
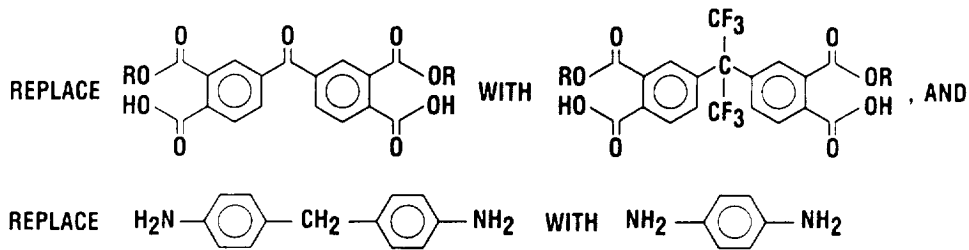
APPROACHES TO ELIMINATE IN-SERVICE MICROCRACKING:

- 1) TOUGHER POLYMER MATRIX RESIN
- 2) REPLACING SOME UNIDIRECTIONAL PLIES WITH RANDOM FIBER MAT



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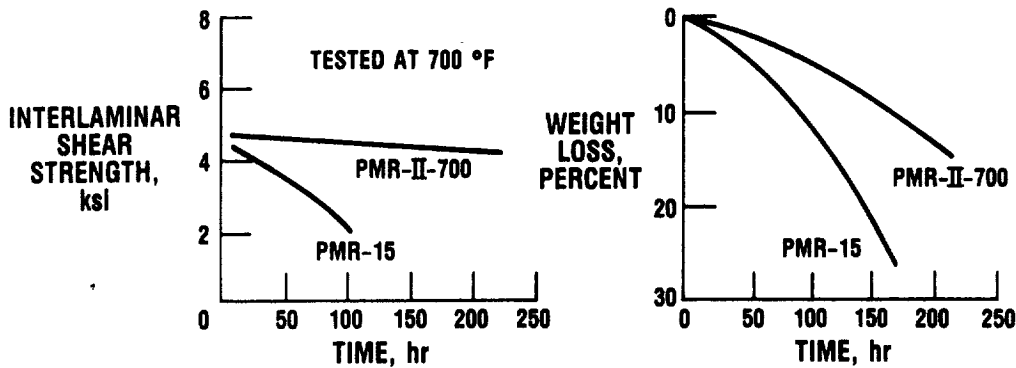
Figure 10. - Eliminating microcracking during in-service thermocycling.



COMPARISON OF FLEXURAL STRENGTH OF PMR-15/GRAPHITE FIBER COMPOSITE WITH PMR-II/GRAPHITE FIBER COMPOSITE EXPOSED AND TESTED AT 600 °F IN AIR

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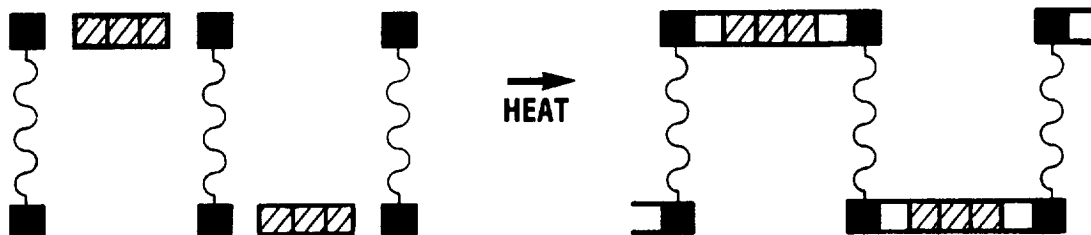
Figure 11. - PMR-II: better retention of properties through use of more stable monomers.



PROPERTIES OF GRAPHITE FIBER/PMR RESIN COMPOSITES AFTER EXPOSURE TO AIR AT 700 °F AND 60 PSIA

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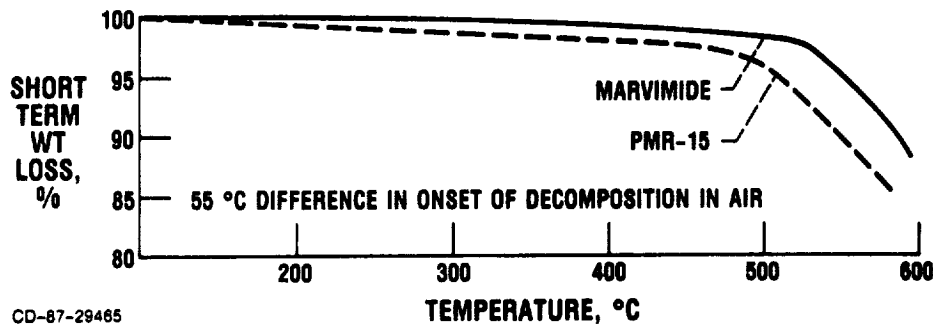
Figure 12. - PMR-II-700: entry into 700 °F applications.



- PROCESSABLE (THERMOPLASTIC ?)
- HIGH SOFTENING TEMPERATURES
- STABLE LADDER STRUCTURES

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Figure 13. - MARVIMIDES: linear addition copolymers with partial ladder structure.



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Figure 14. - Comparison of short-term weight loss of samples of MARVIMIDE and PMR-15.