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HIGH TEMPERATURE POLYMER MATRIX COMPOSITES

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ABSTRACT

With the increased emphasis on high performance aircraft the need for lightweight, thermal/oxidatively stable materials is growing. Because of their ease of fabrication, high specific strength, and ability to be tailored chemically to produce a variety of mechanical and physical properties, polymers and polymer matrix composites present themselves as attractive materials for a number of aeropropulsion applications. In the early 1970's researchers at the NASA Lewis Research Center developed a highly processable, thermally stable (600 °F) polyimide, PMR-15. Since that time, PMR-15 has become commercially available and has found use in military aircraft, in particular, the F-404 engine for the Navy's F/A-18 strike fighter. NASA Lewis's contributions to high temperature polymer matrix composite research will be discussed as well as current and future directions.

WHY POLYMERS?

Polymers have a number of properties which make them attractive candidates for aeropropulsion materials. They are lightweight (typically densities are on the order of 1.0 g/cc), corrosion resistant, and can be easily molded or shaped into complex forms. In addition to this, their chemical structure can be altered to meet a number of specific performance requirements - thermal/oxidative stability, toughness, thermal or electrical conductivity, etc.

WHY POLYMERS ?

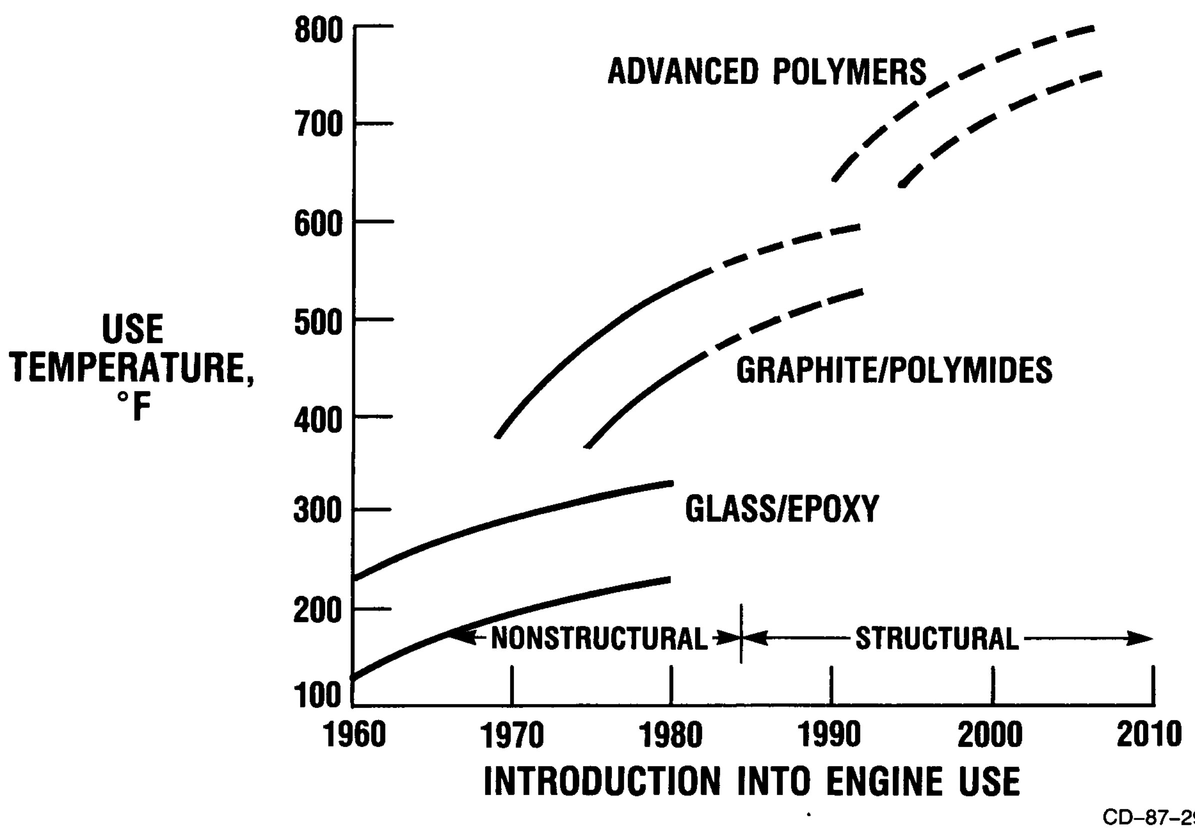
- CAN BE SHAPED OR FORMED EASILY
- LIGHTWEIGHT
- CORROSION RESISTANT
- CAN BE TAILORED TO SPECIFIC NEEDS

CD-87-29452

TRENDS FOR POLYMER COMPOSITES IN ENGINES

Polymer matrix composites have been used in engine applications since fiberglass/epoxy composites were introduced in the 1960's. Since that time, different reinforcement/resin combinations have been developed to meet increased temperature requirements. Current state-of-the-art graphite/polyimide composites are stable for thousands of hours at 600 °F. Research at the Polymers Branch of the Lewis Research Center is aimed at the development of new polymer matrix composite systems for use at 700 °F and beyond.

TRENDS FOR POLYMER COMPOSITES IN ENGINES



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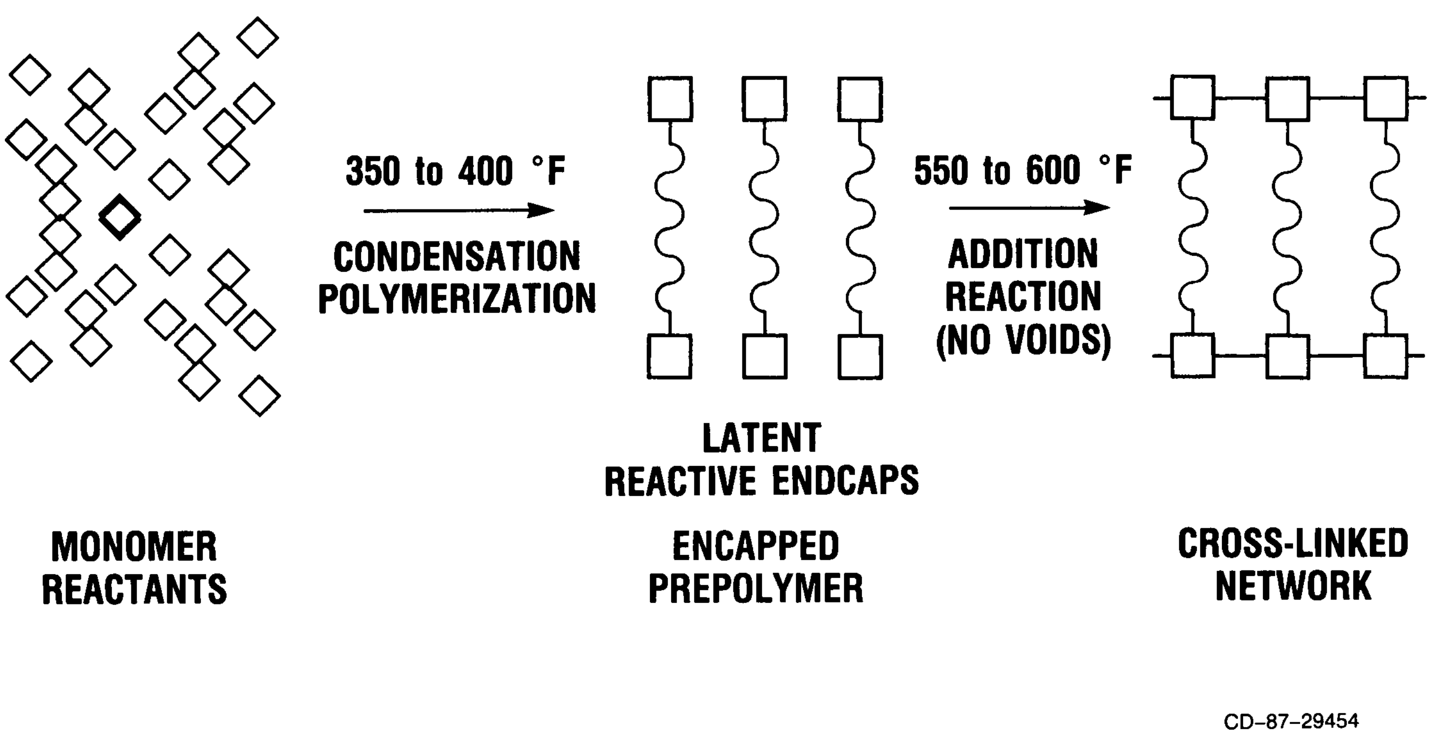
REACTION SCHEME FOR ADDITION POLYIMIDES

Composites which contain a number of air-pockets, or voids, generally have inferior mechanical properties and thermal/oxidative stability. Therefore, one of the major concerns in processing polymer matrix composites is minimizing the void content in the final composite. One approach to this (depicted in this figure) involves a two-step cure procedure. In this method a prepolymer is formed in the first step. Generally, this step involves formation of low molecular weight materials and produces volatile byproducts (condensation reaction). This prepolymer is end-capped with a group which undergoes a cross-linking reaction at a higher temperature to form a more thermally stable, tougher polymer network. Unlike the first step, the cross-linking reaction proceeds with no formation of byproducts. The result is a highly processable, void-free composite.

REACTION SCHEME FOR ADDITION POLYIMIDES

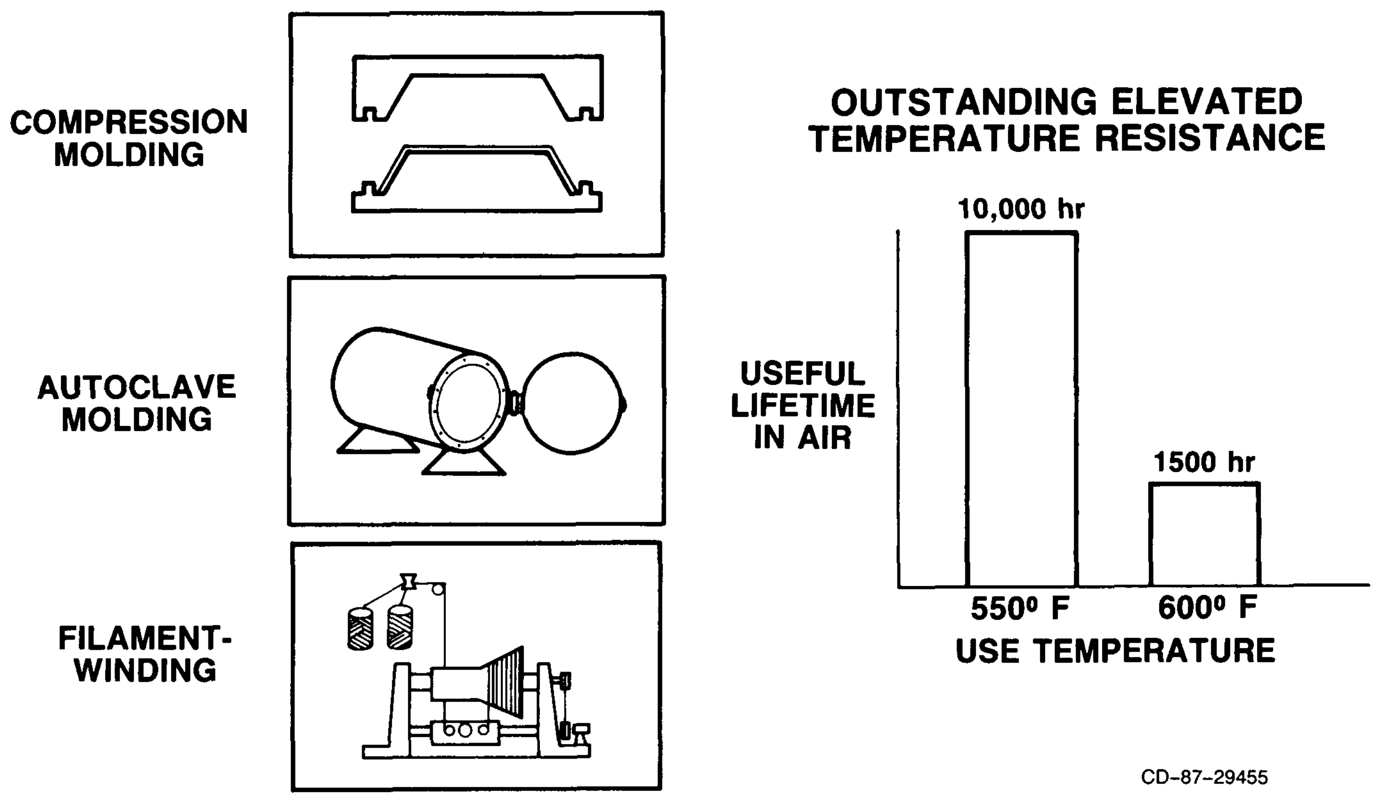


PMR POLYIMIDES

In the early 1970's researchers at NASA Lewis Research Center developed an additional curing polymide resin system known as PMR (polymerization of monomer reactants) polyimides. These polyimides, in particular PMR-15, afford exceptional thermal stability coupled with good processability. The useful lifetimes (in 60 psia) are 10 000 hr at 550 °F and 1500 hr at 600 °F.

LEWIS DEVELOPED PMR-15 POLYIMIDE TECHNOLOGY

EXCELLENT PROCESSABILITY



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NAVY MANUFACTURING TECHNOLOGY

A study performed under contract to the Navy indicated that inclusion of PMR-15/graphite composites in a number of military aircraft engines, such as the F-404, F-110, and F-101, would result in considerable savings in weight and manufacturing costs.

ORIGINAL PAGE IS
OF POOR QUALITY

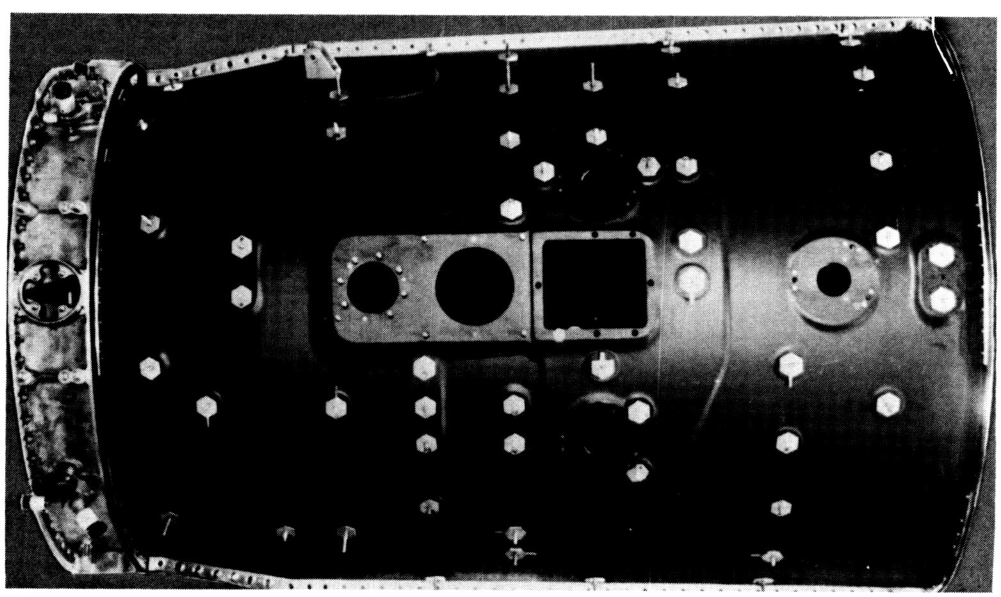
GRAPHITE/PMR-15 TITANIUM REPLACEMENT F-404 OUTER DUCT

GE is currently producing a graphite PMR-15/graphite duct for their F-404 engine. Originally made out of titanium, this duct was manufactured by forming and machining titanium plates followed by chem-milling to reduce the final weight. In initial tests, the graphite/PMR-15 replacement duct successfully completed over 1000 accelerated mission test cycles for a total engine exposure time of 700 hr. Replacement of the original titanium duct by the PMR-15/graphite ducts has resulted in a total weight savings of 7 pounds per engine. In-house studies by GE indicate that PMR-15/graphite could be used in other areas of this engine to provide similar weight reductions and production cost savings.

NAVY/NASA LeRC/GE JOINT DEVELOPMENT

WEIGHT SAVINGS — **7 POUNDS/ENGINE**

PRODUCTION QUALITY DUCT



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NASA LEWIS LEADS THE WAY IN HIGH TEMPERATURE POLYMERS WITH PMR-15

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 matrix resins for 550 °F applications. Currently there are eight commercial licenses for PMR resins.

NASA-LEWIS LEADS THE WAY IN HIGH TEMPERATURE POLYMERS WITH PMR-15

- **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 RESIN FOR 550 °F APPLICATIONS.**

CD-87-29458

LEWIS POLYMERS BRANCH WORKS CLOSELY WITH INDUSTRY

Since the development of PMR polyimides, the Polymers Branch at NASA Lewis Research Center has responded to industry needs for improvements in these resins, understanding the mechanisms for their thermal/oxidative degradation, and developing quality control methods. This work has resulted in a substantial contribution to the scientific literature and has resulted in a number of patents.

LEWIS POLYMERS BRANCH HAS WORKED CLOSELY WITH *INDUSTRY* RESPONDING TO *NEEDS* FOR IMPROVEMENTS AND FURTHER UNDERSTANDING OF THESE MATERIALS, INCLUDING:

- 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

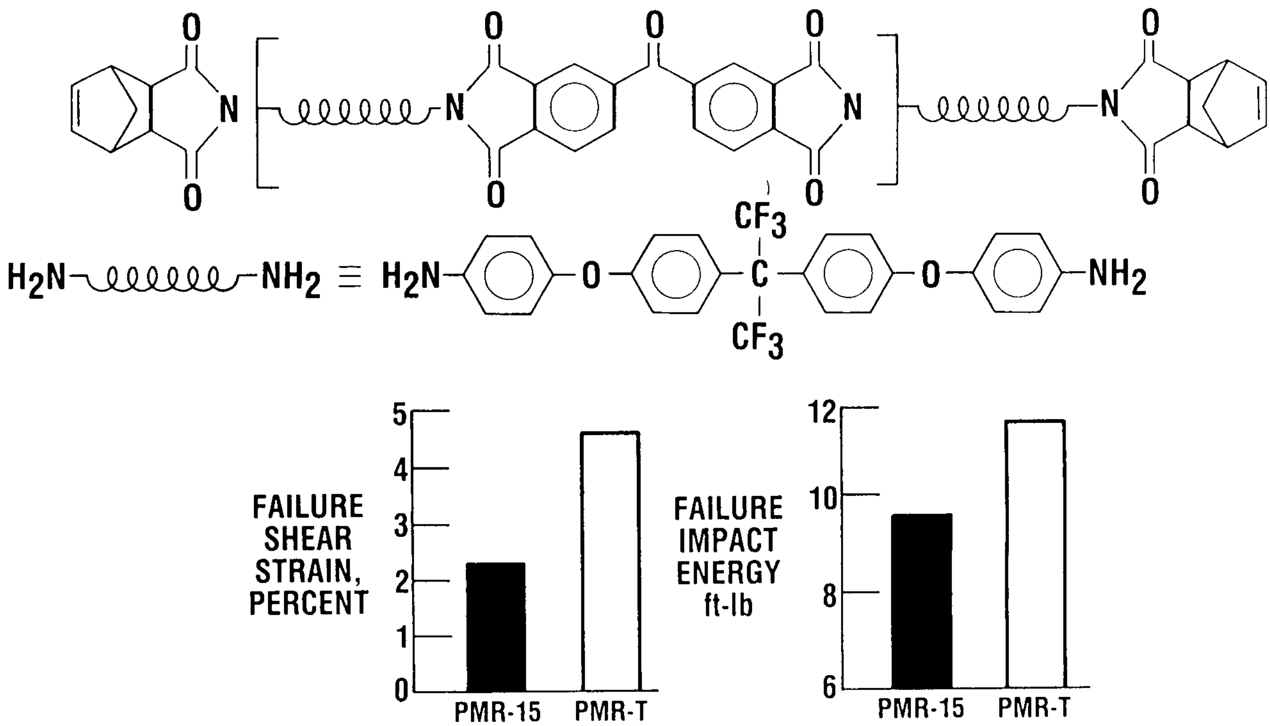
THIS WORK HAS LED TO OVER SEVENTY SCIENTIFIC PUBLICATIONS, TWELVE PATENTS AND SEVEN PATENTS PENDING.

CD-87-29459

PMR POLYMIDES WITH IMPROVED TOUGHNESS

A toughened PMR polyimide, PMR-T, was produced by substituting a flexible monomer into the original PMR formulation. The result is a two-fold increase in failure shear strain and an improvement in the impact strength.

PMR POLYIMIDES WITH IMPROVED TOUGHNESS



COMPARISON OF COMPOSITE PROPERTIES WHICH AFFECT COMPOSITE TOUGHNESS

CD-87-29460

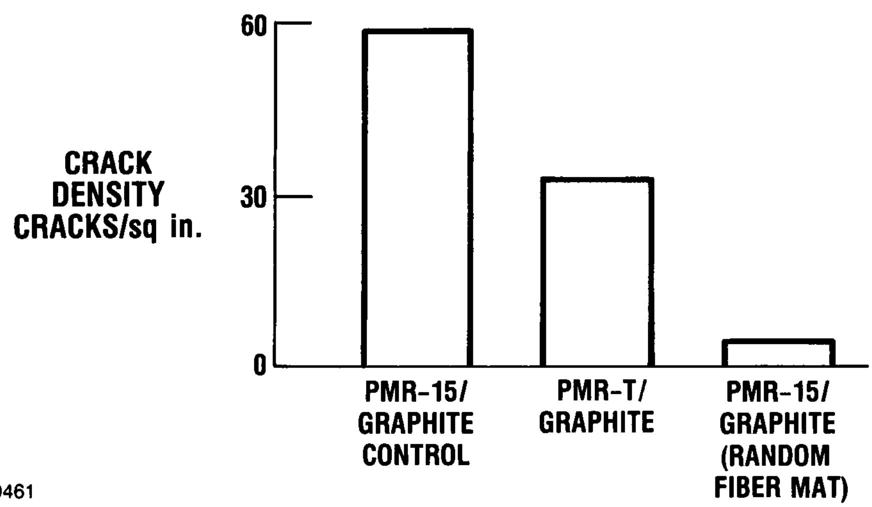
GRAPHITE/PMR COMPOSITE MATERIALS DEVELOP MICROCRACK DURING IN-SERVICE THERMOCYCLING

One concern that has arisen with graphite/PMR-15 is that these composites experience some microcracking during thermal cycling. 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 trans-ply crack density after 1000 cycles (0 to 450°F). Use of a random fiber mat finish virtually eliminated microcracking in a graphite/PMR-15 composite during the same thermal cycling test.

GRAPHITE/PMR COMPOSITE MATERIALS DEVELOP MICROCRACKS DURING IN-SERVICE THERMOCYCLING WHICH CAN AFFECT MECHANICAL PROPERTIES

APPROACHES TO ELIMINATE IN-SERVICE MICROCRACKING:

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



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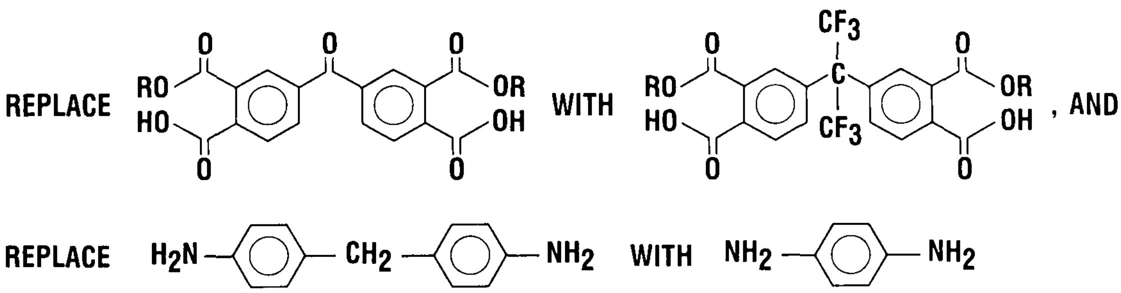
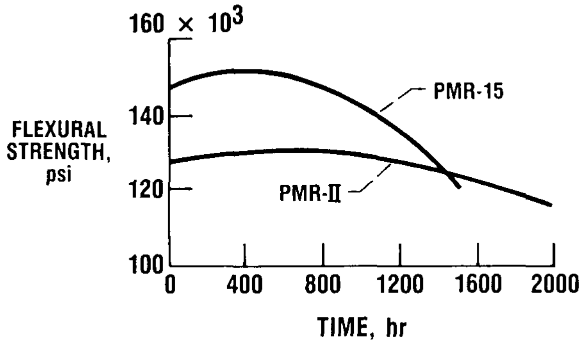
PMR-II: BETTER RETENTION OF PROPERTIES THROUGH USE OF MORE STABLE MONOMERS

Enhanced thermal/oxidative stability was achieved by the substitution of more thermally stable monomers into the original PMR composition. The resulting resin, PMR-II, a 1977 IR-100 award winner, yielded increased mechanical property retention at 600 °F in air over PMR-15.

PMR-II: BETTER RETENTION OF PROPERTIES THROUGH USE OF MORE STABLE MONOMERS





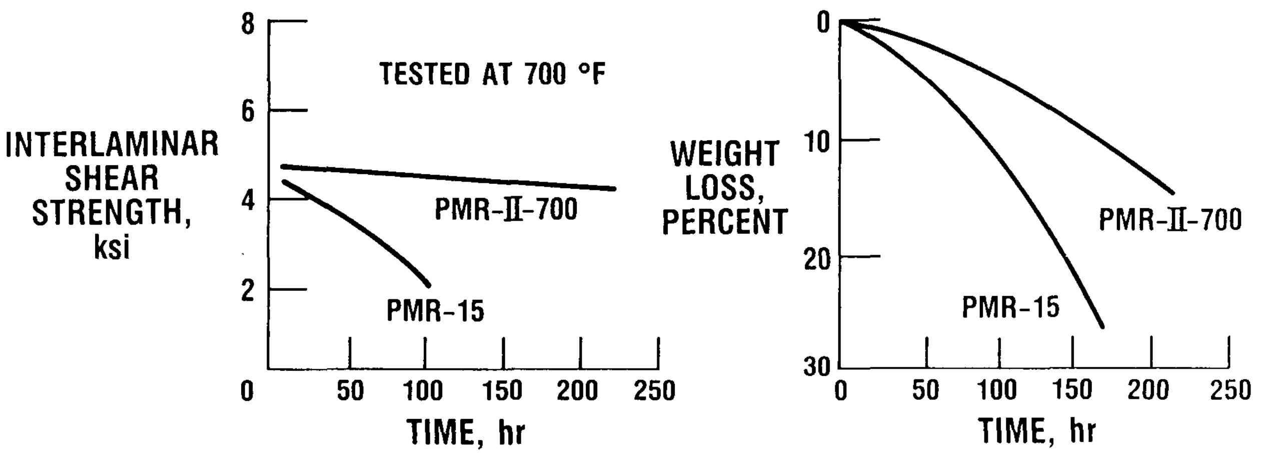
COMPARISON OF FLEXURAL STRENGTH OF PMR-15/GRAPHITE FIBER COMPOSITE WITH PMR-II/GRAPITE FIBER COMPOSITE EXPOSED AND TESTED AT 600 °F IN AIR

CD–87–29462

PMR-II-700: ENTRY INTO 700 °F APPLICATIONS

A higher molecular weight formulation of PMR-II, PMR-II-700, shows some promise as a 700 °F resin candidate. This resin has improved property retention and reduced weight loss over PMR-15 at 700 °F in air.

PMR-II-700: ENTRY INTO 700 °F APPLICATIONS



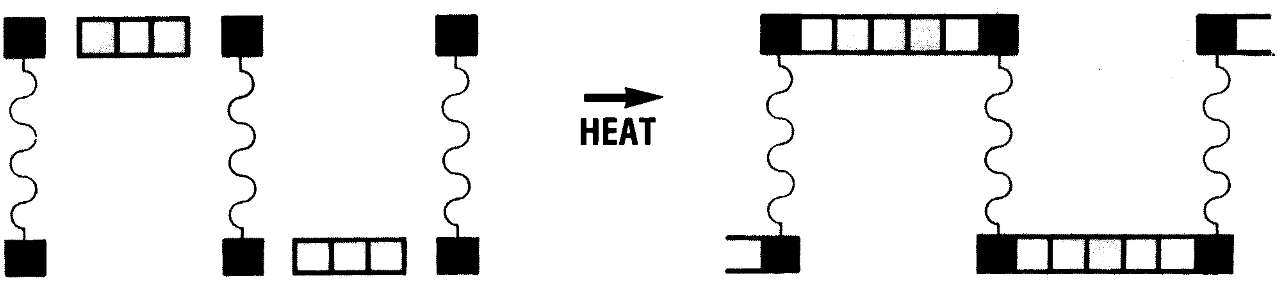
PROPERTIES OF GRAPHITE FIBER/PMR RESIN COMPOSITES AFTER EXPOSURE TO AIR AT 700 °F AND 60 PSIA

CD-87-29463

MARVIMIDES: LINEAR ADDITION COPOLYMERS WITH PARTIAL LADDER STRUCTURE

Mechanistic studies have revealed that the end cap is responsible for much of the thermal degradation in PMR-15 and similar polyimides. This is substantiated by the improved thermal/oxidative stability of PMR-II-700 in which the weight percentage of end cap is reduced by using higher molecular weight formulations. However, if use temperatures greater than 700 °F are to be realized, other approaches to high temperature matrix resins have to be developed. One such approach is MARVIMIDE, which employs a thermally stable cross-linking agent.

MARVIMIDES: LINEAR ADDITION COPOLYMERS WITH PARTIAL LADDER STRUCTURE

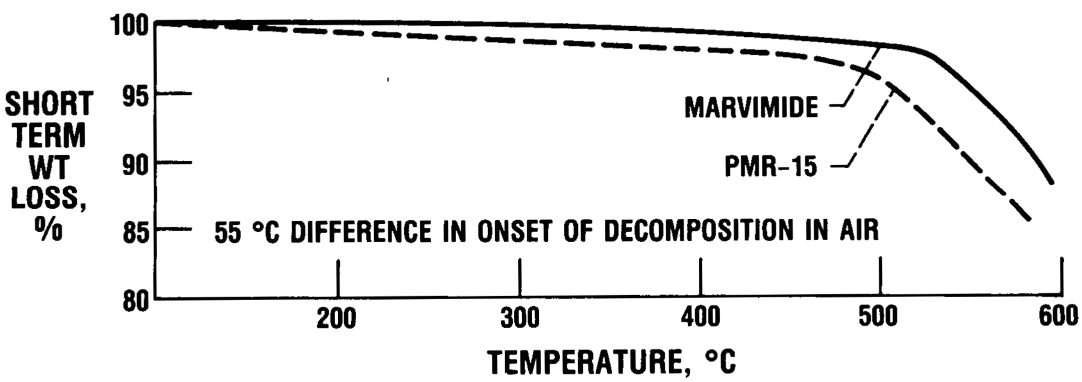


- PROCESSABLE (THERMOPLASTIC ?)
- HIGH SOFTENING TEMPERATURES
- STABLE LADDER STRUCTURES

MARVIMIDE HAS USE TEMPERATURES POTENTIALLY HIGHER THAN STATE OF THE ART (PMR-15)

The MARVIMIDE system offers good processablity, good resin flow, and produces matrix resins with superior thermal/oxidative stability and high softening temperatures (glass transition points, T_g, for unpostcured resins are as high as 420 °C). MARVIMIDE has a 100 °F higher onset of decomposition than PMR-15 in air.

MARVIMIDE HAS USE TEMPERATURES POTENTIALLY HIGHER THAN STATE OF THE ART (PMR-15)



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