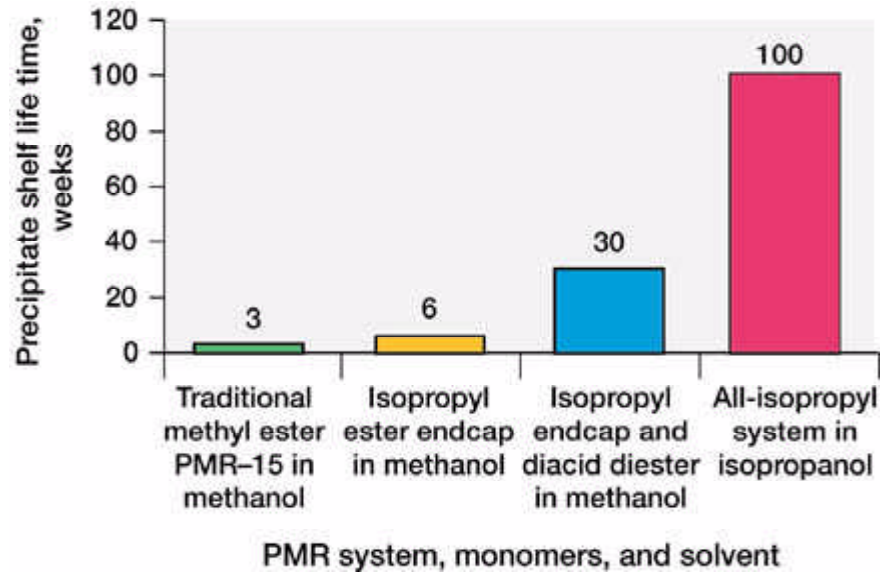


# Shelf Life of PMR Polyimide Monomer Solutions and Prepregs Extended

PMR (Polymerization of Monomeric Reactants) technology was developed in the mid-1970's at the NASA Glenn Research Center at Lewis Field for fabricating high-temperature stable polyimide composites. This technology allowed a solution of polyimide monomers or prepreg (a fiber, such as glass or graphite, impregnated with PMR polyimide monomers) to be thermally cured without the release of volatiles that cause the formation of voids—unlike the non-PMR technology used for polyimide condensation type resins. The initial PMR resin introduced as PMR-15 is still commercially available and is used worldwide by aerospace industries as the state-of-the-art resin for high-temperature polyimide composite applications. PMR-15 offers easy composite processing, excellent composite mechanical property retention, a long lifetime at use temperatures of 500 to 550 °F, and relatively low cost. Later, second-generation PMR resin versions, such as PMR II-50 and VCAP-75, offer improvements in the upper-use temperature (to 700 °F) and in the useful life at temperature without major compromises in processing and property retention but with significant increases in resin cost. Newer versions of nontoxic (non-methylene dianiline) PMR resins, such as BAX PMR-15, offer similar advantages as originally found for PMR-15 but also with significant increases in resin cost. Thus, the current scope of the entire PMR technology available meets a wide range of aeronautical requirements for polymer composite applications.

A major problem with PMR technology is that PMR polyimide monomer solutions and prepregs all suffer from a short shelf life. State-of-the-art PMR-15 has a maximum shelf life of 3 weeks at room temperature. Second-generation versions of PMR monomer solutions and prepregs and newer nontoxic versions of non-methylene dianiline PMR monomer solutions and prepregs exhibit an even shorter shelf life—over an order of magnitude less than that of state-of-the-art PMR-15. This problem has plagued industry since PMR's inception until now. Researchers at Glenn recently discovered that PMR's shelf life is dramatically improved by using secondary alcohols (preferably isopropanol) instead of conventional primary alcohols (methanol or ethanol) to both esterify the PMR monomer mix and dissolve it. In-house researchers also found that PMR monomer solutions and prepregs made with this alternative ester approach are less reactive during comparable storage and handling temperatures without affecting typical curing temperatures. The graph illustrates PMR-15's extended shelf life at room temperature when the new alternative ester approach is used. In the best case, using an all isopropyl system, a thirty-three-fold increase in shelf life is seen before the PMR-15 solution forms precipitates. For second-generation and nontoxic PMR monomer solutions and prepregs, the shelf life improvement is about an order of magnitude. Thus, this discovery has widespread application to improve the shelf life of many PMR systems.



*PMR-15 solution stability as a function of time to precipitate.*

This method of improving PMR shelf life could also offer several additional advantages over conventional PMR technology because of its greater temperature stability, providing an increased tolerance to the mishandling of PMR solutions and prepregs. These advantages translate into (1) reduced shipping and handling costs by eliminating the need for refrigeration, (2) reduced variability between PMR monomer batches that results in more consistent processability, (3) improved hot-melt PMR prepreg manufacturing, (4) reduced scrap rates, (5) improved safety because isopropanol is less toxic than methanol and ethanol, and (6) improved adaptability to some processing techniques such as solvent-assisted resin transfer molding. Further work is ongoing to exploit all these advantages.

**U.S. Army Research Laboratory at Glenn contact:** Dr. William B. Alston, (216) 433-3220, William.B.Alston@grc.nasa.gov

**Dynacs Engineering Co., Inc., contact:** Daniel A. Scheiman, (216) 433-3223, Daniel.A.Scheiman@grc.nasa.gov

**Authors:** Dr. William B. Alston and Daniel A. Scheiman

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