



## Commercialization of LARC™-SI Polyimide Technology

The resulting material is now used in medical, aircraft, consumer products, and electronics applications.

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LARC™-SI, Langley Research Center-Soluble Imide, was developed in 1992, with the first patent issuing in 1997, and then subsequent patents issued in 1998 and 2000. Currently, this polymer has been successfully licensed by NASA, and has generated revenues, at the time of this reporting, in excess of \$1.4 million. The success of this particular polymer has been due to many factors and many lessons learned to the point that the invention, while important, is the least significant part in the commercialization of this material.

Commercial LARC™-SI is a polyimide composed of two molar equivalents of dianhydrides: 4,4'-oxydiphthalic anhydride (ODPA), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 3,4'-oxydianiline (3,4'-ODA) as the diamine. The unique feature of this aromatic polyimide is that it remains soluble after solution imidization in high-boiling, polar aprotic solvents, even at solids contents of 50-percent by weight. However, once isolated and heated above its  $T_g$  of 240 °C, it becomes insoluble and exhibits high-temperature thermoplastic melt-flow behavior. With these unique structure property characteristics, it was thought this would be an advantage to have an aromatic poly-

imide that is both solution and melt processable in the imide form. This could potentially lead to lower cost production as it was not as equipment- or labor-intensive as other high-performance polyimide materials that either precipitate or are intractable.

This unique combination of properties allowed patents with broad claim coverage and potential commercialization. After the U.S. Patent applications were filed, a Small Business Innovation Research (SBIR) contract was awarded to Imtec, Inc. to develop and supply the polyimide to NASA and the general public. Some examples of demonstration parts made with LARC™-SI ranged from aircraft wire and multilayer printed-circuit boards, to gears, composite panels, supported adhesive tape, composite coatings, cookware, and polyimide foam. Even with its unique processing characteristics, the thermal and mechanical properties were not drastically different from other solution or melt-processable polyimides developed by NASA. LARC™-SI risked becoming another interesting, but costly, high-performance material.

A licensee was sought, and a specific application was developed, the THUNDER piezoelectric actuator. This actua-

tor used the polyimide as the adhesive to thermally bond metal shims to the piezoelectric ceramic. This gave the THUNDER actuator a mechanical pre-stress, resulting in enhanced solid-state motion. Because this actuator had separate fields of use, and all the test data was developed using LARC™-SI as one of the components, the commercial THUNDER actuator used LARC™-SI as the adhesive, and was thus partially responsible for keeping LARC™-SI in the public spotlight.

Both LARC™-SI and THUNDER were licensed to several companies, including a known company that was actively investing in marketing a material developed by NASA (Dominion Resources, Inc.). It was important to find a large company that had continuous sales of high-value-added products that could support the initial price and benefit from the use of an expensive new material to gain market share. It was a medical products industry company that licensed LARC™-SI for use as a new wire varnish for pacemaker leads, an application that was never envisioned.

*This work was done by Robert G. Bryant for Langley Research Center. Further information is contained in a TSP (see page 1). LARC-15205-1*

## Novel Low-Density Ablators Containing Hyperbranched Poly(azomethine)s

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An ablative composite is low-density (0.25 to 0.40 g/cm<sup>3</sup>), easy to fabricate, and superior to the current state-of-the-art ablator (phenolic impregnated carbon ablator, PICA) in terms of decomposition temperature, char yield, and mechanical strength. Initial ablative testing with a CO<sub>2</sub> laser under high-heat-flux (1,100 W/cm<sup>2</sup>) conditions showed these new ablators are over twice as effective as PICA in terms of

weight loss, as well as transfer of heat through the specimen.

The carbon fiber/poly(azomethine) composites have the same density as PICA, but are 8 to 11 times stronger to irreversible breaking by tensile compression. In addition, polyazomethine char yields by thermogravimetric analysis are 70 to 80 percent at 1,000 °C. This char yield is 10 to 20 percent higher than phenolic resins, as well as one of the highest

char yields known for any polymer. A high char yield holds the composite together better toward shearing forces on reentry, as well as reradiates high heat fluxes. This innovative composite is stronger than PICA, so multiple pieces can be sealed together without fracture.

Researchers have also studied polyazomethines before as linear polymers. Due to poor solubility, these polymers precipitate from the polymerization sol-