

imide, bis-perfluoro-*n*-octylsulfonic acid imide (C8-C8 imide), or perfluoro-*n*-butyl-perfluoro-*n*-octylsulfonic acid imide. The experiments involved electro-oxidation of methanol on each anode installed as one of the electrodes in a three-electrode electrochemical test cells. The performances of the electrodes were characterized by galvanostatic polarization measurements and cyclic voltammetry. Of the compounds investigated, C12 acid and C8-C8 imide were found to afford the greatest increases in rates of ox-

idation of methanol and the greatest reductions in levels of polarization (see figure), relative to those of Nafion™-H.

This work was done by G. K. Surya Prakash, Qun-jie Wang, and George A. Olah of the University of Southern California and Marshall C. Smart, Sekharipuram Narayanan, and Subbarao Surampudi, of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).

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Advanced Ablative Insulators and Methods of Making Them

Reinforced, filled silicones and carbon phenolics are laser-milled to final shapes.

Lyndon B. Johnson Space Center, Houston, Texas

Advanced ablative (more specifically, charring) materials that provide temporary protection against high temperatures, and advanced methods of designing and manufacturing insulators based on these materials, are undergoing development. These materials and methods were conceived in an effort to replace the traditional thermal-protection systems (TPSs) of re-entry spacecraft with robust, lightweight, better-performing TPSs that can be designed and manufactured more rapidly and at lower cost. These materials and methods could also be used to make improved TPSs for general aerospace, military, and industrial applications.

The ablative materials belong to two families. One family comprises filled,

fiber-reinforced elastomeric carbon phenolics with mass densities that range from 18 to 40 lbm/ft³ (288 to 641 kg/m³); these materials are designed to protect against heating rates up to about 1,300 Btu/(ft²s) [\approx 15 MW/m²]. The other family comprises filled, fiber-reinforced silicones with mass densities that range from 12 to 50 lbm/ft³ [192 to 800 kg/m³]; these materials are designed to protect against heating rates from 5 to about 400 Btu/(ft²s) [about 0.06 to about 4.5 MW/m²]. The fillers in these materials help to minimize their mass densities, while the fibers help to maximize their strengths.

Design and manufacture of TPSs according to the present approach involve the use of computer-aided design

and computer-aided manufacturing (CAD/CAM) methods, including computer numerically controlled (CNC) laser milling. This approach eliminates the labor-intensive steps of machining, fitting, and trimming heat-shield parts in the prior approach to manufacturing. In the present approach, molded panels of the ablative materials are CNC-laser-milled to precise final sizes and shapes and are thus made ready for bonding to heat-shield structures.

This work was done by William M. Congdon of Applied Research Associates, Inc., for Johnson Space Center. For further information, contact the Johnson Technology Transfer Office at (281) 483-3809. MSC-23141

PETIs as High-Temperature Resin-Transfer-Molding Materials

PETI-matrix/carbon-fiber composites made by resin-transfer molding have excellent properties.

Langley Research Center, Hampton, Virginia

Compositions of, and processes for fabricating, high-temperature composite materials from phenylethynyl-terminated imide (PETI) oligomers by resin-transfer molding (RTM) and resin infusion have been developed. Composites having a combination of excellent mechanical properties and long-term high-temperature stability have been readily fabricated. These materials are particularly useful for the fabrication of high-temperature structures for jet-engine components, structural components on high-speed aircraft, spacecraft, and missiles.

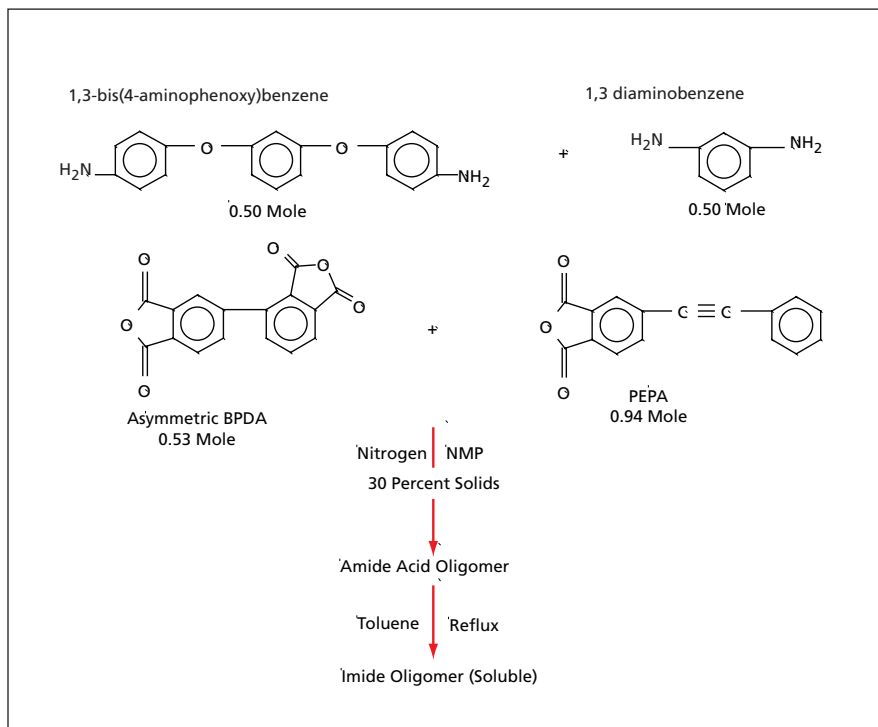
Phenylethynyl-terminated amide acid oligomers that are precursors of PETI oligomers are easily made through the reaction of a mixture of aromatic diamines with aromatic dianhydrides at high stoichiometric offsets and 4-phenylethynylphthalic anhydride (PEPA) as an end-capper in a polar solvent such as *N*-methylpyrrolidinone (NMP). These oligomers are subsequently cyclodehydrated — for example, by heating the solution in the presence of toluene to remove the water by azeotropic distillation to form low-molecular-weight imide

oligomers. More precisely, what is obtained is a mixture of PETI oligomeric species, spanning a range of molecular weights, that exhibits a stable melt viscosity of less than approximately 60 poise (and generally less than 10 poise) at a temperature below 300 °C. After curing of the oligomers at a temperature of 371 °C, the resulting polymer can have a glass-transition temperature (T_g) as high as 375 °C, the exact value depending on the compositions.

As an example, one PETI oligomer, denoted PETI-330, was synthesized as

shown in the figure. First, 0.53 mole of 2,3,3',4'-biphenyltetracarboxylic dianhydride (BPDA) and 0.94 mole of PEPA were reacted with 0.50 mole of 1,3-bis(4-aminophenoxy)benzene and 0.50 mole of 1,3-diaminobenzene in NMP to form the phenylethynyl-terminated amide acid oligomer. Then, by azeotropic distillation using toluene, the phenylethynyl-terminated amide acid oligomer was converted to the PETI oligomer having a calculated repeat unit molecular weight of 750 g/mole. The imide oligomer was isolated, washed well with water, and dried. The melt viscosity of the imide oligomer was found to be 0.6 poise initially at a temperature of 280 °C and 0.9 poise after 2 hours at that temperature.

The imide oligomer was degassed, then injected, at a temperature of 280 °C, into a preform made of a fabric of T650 carbon fibers in 8-harness satin weave. The oligomer was then cured for 1 hour at a temperature of 371 °C and a pressure of 200 psi (≈ 1.4 MPa). The resulting quasi-isotropic composite was found to have an open-hole compressive strength of 39 kpsi (≈ 0.27 GPa) at a temperature of 23 °C and 29 kpsi (≈ 0.2 GPa) at a temperature of 288 °C. After aging for 1,000 hours at 288 °C in air, the open-hole compressive strength was found to be 32 kpsi (≈ 0.22 GPa) at 23 °C. The unnotched compressive strength was found to be 75 kpsi (≈ 0.52 GPa) at 23 °C. The composite exhibited no microcracking, either



PETI-330 is Synthesized in this sequence of reactions.

immediately after cure or after 200 subsequent thermal cycles from -55 °C to $+288$ °C. The T_g of the composite was found to be 330 °C.

Another such PETI oligomer, denoted PETI-375, was synthesized and used to make an RTM composite with a carbon-fiber cloth of the type described above. The open-hole compressive strength of this composite was found to be 43.5 kpsi

(≈ 0.3 GPa) at 23 °C, 34.8 kpsi (≈ 0.24 GPa) at 288 °C, and 32.2 kpsi (≈ 0.22 GPa) at 316 °C. The T_g of the composite was found to be 370 °C.

This work was done by John W. Connell, Joseph G. Smith, Jr., and Paul M. Hergenrother of Langley Research Center. Further information is contained in a TSP (see page 1). LAR-15834-1

Stable Polyimides for Terrestrial and Space Uses

Low-color films exhibit high resistance to space environment.

Langley Research Center, Hampton, Virginia

Polyimides of a recently developed type have an attractive combination of properties, including low solar absorptivity (manifested as low color) when cast into thin films, resistance to atomic oxygen and ultraviolet radiation, solubility in organic solvents, high glass-transition temperatures (T_g s), and high thermal stability. The focus of the development work was on polymers that can endure the space environment and that have specific combinations of properties for use on Gossamer spacecraft. Because of their unique combination of properties, these polymers are also expected to find use in a variety of other applications on Earth as well as in space.

Examples of other space applications include membranes on antennas, second-surface mirrors, thermal optical coatings, and multilayer thermal insulation. For both terrestrial and space applications, these polyimides can be processed into various forms, including films, fibers, foams, threads, adhesives, and coatings.

In preparation for synthesizing a polyimide of this type, one makes [2,4-bis(3-aminophenoxy)phenyl]diphosphine oxide (hereafter denoted "the phosphine oxide diamine"), which is a novel aromatic diamine. In an experiment, this aromatic diamine was made from commercially available starting ma-

terials in a two-step process in relatively high yield. Then, in experimental syntheses of polyimides of this type, the phosphine oxide diamine was reacted with aromatic dianhydrides in polar aprotic solvents. In other experiments, copolyimides were synthesized by use of the phosphine oxide diamine in combination with other commercially available aromatic diamines. These various syntheses made it possible to tailor the polymers to reduce costs and obtain hitherto unavailable combinations of properties.

The figure illustrates the example of one synthesis, in which the phosphine oxide diamine was reacted with oxydiphthalic anhydride (ODPA) in N-methyl-