



Materials & Coatings

Fire-Retardant Polymeric Additives

Mechanical properties are retained or even enhanced.

John F. Kennedy Space Center, Florida

Polyhydroxyamide (PHA) and polymethoxyamide (PMeOA) are fire-retardant (FR) thermoplastic polymers and have been found to be useful as an additive for imparting fire retardant properties to other compatible, thermoplastic polymers (including some elastomers). Examples of compatible flammable polymers include nylons, polyesters, and acrylics. Unlike most prior additives, PHA and PMeOA do not appreciably degrade the mechanical properties of the matrix polymer; indeed, in some cases, mechanical properties are enhanced. Also, unlike some prior additives, PHA and PMeOA do not decompose into large amounts of corrosive or toxic compounds during combustion and can be processed at elevated temperatures.

PMeOA derivative formulations were synthesized and used as an FR additive in the fabrication of polyamide (PA) and

polystyrene (PS) composites with notable reduction (>30 percent for PS) in peak heat release rates compared to the neat polymer as measured by a Cone Calorimeter (ASTM E1354). Synergistic effects were noted with nanosilica composites. These nanosilica composites had more than 50-percent reduction in peak heat release rates.

In a typical application, a flammable thermoplastic, thermoplastic blend, or elastomer that one seeks to render flame-retardant is first dry-mixed with PHA or PMeOA or derivative thereof. The proportion of PHA or PMeOA or derivative in the mixture is typically chosen to lie between 1 and 20 weight percent. The dry blend can then be melt-extruded. The extruded polymer blend can further be extruded and/or molded into fibers, pipes, or any other of a variety of objects that may be required to be fire-retardant.

The physical and chemical mechanisms which impart flame retardancy of the additive include inhibiting free-radical oxidation in the vapor phase, preventing vaporization of fuel (the polymer), and cooling through the formation of chemical bonds in either the vapor or the condensed phase. Under thermal stress, the cyclic hydroxyl/methoxy component forms polybenzoxazole (PBO) in a reaction that absorbs heat from its surroundings. PBO under thermal stress cross-links, forming a protective char layer, which thermally insulates the polymer. Thus, the formation of the char layer further assists to extinguish the fire by preventing vaporization of the polymeric fuel.

This work was done by Martha K. Williams and Trent M. Smith of Kennedy Space Center. For further information, contact the Kennedy Innovative Partnerships Office at (321) 861-7158. KSC-12697

Catalytic Generation of Lift Gases for Balloons

Relatively lightweight, low-power gas generators are based on methanol reforming.

Goddard Space Flight Center, Greenbelt, Maryland

A lift-gas cracker (LGC) is an apparatus that generates a low-molecular-weight gas (mostly hydrogen with smaller amounts of carbon monoxide and/or carbon dioxide) at low gauge pressure by methanol reforming. LGCs are undergoing development for use as sources of buoyant gases for filling zero-gauge-pressure meteorological and scientific balloons in remote locations where heavy, high-pressure helium cylinders are not readily available. LGCs could also be used aboard large, zero-gauge-pressure, stratospheric research balloons to extend the duration of flight.

Methanol reforming has been investigated as a means of generating hydrogen for fuel cells. Although the product-gas specifications, process-stream, and control requirements for fuel-cell applications differ from those of lift-gas applications, the underlying methanol-re-

forming principle is the same for both classes of applications, and some of the heat-exchange and catalyst design requirements from fuel-cell applications are adaptable to lift-gas applications.

In the methanol reforming reactor that lies at the heart of an LGC, methanol is catalytically cracked to carbon monoxide and hydrogen in an endothermic reaction, typically at a temperature in the approximate range of 250 to 350 °C and at a pressure that can lie in a range from somewhat below to somewhat above standard sea-level atmospheric pressure. A small portion of the methanol feed is diverted to a low-pressure combustor to provide the heat for the endothermic reforming reaction and maintain the reactor at the reaction temperature.

When the feedstock is pure methanol, the overall chemical reaction is $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$. In a steam-reforming vari-

ant, the feedstock is a mixture of methanol and steam, typically comprising equal numbers of methanol and water molecules, in which case the overall chemical reaction is $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$. The optimum choice of temperature, pressure, and catalyst depends on details of the specific application. The exact formulations of methanol-reforming catalysts are proprietary; what is known is that most of them include copper oxide and zinc oxide on alumina supports.

The only consumables needed for the methanol-reforming process in an LGC, other than methanol, are air and a small amount of electrical power for an air blower and for instrumentation. In principle, an apparatus that generates hydrogen by electrolysis of water could be used as an alternative to an LGC, but an electrolytic apparatus would be less ad-

	Lift-Gas Cracker	Electrolytic Generator
Mass, kg	<100	>2,000
Area, m ²	<1	>4
Electrical Power, kW	<0.5	≈100 (From Generator)
Fuel, Grams per Standard Liter of Gas	0.1	1.4
Methanol, Grams per Standard Liter of Gas	0.35	0
Water, Grams per Standard Liter of Gas	0.2	0.8
Cost, Dollars (at 2003 Prices)	<\$10,000	>\$50,000

Selected Parameters are presented in comparison of an LGC capable of generating hydrogen-based lift gas and an electrolytic apparatus capable of generating hydrogen — both at a rate of 100 standard liters per minute.

vantageous in several ways: As shown by example in the table, relative to an electrolytic apparatus capable of producing hydrogen at a given rate, an LGC capable of producing hydrogen-based lift gas at the same rate is much less massive and requires much less electrical power and

much less fuel. Moreover, the LGC is more reliable and robust.

As contemplated for use in extending the duration of flight of a high-altitude balloon, an LGC would provide the lift gas for an auxiliary buoyancy-control balloon separate from a main lift bal-

loon. The buoyancy-control balloon would be used to compensate for changes in buoyancy associated with diurnal/nocturnal variations in temperature. In this application, the LGC would produce the lift gas by catalytic reforming of methanol at night. During the day, some of the lift gas would be burned with atmospheric air to produce water for use as ballast. At night, the water ballast could be dropped or could be recycled to the LGC for steam reforming of methanol. In this approach, the duration of flight could be extended by a factor of as much as four, relative to a conventional approach in which ballast is dropped at night and gas is vented during the day.

This work was done by Robert Zubrin and Mark Berggren of Pioneer Astronautics for Goddard Space Flight Center. Further information is contained in a TSP (see page 1). GSC-14792-1

Ionic Liquids to Replace Hydrazine

Customized ionic liquids offer better safety and convenience than traditional propellants.

Dryden Flight Research Center, Edwards, California

A method for developing safe, easy-to-handle propellants has been developed based upon ionic liquids (ILs) or their eutectic mixtures. An IL is a binary combination of a typically organic cation and anion, which generally produces an ionic salt with a melting point below 100 °C. Many ILs have melting points near, or even below, room temperature (room temperature ionic liquids, RTILs). More importantly, a number of ILs have a positive enthalpy of formation. This means the thermal energy released during decomposition reactions makes energetic ILs ideal for use as propellants. Unlike traditional, storable propellants like hydrazine, ILs also exhibit near-zero vapor pressure. This makes them safer to handle because it eliminates hazardous inhalation — the primary pathway — as a route for toxicity in humans. Thus, ILs are ideal candidates for replacing hydrazine, which is expensive and dangerous, and poses significant handling difficulties.

Another behavior exhibited by ILs that makes them particularly attractive for replacing state-of-the-art, storable propellants is the very wide temperature range in which they remain liquid. A number of ILs have been routinely synthesized to possess glass transition points

below -60 °C (-76 °F), and decomposition temperatures in excess of 140 °C (284 °F). This behavior eliminates the stringent thermal control required for hydrazine, which freezes at 2 °C (35 °F) and boils at 113 °C (235 °F). If an IL-based propulsion system were used, spacecraft power otherwise needed to run heaters that keep hydrazine in a liquid state would be freed up for other power-hungry devices.

Another operations and safety benefit is that researchers have tremendous flexibility for dialing-in the precise behavior desired. The primary method for designing an IL for a specific task has been through careful selection of the two counterions — the cation and anion where each introduces specific properties to the binary, ionically bonded salt.

Scientists estimate there are as many as 10¹⁸ possible binary ILs, which gives considerable design freedom to researchers developing new propellants. This design trade space becomes significantly larger by using eutectic mixtures of ILs. Eutectic mixtures are important because they allow for precise tailoring of decomposition thermochemistry, fluid viscosity, melting point, glass transition point, density, and virtually every other physical attribute. Recently research was completed

that began to exploit eutectic mixture ILs specifically for tailoring their behavior to optimize their use as energetic monopropellants. The goal of that effort was to develop an IL monopropellant with higher Isp (specific impulse) performance than hydrazine.

In this specific work, to date, a baseline set of energetic ILs has been identified, synthesized, and characterized. Many of the ILs in this set have excellent performance potential in their own right. In all, ten ILs were characterized for their enthalpy of formation, density, melting point, glass transition point (if applicable), and decomposition temperature. Enthalpy of formation was measured using a microcalorimeter designed specifically to test milligram amounts of energetic materials. Of the ten ILs characterized, five offer higher Isp performance than hydrazine, ranging between 10 and 113 seconds higher than the state-of-the-art propellant. To achieve this level of performance, the energetic cations 4-amino-1,2,4-triazolium and 3-amino-1,2,4-triazolium were paired with various anions in the nitrate, dicyanamide, chloride, and 3-nitro-1,2,4-triazole families. Protonation, alkylation, and butylation synthesis routes were used for creation of the different salts.