Coatings for Next-Generation Harsh Environment Systems

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ABSTRACT

From space to oil and gas wells, polyimide coatings and films are used to protect critical components such as fiber optic cables, enameled wires, and sensors in harsh environments. Polyimide materials provide exceptional thermal durability, chemical resistance, mechanical toughness, and dielectric properties. Polymer coatings with extended lifetimes above 350 °C at pressures up to 10,000 psi are required to enable the next generation of harsh environment devices, but under these conditions, current polyimide coatings rapidly fail due to thermal and hydrolytic decomposition. Through optimization of polymer structure and synthetic methods, Tetramer Technologies has developed a series of new polyimide coatings that provide up to a 10X increase in useful lifetime between 300 and 350 °C in air compared to current polyimide coatings. In this paper, Tetramer discusses the unique features of each of the new Tetrimide™ coatings and their advantages over current polyimide materials in terms of thermal stability and hydrolytic stability.

Keywords: polymer, coatings, polyimide, fiber, wire, film

1 INTRODUCTION

Polyimide polymers were discovered in the 1950's through DuPont's efforts to develop a processable polymer precursor that could be converted to a final polymer with very high chemical and thermal resistance. The result of this work was the polyimide material known as Kapton®, which possessed a break-through combination of thermal stability, chemical resistance, and mechanical toughness [1]. As Kapton® and other polyimide materials were commercialized, they were integral to numerous technological advancements such as integrated circuit manufacturing and aerospace wiring and thermal insulation. Now, polyimide materials are ubiquitous as coatings and films in high temperature and chemically harsh environments.

Conventional polyimide coatings and films are typically rated for continuous use at temperatures up to 300 °C (572 °F) with short excursions to 350 °C and higher. However, new coatings are needed to enable engineered systems to explore deeper wells and provide real-time monitoring of temperature and mechanical stressors in the harshest aerospace and automotive environments.

1.1 Tetrimide™ Polyimide Materials

The exceptional thermal stability and chemical resistance of conventional polyimides have a draw-back – poor processability. Typically, very slow processing speeds and low solution concentrations are inherent to polyimides with the highest thermal and chemical robustness.

The Tetrimide™ polyimides were developed to provide both exceptional durability in harsh environments and good processability. By implementing understanding of polymer structure-property relationships for thermal stability, chemical resistance, and processability, copolymers where designed to push the threshold of durability without sacrificing the solubility and processing speed of the material. Three Tetrimide™ products were developed with industry-leading thermal stability, each engineered for targeted applications.

Tetrimide™ ICP brings exceptional chemical resistance and hydrolytic stability to down-hole devices. This polyimide is processed like a conventional polyimide material, from the poly(amic acid) precursor, and can be used in continuous manufacturing processes like optical fiber coating.

Tetrimide™ MW possesses enhanced mechanical toughness and adhesion to metal substrates for ultra-high temperature enameled wire. This polyimide has 50 % more elongation than Tetrimide™ ICP and is also processed from the poly(amic acid) precursor.

Tetrimide™ SCP offers revolutionary ease-of-use to users of polyimide optical fiber in avionics, aerospace, and medical applications. This innovative polyimide is solvent processable and applied from a pre-imidized polymer solution. Current commercial polyimide coatings are very difficult to strip from the fiber or wire, requiring expensive stripping devices or chemical stripping with hot (150 °C) sulfuric acid. For this reason, the aerospace industry opts to terminate polyimide optical fibers without stripping the coating, a practice that prevents the use of single mode fiber. The Tetrimide™ SCP coating allows the polyimide coating to be stripped from the fiber with specific, benign solvents while maintaining thermal stability more than an order of magnitude greater than industry standard polyimide coated fiber and retaining resistance to common avionic fluids. These improvements translate to increased reliability, greater ease-of-use, and reduced cost of ownership for avionic fiber systems through improved thermal performance and more facile connectorization.

2 EXPERIMENTAL

2.1 Polymer Synthesis

The Tetrimide™ polyimide coatings were synthesized using conventional polymerization techniques. The aromatic dianhydride monomers were added to a solution of aromatic diamines in n-methyl-2-pyrrolidone (NMP) with a total solids concentration of 20 weight percent.

For Tetrimide™ ICP, which is produced as a poly(amic acid) (PAA) solution, the resulting mixture was stirred until a constant solution viscosity was observed, typically 24 hours, and then diluted to the appropriate solution viscosity for each application, which ranges from 6,000 to 10,000 centipoise (cP).

For the Tetrimide™ SCP coating, which is produced as a pre-imidized polymer solution, the PAA solution is heated to above 200 °C while removing the water that evolves from the imidization reaction until the polymer is fully converted and at the appropriate solution viscosity for the target application.

2.2 Film Preparation

Films were prepared using a temperature controlled Erichsen casting table. The Tetrimide™ solutions were cast at 60 °C with a 12-mil bird bar at a rate of 15 mm/sec. The films were dried at 60 °C for 1 hour, 140 °C for 15 minutes, and then transferred to a curing oven. The curing schedule was comprised of a ramping to 400 °C at 5 °C/min, a 10-minute dwell at 400 °C, and then slowly cooling to room temperature. Curing was performed in a nitrogen atmosphere. This procedure yielded 50 ± 5 µm thick films.

A Kapton® HN film was purchased from McMaster Carr for comparison to the Tetrimide™ films in isothermal mass loss and hydrolytic stability.

2.3 Thermal Analysis

Thermal analysis was performed using a TA Instruments Q500 thermal gravimetric analyzer (TGA). A small sample (approximately 25 mm^2) of the polyimide film was cut or punched from the films and analyzed in a platinum TGA pan.

For isothermal analysis, the polymer sample was raised to the isothermal temperature at 10 °C/min in a nitrogen atmosphere, and then gas inlet was changed to dry air. The isothermal was held until 1000 minutes or until 20 % mass loss was obtained, whichever occurred first.

Thermal lifetime projections were performed as described by Stolev et al [2]. For polyimide coated optical fiber, the fiber was chopped into 4 to 5 mm lengths then loaded onto the TGA pan. Dynamic TGA scans were performed at 2, 5, 7, and 10 °C/min in an air atmosphere (30 mL/min) to 700 °C. The mass of the glass fiber, taken as the minimum mass above 600 °C, was subtracted from the TGA data. Lifetime projections were calculated with a failure criterion of 20 % mass loss. All lifetime analyses possessed correlation factors greater than 0.99 for the Arrhenius relationship of time and rate of mass loss.

2.4 Hydrolytic Stability

Hydrolytic stability was studied by evaluating the polyimide films for change in mechanical properties according to ASTM D882 with respect to hydrolysis time. Strips of film were cut to a width of 0.5 inch and length of at least 6 inches. Mechanical analysis was performed with an Instron universal mechanical tester on a 4-inch gauge length at a rate of 0.5 in/min. At least three film samples were tested for each material and hydrolysis time.

Hydrolysis was performed as described in technical literature for Kapton® and other polyimide films. The film strips were submerged in deionized water at 90 °C inside of borosilicate flasks for up to 16 weeks. Samples were periodically removed and tested for mechanical properties.

3 RESULTS AND DISCUSSION

As previously stated, the downhole conditions in oil and gas wells present one of the most aggressive thermal and chemical environments that polymer coating experience. For this reason, the Tetrimide™ coatings were benchmarked against harsh environmental polyimide coated optical fiber.

In order to estimate the useful life of the Tetrimide™ coatings at high temperature and directly compare their performance against other materials, thermal lifetime analysis was performed on the Tetrimide™ polyimide coatings and six commercial polyimide coated optical fibers that are sold into the oil, gas, and medical fiber markets. As shown in Figure 1, the Tetrimide™ ICP and Tetrimide™ SCP coatings provide similar thermal performance and significantly outperform competitive coatings.

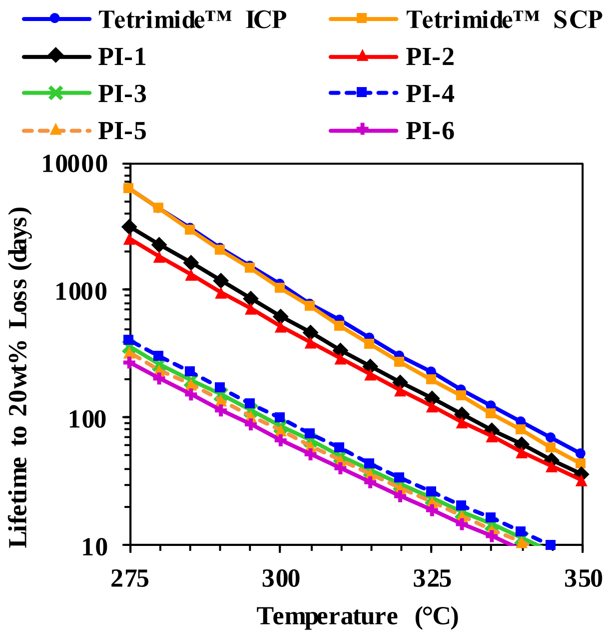

Figure 1: Lifetime projections for the Tetrimide™ coatings and six commercial polyimide optical fiber coatings. Projections were prepared as described in by Stolev et al in air with a failure criterion of 20 % mass loss [2].

While real useful life requirements differ in both service temperature and longevity from one application to another, a service life of 20,000 hours (833 days) is often used for continuous service temperature benchmarking. Considering this longevity metric, the Tetrimide™ coating provide a continuous service temperature of 305 °C, while two of the tested commercial optical fibers provided a service temperature of 295 °C and all others could only be rated for temperatures less than 265 °C.

Alternatively, if considering a use temperature of 300 °C, the Tetrimide™ coatings provide an estimated useful life of 1100 days, compared to 630 days for the nearest commercial fiber – a difference of more than a year of service life.

In other applications such as flexible resistive heaters or corrosion resistant coatings near compulsion elements, excursions to extreme temperatures tend to limit the useful life more than continuous at standard operating conditions. To evaluate excursion stability, the Tetrimide™ coatings were compared to Kapton® HN film in isothermal testing at temperatures of 400 °C and 450 °C in an air atmosphere. A criterion of 20 % mass loss was again used to represent a point at which the mechanical integrity of the polymer has been substantially degraded.

As shown in Figure 2, the Tetrimide™ films lost mass slower than the Kapton® HN film, which lost nearly 10 % of its mass in 1000 minutes at 400 °C and 20 % of its mass in 300 minutes at 450 °C. Comparatively, the Tetrimide™ films retained 80 % mass for more than 450 minutes at 450 °C, and Tetrimide™ SCP lost only 2 % mass in 1000 minutes at 400 °C. In applications where intermittent and short excursions to very high temperatures limit longevity of the device or system, the improved mass retention of the Tetrimide™ materials presents the potential for multiplicative increases in overall useful life.

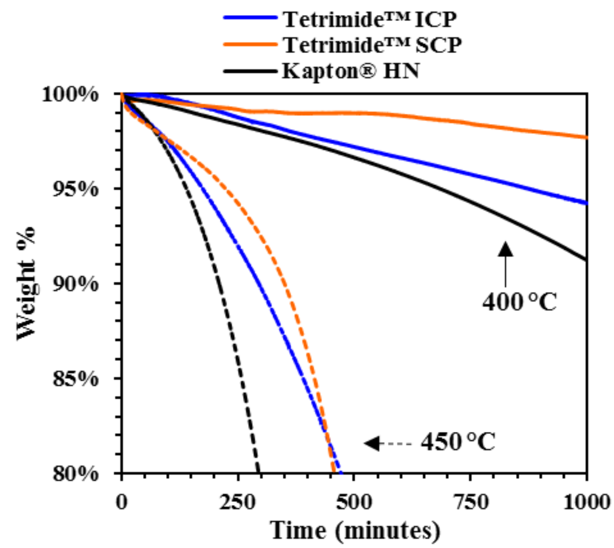

Figure 2: Comparison of mass loss in the Tetrimide™ films to Kapton® HN at 400 °C and 450 °C in air.

Hydrolytic stability at elevated temperature has long been an Achilles' heel for polyimide materials. Degradation of the polymer occurs in a two-step reaction in which the polyimide cycle is broken to regenerate the amic acid linkage or other species, which then readily degrade and break the polymer chain [3].

The hydrolytic stability of the Tetrimide™ materials was compared against Kapton® HN by evaluation of change in mechanical properties with respect to time in 90 °C water over 16 weeks. Tensile modulus, yield strength, and elongation at break were periodically evaluated for at least three samples of each material during the test period.

In general, the mechanical properties of the films exhibited a small degree of change through the hydrolysis test with the exception of elongation at break. Modulus increased by 7-10% and yield strength decreased by 5-7 % for all three materials, but as shown in Figure 3, elongation at break dropped more significantly. The average elongation of Kapton® film rapidly decreased from 59 % to less than 30 % in 500 hours and eventually dropped to only 10 %. By comparison, the Tetrimide™ films lost elongation roughly linearly with respect to time and showed more moderate decreases of their original values; 40 % reduction for Tetrimide™ ICP and 51 % reduction for Tetrimide™ SCP.

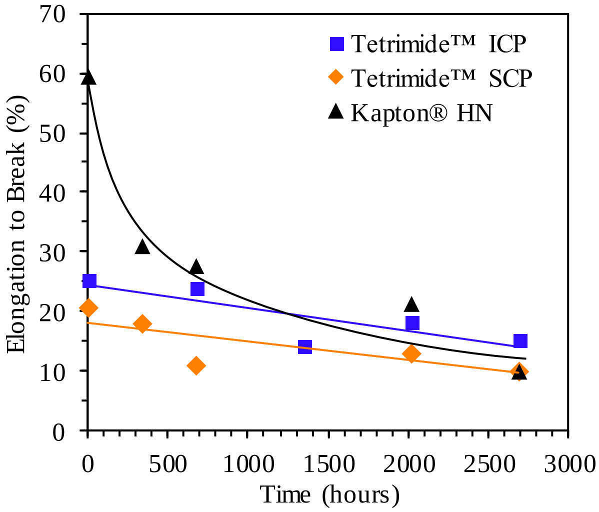

Figure 3: Elongation at break with respect to time at 90 °C in deionized water for Tetrimide™ coatings and Kapton® HN film.

The cause of the difference in degradation behavior between the Tetrimide™ films and the Kapton® film may be related to either intrinsic differences in polymer stability or the presence of extractable small molecules, such as plasticizers or oligomers, in the Kapton® film that increase its initial elongation.

A summary of the average mechanical properties for each of the polyimide films after 16 weeks of hydrolysis is given in Table 1. While the final elongation of the Tetrimide™ and Kapton® films were found to be similar, it is important to consider the material toughness of the hydrolyzed polymers, defined as the total amount of energy per unit volume that a material can absorb before failure. The mechanical properties after hydrolysis show that the Tetrimide™ ICP film provides exceptional toughness even after 16 weeks of hydrolysis, exceeding the toughness of Kapton® film by more than 3X.

Polymer	Yield Strength [3%] (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)	Material Toughness (MPa/mm)
Tetrimide™ ICP	209	7279	15.2	565
Tetrimide™ SCP	78	3923	9.8	164
Kapton® HN	120	3389	9.9	182

Table 1: Summary of mechanical properties after 16 weeks (2700 hours) exposure to 90 °C water for Tetrimide™ coatings and Kapton® HN film

4 CONCLUSIONS

Analysis of both long-term and short exclusion service temperatures successfully differentiated between various polyimide materials. The result showed that the Tetrimide™ polymers provide around twice the useful lifetime compared to the best current commercial materials at relevant service temperatures.

Similarly, testing of long-term hydrolytic stability at 90 °C showed that the Tetrimide™ materials possessed a lower rate of deterioration. Furthermore, the Tetrimide™ ICP polymer provided 3X higher greater material toughness after hydrolysis compared to Kapton® HN.

This material is based up work supported by the National Science Foundation under Grant No. 1330948.

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