A New Class of Perfluoropolymers: High-Temperature Epitaxial Co-Crystalline (ECC) Perfluoropolymer Resins

Jacob Lahijani, Maria P.-Samija, George M. Pruce, John L. Netta

DuPont Chemicals and Fluoroproducts
Fluoropolymer Solutions
Wilmington, Delaware
302-999-2511 jacob.lahijani@usa.dupont.com

Abstract

DuPont has developed a new class of high-temperature, melt-processible perfluoropolymers. This new class demonstrates all of the beneficial properties typical of perfluoropolymers, including chemical resistance, permeation resistance, low dielectric constant, low dissipation factor, and low coefficient-of-friction. However, the new class has enhanced functionality, which primarily results from epitaxial co-crystallization (ECC) within the polymer during post-heat treatment at temperatures approaching 300°C. The melting point for this new resin, prior to heat treatment, is approximately 320°C.

The new high-temperature perfluoropolymer (HTP) resin targets extreme applications requiring a high-temperature rating of up to 300°C in combination with excellent electrical properties and/or chemical resistance. The HTP resin can be melt-processed using standard high-temperature fluoropolymer equipment and at standard operating speeds. In addition, the processing window is large; wire constructions from 5 mils on AWG 30 gauge to 75 mils on AWG 4 gauge have been routinely produced. HTP resin, and products made from it, demonstrate enhanced properties (i.e., modulus retention, improved fatigue resistance, better permeation resistance and higher melting point) when subjected to a post-heat treatment. Qualification trials are underway in a number of applications in the oil and gas, semiconductor, military/aerospace and CPI industries.

Keywords: High-temperature perfluoropolymer; heat aging; melt-processible; thermal transformation; epitaxial co-crystalline; ECC; ECA; HTP resin

1. Introduction

Significant demand has been expressed for a high-temperature polymer that is melt-extrudable, has physical, electrical, and chemical properties characteristic of polytetrafluoroethylene (PTFE) and can operate at prevailing temperatures up to 300°C. In response to that demand, DuPont developed a high-temperature perfluoropolymer for potential use in applications up to 300°C. While HTP resin is still in the early stages of development, it represents a potential step-change in perfluoropolymer performance. The new polymer has excellent chemical resistance, low permeation, and excellent electrical and physical properties commensurate with traditional perfluoropolymers. Testing to confirm the continuous-use temperature rating is underway. This discussion will review some of the unique properties of the HTP resin which are currently known and where those unique properties may be of benefit.

2. HTP Resin Melt Point and Thermal Transformation Behavior

The new HTP resin can be easily processed into shapes, tubes or wire coatings. Once processed and exposed to temperatures in excess of 290°C, the polymer is transformed via epitaxial co-crystallization, which gives the HTP resin its final properties. A melt-point shift is indicative of the co-crystallization effect. Figure 1 demonstrates that upon heat aging and thermal transformation, the HTP resin's melting point increases by as much as 5°C. HTP resin has a melt point of 320°C ± 3°C as measured by differential scanning calorimetry (DSC). After heat-aging at 315°C for 48 hours, HTP resin undergoes a thermal and structural transformation and demonstrates a melt point of 325°C ± 3°C. Figure 2 shows the drop in melt-flow rate (MFR) that occurs with post-treatment. The MFR drops and levels out around 1.0, further confirming the shift in crystalization in the polymer.

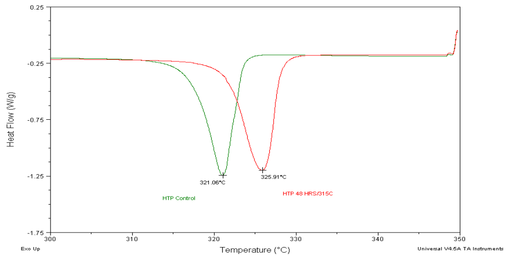

Figure 1. DSC (First Heat Cycle) of HTP Resin

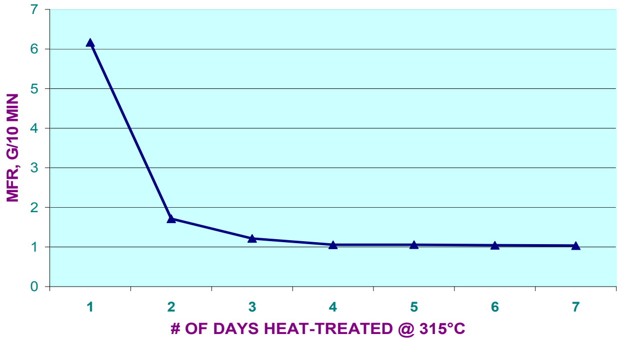

Figure 2. MFR of HTP Resin vs Heat Aging

3. Fatigue and Toughness

Figure 3 demonstrates an increase in flex life/stress-crack resistance post-thermal treatment that is obtained with the new HTP resin. After heat aging, the MIT Flexural Test shows a dramatic increase in stress-crack resistance. This increase in performance offers extended versatility—for example, longer life for current components, the possibility of reducing the wall thickness of parts while maintaining current performance and the ability to use components at higher operating temperatures above the range of current perfluoropolymers.

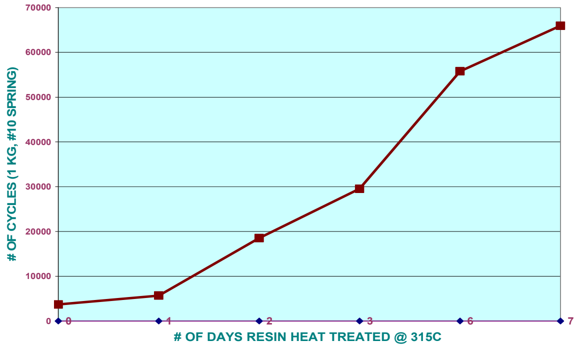

Figure 3. Fatigue/Toughness of HTP Resin vs Heat Aging

4. Modulus Retention

The new HTP resin demonstrates exceptional retention of modulus over time as illustrated in Figure 4. Modulus retention is desirable for high-temperature applications to help prevent creep and deformation, so that wires will retain proper insulation dimensions around the conductor and component parts are less likely to deform under mechanical loading. This level of modulus retention far out-performs current perfluoropolymers.

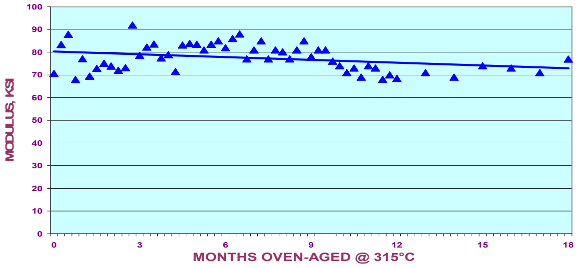

Figure 4. Modulus of HTP Resin vs Time at Temperature

5. Permeation Resistance

In environments where wires, tubes or molded parts are exposed to chemicals, low permeation through the coating is critical to performance. Figures 5, 6 and 7 demonstrate reduction in permeation when HTP resin films treated at 300°C are exposed to CH_4, CO_2 and O_2 respectively. Higher permeation resistance, a result of changes in polymer morphology during heat treatment, is a significant improvement approximating a 50% reduction in permeation over other perfluoropolymers.

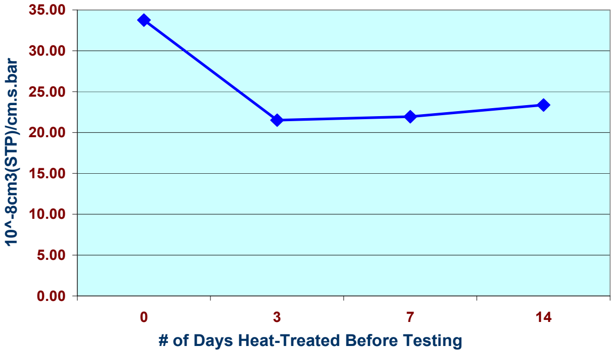

Figure 5. CH_4 Permeation of HTP Resin vs Time at Temperature

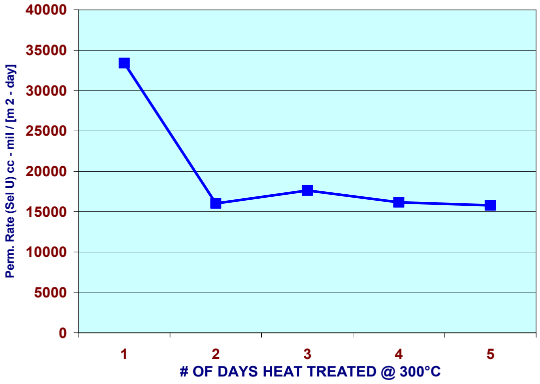

Figure 6. CO_2 Permeation of HTP Resin vs Time at Temperature

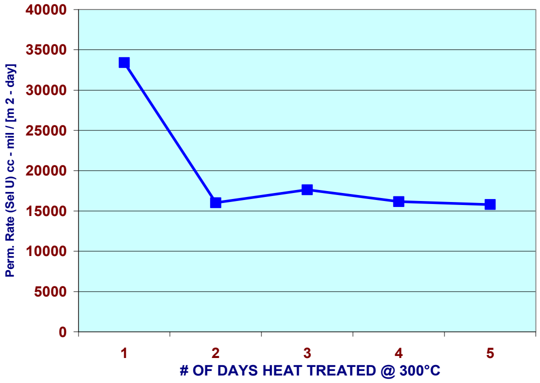

Figure 7. O_2 Permeation of HTP Resin vs Time at Temperature

6. Chemical Resistance

Figures 8 to 11 demonstrate the chemical resistance properties of the new HTP resin to a strong base (35% ammonium hydroxide at 23°C) and a strong acid (98% sulfuric acid at 150°C). The HTP resin demonstrates very little or no loss of tensile strength, some loss in elongation, and a moderate increase in modulus. These results are equivalent to the generally exceptional performance of other perfluoropolymers.

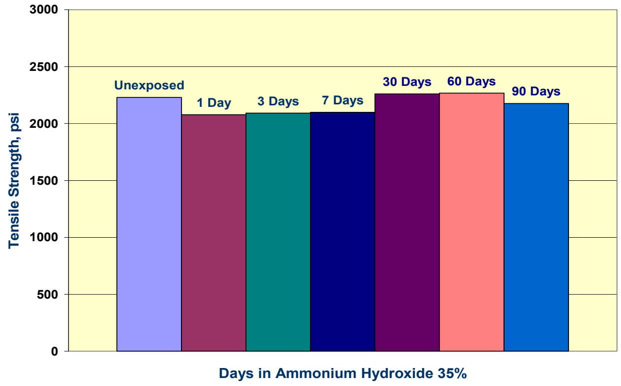

Figure 8. Tensile Strength of HTP Resin in 35% Ammonium Hydroxide at 23°C

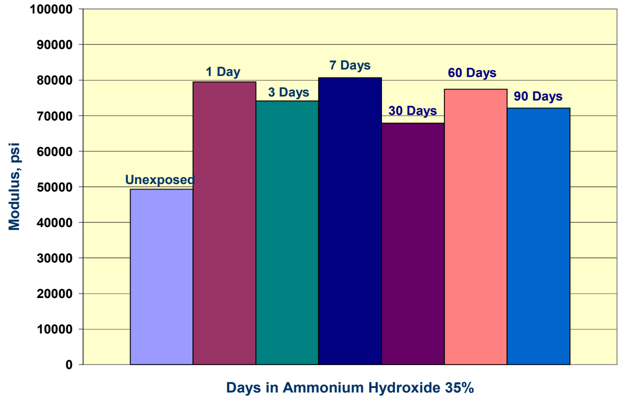

Figure 9. Modulus of HTP Resin in 35% Ammonium Hydroxide at 23°C

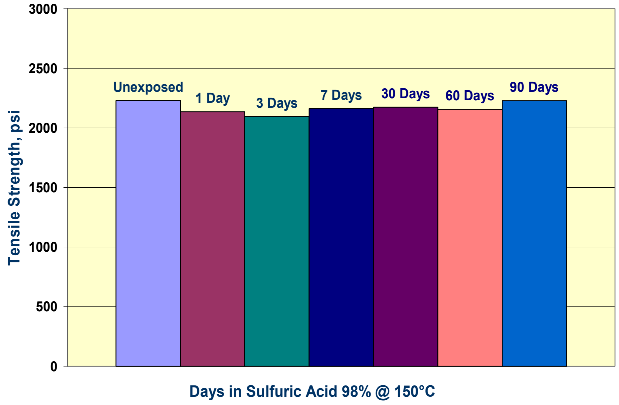

Figure 10. Tensile Strength of HTP Resin in 98% Sulfuric Acid at 150°C

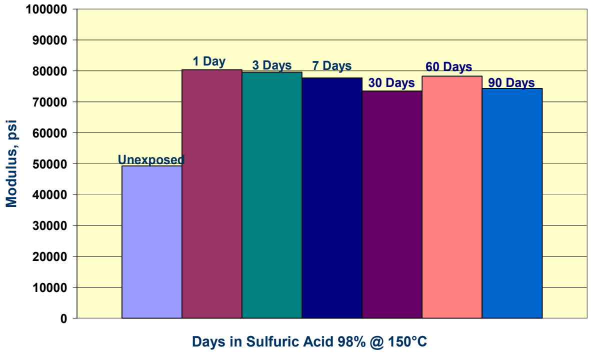

Figure 11. Modulus of HTP Resin in 98% Sulfuric Acid at 150°C

7. Electrical Properties

The new HTP resin demonstrates excellent electrical properties typical of perfluoropolymers. Figure 12 illustrates a lower dissipation factor for HTP resin than standard industrial perfluoroalkoxy (PFA). This level of electrical performance makes the new HTP resin suitable for almost all electronic applications and many power applications.

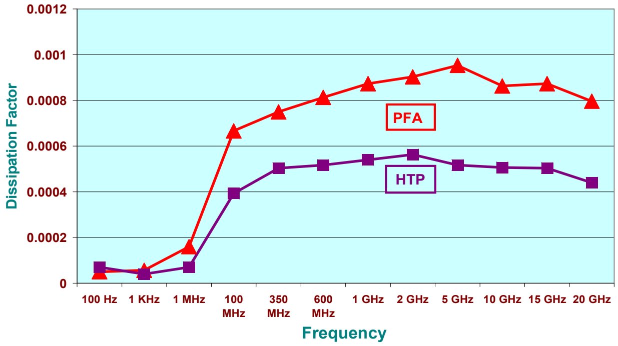

Figure 12. Dissipation Factor of HTP Resin

8. Applications

The new HTP resin drives back the design boundaries in very harsh environments and expands currently available options in wire, tubing and molding once thought to be unattainable with perfluoropolymers. Previously, an upper continuous-use temperature of 260°C was the ultimate limit for exceptional electrical and chemical performance in a perfluoropolymer. HTP resin has the potential to extend the operating range to 300°C.

In the oil and gas market, where wells are being drilled in hotter and deeper environments, the new HTP resin can help carry power to equipment in the well, in addition to facilitating high frequency signals for monitoring the wells. This application would hold true in conventional oil and gas, steam-assisted gravity drainage (SAGD) extraction, and geothermal markets.

In the automotive market, where temperatures underneath the hood continue to rise, the new HTP resin has the potential to stand up to a combination of high temperatures and multiple fuel mixtures. Where signal cables must perform under extreme conditions and in extreme environments, such as in military and aerospace applications, the new HTP resin could allow cable routing in areas previously thought to be outside conventional boundaries. Design options may now be capable of addressing limited space applications with high demand.

In the CPI and semiconductor markets, increased chemical resistance and low permeation could potentially enable new designs with the ability to run at higher temperatures or perform with thinner walls.

The new HTP resin should find its way into a number of well-established markets, exponentially expanding the useful range of current products and catalyzing the emergence of new technologies.

9. Conclusions

The new DuPont high-temperature resin represents a significant breakthrough for perfluoropolymer technology in extreme environments. While HTP resin is still in development, it offers great potential for enhancing the range of applications where perfluoropolymers are currently used, as well as opening up opportunities in new and emerging applications. The potential applications of this new class of HTP resins are expected to grow markedly over the next five years as product designers become more familiar with the unique performance attributes augmenting the well-recognized electrical and chemical properties and extreme performance.

10. Remarks

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11. Author

Jacob Lahijani is a Senior Research Scientist with DuPont Fluoropolymer Solutions, located in Wilmington, Delaware. His primary focus is the development of high-performance perfluoropolymer materials for wire and cable and semiconductor applications. During his 30-year career with DuPont, Jake has served in a number of research positions working in the areas of advanced polymeric materials and fluoropolymer processing. Jake holds a Ph.D. in Chemical Engineering from The Pennsylvania State University. He can be reached at jacob.lahijani@usa.dupont.com.