Abstract

High temperature fluoropolymers are a likely material of choice for critical components in demanding applications. Fabrication methods for producing three-dimensional, thin-walled, hollow objects using polytetrafluoroethylene (PTFE), perfluoroalkoxy (PFA), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE) and ethylene chlorotrifluoroethylene (ECTFE) include assembling films and molded fitments utilizing welding operations. An alternate technique has been developed which eliminates the need for these assembly steps. This method rapidly produces containers suitable for environments between -109°C (-165°F) and 177°C (350°F) while exhibiting superior mechanical, optical, gas barrier and chemical resistance properties.

Background

Application opportunities for fluoropolymers have been developed since the discovery of polytetrafluoroethylene (PTFE) in 1938. A new industry has evolved due to the unique properties of inertness and durability in applications not capable of being served by other polymers. PTFE is unlike other polymers due to its molecular structure of carbon and fluorine. Fluorine is known as the most electronegative of the bondable elements. These strong bonds give PTFE and its derivatives inert and durable properties [1]. A fully fluorinated molecular chain prevents carbon bonding with other elements, hence giving PTFE the non-stick “slick” property for which PTFE is most famous. This is also how it is capable of withstanding high and low temperatures without losing strength. Due to fluorine’s chemically inert condition, solvent bonding of fluoropolymer film is problematic. Melt bonding by other methods such as radio frequency and ultrasonic welding, melt bonding, etc. is only partially successful.

The high melting point, thermal stability, low coefficient of friction, low water ab/adsorptivity, excellent weatherability, and purity are valuable properties of PTFE [1]. PTFE is not melt processible which limits its process options. This has given impetus for material scientists to develop methods to alter its strong molecular bonds to fluorine by alternating fluorine with other elements such as oxygen, hydrogen and chlorine, making partially fluorinated melt processible polymers such as ECTFE, and by branching carbon to carbon and bonding fluorine, or carbon to oxygen bonding then to a group of carbon and fluorine resulting in fully fluorinated and melt processible polymers such as FEP and PFA. These polymers are known as fluoroplastics. Applications for fluoroplastics have grown significantly with each new discovery of a method by which to process them. This sometimes requires additional development of the material science to suit the process method to achieve desired results.

Current methods for producing these fluoropolymer thin-walled containers are labor intensive. These methods utilize sheets of PTFE which is compressed, extruded, sintered, skived, and then calendared to a thickness of 2 to 15 mils. Other methods employ extrusion processes to create fluoroplastic sheets and films of the same thickness (2 to 15 mils). The film is cut to size and components necessary for filling and dispensing are assembled together with the film to produce a bag using laser or heat welding methods. In the case of high temperature fluoropolymers, the weld temperatures can exceed 360°C (680°F) which require specialized exhaust systems to allow for safe evacuation of fumes due to the material out gassing at molten temperatures. All assembly is performed in a clean room environment to prevent the potential of contamination with particles inside the containers.
Complete cycle times to achieve a final product assembly could be as much as 45 minutes per container.

There is a desire in medical and semiconductor markets for an economically-acceptable, high-purity, collapsible container for the packaging of valuable materials. This has inspired research into suitable methods and fluoropolymers to produce these products using a single, efficient process step resulting in a thin-walled container with thicker fitments and connections attached. This paper details the results of the trials of various materials in the development of this technology.

**Methods**

A collaborative team was created consisting of representatives from the manufacturer (FAST Group Houston), a material supplier and process equipment suppliers. The team determined it was necessary to examine multiple fluoroplastics electives in order to discover a resin most suitable for the candidate processes. This involved examination of numerous fluoropolymer materials in several equipment types during the initial discovery stage. During these trials, many resins were determined unsuitable as they did not perform acceptably in the candidate processes.

Using current market literature, the team developed a set of criteria closely matching products manufactured as fluoropolymer welded containers [TABLE 1]. These specifications were used to evaluate containers manufactured in a series of trials. The trials were differentiated by the materials and process specifics utilized during manufacturing.

The first trial produced three-dimensional thin-walled hollow products which were screened by testing physical and mechanical properties. While the processing equipment was incapable of consistently producing acceptable parts using fluoroplastics, the results from this process method proved promising.

The second trial utilized equipment modified specifically for use with high temperatures and the corrosive nature of molten fluoropolymers. The equipment was capable of producing parts with greater clarity and fewer surface imperfections than the previous trial. However, inconsistent cycles prevented further development using this equipment. The mechanical, physical and gas barrier properties of these parts (containers) were tested as detailed in the following Analysis section.

Initially, the third trial did not produce acceptable containers; however, the equipment utilized in this trial was capable of a fast and steady cycle. Given the consistency of the process and the results of previous mechanical property tests, additional modifications of both the equipment and resin were warranted. Once these modifications were complete, more samples were produced. These were sealed in-process and sent for particle content analysis, trace metals, total organic carbon as well as organic and inorganic extractables.

The incremental improvements of the methods employed during the third set of trials resolved the limitations of the equipment and techniques. The material selection was reduced to the best performing candidate. The process for this grade of fluoropolymer with the most consistent cycle was documented and used as the base line target for formulating a new generation of the most suitable material.

The fourth and final set of trials utilized the best performing process and parameters in combination with the new generation of the most optimal of previously tested material, now referred to as Fenner High Temperature Fluoropolymer (FHTF). As in previous trials, containers manufactured during these trials were collected and tested to the specification. The analyses and results of all trials are discussed in the following sections.

**Analysis**

The initial trials of all candidate materials were screened for physical and mechanical properties to confirm that the process could produce a three-dimensional thin-walled (2 to 15 mils) container with a thick (10 to 20 mils) fitment. The analysis performed on samples from various trials is displayed in Table 2. Included in the screens were specific gravity (ASTM D792-08), water absorption (ASTM D570-98), yield strength, tensile at break and tensile modulus (ASTM D882-09). ASTM D-1434 was used to check the gas barrier properties of the film in oxygen (O₂), carbon dioxide (CO₂) and water (H₂O) vapor using an independent testing facility.

The purity of the material was characterized by a series of tests. Solvents were soaked in containers for 90 days. At 30 day intervals, the gas chromatography (GC) technique was used to analyze samples of the soak solvent for organic extractables. Additional samples of the soak solvent were collected to characterize trace metals using inductively coupled plasma mass spectrometry (ICP-MS). A total organic carbon (TOC) analysis determined the mass of organic (oxidizable) carbon deposited all exposed surfaces. This analysis was carried out in a semiconductor lab utilizing a proprietary TOC analyzer using the deionized water (DIW) stored in the fluoropolymer package for 7 days.
Purity analyses via particle counts were performed using a Rion KL-27 particle analyzer. Deionized water was the initial solvent for these analyses. Propylene Glycol Methyl Ether Acetate (PGMEA) and cyclohexanone were also used for this test. This analysis was performed on trials where samples were sealed in-process. The results were the basis for the determination of improvements caused by changes of the material, equipment and process. During these analyses, the solvent was used as a control to ensure its purity.

While not an initial goal, it became evident as testing progressed that the optical clarity of the fluoropolymer would be an attractive characteristic of the material. The initial product trials in the first and second processes resulted in cloudy parts with many imperfections on the surface. As the development matured, parts were crystal clear and had no surface imperfections. Parts were sent to a lab to verify haze (ASTM D1003-07) and light transmission (ASTM D1003-11) properties.

Some fluoropolymers are incapable of maintaining properties after sterilization through gamma irradiation due to cross linking of the polymer chains [6]. One of the market potentials for high purity packaging using these products was in biopharmaceutical manufacturing. This market requires sterilization of the product. Samples were gamma irradiated at 25 kGy and used for protein adsorption testing where film was cut and made into pouches in which testing aliquots were soaked for three weeks. A supplier specializing in investigational investigations for adsorption of bovine serum albumin (BSA) and rabbit immunoglobulin (IgG) soaked and tested the film with and without gamma exposure. The mechanical and physical properties of gamma irradiated material were also tested. These tests were for specific gravity (ASTM D792-08), water absorption (ASTM D570-98), yield strength (ASTM D882-09), tensile at break and tensile modulus (ASTM D882-09).

**Results**

Test results for the typical mechanical and physical properties matched published data for the base materials. These results implied that the process and parameters were not affecting the properties of the materials. All mechanical properties on irradiated and non-irradiated films from the fourth trials utilizing the optimal material (Fenner High Temperature Fluoropolymer) exhibited similar properties.

Samples from the first trial tested high for the gas transmission rate using nitrogen. The material used for the initial prototypes did not perform well in other analyses, so it was removed as a candidate. Upon testing of additional lots, mixed results with gas transmission rates were observed. The high variations between thick- and thin-wall sections were thought to be a source of the variations. For the final tests of the Fenner High Temperature Fluoropolymer, a nominal wall thickness was determined to be most suitable for the gas transmission rate. The results for the Oxygen transmission rate were 33.7 cc/m2/day; a result superior to competitive PFA and PVDF products. Water vapor transmission rate resulted in .046 g/m2/day [Figure 1] which was the lowest of any discovered data on fluoropolymer film. The carbon dioxide transmission rate was comparable to other fluoropolymer films with a rate of 70 cm2/m2/day [Figure 2].

Organic extractables were never detected above the 1000 ppb in any of the solvents that were used in the tests. Initially, there were trace metals detected above allowable levels, however analysis after the final resin formulation and equipment modifications showed these levels well below specification.

Total organic (oxidizable) carbon analysis detected less than 5 ppb at every test, but particle contamination of the containers was shown to be dependant upon the formulation of the resin. The first resin tested for particle contamination had very high counts, but the second resin had minimal counts in Cyclohexanone. The PGMEA results were the same as the Cyclohexanone, and the DIW had high counts for both resins. Improvement in the DIW results through successive generations can be seen in Figure 3. Cyclohexanone and PGMEA exhibited similar improvements.

The thin-walled containers produced during the final trials were used to characterize the optical clarity of the Fenner High Temperature Fluoropolymer. Results for optical clarity included Haze and Transmission, shown in Figure 4 and Figure 5 respectively. The results for haze for PVDF and the Fenner High Temperature Fluoropolymer were compared to Plexiglas®. In this comparison the Fenner material was shown to have the lowest haze percentage. Light transmission results comparing the Fenner High Temperature Fluoropolymer to borosilicate and soda-lime glass illustrated that while the fluoropolymer blocks low-wavelength visible light, the material was comparable to glass from the mid-visible spectrum into the infrared spectrum.

Results from the protein adsorption testing are shown in Figure 6. Unfortunately, similar data was not available for comparison to other fluoropolymers. A comparison with commercially available ethyl vinyl acetate (EVA) film and ultra low density polyethylene (ULDPE) film revealed that both had significantly higher adsorption rates than the fluoropolymer film.
tested in the BSA. Similar results were observed for the IgG.

**Conclusions**

The process and material developed can produce robust thin-walled containers using high-temperature fluoropolymers having all the desired properties of these materials. Parts can be manufactured without secondary operations and can be sealed during the cycle for pristine internal cleanliness, thus eliminating the need for post-mold cleaning. Further, the method can produce products with low organic and inorganic extractables and minimal particle counts in harsh solvents, hence suitable for applications in semiconductor and biopharmaceutical manufacturing.

These containers exhibit excellent properties for gas barrier, water vapor transmission, clarity, and purity all within a thin-walled part configuration. Additionally, the low protein adsorption of these products is superior to that of glass. With lower costs, less complexity and improved properties, this process and material combination represents a novel and superior alternative for current methods of thin-walled fluoroplastic container fabrication.

**References**


**Keywords:** Fluoropolymer, PTFE, Packaging, containers, high-purity, high-temperature

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<th>Test</th>
<th>Method</th>
<th>Media</th>
<th>Conditions</th>
<th>Acceptance</th>
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<td>Organic Extractables</td>
<td>GC-MS</td>
<td>PGMEA, Cyclohexanone, PGMEA/Cyclo. Mix (70/30)</td>
<td>20C, 3 months</td>
<td>&lt;1000 ppb</td>
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<td>Trace Metals</td>
<td>ICP-MS</td>
<td>PGMEA, Cyclohexanone, PGMEA/Cyclo. Mix (70/30), 5% Nitric</td>
<td>20C, 3 months</td>
<td>&lt;5 ppb per Element &lt; 15 ppb Total</td>
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<tr>
<td>Total Organic Carbon</td>
<td>TOC Analyzer</td>
<td>DIW</td>
<td>20C, 7 days</td>
<td>&lt;10 ppb</td>
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<td>Inorganic Extractables</td>
<td>Ion Chromatography</td>
<td>DIW</td>
<td>20C, 3 months</td>
<td>&lt;15 ppb for Fluorine &lt;0.5 ppb for all others</td>
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<td>Liner Purity</td>
<td>Liquid Particle Counts</td>
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<td>Water, CO2, and O2</td>
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**TABLE 1.** The criteria developed for initial requirements.
TABLE 2. Record of the analyses performed from the various trials.

<table>
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<td>PVDF</td>
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<td>Stedim 40®</td>
<td>ULDPE</td>
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<tr>
<td>Stedim 7®</td>
<td>EVA</td>
<td>EVA1</td>
</tr>
<tr>
<td>Sartorius Stedim EVAM®</td>
<td>EVA</td>
<td>EVA2</td>
</tr>
<tr>
<td>Fenner High Temperature Fluoropolymer</td>
<td>Fluoropolymer</td>
<td>FHTF</td>
</tr>
</tbody>
</table>

TABLE 3. Descriptions of the material identifiers for following charts.

Figure 1. Results of testing the water vapor transmission rate of Fenner High Temperature Fluoropolymer at an independent lab and published data [3,4,5] of three other fluoropolymer films using method ASTM D-1434

Figure 2. Results of testing for Carbon Dioxide transmission rate using independent lab and from published data of three other fluoropolymer films [3,4,5] using method ASTM D-1434
Figure 3. Results from purity analysis using particle counts per milliliter in deionized water (DIW) for four versions of materials that were tested using a Rion KL-27 particle counter by an independent testing lab.

Figure 4. Haze percentage of FHTF compared to PMMA as tested at independent testing facility and Meissner [3] commercially published data using method ASTM D1003-07.

Figure 5. Comparing wavelengths of soda lime glass and borosilicate glass standard data with Fenner High Temperature Fluoropolymer in the visible light spectrum using method ASTM D1003-11 Procedure B.

Figure 6. Results and comparison in test report based on results of protein adsorption on films used in biomanufacturing processes.