

# BIOCOMPATIBLE FLUOROPOLYMERS AND ADVANCES IN INJECTION MOLDING THESE MATERIALS FOR MEDICAL DEVICES, DRUG DELIVERY SYSTEMS AND STORAGE COMPONENTS

Performance Plastics LTD., Cincinnati, OH  
513-321-8404 ppl@performanceplastics.com

## Abstract

Injection molded fluoropolymers provide the chemical resistance and material performance needed for the manufacturing, storage and delivery of next generation cancer and biologic drug technologies. Fluoropolymers barrier properties, thermal properties and low surface adhesion characteristics offer advantages for powder and viscous liquid manufacturing, storage and delivery components.

In the past, fluoropolymer were not often considered for high volume parts with complex geometries due to injection molding process limitations. Developments in mold design and tooling steels combined with new manufacturing equipment and processing techniques now allow the use of these biocompatible materials for high volume drug storage and delivery components.

## Introduction

Polyethylenes, polypropylenes and polycarbonates currently used for drug storage containers and delivery components will struggle to meet future efficacy requirements. Next generation drug technologies are bringing new handling and dispensing challenges because of increased chemical resistance and cytotoxicity issues. Long-term storage solutions that maintain performance and extend shelf life will be required. Improvements in dosage control and minimizing or eliminating the use of silicone coating operations in drug delivery components have also become industry wide concerns. Because of the elimination of traditional injection molding process limitations, product design engineers can now cost-effectively use fluoropolymers inherent material property benefits to address these issues.

## Fluoropolymer Material Benefits

Fluoropolymers are chemically inert and pure generally containing no additives that could contaminate liquids or solids during storage or delivery. Fluoropolymers barrier properties resistance to chemical, enzyme and microbiological attack also eliminate biodegradation issues.

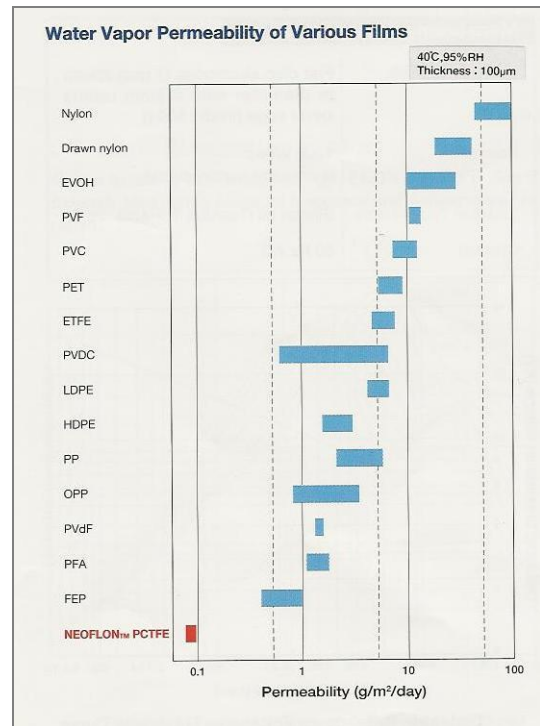


Figure 1. Barrier Properties of Thermoplastics

Compared to current plastics, the barrier properties of fluoropolymers (Figure 1) are exceptional. Aging, even at high temperatures and in the presence of solvents, oils, oxidizing agents, ultraviolet light and other environmental agents, is minimal because fluoropolymers do not use any leachable or degradable stabilizing additives. Fluoropolymers also have a low refractive index and visual appearance that is unchanged after exposure to light. Applications include drug containers and delivery systems components including bottles, vials, syringes and specimen trays.

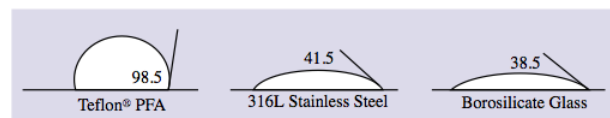


Figure 2. Low Surface Energy Material Comparison

Fluoropolymers have one of the lowest coefficients of friction of any solid material (Figure 2). Low surface energy in its solid state provides an anti-stick, non-wetting contact surface that is hydrophobic and completely resistant to hydrolysis. For sprays and inhalers, fluoropolymer manifolds can minimize drug delivery buildup to assure consistent dosing. Other applications include medical devices, surgical equipment, syringes, plungers, valves and connectors.

### Fluoropolymer Processing

Concerns about fluoropolymer material application and processing limitations are prevalent. It is still generally thought that sintering or machining are the only viable alternatives because of corrosion and thermal issues during the traditional injection molding process. Temperatures of molds and equipment can range from 300°F to 800°F. Highly toxic gases produced have an extremely corrosive effect on both molds and machines. Mold deterioration, runner system scrap rates, melt fracture, delamination and dimensional limitations of traditional gating methods. New fluoropolymers, processing equipment and manufacturing methods have been developed to address both by-product and material waste issues.

### Tooling Challenges

Corrosion of molds and machines has been the primary manufacturing issue. The four main types of products formed during the molding process decomposition are fluoroalkenes, hydrogen fluoride, oxidation products and low molecular weight fluoropolymer particulate. Figure 3 illustrates the severe intergranular chemical attack or hydrofluoric acid on SS420 – a common corrosion resistant mold steel.

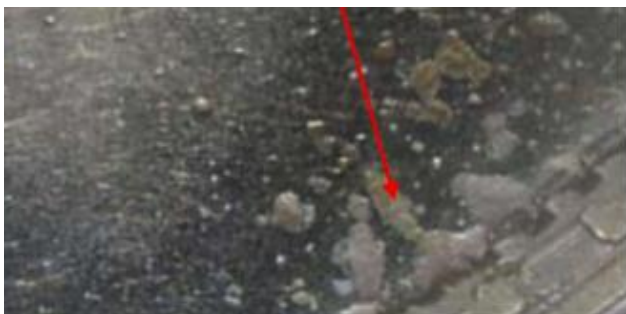


Figure 3. Hydrofluoric Chemical Attack on Stainless Steel

An accelerated corrosion test was developed by Performance Plastics to evaluate other alloys that could survive hydrofluoric attack while maintaining mechanical

performance. Figure 4 details the results of the metallographic analysis of the effect of hydrofluoric acid on each material. The lower the surface alloy depletion thickness, the higher the corrosion resistance of the alloy. *PPL Tip Alloy B* showed an improvement of 250 times the resistance when compared to SS420.

Material	Alloy Depletion	Notes
PPL Tip Alloy B	0.0002	minor phase change at surface
PPL Mold Alloy C	0.00097	Surface Phase change
PPL Mold Alloy B	0.0047	Etched Surface Sev
PPL Mold Alloy A	0.0055	Uniform Surface Alloy Depletion
SS420 Baseline Material	0.05	Severe Intergranular Attack

Figure 4. Metallographic analysis of mold metals

To evaluate the legitimacy of the accelerated test, an empirical test was conducted on four molds over a 12-month period. The area of the mold used to evaluate the materials corrosion resistance was the thermal gate. Tips were fabricated and base-lined against the OEM supplied materials. Part weights were in the 1.0 - 1.50 gram range with average wall thicknesses of 0.3 mm. Fill pressure required to produce these parts was approximately 2,300 bars.

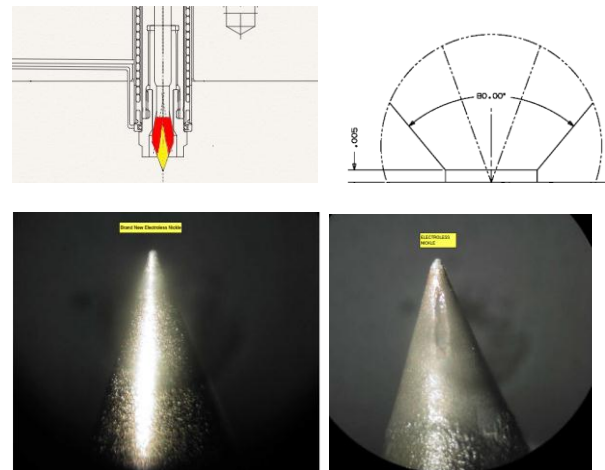


Figure 5. Thermal Gate Tip application and Test Effects

Figure 5 illustrates the area of the mold that the thermal tips are used in and shows the visual effects of pyrolysis due to the hydrofluoric acid. The results of the test are shown in Figure 6. The number of cycles was determined by gate quality, fill pressures, measurement of the tips from design intent and visual inspection.

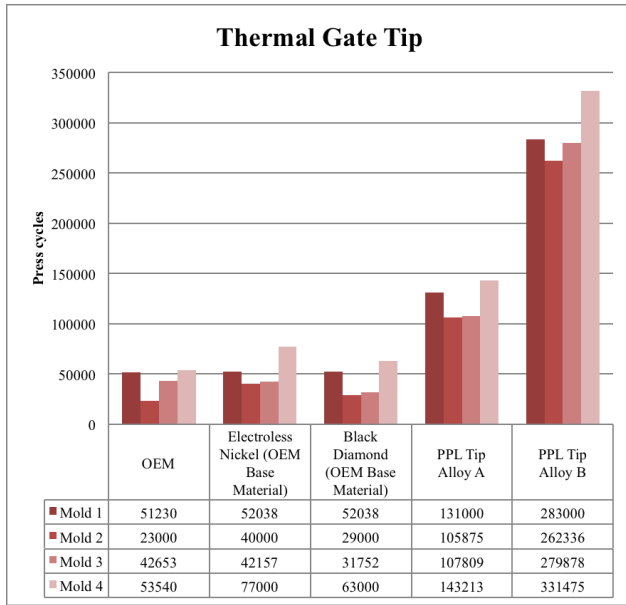


Figure 6. Thermal Gate Tip Test Results

At 43,000 the baseline OEM material showed the fewest cycles. PPL Tip Alloy B showed the best performance averaging 290,000 cycles - a 7-time life improvement.

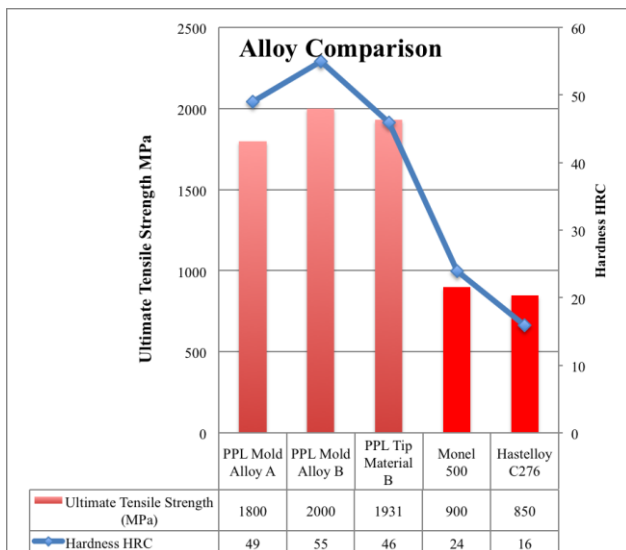


Figure 7. Alloy Comparisons

As shown in Figure 7, the significance of the study shows materials developed by PPL provide significant advantages over materials such as Hastelloy, Inconel, and Monel which are typically used in injection molding of fluoropolymers. While these super alloys have excellent chemical resistance, high nickel content making them significantly softer with surface hardness of only 16 HRC (Rockwell Hardness Scale). This restricts the types of geometries that can be considered because fluoropolymers

have a high propensity to flash at very slight mold clearances. The PPL alloys for tip and mold have hardness values ranging from 46 HRC to 56 HRC to maintain surface integrity and excellent corrosion resistance.

### Manufacturing Challenges

In addition to the tooling challenges, venting and precision thermal management of the equipment required new designs to handle the toxic fumes and high continuous heat generated during processing. High specific gravity and traditional runner system waste for fluoropolymer materials also contributed to making per part costs un-competitive. Working with equipment vendors, molding machines, air handling and thermal management systems were chosen and adapted to the new fluoropolymer processing requirements. Fully automated, robotic workstations using hybrid, hot runner technology with direct gated, multi-cavity molds were developed to enhance fill flow quality and eliminate stem and spruce waste. Figure 8 shows the traditional method and direct gate method. The combination of extended mold life, equipment modifications and direct gating technology now allow quality and cost-efficient injection molding of fluoropolymers in high volumes.

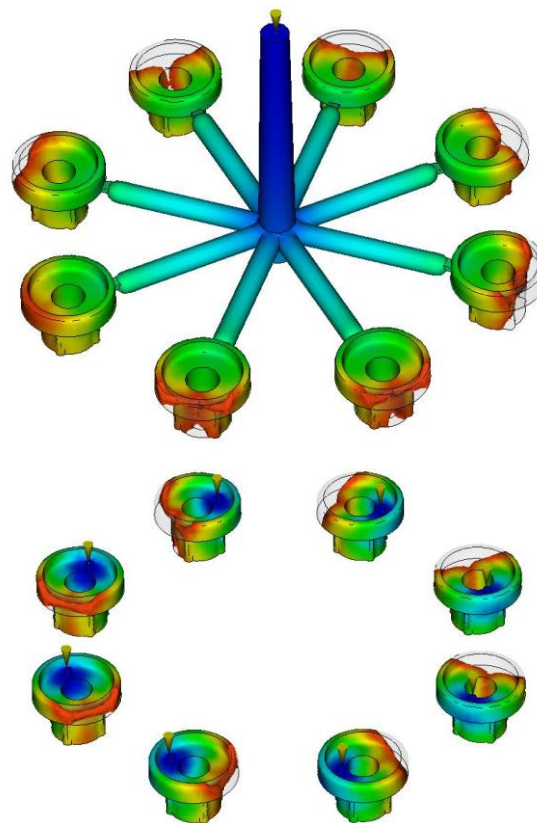


Figure 8. Traditional (top) vs Direct Gate (bottom)

The following illustrates an example of the extended tooling life using the new materials, machines and processes. A traditional 17-4 Stainless Steel mold processing FEP lasted 10 month and 200,000 parts. PPL Mold Alloy A tool has lasted 8 years and produced 40M parts at 0 PPM. Figures 8 and 9 show specific examples of medical applications produced with the equipment and processes described. The syringe has a molded-in membrane. The plunger has undercuts and no parting lines. Eliminating “stick slip” because of low surface adhesion allows smooth plunger action for better delivery control without the need for additional coating.

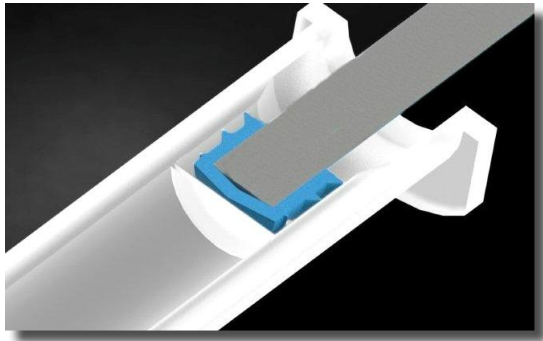


Figure 8. Syringe and plunger with 0.10 mm membrane.

The specimen tray has complex geometry and design details, thin walls and by-passable shut-offs. A single, center gate provides excellent flow for repeatable fill quality.

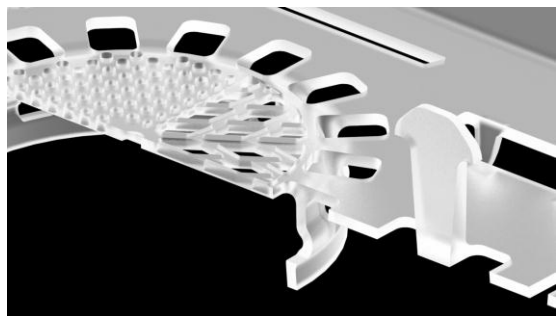


Figure 9. Specimen tray and cross-section

## Conclusions

Meeting new and continually evolving requirements for the production, storage and delivery of new drug technologies can be addressed with fluoropolymers. Biocompatibility, outstanding chemical resistance, inherent inert properties, compatibility with most organic compounds and non-stick properties address many of issues associated with the storage and delivery of both liquids and powders.

Advances in tooling materials, injection molding equipment and processing technology have overcome traditional corrosion and cost obstacles allowing volume manufacturing of fluoropolymer components with complex geometries and tight tolerances. Direct gate, hot runner technology specifically developed for PFA, FEP and other fluoropolymer materials eliminates processing by-products and runner system material waste significantly reducing material usage. These advances give medical device, delivery and storage component designers a viable, high-performance alternative to current plastics.

## References

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