PVDF FOR 3D PRINTING

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The material extrusion method of additive manufacturing using filaments, also known as fused filament fabrication (FFF), was patented in 1992. This method of 3D printing takes a thermoplastic feedstock in filament form, pushes it through a hot nozzle and deposits the melted plastic in a specified pattern layer-by-layer until the part is finished. FFF has gained popularity and rapid adoption due to the simplicity of the technology, availability of inexpensive printers and the ability to use a variety of polymers and polymer composites. Multiple colors or even different materials can be printed in the same part design. FFF is suitable for prototyping, jigs and fixtures, or for repairs where quick access to on-site replacement parts is desirable. Figure 1 shows an example of FFF printing.

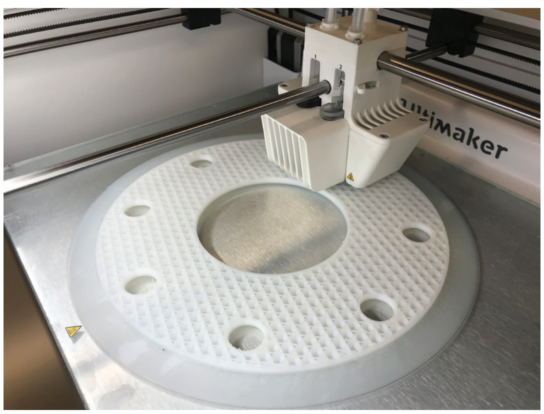

Figure 1: A common printing apparatus, seen here using PVDF filament to print an 8.5" flange.

Materials used for FFF and other 3D printing technologies include polyamide 11, polyamide elastomers and fluoropolymers. A fluoropolymer family that shows promise for use in 3D printing is polyvinylidene fluoride (PVDF) and PVDF copolymers with hexafluoropropylene (HFP). PVDF is considered an engineering fluoropolymer due to its unusually high tensile strength and modulus.

Attributes of PVDF polymers

In the early days of FFF printing, amorphous materials such as acrylonitrile-butadiene-styrene (ABS), polylactic acid (PLA) and glycol modified polyester terephthalate (PETG) were used for their printability and low warpage. As the technology evolved, higher temperature materials, elastomeric materials and semi-crystalline materials were introduced to provide higher performance and meet application needs. However, the material options are limited and there is a need for high-performance products with superior properties in temperature rating, chemical resistance, long-term UV weathering, moisture resistance, flame resistance and mechanical ductility to fill gaps left unserved by the existing materials.

PVDF is a semi-crystalline engineering fluoropolymer that can be adapted in many ways by copolymerization with HFP. Figures 2 and 3 show the monomers used to make PVDF homopolymer and PVDF copolymer. The standard PVDF homopolymer does not pick up moisture, is

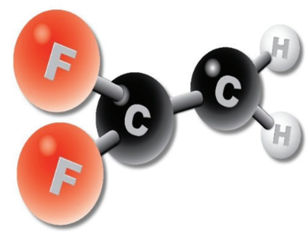

Figure 2: Vinylidene fluoride, the monomer for PVDF homopolymer.

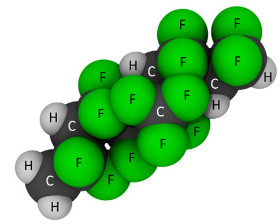

Figure 3: Hexafluoropropylene, which is copolymerized with vinylidene fluoride to make PVDF copolymer.

chemically resistant, has excellent flame resistance, outstanding UV, sunlight, abrasion resistance and radiation resistance. It is used in a range of final components and products such as tubing and piping systems, pump construction, tanks and vessels, membrane and filtration products and coatings. PVDF, unlike most other fluoropolymers, is a polymer with a wide temperature window between its melting point and upper processing temperature limit where it can be safely processed in 3D printing.

When PVDF is copolymerized it can maintain many of the same properties, such as temperature rating, weathering, flame resistance and chemical resistance properties, but the material gains ductility as it is made softer by the reduction in crystallinity.

PVDF can be expected to be fully chemically resistant to solutions from pH below 1 up to 12 for continuous use and to pH 14 for occasional use. PVDF copolymer has an even broader pH range for continuous use, from much less than 1 up to 13.5. All forms of pure PVDF and PVDF copolymers have been studied in Florida 45-degree angle sunlight for long periods without loss of color or physical and mechanical properties. In addition, due to minimal moisture absorption and excellent UV and sunlight resistance, PVDF and PVDF copolymers may be stored indefinitely and do not need to be dried before 3D printing. Many grades of PVDF and PVDF copolymer have been tested for long-term thermal stability to UL® Relative Thermal Index (RTI) standard and some have a RTI temperature rating as high as 150C. Additionally, all grades of PVDF and PVDF copolymer are listed as UL94 V0 for flame resistance (see table 1). These are not grades specifically designed for 3D printing but are included to show the range of properties available in this fluoropolymer family. More specific grades for FFF printing are discussed below.

Printing with PVDF

Despite its promise for 3D printing, PVDF had not been previously available for FFF due to the difficulty of printing highly crystalline materials, which results in the material's shrinkage upon cooling, and PVDF's lack of adhesion to the build plate. However, with recent advances in 3D printing technology and targeted research and development, there are now PVDF formulations available specifically designed for 3D printing that can overcome the challenges faced with printing a crystalline fluoropolymer. Through the manipulation of the polymer composition and printing process, larger, more complicated parts can now be 3D printed with PVDF

Property	Kynar® Resin Grade Range						
	720	2850	2800	3120	2750	3030	2500
Tensile Stress @ yield (PSI)[1]	7,500	5,600	3,900	3,700	2,600	2,200	2,300
Elongation @ yield (%)[1]	8	12	15	25	16	38	17
Tensile Strength @ break (PSI)[1]	4,500	4,500	3,800	4,011	3,200	2,900%	3,400
Elongation @ break (%)[1]	32	33	171	197	747	583	647
Flexural Strength (PSI)[2]	11,000	6,500	3,900	4,000	2,500	2,000	2,000
Flexural Modulus (PSI)[2]	285,000	160,000	85,000	95,000	50,000	40,000	38,000
Impact Resistance (ft*lbf/in)[3]	1.6	6	NB	NB	NB	NB	NB
Relative Thermal Index Rating (°C)	150	140	130	150	Not Tested	Not Tested	Not Tested
UL94 Flame Rating	V0	V0	V0	V0	V0	V0	V0

[1]ASTM D638 Type 1
[2]ASTM D790 Type 1
[3]ASTM D256 1/8 inch bars

Table 1: Property ranges for all grades of Kynar® PVDF.

and its copolymers. Figure 4 shows what is possible with PVDF filament: Two different filaments can be used at the same time to print one part.

There are now filaments available with high flexibility copolymers, moderate flexibility copolymers and high stiffness homopolymers — depending on the mechanical properties required for your applications. All have good chemical resistance and UL94 V0 flame rating. These show strong layer-to-layer adhesion and can be printed with sparse infill all the way to 100 percent infill yielding > 99 percent dense parts depending on the application properties required. A unique feature is the ability to print without having to pre-dry the filaments as many other materials require.

These exciting properties open many different applications for the material in FFF printing. Parts can be printed for functional prototyping purposes, jigs and fixtures, or even for low volume on-demand production parts that allow for a more economical solution when a production environment is stopped due to a broken part. For example, to be injection molded, the part shown in Figure 5 would require a complex and expensive mold. By printing via FFF, users can reduce the cost and lead time for low volume parts. These advantages are especially important to address equipment failures that require immediate resolution, or where the end use takes place in a remote location such as an aircraft carrier at sea. This same thinking can apply to other industrial process equipment, such as flanges, valves and a myriad of other fittings in chemical processing environments, oilfield operations or other fast-paced industries where downtime due to a broken part results in costly situations that can be easily mitigated by FFF printing a replacement part from PVDF.

Figure 4: 3D printed poker chips, used to demonstrate multicolor and multimaterial printing with PVDF.

Figure 5: Complex fitting that has been 3D printed from Kynar® 826-3D PVDF filament after supports have been removed.

Other small, low volume parts have also been printed using formulations of PVDF to provide cost effective solutions where high chemical resistance, high purity and high mechanical strength are required. Some examples can be found in the pharmaceutical industry, where PVDF has been 3D-printed into stoppers and mixers for lab ware. PVDF was chosen as the material of choice due to its high purity and chemical resistance. 3D printing allowed for a cost-effective solution for these low volume parts. The semiconductor industry has also turned to 3D printing PVDF for cost effective, low volume parts for critical fluid handling. Chip manufacturers and toolmakers are turning to 3D printed PVDF parts because they maintain the chemical resistance and high purity of machined parts without the high cost of parts that have traditionally been manufactured by machining. If surface finish is important, PVDF can be readily lapped to reduce the surface roughness of the printed parts.

In addition, by optimizing the polymer composition and printing settings for PVDF 3D printing, you can use the strengths of PVDF to obtain highly dense, robust parts with great layer adhesion. The same property that makes PVDF not adhere to glass is what allows it to adhere to itself very well.

Good adhesion to the buildplate is critical to successfully printing any polymer. PVDF adheres best with PVA glue applied to a glass buildplate. Research has found that Elmer's® Extra Strength glue sticks work very well with PVDF, but other more specialized adhesive solutions also work. Unlike most amorphous polymers, increasing buildplate temperatures does not decrease warping, as the polymer will still crystallize. A build plate temperature of around 158°F/70°C provides the best adhesion and least warping for most PVDF formulations. It is recommended to print PVDF with a brim or a raft to help prevent the corners of the part from peeling up as the part is printed.

PVDF can be printed on most commercially available 3D printers that can process ABS. The nozzle temperature used in PVDF printing range from 464°F/240°C to 518°F/270°C depending on the formulation being printed. A heated build chamber is not required to print PVDF, but an enclosure or regulated build environment may improve part-to-part consistency. Most PVDF formulations require some form of print cooling to resolve fine features. A cooling fan at 30 percent duty cycle works well, but this can vary drastically depending on the power of the print cooling fan. PVDF homopolymer formulations are able to print at higher speeds (50mm/s) than most copolymers and copolymer blends (30mm/s). Stiffer homopolymer and copolymers print well on both Bowden and direct drive extruders, but highly flexible copolymers work much better on direct drive printers.

PVDF formulations for FFF printing

Several grades of PVDF are being used for FFF printing. PVDF homopolymers and copolymers possess the many interesting properties already mentioned. In addition, PVDF can be made conductive, strengthened with added carbon, glass and minerals and alloys are available that improve the material's printability and final part quality. Figure 6 shows an example of a printed part that used a conductive version of PVDF. The conductivity of the final part depends greatly on the loading and type of conductive filler used. Parts printed PVDF formulations with conductive fillers can have resistivity values ranging from 30 Ω*cm to 150 Ω*cm. Carbon fiber fillers can also be added to improve the stiffness of the final part and reduce warping. Example properties of a carbon fiber filled PVDF can be found in table 2.

Depending on the mechanical properties, the chemical resistance and the flexibility required, users can now select from a range of PVDF options in filament form that all have good chemical resistance, excellent UV resistance, are inherently flame retardant and are stable at elevated temperatures. Table 2 summarizes the 3D printed mechanical properties of commercially available filaments. Material suppliers can help in selecting the filament that is most suited to the application requirement. It is important to note that the mechanical properties listed in table 2 are for 3D printing filament grades and their 3D printed mechanical properties, and not to be confused with the mechanical properties listed in table 1.

Another challenge with FFF printing of PVDF is the lack of suitable support materials. Common soluble support materials, such as polyvinyl alcohol (PVA) or breakaway support materials like ABS and PETG, don't stick to

Figure 6: Three parts that have been 3D printed from PVDF resins. The white is an unfilled PVDF and the black PVDF has a conductive filler.

Figure 7: Support materials (black) compatible with PVDF (white), used in 3D printing a tee fitting.

Figure 8: A large flange that has been 3D printed using PVDF filament.

PVDF well or lack the strength to counter PVDF's shrinkage upon cooling. A new breakaway and solvent-soluble support material specifically for PVDF allows users to print larger, more complicated parts. The support material, used in printing a tee fitting, is the black material in figure 7.

Users can now produce high strength, high resolution parts, including parts that need electrostatic dissipation capabilities. For the highest strength, filaments based on homopolymer grades are preferred. For larger parts where high stiffness is not a need, filaments based on copolymer grades are preferred. Larger parts can also be printed using this material. An 8.5" flange, seen in figure 8, is an example of what can be achieved.

Compared to injection molded or extruded samples, 3D printed parts often lose some tensile and elongation properties, especially in the Z direction. Through developing specific Kynar® PVDF homopolymer, PVDF copolymers and blends, it is possible to obtain a range of mechanical

3D Printed Material	Tensile (XY) Strength (MPa)	Tensile (Z) Strength (MPa)	Tensile (XY) Elongation (%)	Flex Modulus (XY) (MPa)	Melting Point (C)	Warping
PVDF Homopolymer	40-45	32-37	25-40%	1400-1700	167	Moderate
PVDF Copolymer I	28-32	23-28	50-150%	700-1000	150	Low
PVDF Copolymer II	13-18	13-18	>250%	250-450	135	Very Low
PVDF ESD	40-45	NA	10-15%	1800-2000	167	Moderate

Table 2: Mechanical properties of commercially available filaments made with PVDF.

properties in the XY direction and maintain most of those properties in the Z direction. This data can be found in table 2. Certain PVDF homopolymer products have high tensile strength in the XY direction and can maintain up to 80 percent of it in the Z direction, but have a lower elongation at break in the Z direction. Other copolymer formulations have lower tensile strength in the XY direction, but maintain up to 100 percent of it in the Z direction. In all cases, the 3D printable PVDF materials maintain the chemical resistance, water resistance, outdoor weathering, flame retardancy and high use temperature rating for which PVDF is known.

Summary

FFF printing is an affordable method of processing low volume parts on demand with custom design parameters and little material waste.

The FFF process is well established with high quality printer suppliers and a network of filament specialists to serve the market.

Recent developments have made PVDF and PVDF copolymers more printable and offer users in the industrial or outdoor component an upgraded, but affordable, material in applications where increased chemical resistance, continuous thermal resistance up to 302°F/150°C for some grades, flame ratings and/or strong sunlight exposure are needed, for years of uninterrupted service.

PVDF has been studied specifically and several variations are available to meet typical applications or for special niche applications such as conductive materials, high strength composites and highly durable and ductile requirements.

Dr. David S. Liu received his Bachelor of Science in chemical engineering from California Institute of Technology and attended graduate school at Massachusetts Institute of Technology where he earned his Mater of Science in chemical engineering practice and his Ph.D. in chemical engineering under the guidance of Prof. Paula Hammond. He joined Arkema Inc. as a scientist in corporate research to explore the use of Arkema's material in 3D printing. He has applied for multiple patents, two granted, on improved materials and methods of printing for UV curing and material extrusion additive manufacturing. From his research, Arkema has commercialized many new thermoplastic materials for material extrusion additive manufacturing.

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