RESINATE

SPECIAL EDITION

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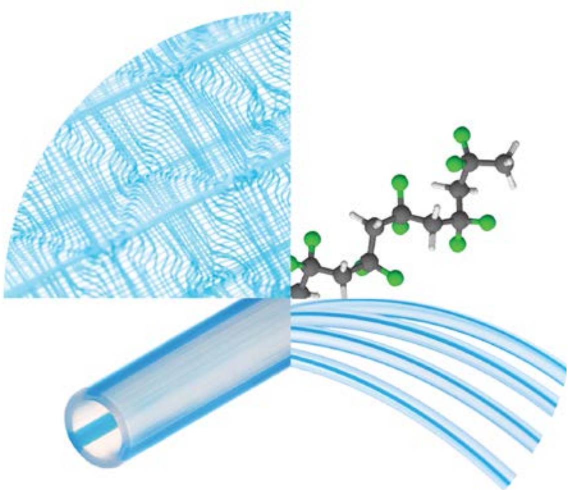
Your quarterly newsletter keeping you informed about trusted products, smart solutions, and valuable updates.

NEW FOCUS ON PVDF



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INTRODUCTION

Polyvinylidene difluoride, or PVDF, is another hallmark fluoropolymer (**Fig. 1**). A descendant of PTFE, PVDF shares many traits with PTFE including very widespread use as a coating. First patented in 1948, PVDF rights have changed hands a number of times, and today this popular material is commonly found as Kynar® (Arkema) or Hylar® (Solvay), to name but two examples [1]. PVDF has many unique facets that set it apart from nearly all other fluoropolymers, including multiple conformations. These differences allow increased manipulation of PVDF during and after processing resulting in many more application possibilities. With this adaptability, PVDF can often go where PTFE cannot. In the relatively short period since its commercialization, PVDF applications have grown and become essential in many unanticipated industries. Consequently, today PVDF occupies the second largest market share among fluoropolymers.

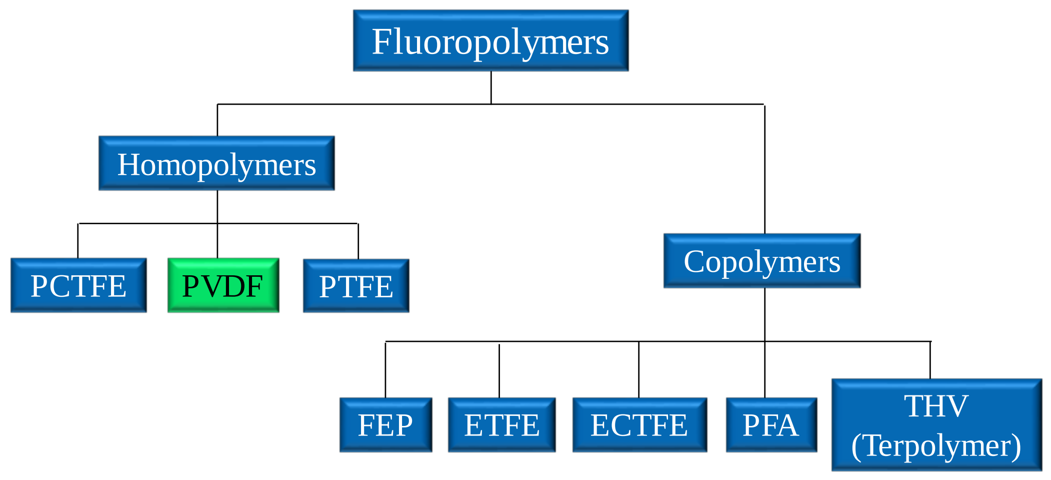

Figure 1: Landscape of popular fluoropolymers. PVDF is a homopolymer produced from the joining of identical monomer units. PVDF is closely related to PCTFE and PTFE.

DISCOVERY, SYNTHESIS, AND STRUCTURE

After the fortuitous discovery of PTFE in the late 1930s by DuPont, PVDF synthesis soon followed [2]. Similarly to PTFE, today PVDF is most commonly produced via a radical reaction to polymerize vinylidene difluoride monomers (**Fig. 2**). PVDF is thus a homopolymer because it is comprised of identical monomer units despite the presence of alternating $–CH_2$ and $–CF_2$ groups along the polymer chain. This simplistic assembly of PVDF may give the false impression that the PVDF polymer molecule, too, is quite simple. PDVF, in fact, is one of the few fluoropolymers which can adopt multiple stable configurations in its crystalline phase. Thus, while similar to PTFE in some ways, PVDF's stable conformational diversity separates it from other fluoropolymers.

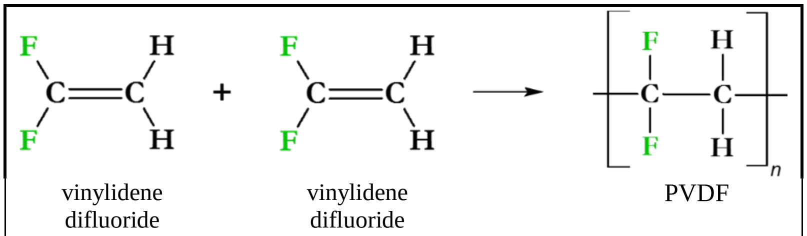

Figure 2: PVDF immediate precursors and synthesis. One canonical means of synthesizing PVDF is via a radical reaction joining vinylidene difluoride monomers.

At the crux of PVDF's multiple conformations are its fluorine atoms. The fluorine atoms possess high electron density due to the six non-bonded (three lone pair) electrons surrounding each of them. This valence shell electron density causes the fluorine atoms to repulse one another. Crystalline PVDF exhibits at least four stable conformations resulting from this fluorine-fluorine repulsion: form I (*β*), form II (*α*), form III (*γ*), and form IV (*δ*). (Amorphous phase PVDF conformations are disordered and undefined). PVDF form I is a canonical zig-zag conformation comparable to an unbranched linear hydrocarbon chain (**Fig. 3A**). However, form II or PVDF *α*, is the one that typically exists at room temperature (**Fig. 3B**). PVDF *α* places neighboring (vicinal) pairs of fluorine atoms further apart from one another than in the zig-zag conformation (form I). PVDF *α* is thus the most stable and therefore the most common form of crystalline phase PVDF. [Information presented henceforth will generally be with respect to PVDF *β* (for illustrative purposes) and to PVDF *α*. Further discussion of PVDF *γ* and *δ* is beyond the scope of this document but can be found in the technical paper, "Drawn Fiber Polymers: Chemical and Mechanical Features" at www.zeusinc.com].

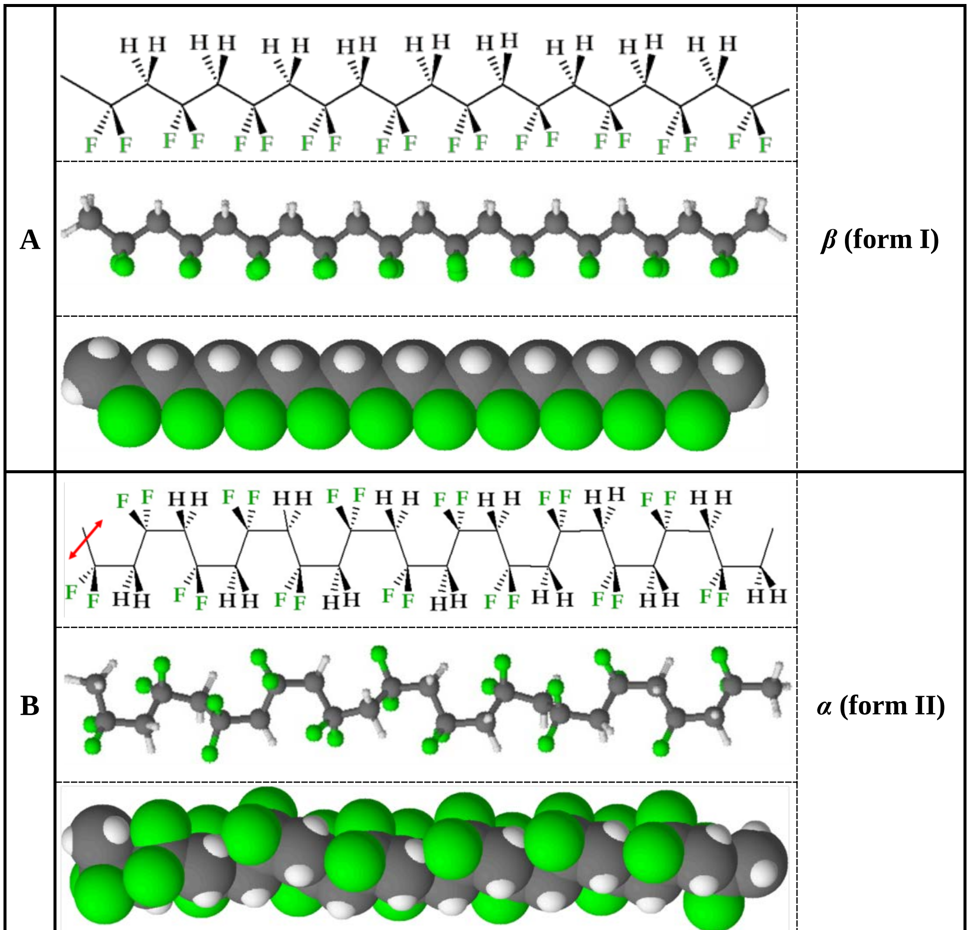

Figure 3: Structure of PVDF *β* (form I) and *α* (form II). A) Form I (*β*) is a typical zig-zag conformation similar to simple saturated hydrocarbon chains. **B)** Form II (*α*) adopts an up-and-down or undulating conformation (as shown in 2-D) and positions the fluoride atoms at a greater distance from one another than in form I. PVDF *α* is more stable than *β* making PVDF *α* the most common form occurring spontaneously and at room temperature. [For **A** and **B**, illustrations are: stereo bond-line drawing (*upper*), ball-and-stick model (*middle*), and space-filling model (*lower*). Conformations of PVDF are variable in melt and amorphous phases].

PROCESSING

One of the significant improvements of PVDF for commercialization is that it is melt-processable unlike PTFE. The inclusion of the alternating $–CH_2$ groups of PVDF rather than all $–CF_2$ groups as PTFE reduces the melting point to ~170 °C (338 °F) for PVDF compared to 327 °C (621 °F) for PTFE. (PVDF melting point may nevertheless vary due to the wide assortment of available PVDF resin grades). Processing of PVDF is easy and can be carried out with most industry-standard equipment [3]. Because additives such as plasticizers and lubricants are generally not required, PVDF processing results in a highly pure product [4]. For injection molding, PVDF does require abundant venting at the conclusion of mold filling to prevent "dieseling," or burning [3]. Some makers also suggest that drying the resin may reduce surface blemishes and improve the appearance of the PVDF product [3]. With respect to products, PVDF is amenable to all common manufacturing processes including extrusion, injection and blow molding, compression molding, and impregnation and coating applications (**Table 1**). For injection molding, nickel or chrome plating is preferred for surfaces that may come in contact with the PVDF [3]. Plating helps to mitigate pitting of those surfaces. PVDF's production-friendly processing and adaptability are just a few of its features that buoy its continuing prevalence in the industry.

Processing Method	Suitability
Injection molding	**Yes**
Extrusion (profiles, films, sheet, tubing, and coating)	**Yes**
Blow molding (thin films)	**Yes**
Compression molding	**Yes**
Impregnation and coating	**Yes**

Table 1: PVDF processing suitability. PVDF is easily processed with industry-standard equipment and is amenable to most processing and production methods.

PVDF PROPERTIES

PHYSICAL AND MECHANICAL

PVDF offers a mix of properties that rival many of the highest-performing fluoropolymers. PVDF is a high molecular weight polymer due to its generally long-chain molecules. Normal PVDF products are white to translucent in appearance and of light weight (**Table 2**). By comparison, PVDF is heavier than polyether ether ketone (PEEK) but lighter than the perfluorinated polymers PTFE or fluorinated ethylene propylene (FEP). The very short and strong C–H and C–F bonds of PVDF are very disinclined to react chemically. This feature gives PVDF excellent chemical resistance (including at high temperatures) in addition to very low water absorption. PVDF can be steam cleaned at 140 °C (284 °F) for autoclaving, and it also tolerates ETO and gamma sterilization (though gamma is least preferred) [3].These attributes support PVDF's use as a biocompatible product, and PVDF is a USP Class VI approved plastic. This biocompatibility has gained PVDF significant market share in the medical and biomedical research sectors in addition to its long-standing industrial use where its properties were initially applied. Furthermore, the multiple forms of PVDF with their distinctive properties have created applications and markets exclusive to this polymer. On the other hand, for areas where PVDF performance may fall short, its ease of processing is often a deciding factor in choosing this versatile polymer.

Property	ASTM	Value (natural polymer)
Appearance	–	**Whitish to translucent**
Density (g/cm^3)	D792	**1.76 - 1.82**
Specific Gravity (23 °C)	D792	**1.76 – 1.82**
Water Absorption (50% rh; %)	D570 / ISO 62-1	**0.02 - 0.07**
Refraction Index	D542	**1.41**
Limiting Oxygen Index (LOI) 3.2 mm thickness	D2863	**44**
Biocompatible	USP Class VI	**Yes**
Chemical Resistance	–	**Excellent**
Sterilization	–	**Autoclave, ETO, and gamma**

Table 2: PVDF typical physical properties. PVDF chemical structure gives it many exceptional properties including chemical resistance and biocompatibility. For sterilization, autoclave and ETO are preferred over gamma irradiation. (Methods are ASTM test standards except where indicated).

The mechanical properties accompanying PVDF further highlight its diverse uses. PVDF is a semi-crystalline material with an average of approximately 50% crystallinity. While PVDF displays excellent dimensional stability, highly crystalline (nearing 70%) PVDF parts will likely exhibit shrinkage [3]. This phenomenon should be taken into account for parts with critical dimensions. Highly crystalline PVDF could also produce voids during some molding operations [3]. PVDF shows excellent hardness and abrasion resistance compared to other fluoropolymers, and it is also quite rigid (**Table 3**). PVDF possesses high mechanical strength, while its tensile strength is comparable to that of PEEK. PVDF, however, provides an alternative to this end where aromatic moieties are not preferred. PVDF performs very well under load-bearing conditions and shows minimal creep when compared to many melt-processable plastics. The coefficient of friction of PVDF is moderately low besting most fluoropolymers but does not exceed the most widely known and highly lubricious fluoropolymer, PTFE. PVDF physical properties show minimal effects from long-term UV exposure making it a highly preferred material for outdoor use. Strength, mechanical toughness, dimensional stability, and crystalline nature are the hallmarks some of the highest-performing fluoropolymers – including PVDF.

Property	ASTM	Value (natural polymer)
Tensile Strength (MPa)	D638	**14 - 55**
Elongation at Break (%)	D638	**20 – 800**
Modulus of Elasticity (GPa)	D638	**1.3 – 2.2**
Flexural Modulus (GPa)	D790	**1.38 – 2.31**
Flexural Strength (MPa)	ISO 178 / D790	**37 – 80**
Hardness (Shore D)	D2240	**50 – 80**
Impact Strength (23 °C; kJ/m^2)	ISO 180	
notched		**8**
unnotched		**no break**
Coefficient of Friction	D1894	**0.14 – .54**

Table 3: Typical PVDF mechanical properties. PVDF possesses excellent mechanical properties even at the upper range of its working temperature. PVDF also performs well under load. (Methods are ASTM test standards except as indicated).

THERMAL

PVDF exhibits good thermal performance throughout its service temperature range. With its moderate maximum of 150 °C (302 °F), PVDF is quite stable thermally even down to sub-zero temperatures (**Table 4**). In fact, 250 °C (482 °F) molten PVDF does not result in weight loss of the resin [3]. PVDF exhibits low thermal conductivity allowing it to be used as a heat barrier. Similarly, PVDF is difficult to burn and requires at least 40% oxygen to sustain combustion (compare to 21% oxygen in normal air). PVDF is self-extinguishing (low smoke) and UL 94 V-0 rated for flammability – a particular benefit for applications such as aerospace and automotive. These properties and others make PVDF one of the preferred options for use in sustained hot environments.

Property	Method	Value (natural polymer)
Thermal Conductivity (W/m-K)	D433 / ISO 22007-4 / C-177	**0.14 – 0.20**
Maximum Service Temperature (°C)	UL 746	**150**
Minimum Service Temperature (°C)	UL 746	**-40**
Melting Point (°C)	D4591 / D3418/ ISO 12086 / DOW Method	**117 – 172**
Glass Transition Temperature (°C)	E1356 (DSC) or E1545 (mechanical)	**-48 to -38**
Decomposition Temperature (°C)	E1131	**375**
Coefficient of Thermal Expansion, Linear (µm/m-°C)	D696	**80 – 194**
Flammability Rating (UL 94)	D2863	**V-0**

Table 4: PVDF thermal properties. While PVDF's upper service temperature may appear comparably moderate, it retains many desirable mechanical properties at these temperatures. PVDF's resistance to burning is also a highly preferred trait. (Methods are ASTM test standards except where indicated).

ELECTRICAL

PVDF exhibits moderate insulating properties (**Table 5**). PVDF α is the only non-polar conformation of PVDF and thus does not exhibit piezoelectric or pyroelectric properties [5, 6]. α PVDF, therefore, is a better insulator over the other three forms (β, γ, and δ). Invariably, however, typical solid PVDF also contains a mixture of amorphous polymer reducing its insulating ability reducing insulating capabilities (β, γ, and δ forms aside). Conversely, the weaker insulating traits of PVDF are used to an advantage for applications where static dissipation is preferred. The varying insulating properties of PVDF products are shown by its large range of dielectric strength, or breakdown voltage (the voltage at which the material fails). Thus, for applications where dielectric properties are important, users should understand and be able to articulate to their vendor the type of PVDF product they require.

Property	ASTM	Value (natural polymer)
Dielectric Constant (1 MHz)	D150	**4.5 – 13.5**
Dielectric Strength (V/mil)	D149 / IEC 60243-1	**254 – 1100**
Volume Resistivity (Ω–cm)	D257 / IEC 60096	**2×10^{14}**

Table 5: PVDF electrical properties. PVDF possesses moderate dielectric traits compared to perfluorinated polymers. PVDF dielectrics, however, can be influenced during processing to alter dielectric properties. (Methods are ASTM except where indicated).

FINISHING

PVDF can be produced in almost any form that is amenable to the processes described in Table 1. Rods, sheets, tubing, monofilament and drawn fiber, films, membranes, and cast parts are just a few of the items commonly produced from PVDF. Finishing and machining, too, are advantages for PVDF over some other plastics. PVDF is easily machined and can be performed using the same common methods as for polyamides. Good machine practice suggests allowing unfinished PVDF products to equilibrate to the environment overnight before fine machining. Certain operations such as milling and turning require caution and may produce chip melting. In those cases, a cooling fluid may be required, and PVDF's chemical resistance allows for a wide range of choices. Pre-drilling and rough reaming are also recommended before performing those final operations. To assist in the machining process, many manufacturers offer guidelines to address critical issues and to help achieve precision parts fashioned from PVDF.

APPLICATIONS

PVDF is a highly adaptable polymer. Its properties lend themselves to a wide variety of industries and applications most of which are focused around operations that require heat tolerance, chemical resistance, and strength and toughness (**Table 6**). Because of its excellent chemical resistance and high purity, PVDF is frequently used as a liner inside of piping or fluid tanks that are used to carry chemicals. In chemical manufacturing plants, PVDF valves and fittings are also abundant. Similarly, and also because of its toughness and abrasion resistance, PVDF pump parts, flanges, and spacers are commonplace. Some PVDF grades are FDA or USDA approved for contact with food. Here, PVDF food trays can be used because they can tolerate the high heat used in their cleaning without warping or deforming. Similarly, PVDF has a strong presence in the pharmaceutical industry, not only for its chemical resistance but also for its heat tolerance (such as for autoclaving) and excellent performance under load. Certainly, operations that require high heat and mechanical loading will likely prefer PVDF. Dielectric aspects of PVDF work in its favor for applications desiring static dissipation. Conversely, PVDF that has been designed with good insulating characteristics is used to cover wiring in critical applications such as the aerospace industry while also working as a heat barrier. This application also fits well with PVDF's non-burning and V-0 flammability rating, critical aspects for vehicles and for the transportation industry as a whole. Lastly, PVDF's performance under UV exposure has led to its use in a variety of outdoor applications including as a protective film over other surfaces and as a component in paints to increase their longevity. Indeed, the hallmarks of PVDF – chemical resistance and mechanical toughness in heat and under load – have helped to create the second largest fluoropolymer market for this well-rounded and frequently preferred material.

Application or Industry	Key Benefits
Aerospace and automotive	UL 94 V-0 flammability rating, low smoke
Chemical manufacturing	Chemical, heat resistance; toughness
Energy (oil and gas)	Chemical resistance
Exterior (outdoors)	Protective UV coating or paint additive to increase product longevity
Fluid handling	Chemical resistance, purity
Pharmaceutical, food processing	Biocompatibility; chemical and heat resistance; mechanical performance under load
General industrial	Toughness, easily machined

Table 6: Survey of PVDF applications. PVDF's key properties such as mechanical strength and toughness and its purity and chemical resistance are highly preferred over a broad spectrum of industries. PVDF's ease of processing gives it additional advantages in these areas over other comparable polymers.

SUMMARY

PVDF provides an excellent balance of properties with the added advantage of being very easily processed. The inclusion of the $–CH_2$ groups significantly lowers the melting point of PVDF compared to PTFE rendering PVDF melt-processable. Unique to PVDF is that it exhibits at least four stable conformations in its crystalline phase: *α*,

β, γ and δ. Of these, PVDF α is the most stable and therefore the most common at room temperature. PVDF α is also the only non-polar form and does not possess piezoelectric or pyroelectric properties. PVDF stands out for its ability to maintain many of its mechanical attributes at the upper end of its service temperature. PVDF possesses excellent tensile strength and chemical resistance; it also performs exceptionally well at high temperatures while under mechanical load. PVDF is difficult to burn making it especially preferred for applications such as aerospace where fire is particularly detrimental. PVDF biocompatibility allows it to be used in medical applications, and some grades are approved for contact with food. PVDF is highly pure making it very desirable for chemical and pharmaceutical applications. While not ideal as an insulator, PVDF is frequently used for static dissipation applications. PVDF can easily be produced in multiple forms from tubing to membranes to films and more. PVDF parts can be machined with common plastic machining methods and tools requiring no specialization. While PVDF may not reach some of the highest performing fluoropolymer attributes, they are balanced by its versatility and highly manufacturable nature resulting in a popular and remarkably beneficial material.

Advantages / Benefits (+)	Limitations (–)
• Ease of processing (melt processable) • Mechanical strength • Retention of mechanical properties • Chemical and dimensional stability • Excellent chemical resistance • Low weight • Excellent UV resistance	• Incompatible with glass fiber • Cost • Moderate upper service temperature • Moderate insulating capability

Table 7: PVDF advantages and limitations. PVDF provides a balance of properties allowing it to compete with other more costly polymers. PVDF also shows exceptional long-term UV (outdoor) performance.

ABOUT ZEUS

Zeus is the world's leader in polymer extrusion technologies. For over 50 years, Zeus has been serving the medical, aerospace, energy exploration, automotive, and fiber optics industries. Headquartered in Orangeburg, South Carolina, Zeus employs approximately 1,500 people worldwide and operates multiple facilities in North America and internationally. You can find us at www.zeusinc.com.

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