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FLUORINE-CONTAINING POLYMERS, POLY(VINYLIDENE FLUORIDE)

Poly(vinylidene fluoride) [24937-79-9] is the addition polymer of 1,1-difluoroethene [75-38-7], commonly known as vinylidene fluoride and abbreviated VDF or VF_2. The formula of the repeat unit in the polymer is $-CH_2-CF_2-$. The preferred acronym for the polymer is PVDF, but the abbreviation PVF_2 is also frequently used. The history and development of poly(vinylidene fluoride) technology has been reviewed (1–3).

PVDF is a semicrystalline polymer that contains 59.4 wt % fluorine and 3 wt % hydrogen and is commercially polymerized in emulsion or suspension using free-radical initiators. The spatial arrangement of the CH_2 and CF_2 groups along the polymer chain accounts for the unique polarity, unusually high dielectric constant, polymorphism, and high piezoelectric and pyroelectric activity of the polymer. It has the characteristic resistance of fluoropolymers to harsh chemical, thermal, ultraviolet, weathering, and oxidizing or high energy radiation environments. Because of these characteristics it has many applications in wire and cable products, electronic devices, chemical and related processing fields, as a weather-resistant binder for exterior architectural finishes, and in many specialized uses. The polymer is readily melt-processed using conventional molding or extrusion equipment; porous membranes are cast from solutions, and finishes are deposited from dispersions using specific solvents. PVDF contains an extremely low level of ionic contamination and does not require additives for stabilization during melt-processing, thereby qualifying it for applications such as ultrapure water systems where high purity is demanded from materials of construction.

There is growing commercial importance and escalating scientific interest in PVDF. The World Patent database, including the United States, lists 678 patents that cite the term poly(vinylidene fluoride) for the period 1963–1980 and 2052 patents for the period 1981–1992; *Chemical Abstracts* files covering the years 1967–1992 contain 5282 references for the same term. Thirty years ago there was only one commercial producer of PVDF in the world; now there are two in the United States, two in Japan, and three in Europe.

1. Monomer

1.1. Properties

Vinylidene fluoride is a colorless, flammable, and nearly odorless gas that boils at $-82^{\circ}C$. Physical properties of VDF are shown in Table 1. It is usually polymerized above its critical temperature of 30.1°C and at pressures above 3 MPa (30 atm); the polymerization reaction is highly exothermic.

1.2. Preparation

Thermal elimination of HCl from 1-chloro-1,1-difluoroethane (HCFC-142b) [75-68-3] is the principal industrial route to VDF covered by numerous patents (8–19). Dehydrohalogenation of 1-bromo-1,1-difluoroethane (20), or 1,1,1-trifluoroethane (HFC-143a) (21–25), or dehalogenation of 1,2-dichloro-1,1-difluoroethane (26–28) are investigated alternative routes (see Fluorine compounds, organic–fluorinated aliphatic compounds).

Table 1. Properties of Vinylidene Fluoride

Property	Value	Reference
molecular weight	64.038	
boiling point, °C	−84	
freezing point, °C	−144	
vapor pressure at 21°C, kPa[a]	3683	
critical pressure, kPa[a]	4434	4
critical temperature, °C	30.1	
critical density, kg/m^3	417	
explosive limits, vol % in air	5.8–20.3	5
heat of formation at 25°C, kJ/mol[b]	−345.2	6
heat of polymerization at 25°C, kJ/mol[b]	−474.21	7
solubility in water, cm^3/100 g at 25°C, 10 kPa[a]	6.3	

[a] To convert kPa to atm, divide by 101.3.
[b] To convert kJ to kcal, divide by 4.184.

The commercially preferred monomer precursor HCFC-142b has been prepared by hydrofluorination of acetylene (29), vinylidene chloride (30–32), or 1,1,1-trichloroethane (33–39).

$$CH{\equiv}CH \xrightarrow{+2\ HF} CH_3{-}CHF_2 \xrightarrow{+Cl_2} CH_3{-}CClF_2 + HCl$$

$$CH_2{=}CCl_2 \xrightarrow{+2\ HF} CH_3{-}CClF_2 + HCl$$

$$CH_3{-}CCl_3 \xrightarrow{+2\ HF} CH_3{-}CClF_2 + 2\ HCl$$

The monomer can also be continuously prepared by the pyrolysis of trifluoromethane (CHF_3) in the presence of a catalyst and either methane or ethylene (40–43). Passing 1,1-difluoroethane ($CH_3{-}CHF_2$), oxygen, and CO_2 over a catalyst gives a mixture of VDF and vinyl fluoride (44). Using either methanol or dichloromethane as a source of the carbene moiety, VDF can be continuously prepared from chlorodifluoromethane (HCFC-22) (CHF_2Cl) (45, 46). Pyrolysis of dichlorodifluoromethane (CFC-12) (CCl_2F_2) with either methane (47) or methyl chloride yields the monomer (48, 49). Copyrolysis of methane and either bromotrifluoro-($CBrF_3$) or chlorotrifluoromethane ($CClF_3$) yields VDF (50). Deuterated VDF has also been prepared (51).

1.3. Storage and Shipment

VDF or HFC-1132a is stored and shipped in gas cylinders or high pressure tube trailers without polymerization inhibitor and is placarded as flammable compressed gas. Terpenes or quinones can be added to inhibit polymerization. Elf Atochem North America, Inc. and Ausimont USA, Inc. supply VDF in the United States; other producers are in Japan and Europe.

1.4. Health and Safety Factors

VDF is a flammable gas; its combustion products are toxic. Liquid VDF on contact with the skin can cause frostbite. Acute inhalation toxicity of VDF is low; median lethal concentrations (LC_{50}) for rats were 128,000 ppm after a single 4-h exposure (52) and 800,000 ppm after a 30-min exposure (53). Cumulative toxicity is low;

exposure of rats and mice at levels of up to 50,000 ppm for 90 days did not cause any systemic toxicity (54, 55). No teratogenic or reproductive effects were found in rats. VDF was positive in bacterial gene mutation assay but negative in mammalian gene mutation, chromosomal aberration, and cell transformation assays. In 1979, a paper reported that rats developed lipomas after being given over 52 weeks' oral doses of VDF dissolved in olive oil (56). More relevant, lifetime (18 months) inhalation studies on rats and mice have not detected chronic or carcinogenic effects up to 10,000 ppm VDF (57, 58). Additional information is available (59, 60). Toxicology test data on VDF were submitted to the EPA pursuant to a final test rule and consent order under the Toxic Substances Control Act (TSCA) (61).

1.5. Uses

Vinylidene fluoride is used for the manufacture of PVDF and for copolymerization with many fluorinated monomers. One commercially significant use is the manufacture of high performance fluoroelastomers that include copolymers of VDF with hexafluoropropylene (HFP) (62) or chlorotrifluoroethylene (CTFE) (63) and terpolymers with HFP and tetrafluoroethylene (TFE) (64) (see Elastomers, synthetic–fluorocarbon elastomers). There is intense commercial interest in thermoplastic copolymers of VDF with HFP (65, 66), CTFE (67), or TFE (68). Less common are copolymers with trifluoroethene (69), 3,3,3-trifluoro-2-trifluoromethylpropene (70), or hexafluoroacetone (71). Thermoplastic terpolymers of VDF, HFP, and TFE are also of interest as coatings and film. A thermoplastic elastomer that has an elastomeric VDF copolymer chain as backbone and a grafted PVDF side chain has been developed (72).

2. Polymer

2.1. Polymerization

The first successful polymerizations of VDF in aqueous medium using peroxide initiators at 20–150°C and pressures above 30 MPa were described in a patent issued in 1948 (73). About a year later, the first copolymerizations of VDF with ethylene and halogenated ethylenes were also patented (74). After a hiatus of over 12 years a commercially feasible process was developed and PVDF was ready for market introduction (2).

PVDF is manufactured using radical initiated batch polymerization processes in aqueous emulsion or suspension; operating pressures may range from 1 to 20 MPa (10–200 atm) and temperatures from 10 to 130°C. Polymerization method, temperature, pressure, recipe ingredients, the manner in which they are added to the reactor, the reactor design, and post-reactor processing are variables that influence product characteristics and quality.

Emulsion polymerization of VDF is a heterogeneous reaction that requires, as is typical with most fluorine-containing monomers, addition of a polyfluoroalkanoic acid salt as surfactant (75) to avoid radical scavenging reactions during polymerization. Sometimes chain-transfer agents or buffers, or both, are used in the emulsion process. Radical generators that initiate polymerization of VDF are either water-soluble, eg, persulfate salts (76–78), disuccinic acid peroxide (79), β-hydroxyalkyl peroxide (80, 81), alkylperoxybutyric acid (82) or monomer soluble, eg, di-*tert*-butyl peroxide (83, 84), dialkylperoxydicarbonate (85–88), or *tert*-butylperoxybutyrate (89). A radiotracer study found that the number of end groups formed in the polymer from primary radicals of the initiator decreased during emulsion polymerization of PVDF, whereas overall branching increased (90). Upon completion of the polymerization, the discharged reactor product is a milky white colloidal dispersion or latex that is subsequently filtered, coagulated, thoroughly washed and usually spray-dried to produce a very fine powder. It is typical of emulsion polymerization that the polymer solids in latex are spheres of about 250 nm in diameter and the dried powders contain agglomerates of about 2 to 5 μm in diameter. The powder is either packaged or processed as required for the intended use.

Suspension polymerization of VDF in water are batch processes in autoclaves designed to limit scale formation (91). Most systems operate from 30 to 100°C and are initiated with monomer-soluble organic free-radical initiators such as diisopropyl peroxydicarbonate (92–96), *tert*-butyl peroxypivalate (97), or *tert*-amyl peroxypivalate (98). Usually water-soluble polymers, eg, cellulose derivatives or poly(vinyl alcohol), are used as suspending agents to reduce coalescence of polymer particles. Organic solvents that may act as a reaction accelerator or chain-transfer agent are often employed. The reactor product is a slurry of suspended polymer particles, usually spheres of 30–100 μm in diameter; they are separated from the water phase thoroughly washed and dried. Size and internal structure of beads, ie, porosity, and dispersant residues affect how the resin performs in applications.

Solution polymerization of VDF in fluorinated and fluorochlorinated hydrocarbons such as CFC-113 and initiated with organic peroxides (99), especially bis(perfluoropropionyl) peroxide (100), has been claimed. Radiation-induced polymerization of VDF has also been investigated (101, 102). Alkylboron compounds activated by oxygen initiate VDF polymerization in water or organic solvents (103, 104). Microwave-stimulated, low pressure plasma polymerization of VDF gives polymer film that is <10 μm thick (105). Highly regular PVDF polymer with minimized defect structure was synthesized and claimed (106). Perdeuterated PVDF has also been prepared and described (107).

2.2. Polymer Properties

PVDF is a tough, semicrystalline engineering polymer. Compared to the softer and mechanically less robust perfluorocarbon polymers, PVDF has high mechanical and impact strength, and excellent resistance to both creep under long-term stress and fatigue upon cyclic loading (108, 109). PVDF also has excellent abrasion resistance and thermal stability, and resists damage from most chemicals and solvents, as well as from ultraviolet and nuclear radiation. Typical PVDF design properties are shown in Table 2.

Properties of PVDF depend on molecular weight, molecular weight distribution, chain configuration, ie, the sequence in which the monomer units are linked together, including side groups or branching, and crystalline form. The morphology of PVDF reflects differences in both the utilized polymerization procedure and the thermomechanical treatment that followed polymerization. During radical-initiated polymerization, the head-to-tail addition of VDF molecules predominates, in which $-CF_2-$ is denoted as "head" and $-CH_2-$ as "tail," but reversed monomeric addition leading to head-to-head and tail-to-tail defects does occur; the extent of defects is influenced by polymerization process conditions, particularly temperature (110). The incidence of these defects is best determined by high resolution ^{19}F nmr (111, 112); infrared (113) and laser mass spectrometry (114) are alternative methods. Typical commercial polymers show 3–6 mol % defect content. Polymerization methods have a particularly strong effect on the sequence of these defects. In contrast to suspension polymerized PVDF, emulsion polymerized PVDF forms a higher fraction of head-to-head defects that are not followed by tail-to-tail addition (115, 116). Crystallinity and other properties of PVDF or copolymers of VDF are influenced by these defect structures (117).

Crystallinity affects toughness and mechanical strength as well as impact resistance. PVDF crystals are seen in the optical microscope as spherulites that are lamellae of polymer chain segments, which are packed crystallographically; the interposed amorphous regions consist of disordered chains. The crystallinity can range between 35 and 70%. Various parameters, including molecular weight, molecular weight distribution, polymerization method, thermal history, and cooling rates influence crystallization kinetics (118).

Unlike other synthetic polymers, PVDF has a wealth of polymorphs; at least four chain conformations are known and a fifth has been suggested (119). The four known distinct forms or phases are alpha (II), beta (I), gamma (III), and delta (IV). The most common α-phase is the trans-gauche (tgtg$'$) chain conformation placing hydrogen and fluorine atoms alternately on each side of the chain (120, 121). It forms during polymerization and crystallizes from the melt at all temperatures (122, 123). The other forms have also been well characterized

Table 2. Properties of Poly(vinylidene fluoride)

Property	Method	Value
specific gravity	ASTM D792	1.75–1.80
water absorption, 24 h at 23°C, %	ASTM D570	0.04
refractive index, n_D	ASTM D542	1.42
melting peak, T_m, °C	ASTM D3418	156–180
crystallization peak, T_c, °C	ASTM D3418	127–146
glass transition, T_g, °C	ASTM D2236	−40
brittleness temperature, °C	ASTM D746	−62 to −64
deflection temperature at 1.82 MPa,[a] °C	ASTM D648	84–115
specific heat, kJ/kg·K[b]	DSC	1.26–1.42
thermal conductivity, W/Km	ASTM D433	0.17–0.19
tensile stress at yield, MPa[a]	ASTM D638	28–57
tensile stress at break, MPa[a]	ASTM D638	31–52
elongation at break, %	ASTM D638	50–250
compressive strength, MPa[a]	ASTM D695	55–110
flexural strength, MPa[a]	ASTM D790	59–94
modulus of elasticity, MPa[a]		
in tension	ASTM D882	1040–2600
in flexure	ASTM D790	1140–2500
impact strength at 25°C, J/m[c]	ASTM D256	
unnotched		800–4270
notched		107–214
limiting oxygen index, %	ASTM D2863	43
vertical burn	UL 94	V-0
sand abrasion, m^3/mm	ASTM D968	4.0

[a] To convert MPa to psi, multiply by 145.
[b] To convert kJ to kcal, divide by 4.184.
[c] To convert J/m to ftlbf/in., divide by 53.38.

(124–128). The density of the α polymorph crystals is 1.92 g/cm^3 and that of the β polymorph crystals 1.97 g/cm^3 (129); the density of amorphous PVDF is 1.68 g/cm^3 (130).

Relaxations of α-PVDF have been investigated by various methods including dielectric, dynamic mechanical, nmr, dilatometric, and piezoelectric and reviewed (3). Significant relaxation ranges are seen in the loss-modulus curve of the dynamic mechanical spectrum for α-PVDF at about 100°C (α'), 50°C (α''), −38°C (β), and −70°C (γ). PVDF relaxation temperatures are rather complex because the behavior of PVDF varies with thermal or mechanical history and with the testing methodology (131).

Suspension- and emulsion-polymerized PVDF exhibit dissimilar behavior in solutions. The suspension resin type is readily soluble in many solvents; even in good solvents, solutions of the emulsion resin type contain fractions of microgel, which contain more head-to-head chain defects than the soluble fraction of the resin (116). Concentrated solutions (15 wt %) and melt rheology of various PVDF types also display different behavior (132). The Mark-Houwink relation ($\eta = KM^a$) for PVDF in N-methylpyrrolidinone (NMP) containing 0.1 molar LiBr at 85°C, for the suspension (115) and emulsion (116) respectively is: $\eta = (4.5 \pm 0.3) \times 10^{-4} M^{0.70}$ and $\eta = 1.4 \times M^{0.96}$.

Unlike most crystalline polymers, PVDF exhibits thermodynamic compatibility with other polymers (133). Blends of PVDF and poly(methyl methacrylate) (PMMA) are compatible over a wide range of blend composition (134, 135). Solid-state nmr studies showed that isotactic PMMA is more miscible with PVDF than atactic and syndiotactic PMMA (136). Miscibility of PVDF and poly(alkyl acrylates) depends on a specific interaction between PVDF and oxygen within the acrylate and the effect of this interaction is diminished as the hydrocarbon content of the ester is increased (137). Strong dipolar interactions are important to achieve miscibility with

Table 3. Electrical Properties of Poly(vinylidene fluoride)

Property	Method	Value
volume resistivity, Ωcm	ASTM D257	$1.5 - 5 \times 10^{14}$
surface arc resistance, s	ASTM D495	50–60
dielectric strength, kV/mm	ASTM D149	63–67
dielectric constant at 25°C	ASTM D150	
1 kHz		8.15–10.46
10 kHz		8.05–9.90
100 kHz		7.85–9.61
dissipation factor		
1 kHz		0.005–0.026
10 kHz		0.015–0.021
100 kHz		0.039–0.058

poly(vinylidene fluoride) (138). PVDF blends are the object of many papers and patents; specific blends of PVDF and acrylic copolymers have seen large commercial use.

PVDF cross-links readily when subjected to electron beam radiation (139) or gamma radiation (140). Cross-linking efficiency is proportional to molecular weight, molecular weight distribution, or extent of head-to-head chain defects (141). The cross-linked PVDF, when highly stressed or compressed above the melting point, exhibits thermodynamic and physical properties similar to polyethylene and polypropylene (142). Polyfunctional monomers having good solubility in PVDF increase the cross-linking rate (143, 144). The effect of radiation on the structure and properties of PVDF has been reviewed (145).

Some electrical properties are shown in Table 3. Values of other parameters have been published (146). Polymorphism of the PVDF chains and the orientation of the two distinct dipole groups, $-CF_2-$ and $-CH_2-$, rather than trapped space charges (147) contribute to the exceptional dielectric properties and the extraordinarily large piezoelectric and pyroelectric activity of the polymer (146, 148, 149).

Prolonged exposure of PVDF to processing temperatures exceeding 300°C could lead to discoloration and chemical reactions that present hazards. The primary reaction at high temperature is loss of hydrogen fluoride (HF) that results in conjugation, $-CH{=}CF-CH{=}CF-$, along the chains; this explains the observed discoloration. The extent and rate of discoloration is not homogeneous among PVDF resins and may be commensurate with chain perfection, ie, percentage of head-to-tail repeat units in the chain (150); reversed repeat units may interrupt dehydrofluorination (151). If the temperature exceeds 375°C in air, rapid thermal decomposition takes place and HF gas evolves. After 70 wt % loss, at about 480°C, the residue is char that eventually burns completely at higher temperature. The charring phenomenon is considered basic to the superior performance of PVDF in severe fire tests such as the Underwriters Laboratories UL 910 Modified Steiner Tunnel Test (152).

2.3. Fabrication and Processing

PVDF is available in a wide range of melt viscosities as powder or pellets to fulfill typical fabrication requirements; latices are also commercially available.

PVDF is readily molded in conventional compression , transfer, and injection-molding equipment (153–155); typical molding temperatures for the cylinder and nozzle are 180–240°C and molds are at 50–90°C. PVDF resins do not require drying because the resin does not absorb moisture. As a crystalline polymer, it shows a relatively high mold shrinkage of ca 3%. To obtain a high dimensional stability, carbon-filled, mica-filled, or carbon–fiber-reinforced (156) grades are used. To achieve best results and avoid warping or voids, it is essential to coordinate the cooling rate with the crystallization of the resin or anneal the part at 140–150°C. For compression or transfer molding the PVDF pellets are preheated in an oven to 210–240°C and transferred to the mold that is heated to 190–200°C. The resin in the filled mold is placed under sufficient pressure to complete flow and fusion. Sufficient time must be allowed to cool the molded part under pressure to 90°C to prevent vacuum voids and distortion.

Smooth PVDF profiles of all types—film, sheet, rod, profile, pipe, tubing, fiber, monofilament, wire insulation, and cable-jackets—can be extruded; no heat stabilizers are needed. In both molding and extrusion operations, care must be exercised to eliminate hang-up zones in the equipment where molten resin (at 230–260°C) can stagnate and thermally decompose with time. Equipment built with material of construction used for processing polyolefins or PVC is adequate; for long-term or high shear processing, a highly wear-resistant alloy such as Xaloy 306 for barrel liner and SAE 4140 steel for the screw is suggested. Gradual transition-type screws having L/D ratios at least 20:1, ample metering sections, and compression ratio of about 3 are recommended. Temperature profiles vary from 190 to 290°C depending on resin grade and shape being extruded. Water quenching is practiced for wire insulation, tubing, and pipe, whereas sheet and flat film are melt-cast on polished steel rolls operating at 65–150°C (157).

PVDF sheets can be backed during extrusion-calendering using fabrics of glass (158), polyamide, or polyester fibers; they can also be press-laminated with the fabrics at 185 to 200°C (159). Nonvulcanized rubber can also be press-laminated with PVDF sheet at 150°C (160). Melt-cast PVDF sheets can be oriented uniaxially or biaxially to produce films with vastly increased mechanical strength, specular transmission, or ferroelectric activity (161). Blown-film equipment typically used for HDPE can also be used for extrusion of blown PVDF film. Monofilaments are usually extruded or spun at 240–260°C into a 30–50°C water bath and then reheated to 130–160°C, oriented using draw ratios of 3:1 to 5:1, and heat-set at elevated temperatures to produce high strength filament having tenacities of 350–440 mN/tex (4–5 gf/den) (162, 163). Coextrusion of PVDF with other polymers is the subject of several patents. Interlayer adhesion is critical, although matching the coefficients of thermal expansion and melt viscosities are other important considerations (164). To promote interleaf bond, an adhesive “tie-layer” consisting of a polymer that is partially compatible both with PVDF and the incompatible polymer layer, such as ABS (165 and polyolefins (166), has been used in coextrusion.

Semifinished PVDF products can be machined and processed by methods used for other thermoplastics (155). PVDF parts can be joined by standard welding methods. Pipe, fittings, or sheets can be welded using a hot-air gun with a welding rod or a heated tool for butt or socket welding. Films can be bonded by heat sealing, high frequency welding, or ultrasonic welding.

Manufactured PVDF parts can be cross-linked using high energy radiation to produce high temperature wire insulation, and heat-shrinkable tubing or film.

Organosol dispersions of PVDF used extensively for exterior architectural finishes can be produced from the very fine powder obtained only by the emulsion polymerization method. These dispersions include the very fine PVDF powder, pigments, acrylate or methacrylate copolymer, and selected solvents (167–170); comparable water-based coating compositions can also be prepared (171–174). These dispersions are factory applied by spray or roller to primed steel or aluminum surfaces and oven-fused at 230–260°C to form continuous films that adhere firmly to the substrata. Other organic dispersions of PVDF are formulated for spray applications of relatively thick coatings to protect metals from corrosive environments. Powders for electrostatic spraying, fluidized-bed deposition, or rotomolding are obtained by melt compounding PVDF with appropriate ingredients, cryogenic grinding, and classification to desirable particle-size range for the application.

Microporous filtration membranes from VDF polymers are made by casting a polymer solution on a rigidly supported backing belt, then passing the belt through a bath to form the membrane, followed by extraction of any residual solvent from and drying of the membrane (175). Formation of microporous PVDF membranes has been reviewed (176). To improve performance, PVDF membranes are often chemically modified (177–181). Hollow fibers useful for microfiltration are produced by extruding a spinning solution of PVDF from an annular spinning orifice into coagulating liquids (182). Porous structures can also be made by sintering very fine granules under controlled conditions (183), from extruded compounds that contain leachable additives that

Table 4. Producers and Trademarks of Poly(vinylidene fluoride)

Producer	Country	Trademark
Ausimont USA, Inc.	United States	Hylar
Elf Atochem North America, Inc.	United States	Kynar
Elf Atochem, SA	France	Foraflon
Solvay & Cie, SA	Belgium	Solef/Vidar
Hüls, AG	Germany	Dyflor
Daikin Kogyo Co., Ltd.	Japan	Neoflon
Kureha Chemical Industry Co., Ltd.	Japan	KF Polymer

upon extraction leave voids in the product, or by extrusion of compounds containing chemical blowing agents (184, 185).

3. Economic Aspects

Because of its excellent combination of properties, processibility, and relatively low price compared to other fluoropolymers, PVDF has become the largest volume fluoropolymer after PTFE; consumption in the United States has grown from zero in 1960 to about 6200 metric tons in 1991 (186). About 49% of the consumed volume is PVDF modified by copolymerization with 5–12-wt % HFP to enhance flexibility. In 1992, list price for homopolymer powders was \$15.32/kg, and for pellets \$15.42/kg; the reported market price was \$14.09–14.22/kg (187). In the United States, almost all PVDF is supplied by Ausimont USA, Inc., Elf Atochem North America, Inc., and Solvay Polymers, Inc. Ausimont and Elf Atochem are producers; Solvay is an importer of the resin. Small amounts of resin are imported from Germany by Hüls America, Inc. and from Japan by Kureha Chemical Industry Co., Ltd. PVDF producers and their trademarks are listed in Table 4.

After 10 years of unabated rapid growth in the plenum wire and cable market, fluoropolymers including PVDF, primarily the flexible VDF/HFP copolymer, are beginning to lose market share to lower priced PVC-alloys. The loss of market share in the plenum market probably will be compensated by growth of PVDF in other fields; thus during the mid-1990s the total volume of PVDF may not grow (188).

3.1. Specifications and Standards

Commercial PVDF resin types and standards are defined in ASTM D3222. A list of military and industrial specifications covering applications, material suppliers, and PVDF resin grades can be found in Reference 189.

4. Health and Safety Factors

PVDF is a nontoxic resin and may be safely used in articles intended for repeated contact with food (190). Based on studies under controlled conditions, including acute oral, systemic, subchronic, and subacute contact; implantation; and tissue culture tests, no adverse toxicological or biological response has been found in test animals (191, 192). PVDF is acceptable for use in processing and storage areas in contact with meat or poultry products prepared under federal inspection and it complies with the 3-A sanitary standards for dairy equipment.

PVDF is not hazardous under typical processing conditions. If the polymer is accidentally exposed to temperatures exceeding 350°C, thermal decomposition occurs with evolution of toxic hydrogen fluoride (HF).

Some silica-containing additives such as glass and titanium dioxide lower the thermal stability of PVDF and should be used with caution. Processors should consult the resin producer about safe processing practice.

5. Uses

PVDF is used in many diverse industrial applications for products that require high mechanical strength and resistance to severe environmental stresses. The most important fields of application for PVDF resins include electric and electronic industry products, architectural and specialty finishes, products for the chemical and related industries, and rapidly growing specialized uses.

In the electric and electronics field the largest usage of PVDF is for plenum wire and cables, plenum being the space between the suspended and structural ceiling in high rise buildings. PVDF-insulated wire and cables jacketed with the flexible VDF–HFP copolymer pass the UL 910 specification for low smoke generation and flame spread and are approved for remote-control, signaling and power-limited circuits, fire protective signaling systems, and communication systems. Other important wire constructions include cross-linked PVDF jackets (193) for commercial aircraft, industrial power control, and cathodic protection wires and cables. Self-limiting strip heaters consisting of a cross-linked conductive PVDF core, which separates two parallel conductors, and a fluoropolymer jacket are useful for heating pipes or other process fluid-handling equipment (194, 195). Cross-linked heat-shrinkable PVDF tubings (196) are used as connector sleeves for wires and cables, or to coat ordnance (197). Some sleeves incorporate a ring of solder, forming a so-called solder sleeve for power control, electronic, aircraft, and communication wiring.

Uniaxially or biaxially oriented PVDF film upon metallization and poling under a high dielectric field is a flexible, tough, light, and active transducer for many piezo- and pyroelectric applications (198, 199). Current applications include infrared detectors (200); audio devices, eg, stereo speakers, microphones, headphones, phonograph cartridges, hydrophones for long-range tracking in ocean depth; pressure or stress sensors (201); contactless keyboards (202); motion detectors (203); and medical devices, eg, detectors for heartbeat and breathing rate, or sensors for ultrasonic imaging.

The largest commercial application for PVDF homopolymer powder is as a base for long-lasting decorative finishes on aluminum and galvanized steel siding, curtain-wall panels, roofing systems, aluminum extrusions and other building components (204) that are used on power plants, schools, airport buildings, department stores, high rise office and hotel buildings, sports stadiums, and, to a lesser extent, residential buildings. These organosol finishes, available in many colors from paint companies throughout the world, are factory-applied by conventional state-of-the-art coil or spray-coating procedure to the primed base metal (205). Usually, the coating consists of a suitable primer layer up to about 5 μm thick and a 20–30 μm finishing layer of a PVDF topcoat. Accelerated weathering tests along with the experience with buildings erected since the 1960s prove that these finishes are unique in durability in terms of film integrity, color retention, corrosion resistance, flexibility, sand-abrasion resistance, and chemical resistance (206). Similar PVDF organosol dispersions are also being used for corrosion-protection coating of automotive break-line tubings. Pigmented thin film that is continuously cast from PVDF solutions or dispersions is used for decorative laminates and has been specified for body trim by principal automobile manufacturers. PVDF-based powders analogous in composition to the liquid finishes have been proposed as decorative protective coatings for metallic substrata (207). PVDF-based powder for rotomolding, eg, for tanks, valves, or fittings, and for fluidized-bed deposition and electrostatic spraying are available (208).

Fluid-handling systems in the chemical processing and related fields are also large users of PVDF products such as solid or lined pipes, valves, pumps, tower packing, and tank and trailer linings (209, 210). Because PVDF is manufactured by methods that assure extremely low ionic contamination, it has qualified for use in ultrapure water systems (211–213), including WFI (water for injection) and *U.S. Pharmacopoeia* (USP) standards (214). Blow-molded PVDF bottles are used for shipping or storing high purity chemicals in the semiconductor industry (215). Extruded monofilament woven into coarse fabric is used widely for drum filtration during bleaching of wood pulp with chemicals, eg, sodium hypochlorite or chlorine dioxide and caustic soda. Like other fluoropolymers, PVDF is used as a binder for asbestos-fiber-based diaphragms used in cells for the electrolysis of brine to produce chlorine and caustic soda (216, 217).

PVDF-based microporous filters are in use at wineries, dairies, and electrocoating plants, as well as in water purification, biochemistry, and medical devices. Recently developed nanoselective filtration using PVDF membranes is 10 times more effective than conventional ultrafiltration (UF) for removing viruses from protein products of human or animal cell fermentations (218). PVDF protein-sequencing membranes are suitable for electroblotting procedures in protein research, or for analyzing the phosphoamino content in proteins under acidic and basic conditions or in solvents (219).

Pigmented PVDF and ABS laminates manufactured by coextrusion with a tie-coat exhibit excellent weather resistance resulting from the protective PVDF cap layer; they are used in Europe for thermoformed automotive dash panels, trailer and tractor roofs, motorcycle gas tank housings, and lawn-mower blade guards (220). A PVDF alloy which is a blend of PVDF and alkyl methacrylate homo- or copolymer is coextruded with acrylate or methacrylate resin blend to form a sheet for hydrosanitary components (221). Similar blends of PVDF and compatible resins can be coextruded both with PVC, to form home siding panels with outstanding resistance to weather (222), and with an engineering resin, ie, polycarbonate, polyurethane, polyamide, polyester, or ABS, or their compounds (223).

In Japan, PVDF monofilament for fishing lines for both commercial and sport fishing is a specialty in demand (224–226) because it displays no water absorption, is not visible in water, and has high knot strength and high specific gravity. PVDF as a processing aid eliminates melt fracture and other flow-induced imperfections in blown LLDPE and HDPE films (227). Optical disk memory devices utilize the decrease in transmittance on crystallization of PVDF and thus provide an overwritable memory (228). The exceptional dielectric properties of PVDF are utilized in electrophotographic carrier (toner) compositions (229).

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