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POLY (VINYL FLUORIDE)

Vinyl fluoride can be polymerized into homopolymers and copolymers with the aid of a free-radical generating catalyst (initiator), usually under high pressure. Du Pont first commercialized a poly(vinyl fluoride) (PVF) based film in 1961 under the trade name Tedlar and is the only known supplier of this polymer. PVF homopolymers and copolymers have excellent resistance to sunlight degradation, chemical attack, water absorption, and solvent, and have a high solar energy transmittance rate. These properties have resulted in the utilization of PVF film and coating in outdoor and indoor functional and decorative applications. These films have found use where thermal stability, outdoor durbility, stain resistance, adherence, and release properties are required.

1. Monomer

Vinyl fluoride [75-02-5] (VF) (fluoroethene) is a colorless gas at ambient conditions. It was first prepared by reaction of 1,1-difluoro-2-bromoethane [359-07-9] with zinc (1). Most approaches to vinyl fluoride synthesis have employed reactions of acetylene [74-86-2] with hydrogen fluoride (HF) either directly (2–5) or utilizing catalysts (3, 6–10). Other routes have involved ethylene [74-85-1] and HF (11), pyrolysis of 1,1-difluoroethane [624-72-6] (12–15) and fluorochloroethanes (16–20), reaction of 1,1-difluoroethane with acetylene (21, 22), and halogen exchange of vinyl chloride [75-01-4] with HF (23–25). Physical properties of VF are given in Table 1.

2. Polymerization

Vinyl fluoride undergoes free-radical polymerization. The first polymerization involved heating a saturated solution of VF in toluene at 67°C under 600 MPa (87,000 psi) for 16 h (26). A wide variety of initiators and polymerization conditions have been explored (27–29). Examples of bulk (30, 31) and solution (27, 30, 32, 33) polymerizations exist; however, aqueous suspension or emulsion methods are generally preferred (28, 34–43). VF volatility dictates that moderately high pressures would be required. Photopolymerizations, usually incorporating free-radical initiators, are also known (28, 30, 31, 37).

The course of VF polymerizations is dominated by the high energy, and hence high reactivity of the propagating VF radical. The fluorine substituent provides little resonance stabilization, leading to a propagating intermediate that is indiscriminant in its reactions. Monomer reversals, branching, and chain-transfer reactions are common. The reactivity of the VF radical limits the choice of polymerization medium, surfactants, initiators, or other additives and makes impurity control important. Species that can participate in chain transfer or incorporate in the polymer can depress molecular weight or degrade the thermal stability characteristics of the final polymer.

The combination of triisobutylborane [1116-39-8] and oxygen has been used to polymerize VF at reduced temperature and pressure (44). Polymerization temperature was varied from 0 to 85°C with a corresponding drop in melting point from ~ 230°C (0°C polymerization) to ~ 200°C (85°C polymerization). This dependance

Table 1. Physical Properties of Vinyl Fluoride

Property	Value
molecular weight	46.05
boiling point, °C	−72.2
freezing point, °C	−160.5
critical temperature, °C	54.7
critical pressure, MPa[a]	5.1
critical density, g/cm^3	0.320
liquid density at 21°C, g/cm^3	0.636
vapor pressure at 21°C, MPa[a]	2.5
solubility in water at 80°C, g/100 g H_2O	
at 3.4 MPa[a]	0.94
at 6.9 MPa[a]	1.54

[a] To convert MPa to atm, divide by 0.101.

of melting temperature, and degree of crystallinity, have been interpreted in terms of variations in the extent of monomer reversals during polymerization (45). Copolymers of VF with vinylidene fluoride [75-38-7] and tetrafluoroethylene [116-14-3] also have been prepared with this initiation system. VF tends toward alternation with tetrafluoroethylene and incorporates preferentially in copolymerization with vinylidene fluoride (see Fluorine compounds, organic–polytetrafluoroethylene; poly(vinylidene fluoride)). More recently, interpolymers of VF have been reported with tetrafluoroethylene and other highly fluorinated monomers such as hexafluoropropylene, perfluorobutylethylene, and perfluoroethylvinylether (46, 47). Polymerization reaction took place in an aqueous medium using an initiator consisting of water-soluble organic azo compounds or salts of inorganic peracids, examples of which include 2,2′-azobis(2-amidinopropane) dihydrochloride and ammonium persulfate. Reaction conditions were relatively mild at temperatures of 60–100°C and pressures of 1–12 MPa in the absence of any surfactant.

Copolymers of VF and a wide variety of other monomers have been prepared (6, 44, 45, 48–53). The high energy of the propagating VF radical strongly influences the course of these polymerizations. VF incorporates well with other monomers that do not produce stable free radicals, such as ethylene and vinyl acetate, but is sparingly incorporated with more stable radicals such as acrylonitrile [107-13-1] and vinyl chloride. An Alfrey-Price Q value of 0.010 ± 0.005 and an e value of 0.8 ± 0.2 have been determined (54). The low value of Q is consistent with little resonance stability and the e value is suggestive of an electron-rich monomer.

3. Polymer Properties

Poly(vinyl fluoride) [24981-14-4] (PVF) is a semicrystalline polymer with a planar, zig-zag configuration (55). The degree of crystallinity can vary significantly from 20–60% (56) and is thought to be primarily a function of defect structures. Wide-line Nuclear magnetic resonance (nmr) and X-ray diffraction studies show the unit cell to contain two monomer units and have the dimensions of $a = 0.857$ nm, $b = 0.495$ nm, and $c = 0.252$ nm (57). Similarity to the phase I crystal form of poly(vinylidene fluoride) suggests an orthorhombic crystal (58).

The relationship of polymer structure to melting point and degree of crystallinity has been the subject of a number of studies. Head-to-head regio irregularities in PVF are known (56, 59, 60) and the concentration of such units has been suggested as the source of variations in melting point (45, 52, 61). Commercial PVF contains $\sim 12\%$ head-to-head linkages by ^{19}F- nmr and displays a peak melting point of ~ 190°C (52, 53, 62, 63). Both nmr and infrared (ir) studies have shown PVF to be atactic (52, 56, 59, 60, 64–67) and, as such, variations in stereoregularity are not thought to be a contributor to variations in melting point.

PVF with controlled amounts of head-to-head units varying from 0 to 30% have been prepared (52, 53) by using a chlorine substituent to direct the course of polymerization of chlorofluoroethylenes and then reductively dechlorinating the products with tributyltin hydride. This series of polymers shows melting point distributions ranging from ∼ 220°C for purely head-to-tail polymer down to ∼ 160°C for polymer containing 30% head-to-head linkages. This study, however, does not report the extent of branching in these polymers. Further work has shown that the extent of branching has a pronounced effect upon melting temperature (62, 63). Change of polymerization temperature from 90 to 40°C produces a change in branch frequency from 1.35 to 0.3%, while the frequency of monomer reversals is nearly constant $(12.5 \pm 1\%)$. The peak melting point for this series varies from 186°C (90°C polymerization) to 206°C (40°C polymerization).

PVF displays several transitions below the melting temperature. The measured transition temperatures vary with the technique used for measurement. T_g (L) (lower) occurs at -15 to $-20°C$ and is ascribed to be relaxation free from restraint by crystallites. T_g (U) (upper) is in the 40–50°C range and is associated with amorphous regions under restraint by crystallites (68). Another transition at $-80°C$ has been ascribed to short-chain amorphous relaxation and one at 150°C associated with premelting intracrystalline relaxation.

PVF has low solubility in all solvents below ∼ 100°C (66). Polymers with greater solubility have been prepared using 0.1% 2-propanol polymerization modifier and were characterized in dimethylformamide (DMF) solution containing $0.1\,N$ LiBr. M_n ranged from 76,000 to 234,000 (osmometry), and M_s from 143,000 to 654,000 (sedimentation velocity). Sedimentation velocity molecular weights can be related to intrinsic viscosity using the Mark–Houwink equation:

$$\eta_{\mathrm{inh}} = KM^a$$

Using an a value of 0.80, which is typical of an extended polar polymer in good solvent, K is determined to be 6.52×10^{-5} (69).

The conformational characteristics of PVF are the subject of several studies (58, 70). The rotational isomeric state (RIS) model has been used to calculate mean square end-to-end distance, dipole moments, and conformational entropies. ^{13}C nmr chemical shifts are in agreement with these predictions (71). The stiffness parameter (†) has been calculated (72) using the relationship between chain stiffness and cross-sectional area (73). In comparison to polyethylene, PVF has greater chain stiffness that decreases melting entropy, ie, $(\Delta S)_m$ = 8.58 J/(moK) [2.05 cal/(mol·K)] vs 10.0 J/(mol·K) [2.38 cal/(moK)].

A solubility parameter of $24.5 - 24.7\,\mathrm{MPa}^{1/2}$ $[12.0 - 12.1\,(\mathrm{cal/cm}^3)^{1/2}]$ has been calculated for PVF using room temperature swelling data (74). The polymer lost solvent to evaporation more rapidly than free solvent alone when exposed to air, which was ascribed to reestablishment of favorable dipole–dipole interactions within the polymer. Infrared spectral shifts for poly(methyl methacrylate) in PVF have been interpreted as evidence of favorable acid–base interactions involving the H from CHF units (75). This is consistent with the greater absorption of pyridine than methyl acetate despite a closer solubility parameter match with methyl acetate.

PVF is more thermally stable than other vinyl halide polymers. High molecular weight PVF is reported to degrade in an inert atmosphere, with concurrent HF loss and backbone cleavage occurring at ∼ 450°C (76, 77). In air, HF loss occurs at ∼ 350°C, followed by backbone cleavage ∼ 450°C.

More recent work reports the onset of thermal degradation at lower temperatures and provides a clearer picture of the role of oxygen (78–80). In the presence of oxygen, backbone oxidation and subsequent cleavage reactions initiate decomposition. In the absence of oxygen, dehydrofluorination eventually occurs, but at significantly higher temperatures.

PVF is transparent to radiation in the ultraviolet (uv), visible, and near-ir regions, transmitting 90% of the radiation from 350 to 2500 nm. Radiation between 7000 and 12,000 nm is absorbed (81). Exposure to low dose γ irradiation produces cross-links in PVF and actually increases tensile strength and etching resistance, whereas the degree of crystallinity and melting point are reduced (82). PVF becomes embrittled upon exposure to electron beam radiation of 10 MGy (10^9 rad), but resists breakdown at lower doses. It retains its strength at 0.32 MGy (32×10^6 rad) while polytetrafluoroethylene is degraded at 0.02 MGy (2×10^6 rad) (83).

4. Fabrication and Processing

Commercial PVF is insoluble at room temperature because of the large number of hydrogen bonds and high degree of crystallinity. Some latent solvents solvate PVF at temperatures > 100°C. PVF is converted to thin films and coatings. Processing of PVF, eg, by melt extrusion, depends on latent solvation of PVF in highly polar solvents and its subsequent coalescence. An example is plasticized melt extrusion of PVF into thin films (84). Pigments, stabilizers, plasticizers, and other additives can be incorporated in the film by dispersing them with the polymer in the latent solvent. The solvent is recovered by evaporation after extrusion. The extruded film can be biaxially oriented to varying degrees.

PVF can be applied to substrates with solvent-based or water-borne dispersions, or by powder-coating techniques. Viscosity modifiers are often needed to obtain a coatable dispersion. Dispersions can be applied by spraying, reverse roll coating, dip coating, and centrifugal casting. Other methods include casting on a continuous belt, extrusion into a hot liquid (85), and dipping a hot article into the dispersion (86).

Table 2 lists properties of PVF films. Various multilayer cast PVF films have been reported (87). Physical and tensile properties of the film depend on the extent of its orientation (88).

Table 2. Properties of Poly(vinyl fluoride) Film

Property	Value	ASTM[a] test method
	Physical and thermal properties	
bursting strength, kPa[b]	200–450[c]	D774
coefficient of friction with metal	0.18–0.21	D1894-78
density, g/cm^3	1.38–1.72	weighed samples
impact strength, kJ/m[d]	43–90	D3420-80
refractive index, n_D	1.46	D542; Abbe refractometer, 30°C
tear strength, kJ/m[d]		
propagated	6–22	D1922-67
initial	129–196	D1004-66
tensile modulus, MPa[e]	44–110	D882
ultimate elongation, %	115–250	D882
ultimate yield strength, MPa[e]	33–41	D882
linear coefficient of expansion, cm/(cm·°C)	0.00005	air oven, 30 min
useful temperature range, °C		
continuous use	−70 to +107	
short cycle (1–2 h)	175	
zero strength, °C	260–300	hot bar
thermal conductivity (1°C/cm), W/(m·K)		
−30°C	0.14	
60°C	0.17	
self-ignition temperature, °C	390	D1929
solar energy transmittance, 359–2500 nm, %	90	E427-71
	Permeability	
moisture absorption, %	0.5	D570-81
moisture vapor transmission,[f] nmol/(m^{2}s)[g]		
at 7.0 kPa,[h] 39.5°C	4.65–29.4	E96-58T
gas permeability,[f] nmol/(m·sGPa)[i] at		
98 kPa,[h] 23°C		D1434
carbon dioxide	22.4	
helium	302	

Table 2. ***Continued***

Property	Value	ASTM[a] test method
hydrogen	117	
nitrogen	0.5	
oxygen	6.6	
vapor transmission rate,[j] nmol/(m^2s)[k] at 23.5°C		E96, modified
acetic acid	4.9	
acetone	1570	
benzene	13	
carbon tetrachloride	3.9	
ethyl acetate	13	
hexane	10	
water[l]	22	
Electrical properties[m]		
corona endurance, h at 60 Hz, 40 V/μm	2.5–6.0	D2275
dielectric constant at 1 MHz, 23°C	6.2–7.7	D150-81
dielectric strength,		D150-81
short term ac, kV/μm	0.08–0.13	
short term dc, kV/μm	0.15–0.19	
dissipation factor, %		D150-81
1 MHz at 23°C	0.17–0.28	
1 MHz at 100°C	0.09–0.21	
10 kHz at 23°C	0.019–0.019	
10 kHz at 100°C	0.21–0.067	
volume resistivity for transparent film, GΩm		D257
23°C	2000–700	
100°C	0.7–2	
surface resistivity, GΩm		D257
23°C	60,000–20,000	
100°C	7–20	

[a] Unless otherwise noted.
[b] To convert kPa to psi, multiply by 0.145.
[c] Range dependent on composition and tensile modification.
[d] To convert kJ/m to ft·lbf/in., divide by 0.0534 (ASTM D256).
[e] To convert MPa to psi, multiply by 145.
[f] Measurements made on films of nominal 25 μm thickness.
[g] To convert nmol/(m^2·s) to g/(m^2·d), multiply by 1.94.
[h] To convert kPa to mm Hg, multiply by 7.5.
[i] To convert nmol/(m·s·GPa) to mL·mil/(m^2·d·atm), multiply by 7.725.
[j] At partial pressure of vapor at given temperature.
[k] To convert nmol/(m^2·s) to g/(m^2·d), multiply by 1.94 and by the density.
[l] At 39.5°C.
[m] Range of electrical properties is given; the first value refers to 54.8-μm transparent film, and the second value to 54.8-μm white pigmented film.

Adherability of the film may be enhanced by its treatment with flame, electric discharge, boron trifluoride gas, activated gas plasma, dichromate sulfuric acid, and a solution of alkali metal in liquid ammonia (89–92). A coating of polyurethane, an alkyl polymethacrylate, or a chlorinated adhesive can be applied to PVF surfaces to enhance adhesion (85, 93, 94).

5. Economic Aspects

PVF is available from Du Pont both as transparent and pigmented films and as a resin under the trademark *Tedlar* PVF film. Films are available in nonoriented and oriented grade in several tensile modifications and thicknesses, with either adherable or nonadherable release-grade surfaces. Nonorieted films exhibit extensive conformability to various shapes. PVF films are available in single layer and integrated multilayers where the top layer of the latter is clear and the bottom layer may possess aesthetic effects such as color, metallic appearance or pearlescenc. The prices in the year 2000 ranged from $30 to 70/kg. Prices for specially tailored films were significantly higher.

6. Health and Environment

A number of studies and reviews of the toxicological effects of exposure to VF have been conducted (95–97). A 1995 report (98) by *International Agency for Research on Cancer* (IARC) has evaluated the preceding data for VF and a classification of "probably carcinogenic to humans" was assigned to VF. In 1998, *American Conference of Government Industrial Hygienist* (ACGIH) classified VF as an A2 carcinogen defined as "suspected human carcinogen". These classifications are based only on animal data since sufficient epidemiology data do not exist. The oncogenic potential of VF has been studied in male and female rats and mice administered VF via inhalation. Exposure concentrations ranged from 0 to 2500 ppm for 6 h/day, 5 days/week for up to 2 yr (95). Under the conditions of this study, VF was found carcinogenic, similar to other monohaloethylenes, at concentrations of 25 ppm or greater. Mice were more susceptible than rats to the carcinogenic effects of VF and were found to metabolize VF more readily than rats or humans (99). A metabolite of VF is the suspected carcinogenic species. VF is metabolized to the suspected carcinogenic intermediate at a rate approximately one-fifth that of vinyl chloride (100–104).

VF is flammable in air between the limits of 2.6 and 22% by volume. Minimum ignition temperature for VF and air mixtures is 400°C. A small amount, $<0.2\%$, of terpenes is added to VF to prevent spontaneous polymerization. The U.S. Department of Transportation has classified the inhibited VF as a flammable gas.

The self-ignition temperature of PVF film is 390°C. The limiting oxygen index (LOI) for PVF is 22.6% (105), which can be raised to 30% in antimony oxide-modified film (106). Hydrogen fluoride and a mixture of aromatic and aliphatic hydrocarbons (107) are generated from the thermal degradation of PVF. Toxicity studies, ie, survival and time to incapacitation, of polymers, cellulosics (108, 109), and airplane interior materials (110) expose mice to pyrolysis products and show PVF thermal degradation products to have relatively low toxicity.

7. Uses

The uses of PVF depend on its weatherability, strength over a wide range of temperatures, and inertness toward a wide variety of chemicals, corrosives, and staining agents. It finds wide use as a protective or decorative coating. It can be applied as a preformed film in a laminating step or from a dispersion in a coating step. It may be transparent or pigmented in a variety of colors. PVF film is laminated to cellulosics, flexible vinyls, plastics, rubbers, and resin-impregnated felt. These laminated products are applied to exterior wall panels for buildings (111, 112), highway sound barriers (113), automobile trim, truck and trailer siding (114), vinyl awnings, backlit signs (115), pipe covering (116), stain-resistant wall coverings, and aircraft cabin interiors (117, 118).

On metal or plastics, PVF surfaces serve as a primer coat for painting, eg, automobile parts, or where improved adhesion is desired (119). Because of its moisture impermeability and wide operating temperature range, PVF film is used to fabricate bags to contain glass fiber mats for insulating exterior airplane walls and cargo space, and air conditioning ducts. PVF has long been used to construct bags for sampling gases (120).

Fiber-reinforced panels covered with PVF have been used for greenhouses. Transparent PVF film is used as the cover for flat-plate solar collectors (121) and photovoltaic cells (qv) (122). White PVF pigmented film is used as the bottom surface of photovoltaic cells. Nonadhering film is used as a release sheet in plastics processing, particularly in high temperature pressing of epoxy resins for circuit boards (123–125) and aerospace parts. Dispersions of PVF are coated on the exterior of steel hydraulic brake tubes and fuel lines for corrosion protection.

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