Designation: ~~D3222 – 18a~~ D3222 – 20

Standard Specification for Unmodified Poly(Vinylidene Fluoride) (PVDF) Molding Extrusion and Coating Materials[1]

This standard is issued under the fixed designation D3222; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This specification covers melt processable molding and extrusion materials, as well as coating materials of poly(vinylidene fluoride) fluoroplastic, commonly abbreviated PVDF (or PVF_2 in scientific literature). This specification covers thermoplastic resin materials supplied in pellet or powder form.

1.2 This specification applies only to the virgin homopolymer prepared from vinylidene fluoride, not copolymers, reinforced, filled grades or special grades with additives or treatments for modification of attributes.

1.3 The tests involved are intended to provide information for specification of unmodified PVDF homopolymer resins. It is not the purpose of this specification to provide engineering data for design purposes.

1.4 PVDF fluoroplastics melt between 156 and 180°C (312 and 356°F) and are thermally stable up to about 370°C (698°F). (**Warning—**Evolution of corrosive and toxic hydrogen fluoride can occur under certain conditions.)

1.5 The values stated in SI units, as detailed in IEEE/ASTM S-10, are to be regarded as the standard. The values given in parentheses are for information only.

NOTE 1—PVDF exhibits polymorphism.[2] The type and extent of crystalline structure varies with the thermomechanical history of the sample. Specimens prepared by techniques different than prescribed in this specification can have properties that vary from the values specified.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 10.

NOTE 2—There is no equivalent ISO standard for this specification. Information in this specification is technically equivalent to related information in ISO 12086-1 and ISO 12086-2.

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

[1] This specification is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.15 on Thermoplastic Materials.
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[2] Lovinger, A. J., "Poly(Vinylidene Fluoride)" *Developments in Crystalline Polymers*, Vol 1, Chapter 5, D. C. Bassett, Ed., Applied Science, London, 1982.

***A Summary of Changes section appears at the end of this standard**

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D149 Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials at Commercial Power Frequencies
D150 Test Methods for AC Loss Characteristics and Permittivity (Dielectric Constant) of Solid Electrical Insulation
D256 Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics
D257 Test Methods for DC Resistance or Conductance of Insulating Materials
D542 Test Method for Index of Refraction of Transparent Organic Plastics
D618 Practice for Conditioning Plastics for Testing
D638 Test Method for Tensile Properties of Plastics
D790 Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials
D792 Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement
D883 ~~Terminology Relating to Plastics~~
D1238 Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer
D2863 Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)
D3418 Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry
D3835 Test Method for Determination of Properties of Polymeric Materials by Means of a Capillary Rheometer
D3892 Practice for Packaging/Packing of Plastics
IEEE/ASTM S-10 Use of the International System of Units (SI): The Modern Metric System

2.2 *IEC and ISO Standards:*

ISO 12086-1 Plastics—Fluoropolymer Dispersion and Moulding and Extrusion Materials—Part 1: Designation and Basis for Specification[4]
ISO 12086-2 Plastics—Fluoropolymer Dispersion and Molding and Extrusion Materials—Part 2: Preparation of Test Specimens and Determination of Properties[4]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of plastics terms used in this specification, see Terminology D883.

3.1.2 *lot, n*—one production run or a uniform blend of two or more production runs.

4. Classification

4.1 This specification covers two types[5] of natural, unmodified PVDF fluoroplastics supplied in pellet form for molding and extrusion, and in powder form for solutions, dispersions, or coatings.

4.1.1 *Type I*—PVDF fluoroplastics are polymerized in emulsion. Depending upon the polymerization conditions, the peak melting point of the resin can be varied between 156 and 172°C. The diameter of the primary particle isolated from the emulsion is typically less than 1 µm; the dried powder has an average agglomerate diameter range of 3 to 15 µm.

4.1.1.1 Two distinctly different Type I emulsion PVDF resins are available commercially. These are differentiated by peak melting endotherm values, as shown in Table 1, and this difference is the basis for subdividing Type I resins into Grades 1 and 2. Table 1 shows the melt viscosity ranges encompassing resin grades available from several sources and are provided for information purposes only.

4.1.2 *Type II*—PVDF fluoroplastics are polymerized in suspension. Peak melting temperatures of these resins range from 164 to 180°C. The particles isolated from suspension are spherical and range typically from 20 to 150 µm in diameter.

4.1.2.1 Type II resins are available commercially, and the data of Table 1 reflect ranges encompassing values typical for the properties of available grades.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.
[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.
[5] Dohany, J. E., and Robb, L. E., "Poly(Vinylidene Fluoride)" *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol 11, 3rd Edition, 1980, pp. 64–74.

TABLE 1 Classification of PVDF Resins

Property		Typical Values or Ranges		
		Type I		Type II
		Grade 1	Grade 2	
Specific Gravity	Gms/cc	1.75-1.79	1.75-1.79	1.76-1.79
~~Peak Melting Endotherm~~	~~°C~~	~~156-162~~	~~162-172~~	~~164-180~~
Peak Melting Endotherm	°C	156-162	161-172	164-180
Melt Flow Rate	g/10 min (wt in Kg)			
	~~Ultra High Viscosity~~	~~...~~	~~...~~	~~0.5-10[A]~~
	Ultra High Viscosity	...	0.1-2[A]	0.5-10[A]
	High Viscosity	0.5-8[A]	5-8[B]	0.5-10[C]
	Medium Viscosity	4-18[A]	5-36[B]	0.5-30[D]
	Low Viscosity	...	3.5-45[E]	0.5-60[F]
Apparent Melt Viscosity	Pa's:[G]			
	~~High Viscosity~~	~~2800-3800~~	~~2800-3700~~	~~2500-4000~~
	High Viscosity	2800-3800	2800-3900	2500-4000
	Medium Viscosity	2300-2800	1300-2800	1300-2500
	~~Low Viscosity~~	~~...~~	~~250-1300~~	~~250-1300~~
	Low Viscosity	...	100-1300	250-1300

Note: For measuring MFR values of PVDF, the load must be selected based on the viscosity as follows:

[A] = 21.6 Kg
[B] = 12.5 Kg
[C] = 10.0 Kg
[D] = 5 Kg
[E] = 3.8 Kg
[F] = 2.16 Kg
[G] Reported for a shear rate of 100 s^{-1} determined by capillary rheometry at 232°C (450°F) using 0.027 radian (60°) entrance angle die with L/D of 15 and in accordance with procedures of Test Method D3835. Multiply the pascal second values by ten to obtain poise values.

4.2 The system uses predefined cells to refer to specific aspects of this specification, as illustrated below.

Specification				
Standard Number Block	Type	Grade	Class	Special Notes
Example: Specification D3222	I	2	...	...

For this example (D3222, I2), the line callout describes a PVDF resin polymerized in emulsion, having a specific gravity between 1.75 and 1.79, and a peak melting endotherm between ~~162~~161 to 172°C. A comma is used as the separator between the Standard Number and the Type. Separators are not needed between the Type, Grade, and Class.[6] Provision for Special Notes is included so that other information, such as a preferred viscosity range, can be provided when required. When special notes are used, they shall be preceded by a comma.

5. General Requirements

5.1 The material shall be of uniform composition and free of foreign matter.

6. Detail Requirements

6.1 *General Attributes:*

6.1.1 *Peak Melting Endotherm*—The material covered by this specification shall have a minimum peak melting endotherm for the type and class as shown in Table 1 when tested in accordance with Test Method D3418. For Type I resins, this shall involve heating a solid specimen of 5 ± 1 mg from room temperature to 200°C at 10°C/min, maintaining the temperature at 200°C for 5 min, followed by cooling at a controlled rate of 10°C/min to about 30°C, then reheating at 10°C/min to 200°C. Record the peak melting endotherm during the second melting cycle.

6.1.1.1 *Temperature*—Test Type II resins likewise except that the maximum is ~~250°C.~~230°C.

6.1.2 *Specific Gravity*—A solid specimen of the material covered by this specification shall have the specific gravity indicated in Table 1 when tested in accordance with Test Method D792.

[6] See the ASTM *Form and Style for ASTM Standards*, available from ASTM Headquarters.

NOTE 3—~~Test attached to the specimen upon immersion.~~ Dipping the specimens in a very dilute solution (less than 0.1 weight percent) of an ammonium perfluorooctanoate surfactant minimizes ~~this problem.~~issues with the water-sample interface and gives more accurate results.

6.1.3 *Refractive Index*—The material covered in this specification shall have a refractive index of 1.42 when measured at the sodium D line at 25°C (77°F) in accordance with the refractometer procedure in Test Methods D542, using specimens that have not been subjected to any processes which induce orientation of the polymer chains or crystal-lites. Compression-molded specimens at least 2-mm (0.079-in.) thick that have been quenched rapidly in water are preferred.

6.1.4 *Limiting Oxygen Index*—The material covered in this specification shall have a minimum limiting oxygen index of 42 when tested in accordance with Test Method D2863.

NOTE 4—If a column with a restricted opening is used, position the top of the specimen 40 mm below the opening.

6.2 *Processing Related Attributes:*

6.2.1 *Flow Rate*—Materials conforming to this specification shall be tested for melt flow rate in accordance with Test Method D1238 using loads shown in parentheses in Table 1.

6.2.2 *Rheological Properties*—The apparent melt viscosity of these materials shall be tested in accordance with Test Method D3835 at 231 ± 1°C (450°F) using a die with an entrance angle of 60° (cone angle of 120°) and a minimum capillary L/D of 15. See Table 1.

6.3 *Mechanical Properties:*

6.3.1 *Tensile Properties*—The material covered in this specification shall have a tensile yield strength exceeding 36 MPa (5200 psi) at 23°C (74°F) and a minimum elongation at break of 10 % when tested in accordance with Test Method D638 at 51 mm (2 in.)/min, using Type I specimens 3.2-mm (0.125-in.) thick as specified in Test Method D638. Preferably, compression-molded samples are used (see Section 8), but injection molded specimens also are used, providing that the samples yield and rupture in the gage region and not near the heel. Specimens shall be molded under conditions specified by the resin suppliers. Generally, injection molded specimens show low and variable elongation values compared to compression-molded specimens. Typically, the melt temperature is 30 to 60°C higher than the upper peak melting endotherm value depending on the grade. Mold temperature is ~~120 ± 10°F.~~53 ± 10°C (128 ± 18°F).

6.3.2 *Flexural Properties*—The material covered in this specification shall have a minimum flexural modulus of 1.31 GPa (190×10^3 psi) when tested in accordance with Method I of Test Methods D790, using 6.4-mm (0.25-in.) thick specimens prepared by injection molding under conditions specified by the resin supplier. Alternatively, compression-molded samples are used (see Section 8) and tested after the 16-h conditioning period.

6.3.3 *Impact Resistance*—Type I material of medium or high viscosity shall have a minimum impact strength of 80.0 J/m (1.50 ft·lbf/in.). Type I material of low viscosity shall have a minimum impact strength of 40.0 J/m (0.75 ft-lbf/in.). The impact strength shall be determined by Test Methods D256 using 6.4-mm (0.25-in.) thick specimens prepared by injection molding under conditions specified by the manufacturer. Alternatively, specimens are compression-molded and tested after the conditioning period as specified above. For Type II material, impact testing is not required.

6.4 *Electrical Properties:*

6.4.1 *D-C Resistance*—The material covered in this specification shall have a d-c volume resistivity greater than 1.2Ω·m (1.2×10^{14} Ω·cm) when tested as a 0.76-mm (0.030-in.) compression-molded specimen (see Section 8) in accordance with Test Methods D257.

6.4.2 *Dielectric Strength*—The material covered in this specification shall have a dielectric strength in air no less than 57 kV/mm (1280 V/0.001 in.) by the "short-time" method of Test Methods D149 with 0.13-mm (0.05-in.) thick compression-molded specimens (see Section 8) tested in air using 25.4-mm (1-in.) Type 3 electrodes.