Designation: D 3222 – 99

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

This standard is issued under the fixed designation D 3222; 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.

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).

NOTE 1—**Warning:** Evolution of corrosive and toxic hydrogen fluoride can occur under certain conditions.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

NOTE 2—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 could have properties that may 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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Note 1 and Section 10.

NOTE 3—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.

2. Referenced Documents

2.1 *ASTM Standards:*

D 149 Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials at Commercial Power Frequencies[3]

D 150 Test Methods for A-C Loss Characteristics and Permittivity (Dielectric Constant) of Solid Electrical Insulating Materials[3]

D 256 Test Methods for Impact Resistance of Plastics and Electrical Insulating Materials[4]

D 257 Test Methods for D-C Resistance or Conductance of Insulating Materials[3]

D 542 Test Methods for Index of Refraction of Transparent Organic Plastics[4]

D 618 Practice for Conditioning Plastics and Electrical Insulating Materials for Testing[4]

D 638 Test Method for Tensile Properties of Plastics[4]

D 790 Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials[4]

D 792 Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement[4]

D 883 Terminology Relating to Plastics[4]

D 1238 Test Method for Flow Rates of Thermoplastics by Extrusion Plastometer[4]

D 1505 Test Method for Density of Plastics by the Density-Gradient Technique[4]

D 1898 Practice for Sampling of Plastics[4]

D 2863 Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-like Combustion of Plastics (Oxygen Index)[5]

D 3295 Specification for PTFE Tubing[5]

D 3418 Test Method for Transition Temperatures of Polymers by Thermal Analysis[5]

D 3835 Test Method for Determination of Properties of

[1] This specification is under the jurisdiction of ASTM Committee D-20 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.

[3] *Annual Book of ASTM Standards*, Vol 10.01.

[4] *Annual Book of ASTM Standards*, Vol 08.01.

[5] *Annual Book of ASTM Standards*, Vol 08.02.

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

Polymeric Materials by Means of a Capillary Rheometer[6]
D 3892 Practice for Packaging/Packing of Plastics[5]
D 4895 Specification for Polytetrafluoroethylene (PTFE) Resins Produced From Dispersion[6]
E 380 Practice for Use of the International System of Units (SI)[7]

2.2 *IEC and ISO Standards:*

ISO 12086-1 Plastics—Fluoropolymer Dispersion and Moulding and Extrusion Materials—Part 1: Designation and Basis for Specification[8]
ISO 12086-2 Plastics—Fluoropolymer Dispersion and Molding and Extrusion Materials—Part 2: Preparation of Test Specimens and Determination of Properties[8]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of plastics terms used in this specification, see Terminology D 883.

3.2 *Abbreviations:Units, Symbols, and Abbreviations:*

3.2.1 For units, symbols and abbreviations used in this specification see Practice E 380.

4. Classification

4.1 This specification covers two types[9] 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 170°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.

4.2 A one-line system may be used to specify materials covered by this specification. 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 D 3222 – 97	I	2	...	...

For this example (D 3222 – 97, 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 to 170°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.[10] 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 should be preceded by a comma.

5. General Requirements

5.1 The material shall be of uniform composition and free of foreign matter to the contamination level agreed upon between the purchaser and seller.

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 D 3418. 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.

6.1.2 *Specific Gravity*—A solid specimen of the material covered by this specification shall have the minimum specific gravity indicated in Table 1 (1.75 for Type I, Class 1 and 1.76 for all others) when tested in accordance with Test Methods D 792 or D 1505.

6.1.3 *Refractive Index*—The material covered in this specification shall have a refractive index of 1.42 when measured at

TABLE 1 Classification of PVDF Resins

Property	Typical Values or Ranges		
	Type I		
	Grade 1	Grade 2	Type II
Specific Gravity	1.75 to 1.79	1.75 to 1.79	1.76 to 1.79
Peak Melting Endotherm, °C	156 to 162	162 to 170	164 to 180
Apparent Melt Viscosity,[A] Pa·s:			
High Viscosity	2800 to 3800	2800 to 3100	2500 to 4000
Medium Viscosity	2300 to 2800	1300 to 2800	1300 to 2500
Low Viscosity	...	500 to 1300	500 to 1300

[A] 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 according to procedures of Test Method D 3835. Multiply the pascal second values by ten to obtain poise values.

[6] *Annual Book of ASTM Standards*, Vol 08.03.
[7] *Annual Book of ASTM Standards*, Vol 14.02.
[8] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.
[9] Dohany, J. E., and Robb, L. E., "Poly(Vinylidene Fluoride)" *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol 11, 3rd Edition, 1980, pp. 64–74.
[10] See the ASTM *Form and Style for ASTM Standards*, available from ASTM Headquarters.

the sodium D line at 25°C (77°F) in accordance with the refractometer procedure in Test Methods D 542, 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 D 2863.

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

6.2 *Processing Related Attributes*:

6.2.1 *Flow Rate*—Materials conforming to this specification may be tested for melt flow rate according to Test Method D 1238, using 232°C and 21.6-kg load for medium or high melt viscosity grades; low melt viscosity grades may be tested at 232°C (450°F) using a 5 kg weight.

6.2.2 *Rheological Properties*—The preferred method for measuring flow characteristics is capillary rheometry. Thus rheological properties of the materials should be tested according to Test Method D 3835 at 232°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 according to Test Method D 638 at 51 mm (2 in.)/min, using Type I specimens 3.2-mm (0.125-in.) thick as specified in Test Method D 638. Condition in accordance with Procedure A of Test Method D 638, except that a minimum time of 16 h before testing is satisfactory. Preferably, compression-molded samples should be used (see Section 8), but injection molded specimens may be used, providing that the samples yield and rupture in the gage region and not near the heel. Specimens should be molded under conditions specified by the resin suppliers. Generally, injection molded specimens show low and variable elongation values compared to compression-molded specimens.

6.3.2 *Flexural Properties*—The material covered in this specification shall have a minimum flexural modulus of 1.38 GPa (190×10^3 psi) when tested according to Method I of Test Methods D 790, using 6.4-mm (0.25-in.) thick specimens prepared by injection molding under conditions specified by the resin supplier. Samples should be conditioned in accordance with Procedure A of Methods D 618 except that a minimum time of 16 h before testing is satisfactory. Alternatively, compression-molded samples may be used (see Section 8) and tested after the 16-h conditioning period.

6.3.3 *Impact Resistance*—The material covered in this specification shall have a minimum impact strength of 101.4 J/m (1.90 ft·lbf/in.) determined by Test Methods D 256 using 6.4-mm (0.25-in.) thick specimens prepared by injection molding under conditions specified by the manufacturer. Specimens shall be conditioned in accordance with the provisions of Procedure A of Methods D 618, except that the conditioning period prior to testing shall be at least 16 h. Alternatively, specimens may be compression-molded and tested after the conditioning period as specified above.

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 $1.2\Omega \cdot m$ (1.2×10^{14} $\Omega \cdot cm$) when tested as a 0.76-mm (0.030-in.) compression-molded specimen (see Section 8) in accordance with Test Methods D 257.

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 D 149 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.

6.4.3 *Dielectric Constant*—The material covered in this specification shall have a dielectric constant less than 11.0 at 100 Hz and greater than 7.2 at 1 MHz when tested as a 3.2-mm (0.125-in.) thick compression-molded specimen (see Section 8) according to Test Methods D 150 at 23°C (73°F).

6.4.4 *Dissipation Factor*—The material covered in this specification shall have a dissipation factor of less than 0.045 at 100 Hz and less than 0.24 at 1 MHz when tested as 3.2-mm (0.125-in.) compression-molded specimens (see Section 8) according to Test Methods D 150 at 23°C (73°F).

NOTE 5—Since this material has very low water-absorption characteristics, maintenance of constant humidity during testing or specimen preparation is not necessary except as required for a specific test method. However, no moisture should be present in the resin when preparing specimens for testing. Heat the resin sample at 110°C (230°F) in an air-circulating oven until the adventitious moisture is removed.

7. Sampling

7.1 Materials shall be sampled in accordance with Practice D 1898. Adequate statistical sampling shall be considered an acceptable alternative.

8. Preparation of Compression Molded Specimens

8.1 *Equipment*:

8.1.1 Press with approximately 180 kN (20 ton) capacity and heating capability for maintaining platens between 220 and 240°C (428 to 464°F).

8.1.2 Two smooth chromium-finished plates with approximate dimensions $150 \times 250 \times 5$ mm ($10 \times 10 \times 0.02$ in.), or, if more appropriate to the press type, $150 \times 150 \times 5$ mm ($6 \times 6 \times 0.02$ in.).

8.1.3 Flat open-cavity steel molds, that is, frames, to provide the shape and thicknesses requisite for the specific tests.

8.1.4 Timing device.

8.1.5 Appropriate equipment to handle the hot mold assembly when removed from the press.

8.1.6 Balance and containers for weighing the resin samples.

8.1.7 Water-filled container to quench-cool the samples in the mold frame.

8.1.8 Aluminum foil approximately 0.1-mm thick (0.004-in.).

8.2 *Compression Molding Specimens Less Than 2 mm (0.08 in.)*:

8.2.1 For the given mold cavity establish, by initial trial preparations, the amount of material necessary to overfill slightly and yield a minimum flash after forming.

8.2.2 Place the appropriate amount of material in the center of the mold between thin sheets of polished aluminum foil.

8.2.3 Place the assembly between the chrome-finished plates.

8.2.4 Place the mold assembly in the press so that it is in contact with the hot platens, using a ram force that barely registers on the force gage and hold for a 5-min period. The temperature preferably should be 230°C (446°F) but may be as slow as 228°C (442°F) and as high as 232°C (450°F).

8.2.5 After the preheat period, slowly increase the ram force to 130 kN (30 000 lbf) and hold for 1 min.

8.2.6 Remove the sandwiched material and immediately quench in cold water.

8.2.7 After standing for 1 min, disassemble and remove the molded plaque from the frame.

NOTE 6—The alternative method of allowing the assembly to cool at ambient room temperature under a heavy weight, or under pressure in a cold press, may result in specimens having properties that may vary from values in specification tests.

8.2.8 If the mold shape is not appropriate for the test, cut test specimens from the molded sample.

NOTE 7—The edges of the specimen may affect performance in mechanical tests. Die-cutting is the preferred method to prepare such specimens; the cutting edges should be leveled and sharp.

8.3 *Compression Molding Specimens Thicker Than 2 mm (0.08 in.)*:

8.3.1 Pellets of PVDF can be compression-molded directly in thick sections without difficulty.

8.3.2 Powdered PVDF samples tend to entrap air when thick sections are molded under compression. Such specimens are not suitable for any tests in this specification. The preferred method to obtain bubble-free thick moldings involves preparation of thin compression-molded sheets, as described in 8.2, and a subsequent second molding cycle filling the thick section mold with several layers of the thin sheet specimens cut to fill the mold dimension. To assure complete filling, the stack of thin samples must be slightly higher than the mold cavity thickness.

9. Test Conditions

9.1 *Specific Gravity, Mechanical Properties, and Electrical Properties*:

9.1.1 Condition the molded test specimens in accordance with Procedure A of Practice D 618, except that the period shall be at least 16 h prior to test.

9.1.2 Conduct tests at the standard laboratory temperature of 23 ± 2°C (73.4 ± 3.6°F).

NOTE 8—PVDF is a partially crystalline polymer. Unless molded and conditioned equivalently for a sufficient period to assure consistent crystallinity, samples prepared by any other method may give variable results.

9.1.3 The specific gravity of two specimens cut from a compression-molded sample shall be determined according to Test Methods D 792 or D 1505. If the latter method is used, the tube should have a linear gradient over the range from about 1.65 to 1.90.

NOTE 9—Test Methods D 792 is particularly convenient, but care must be exercised to eliminate air bubbles that may be 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.

9.2 *Melting Temperature*—Determine the melting endotherm peak on the as-received resin sample according to Test Method D 3418 by differential scanning calorimetry under conditions given in 5.1.1. The test for melting endotherm peak requires no conditioning.

10. Handling

10.1 As is the case with any synthetic resin, it is advisable to wear a dust mask when handling large quantities of powder grades to prevent ingestion.

11. Packaging

11.1 The packing, packaging, and marking provisions of Practice D 3892 shall apply to this standard.

12. Precision and Bias

12.1 The precision and bias statements of ASTM test methods referenced herein apply to the specific tests required in this specification.

13. Keywords

13.1 extrusion materials; fluorohydrocarbon plastics; fluoropolymers; molding materials; polyvinylidene fluoride (PVDF)

SUMMARY OF CHANGES

This section identifies the location of selected changes to this specification. For the convenience of the user, Committee D-20 has highlighted those changes that may impact the use of this specification. This section may also include descriptions of the changes or reasons for the changes, or both.

D 3222 – 97:

(*1*) Changed SI statement (1.5).

(*2*) Added new Note 3.

(*3*) Added ISO 12086-01 and ISO 12086-02 and Terminology D 883 to list of referenced documents.

(*4*) Removed reference to Military specifications.

(*5*) Added new Sections 3, 3.1, and 3.2.

(*6*) In Table 1, changed Class 1 and 2 classifications to Grades 1 and 2 classifications.

(*7*) Changed 5.1.1.1 to reflect change from class to grade and qualified the inclusion of viscosity ranges in Table 1 as information only.

(*8*) In 5.2 changed one-line callout example to refer to D 3222 – 97.

D 3222 – 99:

(*1*) Revised the impact strength to 101.4 J/m (1.90 ft·lbf/in.) in 6.3.3.