



Standard Test Method for Determining Inherent Viscosity of Poly(Ethylene Terephthalate) (PET) by Glass Capillary Viscometer¹

This standard is issued under the fixed designation D 4603; 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 test method is for the determination of the inherent viscosity of poly(ethylene terephthalate) (PET) soluble at 0.50 % concentration in a 60/40 phenol/1,1,2,2-tetrachloroethane solution by means of a glass capillary viscometer. Highly crystalline forms of PET that are not soluble in this solvent mixture will require a different procedure.

1.2 The inherent viscosity values obtained by this test method are comparable with those obtained using differential viscometry described in Test Method D 5225.

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

1.4 *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 hazards statements are given in Section 8.

NOTE 1—This test method and ISO 1628-5 are similar but not technically equivalent. This ISO standard gives an option of solvents for PET. Solvent specified in this ASTM test method is one of the options in the ISO method. ISO also uses Type 1C Ubbelohde viscometer, rather than the 1B, and reports viscosity number, rather than inherent viscosity.

2. Referenced Documents

2.1 ASTM Standards:

D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)²

D 446 Specification for Operating Instructions for Glass Capillary Kinematic Viscometers²

D 1972 Practice for Generic Marking of Plastic Products³

¹ This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods (D20.70.05).

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² Annual Book of ASTM Standards, Vol 05.01.

³ Annual Book of ASTM Standards, Vol 08.01.

D 5225 Test Method for Measuring Solution Viscosity of Polymers with a Differential Viscometer⁴

E 1 Specification for ASTM Thermometers⁵

E 380 Practice for Use of the International System of Units (SI)⁶

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁶

2.2 ISO Standard:

1628/5–1998 Determination of the Viscosity of Polymers in Dilute Solution Using Capillary Viscometers - Part 5: Thermoplastic Polyester (TP) homopolymers and Copolymers.⁷

2.3 NIST Standard:

C 602 Testing of Glass Volumetric Apparatus⁸

3. Terminology

3.1 Units, symbols, and abbreviations used in this test method are those recommended in Practice E 380.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *inherent viscosity* (also known as the logarithmic viscosity number)—defined by the equation given in 11.1.

3.2.2 *PET*—as outlined in Practice D 1972. The PET acronym may be used to avoid trademark infringement and to comply with various state or federal laws.

4. Summary of Test Method

4.1 The inherent viscosity is determined by measuring the flow time of a solution of known polymer concentration and the flow time of the pure solvent in a capillary viscometer at a fixed temperature. The inherent viscosity value is calculated from the flow time values.

⁴ Annual Book of ASTM Standards, Vol 08.03.

⁵ Annual Book of ASTM Standards, Vol 14.03.

⁶ Annual Book of ASTM Standards, Vol 14.02.

⁷ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

⁸ Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 3460, Gaithersburg, MD 20899-3460.

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

5. Significance and Use

5.1 The inherent viscosity is relatable to the composition and molecular weight of a polyester resin. It must be controlled so that the processability and end properties of the resin remain in a desired range.

6. Apparatus

6.1 *Cannon Ubbelohde Type 1B Viscometer*, as described in Specifications and Operating Instructions D 446.

6.2 *Viscometer Holder*.

6.3 *Electric Timer*, readable to 0.1 s, as described in Test Method D 445.

6.4 *Constant Temperature Bath*, control label at 30°C [86°F] ± 0.01°C [0.02°F].

6.5 *Kinematic Viscosity Thermometer ASTM 118* (for use at 30°C), conforming to Specification E 1.

6.6 *Temperature Controllable Magnetic Stirring Hot Plate*.

6.7 *TFE-Fluorocarbon Plastic-Coated Stirring Bars and a Magnetic Bar Retriever*.

6.8 *Volumetric Flasks and Stoppers*, 50-mL capacity, conforming to the standards of accuracy in NIST Circular No. C 602.

6.9 *Analytical Balance*, with readout to 0.0001 g.

6.10 *Borosilicate Funnels*.

6.11 *Stainless Steel Filter Screening*, 325-mesh or finer.

6.12 *Aspirator*.

6.13 *Wiley Mill Grinder*, with 20-mesh stainless steel screen.

6.14 *Drying Oven*, for equipment.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁹ Other grades are permitted to be used, providing it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Phenol/1,1,2,2-tetrachloroethane Solution*, 60/40 weight % mixture (0.5 % moisture maximum, protected in such a manner as to maintain this maximum level). Protect PET against the degradation which has been found to occasionally occur during the heating stage in 10.3 through the addition of a hydrogen chloride scavenger to the solvent, such as 0.2 weight % *n*-octyl-bis-(isoethyl mercaptoacetate).¹⁰

7.3 *Reagent Grade Methylene Chloride and Acetone*, rinsing solvents.

7.4 *Chromic Acid*, cleaning solution.

⁹ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

¹⁰ Available from M&T Chemicals, Inc., P. O. Box 1104, Rahway, NJ 07065.

8. Hazards

8.1 The solvent used in this procedure is a mixture of 60 weight % phenol and 40 weight % 1,1,2,2-tetrachloroethane. Both compounds and the mixture are toxic and require care in handling. Make reference to the material safety data sheets available from the suppliers of these compounds for dealing with the hazards they present. In addition to using a hood for adequate ventilation in handling these materials, protection against skin contact is essential.

8.2 Obtain the material safety data sheets for methylene chloride, acetone, and the chromic acid solution used for cleaning the testing equipment from their suppliers. Consult the material safety data sheets before using the materials.

9. Conditioning

9.1 If the sample of PET contains 0.5 % or more of inert material such as titanium dioxide or glass fiber, determine the amount of inert material accurately by a procedure suitable for the type of inert material present.

9.2 If the sample is suspected of being wet (in excess of the moisture level derived from exposure to ambient humidity conditions), dry the sample in an oven for a suggested minimum of 2 h at 65°C [149°F] ± 5°C [9°F] or until a constant weight of ± 0.1 % is reached. Moisture picked up from ambient humidity will weigh 0.30 % and is negligible in this procedure. (See Note 2.)

NOTE 2—Use a suitable technical method to determine moisture content.

9.3 If the sample is difficult to dissolve, reduce the sample size by grinding it to a 20-mesh screen size in a Wiley Mill or other size reduction technique. Avoid overheating the sample during the grinding operation. It is possible to maintain a low temperature by grinding in the presence of dry ice or liquid nitrogen. Grind a 15 to 20-g sample, representative of the entire lot being tested. It is likely that drying is necessary after the dry ice grinding step.

10. Procedure

10.1 Accurately weigh between 0.2475 and 0.2525 g (accurate to ±0.0002 g) of sample into a clean, dry 50-mL volumetric flask. If the sample contains more than 0.5 % inert material, weigh the amount of sample necessary to give the specified amount of PET.

10.2 Place a TFE-fluorocarbon plastic-coated stirring bar into the flask and add approximately 25 mL of solvent. Prepare one flask without any sample present. Cap the flasks.

10.3 Place the flasks in steel beakers and place on a magnetic hot plate which has been preheated to 110°C [230°F] ± 10°C [18°F]. Heat the flasks for 15 min while stirring. Remove flasks and inspect for undissolved PET. If a sample does not dissolve completely, extend the stirring time for up to 30 more min while inspecting the sample at 10-min intervals. If the sample fails to dissolve completely at this time, this procedure is not applicable.

10.4 When the samples have completely dissolved, remove the flasks from the hot plate and allow them to cool to approximately room temperature. Remove the stirring bars with a magnetic retriever and wash the bar with fresh solvent,

letting the wash solvent fall back into the volumetric flask. Add additional solvent to a level about 1 cm [0.4 in.] below the 50-mL mark. Place the flasks in the constant temperature bath preset at 30°C [86°F] ± 0.01°C [0.02°F]. Allow the flasks to sit for 10 min to reach the bath temperature. Invert the stoppered flasks to wash down solvent droplets adhering to the flask walls above the polymer solution, and add sufficient solvent to raise the liquid level up to the 50-mL mark.

10.5 Pour the solution into a clean, dry, Cannon-Ubbelohde viscometer by passing it through a funnel and filter screen into the top of the larger viscometer tube. Fill the viscometer to a level between the level lines on the large reservoir bulb at the bottom of the larger tube. Remove the funnel and place the viscometer in the constant temperature bath preset at 30°C [86°F] ± 0.01°C [0.02°F]. Allow at least 15 min for the temperature of the solution in the viscometer to reach equilibrium.

TABLE 1 Inherent Viscosity of PET at 30°C and 0.5 % Polymer Concentration

| Material | Mean | S _r | S _R | I _r | I _R |
|----------|--------|----------------|----------------|----------------|----------------|
| 2 | 0.6615 | 0.005755 | 0.01233 | 0.0163 | 0.0349 |
| 1 | 0.6949 | 0.007436 | 0.01369 | 0.0210 | 0.0387 |
| 3 | 0.7819 | 0.006819 | 0.01118 | 0.0193 | 0.0316 |

10.6 Using suction from an aspirator, draw the solution through the capillary to a level above the top calibration mark. Regulate the level by capping the breather tube with one rubber-gloved finger and carefully applying suction to the top of the capillary tube. Use care to prevent splashing or bubble formation. A valve in the aspirator line has been found to be useful to control the suction.

10.7 Let the sample solution or solvent flow back down the capillary tube by removing the suction from the top of the capillary tube and by removing the finger from the top of the breather tube. The first flow is a rinse to wet the capillary bulb and finally equilibrate the sample solution to the bath temperature.

10.8 After the solution has drained out of the capillary, repeat 10.6 and 10.7 and time the period required for the liquid to fall back from the higher calibration mark to lower calibration mark above the capillary. Use the electric timer for this measurement. The bottom of the meniscus of the liquid surface is used for determining the times at which the liquid surface flows past the calibration marks.

10.9 Record the flow time and repeat the measurement three more times. Average these results unless the range in time exceeds 0.2 s, in which case make additional measurements until four within a range of 0.2 s are obtained for averaging. Measure the solvent flow time in the same manner as the flow time of the solution samples.

10.10 During the measurements, record the bath temperature to the nearest 0.01°C [0.02°F]. Ensure that the range in temperature does not exceed 0.01°C.

10.11 When measurements are completed, remove the viscometer from the bath and carefully pour the solution from the viscometer into a safety disposal container.

11. Calculation

11.1 Determine the inherent viscosity as follows:

$$\eta_{inh}^{30^\circ C, 0.5\%} = \frac{\ln \eta_r}{C} \quad (1)$$

where:

$\eta_{inh}^{30^\circ C, 0.5\%}$ = inherent viscosity at 30°C [86°F] and at a polymer concentration of 0.5 g/dL (dimensions of inherent viscosity are dL/g),
 η_r = relative viscosity = t/t_o ,
 t = average solution flow time, s,
 t_o = average solvent flow time, s, and
 C = polymer solution concentration, g/dL.

11.2 An alternative means for calculating the intrinsic viscosity η from a single measurement of the relative viscosity is by using the Billmeyer relationship:¹¹

$$\eta = 0.25 (\eta_r - 1 + 3 \ln \eta_r)/C \quad (2)$$

12. Report

12.1 Report the following information:

- 12.1.1 Sample identification and description,
- 12.1.2 Sample weight,
- 12.1.3 Percent of inert material,
- 12.1.4 Sample dissolution time and temperature,
- 12.1.5 Average solvent flow time,
- 12.1.6 Average solution flow time,
- 12.1.7 Average viscometer bath temperature,
- 12.1.8 Inherent viscosity (three significant places), and
- 12.1.9 Intrinsic viscosity (optional).

13. Precision and Bias

13.1 Table 1 is based on a round robin¹² conducted in 1984 in accordance with Practice E 691, involving three materials representing different inherent viscosity levels, tested by six laboratories. For each material, all the samples were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Each test result was the average of two individual determinations. Each laboratory obtained one test result done by two different operators for each material each week for three weeks. (**Warning**—The explanations of r and R (13.2-13.2.3) only are intended to present a meaningful way of considering the approximate precision of this test method. Do not apply the data in Table 1 to acceptance or rejection of materials, as these data apply only to the materials tested in the round robin and are unlikely to be rigorously representative of other lot formulations, conditions, materials, or laboratories. Use the principles outlined in Practice E 691 to generate data specific to a particular material or laboratory (or for comparison between specific laboratories). The principles of 13.2-13.2.3 then would be valid for such data.)

¹¹ *Journal of Polymer Science*, Vol 4, 1949, p. 83.

¹² Supporting data are available from ASTM Headquarters. Request RR: D20-1132.

13.2 *Concept of r and R in Table 1*—If S_r and S_R have been calculated from a large enough body of data, and for test results that were averages from testing four specimens for each test result by each operator, then:

13.2.1 *Repeatability*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the r value for that material. r is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

13.2.2 *Reproducibility*—Two test results obtained by different laboratories shall be judged not equivalent if they differ by more than the R value for that material. R is the interval

representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

13.2.3 Any judgment in accordance with 13.2.1 or 13.2.2 would have an approximate 95 % (0.95) probability of being correct.

13.3 There are no recognized standards by which to estimate bias of this test method.

14. Keywords

14.1 glass capillary viscometer; inherent viscosity; poly-(ethylene terephthalate); PET; solution viscosity

SUMMARY OF CHANGES

This section identifies the location of selected changes to this test method. For the convenience of the user, Committee D20 has highlighted those changes that may impact the use of this test method. This section may also include descriptions of the changes or reasons for the changes, or both.

D 4603 – 03:

- (1) Deleted referenced document: Test Method D 4019 and added ISO statement.
- (2) Editorial changes including the removal of non-mandatory language.

D 4603 – 96:

- (1) This edition included a title change and revised precision and bias statement.

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