Designation: D 4603 – 9603

**Standard Test Method for
Determining Inherent Viscosity of Poly(Ethylene
Terephthalate) (PET) by Glass Capillary Viscometer[1]**

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. Some highly Highly crystalline forms of PET may that are not be soluble in this solvent mixture and 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:*

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[1] This test method is under the jurisdiction of ASTM Committee D=20 on Plastics and is the direct responsibility of Subcommittee D20.70.05 D20.70 on Analytical Methods (D20.70.05).

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This edition includes a title change and revised precision and bias statement. approved in 1996 as D 4603 – 96.

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

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 Viscometers[2]

D 1972 Practice for Generic Marking of Plastic Products[3]

D 4019 Test Method for Moisture in Plastics by Coulometry[4]

D 5225 Test Method for Measuring Solution Viscosity of Polymers with a Differential Viscometer[4]

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

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

[4] *Annual Book of ASTM Standards*, Vol 08.023.

E 1 Specification for ASTM Thermometers[5]
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 Method[6]

2.2 *ISO Standard:*

1628/5~-~19986 Determination of ~the~ Viscosity ~Number~ of Polymers in Dilute Solution Using Capillary Viscometers - Part 5: Thermoplastic Polyester (TP) homopolymers and ~Limiting~ ~Number—Part~ ~5~[7] Copolymers.[8]

2.3 *NIST Standard:*

C 602 Testing of Glass Volumetric Apparatus[7]

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[5] *Annual Book of ASTM Standards*, Vol ~08.03.~ 14.03.

[6] *Annual Book of ASTM Standards*, Vol 14.032.

[7] Available from ~American~ National Institute of Standards ~Institute,~ ~11~ ~W.~ ~42nd~ ~St.,~ ~13th~ ~Floor,~ ~New~ ~York,~ ~NY~ ~10036.~ and Technology (NIST), 100 Bureau Dr., Stop 3460, Gaithersburg, MD 20899-3460.

Annual Book of ASTM

[8] Available from American National Standards~,~ ~Vol~ ~14.02.~ Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

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.

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) [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 may 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,* (PET), 60/40 weight % mixture (0.5 % moisture maximum, protected in such a manner as to maintain this maximum level). The Protect PET should be protected 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.

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. Reference should be made 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 TObtain the material safety data sheets for methylene chloride, acetone, and the chromic acid solution used for cleaning the testing equipment should also be obtained from their suppliers and e. Consult the material safety data sheets before using the materials.

[9] Available from

[9] *Reagent Chemicals, American Chemical Society Specifications* , American Chemical Society, Washington, DC. For suggestions on the National Institute testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and Technology, the *United States Pharmacopeia and National Formulary*, U.S. Department of Commerce, Washington, DC 20234. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

Reagent

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

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)~~ [9°F] or until a constant weight of ± 0.1 % is reached. Moisture picked up from ambient humidity will weigh 0.30 % and ~~can be neglected~~ is negligible in this procedure. (See Note ~~1.)~~ 2.)

    NOTE 1—Test Method D 4019 or another 2—Use a suitable technical method ~~may be used~~ to determine moisture content.

9.3 If the sample is difficult to dissolve, reduce the sample size by grinding it ~~may be desirable~~ to ~~grind it to~~ a 20-mesh screen size in a Wiley ~~Mill. Care must be taken not to overheat~~ Mill or other size reduction technique. Avoid overheating the sample during the grinding operation. ~~A~~ It is possible to maintain a low temperature ~~can be maintained~~ 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. ~~Drying may be~~ 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)~~ [230°F] ± 10°C ~~(18°F).~~ [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)~~ [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)~~ [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 ~~may~~ 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~~)~~]. ~~T~~ Ensure that the range in temperature ~~should~~ 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:

$$\eta_{inh} {}^{30°C}_{0.5\%} = \frac{\ln \eta_r}{C}$$

(1)

where:

$\eta_{inh} {}^{30°C}_{0.5\%}$ = inherent viscosity at 30°C (86°F) [86°F] and at a polymer concentration of 0.5 g/dL (dimensions of inherent viscosity are d ʟ/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 T̶An alternative means for calculating the intrinsic viscosity η c̶a̶n̶ ̶a̶l̶s̶o̶ ̶b̶e̶ ̶c̶a̶l̶c̶u̶l̶a̶t̶e̶d̶ from a single measurement of the relative viscosity is by using the Billmeyer relationship:[11]

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

(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 robin[12] 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 w̶h̶i̶c̶h̶ 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 w̶e̶e̶k̶s̶.

N̶O̶T̶E̶ ̶2̶—̶C̶a̶u̶t̶i̶o̶n̶:̶ 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. T̶h̶e̶ Do not apply the data in Table 1 s̶h̶o̶u̶l̶d̶ ̶n̶o̶t̶ ̶b̶e̶ ̶a̶p̶p̶l̶i̶e̶d̶ 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. U̶s̶e̶r̶s̶ ̶o̶f̶ ̶t̶h̶i̶s̶ ̶t̶e̶s̶t̶ ̶m̶e̶t̶h̶o̶d̶ ̶s̶h̶o̶u̶l̶d̶ ̶a̶p̶p̶l̶y̶ Use the principles outlined in Practice E 691 to generate data specific to t̶h̶e̶i̶r̶ ̶m̶a̶t̶e̶r̶i̶a̶l̶s̶ ̶a̶n̶d̶ 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.)

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.

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

J̶o̶u̶r̶n̶a̶l̶ ̶o̶f̶ ̶P̶o̶l̶y̶m̶e̶r̶ ̶S̶c̶i̶e̶n̶c̶e̶,̶ ̶V̶o̶l̶ ̶4̶,̶ ̶1̶9̶4̶9̶,̶ ̶p̶.̶ ̶8̶3̶.̶

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

14. Keywords

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

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SUMMARY OF CHANGES

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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.