Designation: D 5492 – 98 (Reapproved 2003)

Standard Test Method for Determination of Xylene Solubles in Propylene Plastics[1]

This standard is issued under the fixed designation D 5492; 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 to be used for determining the 25°C ortho-xylene-soluble fraction of polypropylene and propylene-ethylene copolymers.

1.2 *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.*

NOTE 1—This standard is similar to ISO 6427-1982 in title only. The technical content is significantly different.

2. Referenced Documents

2.1 *ASTM Standards:*

D 883 Terminology Relating to Plastics[2]

D 1600 Terminology of Abbreviated Terms Relating to Plastics[2]

2.2 *ISO Standard:*

ISO 6427-1982 Plastics—Determination of Matter Extracted by Organic Solvents (Conventional Methods) Annex B Standard Method of Test for Determination of Polypropylene Solubility in Cold Xylene[3]

3. Terminology

3.1 For definitions of plastic terms see Terminology D 883 and for abbreviations see Terminology D 1600.

3.2 There are no terms in this test method that require new or other-than-dictionary definitions.

4. Summary of Test Method

4.1 A weighed amount of sample is dissolved in orthoxylene under reflux conditions. The solution is cooled under controlled conditions and maintained at a 25°C equilibrium temperature so that the crystallization of the insoluble fraction takes place. One of two precipitation-time periods can be used, although the longer precipitation time should be used for homopolymers and copolymers with solubles less than 12 mass %. When the solution is cooled the insoluble portion precipitates and is isolated by filtration. The orthoxylene is evaporated from the filtrate, leaving the soluble fraction in the residue. The percentage of this fraction in the plastic is determined gravimetrically.

5. Significance and Use

5.1 The results of this test provide a relative measure of the total soluble fraction of polypropylene and copolymers. The soluble fraction can be approximately correlated to the amorphous fraction in the polypropylene. Xylene is widely used for determining the soluble fraction in polypropylene. The concentration of a soluble fraction obtained with a specific solvent has been found to relate closely to the performance characteristics of a product in certain applications, for example film and fiber. Data obtained by one solvent and at one precipitation time cannot be compared with data obtained by another solvent or precipitation time, respectively. Xylene is more specific to the atactic fraction than other solvents.

6. Interferences

6.1 Materials with solubilities similar to the polymer fraction, such as additives, may interfere with the measurement of solubles. When present in concentrations that are judged to impart a significant error to the soluble-fraction data, the level of interference must be determined and corrections made.

6.2 Small-particle fillers and pigments that may pass through the filter and insoluble gels present in the polymer may cause errors in the measurement.

6.3 The polymer flakes and spheres must be dried before testing to eliminate moisture that can influence the initial weight of sample added to the flask.

7. Apparatus

7.1 *Reflux-Condenser Apparatus,* 400 mm, with 24/40 glass joint.

7.2 *Flat-Bottom Boiling Flask,* with one or two necks, 400 mL with 24/40 joint, Erlenmeyer flask, or cylindrical bottle.

7.3 *Insulation Disk,* made of fiberglass or rock wool.

7.4 *Electromagnetic Stirrer,* with temperature-controlled heating plate, thermostated oil bath, or heater block capable of maintaining 145 to 150°C.

7.5 *Stirring Bar.*

7.6 *Pipette,* Class A, 200 mL.

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.12 on Olefin Plastics.

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

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

7.7 *Pipette,* Class A, 100 mL.

7.8 *Glass-Stoppered Volumetric Flask,* 250 mL.

7.9 *Thermostatically Controlled Water Bath,* at 25°C.

7.10 *Electromagnetic Stirrers.*

7.11 *Filter Paper,* fluted, Whatman No. 4, No. 541,[4] or equivalent, 200 mm.

7.12 *Funnel,* 60°, 200 mm.

7.13 *Heated Vacuum Oven.*

7.14 *Disposable Aluminum Pans,* 300-mL capacity, with smooth sides.

7.15 *Temperature-Controlled Heating Plate.*

7.16 *Analytical Balance,* with minimum weighing sensitivity to 0.0001 g (a sensitivity of 0.00001 is preferred).

7.17 *Desiccator,* containing appropriate desiccant.

7.18 *Timer with Alarms,* in minutes.

8. Reagents

8.1 *Reagent-Grade Ortho-Xylene (o-Xylene)*—Assay gas chromatography (GC) = 98 % min; less than 2 % ethylbenzene as established by GC; evaporation residue at 140°C less than 0.002 g/100 mL; boiling point 144°C.

9. Procedure

9.1 *Preparation of the o-Xylene:*

9.1.1 It is not necessary to stabilize the o-xylene before using, but it may be stabilized if desired.

NOTE 2—BHT,[5] Irganox 1010,[6] and Santonox R[7] have been found to be effective stabilizers for o-xylene.

9.1.2 Degas the o-xylene. Using nitrogen gas, purge the o-xylene for a minimum of 1 h every 24 h.

9.2 *Determine the Level of Contamination in the o-Xylene (Solvent Blank):*

9.2.1 The purpose of the solvent blank is to determine whether the o-xylene to be used contains significant amounts of evaporation residue or foreign components. A solvent-blank test for residue should be run on every new lot of o-xylene. Run and average the solvent-blank results, for three aliquots per bottle or lot of o-xylene. Each aliquot shall be 200 mL.

NOTE 3—It is recommended that o-xylene be purchased in glass or glass-lined containers and of a size such that the o-xylene will be used within three days, once opened. Containers of larger size may be used if the o-xylene is used up within a short period of time. The purpose of the short time period is to ensure purity and minimize moisture pickup and other contaminants.

9.2.2 Pipet 200 mL of unstabilized or stabilized o-xylene into a clean empty flask.

9.2.3 Place a 200-mm No. 4 filter paper or equivalent in a 200-mm funnel in a funnel rack over a 250-mL glass-stoppered flask.

9.2.4 For each sample blank, pour the contents from the flask into a funnel and allow the filtrate to drip into a second flask. Continue the filtration until all the filtrate has been collected.

9.2.5 Dry the aluminum pans for 30 min in an oven at 150°C. Cool the pans in a desiccator until ready to use. For each sample weigh a clean, dry pan on the analytical balance to the nearest 0.0001 g.

9.2.6 With a Class A pipette, pipet a 100-mL aliquot of the filtered o-xylene into the weighed aluminum pan.

9.2.7 Place the pan on a temperature-controlled heating plate maintained at 145 to 150°C. Allow the aliquot to obtain a rolling boil to prevent splashing. Blanket the pan with a slow stream of nitrogen. Continue heating the pan until the residue in the dish is almost dry.

9.2.8 Place the pan into a vacuum oven at 100 ± 5°C for about an hour at a pressure less than 13.3 kPa.

9.2.9 Cool the pan to room temperature in a desiccator and weigh the pan to the nearest 0.0001 g. Repeat the drying, cooling, and weighing steps until two consecutive weighings agree within 0.0002 g. Calculate the average blank-residual mass of the three determinations.

9.3 *Determine the Percent Soluble Fraction in the Polymer:*

9.3.1 Dry the polypropylene powder or spheres before analysis. It is not necessary to dry the pellets unless it is known that they contain high levels of moisture pellets or spheres before analysis. If necessary, dry the samples in a vacuum oven at 70 ± 5°C, in a vacuum of 13.3 kPa for a minimum of 20 min. Cool the sample in a desiccator to prevent moisture pickup.

NOTE 4—For large pellets or spheres, where there is concern that the polymer sample will not dissolve in a reasonable time frame, the pellets or spheres may be ground to an appropriate size to afford a faster dissolution. Ground material should be dried as specified in 9.3.1.

9.3.2 Weigh out a sample in accordance with Table 1. When the expected solubles level is unknown use a 2.0 ± 0.1 g sample. For referee testing between laboratories a sample 2.0 ± 0.1 g shall be used, unless there is agreement between the laboratories to use a different sample size. Determine mass of the sample to the nearest 0.0001 g. Pour the sample into a flat-bottom boiling flask. Place a magnetic stirring bar in the flask.

NOTE 5—Table 1 provides a choice of sample mass. Use the largest sample mass possible to minimize variability of the test data, unless from prior experience it is known that the polymer/o-xylene solution does not filter readily as in 9.3.11.

9.3.3 Pipet 200 mL of unstabilized or stabilized o-xylene into the flask.

9.3.4 Attach the flask to the condenser.

9.3.5 Place an insulation disk on top of the electromagnetic stirrer plate to prevent localized heating of the flask. Position

TABLE 1 Sample Size

Expected Solubles	Initial Sample Mass, g[A]
<8 % by mass	4.0000 ± 0.1000 or 2.000 ± 0.1000
8.0 to 30.0 % by mass	2.0000 ± 0.1000
>30.0 % by mass	2.0000 ± 0.1000 or 1.0000 ± 0.1000

[A] See Note 1.

[4] Available from Whatman Intl. Ltd., Maidstone, England or from Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219.

[5] Available from Uniroyal Chemical Co., Inc., Specialty Chemicals Division, World Headquarters, Benson Rd., Middlebury, CT 06749.

[6] Available from CIBA-GEIGY Corp., Additive Division, Seven Skyline Drive, Hawthorne, NY 10532.

[7] Available from Monsanto Co., Chemical Group, 800 N. Lindberg Blvd., St. Louis, MO 63167.

the flask and condenser system on top of the insulation disk (see Fig. 1). Position the nitrogen inlet tube in the top of the condenser. Turn on the cooling water to the condenser.

9.3.6 Blanket the contents of the boiling flask with a slow flow of nitrogen directed across the top of the condenser, not directly into the condenser, to minimize possible o-xylene loss. Flow rate should be approximately 2 L/h.

9.3.7 Heat the polymer/o-xylene mixture to reflux temperature while vigorously stirring. The stirring shall be vigorous enough to obtain a deep vortex, which keeps the boiling under control and prevents boiling up into the condenser. This will take approximately 30 min. Ensure that the reflux is gentle so that localized burning and sticking of the polymer to the flask walls does not occur.

9.3.8 Once the reflux temperature is reached, stir the solution for an additional 30 min. The liquid will appear water-clear.

9.3.9 Remove the heating plate from beneath the flask. Detach the flask from the condenser and lightly stopper the flask. Cool the solution temperature from reflux temperature to below 100°C by cooling the flask in air for 12 to 14 min. A timer with alarm must be used to ensure that the solution is cooled to within a narrow range of temperature from run to run.

9.3.10 Transfer the flask to a thermostatically controlled water bath at 25 ± 0.5°C. Shake the flask to break up any precipitate before immersing the flask in the bath.

NOTE 6—Because the rate of cooling affects the crystal size and the rate of crystallization, the time and temperature during the cooling steps are very critical, especially in the short method.

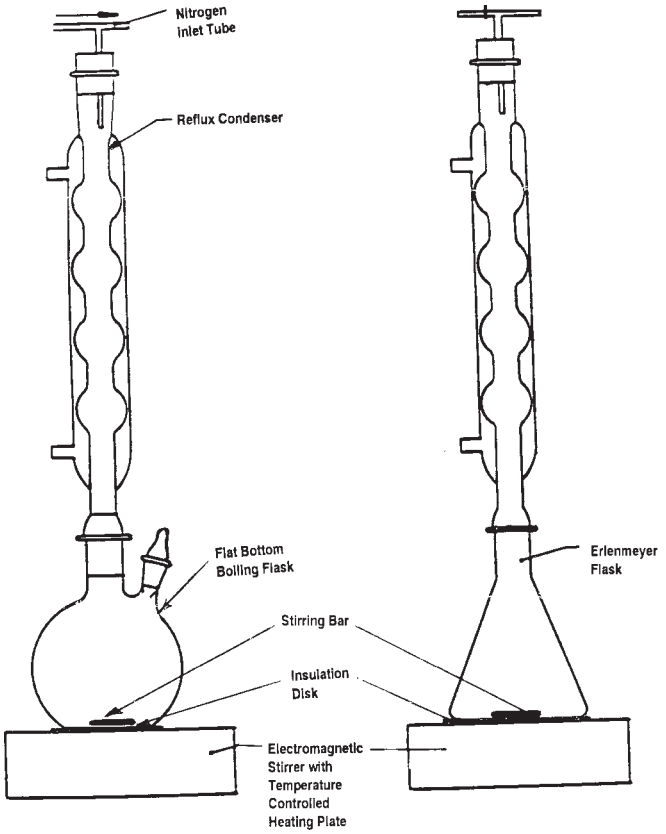

FIG. 1 Equipment Setup

NOTE 7—The water bath must have sufficient cooling capacity to maintain a constant temperature of 25 ± 0.5°C during cooling.

9.3.11 *Precipitation Time:*

9.3.11.1 *Long Precipitation Time*—Allow the flask to stand undisturbed 16 to 20 h at 25 ± 0.5°C. Stir or gently shake the flask to break up any precipitated-polymer gel at the end of the precipitation time, or

9.3.11.2 *Short-Precipitation Time*—Without stirring, cool the solution for 60 min in the temperature-controlled bath at 25 ± 0.5°C. Use a timer with an alarm to ensure that the solution-precipitation time ranges from 60 to 62 min. Remove the flask from the temperature-controlled bath. Stir or gently shake the flask to break up any precipitated-polymer gel.

NOTE 8—The long-precipitation method should be used only for homopolymers and copolymers with solubles of less than 12 %. Results have shown that copolymers with high levels of polymer solubles take as much as three days to reach equilibrium, therefore long precipitation times do not have any advantage over short precipitation times.

9.3.12 Place a 200-mm No. 4 filter paper or equivalent in a 200-mm funnel in a funnel rack over a 250-mL glass-stoppered flask.

9.3.13 For each sample, pour the contents from the flask into a funnel and allow the filtrate to drip into the second flask.

9.3.14 Continue the filtration until all the filtrate has been collected. If the filtered solution is not completely clear it will be necessary to repeat the filtration.

9.3.15 Dry the aluminum pans for 30 min in an oven at 150°C. Cool the pans in a desiccator until ready for use. For each sample weigh a clean, dry pan on the analytical balance to the nearest 0.0001 g.

9.3.16 With the clean Class A pipette, pipet a 100-mL aliquot of the soluble filtrate into the weighed aluminum pan.

9.3.17 Place the pan on a temperature-controlled hot plate maintained at 145 to 150°C. Allow the aliquot to obtain a rolling boil to prevent splashing. Blanket the pan with a slow stream of nitrogen. Continue heating the pan until the residue in the dish is almost dry.

9.3.18 Place the pan in a vacuum oven at 100 ± 5°C for about an hour at a pressure less than 13.3 kPa.

9.3.19 Cool the pan to room temperature in a desiccator and weigh the pan to the nearest 0.0001 g. Repeat the drying, cooling, and weighing steps until two consecutive weighings agree within 0.0002 g.

9.3.20 Obtain the mass of the soluble fraction by subtracting the mass of the pan from the residue-and-pan mass. Adjust the final percent-soluble-fraction data to account for the percent residual contamination from o-xylene.

10. Calculation

10.1 Calculate the mass percent of the soluble fraction by use of the following equation:

$$S_s = ((V_{bo}/V_{b1} \times (W_2 - W_1) - V_{bo}/V_{b2} \times B)/W_o) \times 100$$

where:

S_S = soluble fraction of sample, %,
V_{bo} = original volume of solvent, mL,
V_{b1} = volume of aliquot used for solubles determination, mL,

V_{b2} = volume of aliquot used for blank residuals, mL,
W_2 = mass of pan and solubles, g,
W_1 = mass of pan, g,
W_0 = mass of original sample, g, and
B = average blank residual, g.

10.2 Materials, such as additives, with solubilities similar to the soluble-polymer fraction interfere in the measurement of percent solubility. Corrections are made to the percent soluble fraction only if the material is present in concentrations that are judged to impart a significant error on the soluble-fraction data. The material(s) must be 100 % soluble and the mass percent of the material present in the polymer must be known for the following correction to be made:

$$S_c = S_s - S_m$$

S_c = corrected soluble fraction of sample, %,
S_s = soluble fraction of sample, %, and
S_m = contamination from materials added to polymer, %, where S_m is the sum of the percent for each of the additives in the material formulation known to be 100 % soluble.

11. Report

11.1 Report the following information:

11.1.1 Grade of o-xylene,

11.1.2 Whether long- or short-precipitation time was used,

11.1.3 Initial sample mass added to flask,

11.1.4 Volume of aliquot used, and

11.1.5 Percent-soluble fraction. (If the data is adjusted for soluble additives, report corrected-percent-solubles fraction, percent-solubles fraction, and percent contamination. Report values to three significant figures.)

12. Precision and Bias

12.1 Tables are based on a round robin[8] tests conducted in 1996 in accordance with Practice E 691, involving five materials tested by seven laboratories. One laboratory distributed the five commercial polypropylene formulations chosen for the evaluation. The individual specimens were prepared at the laboratories that tested them. All pellet samples were extracted using both a short and long precipitation times. Each test result was an individual determination. Each laboratory obtained two test results for each material and precipitation method. Results for the short precipitation time are listed in Table 2. Results for the long precipitation time are listed in Table 3.

NOTE 9—**Caution:** The following explanation for *r* and *R* (12.2 through 12.2.3) only are intended to present a meaningful way of considering the approximate precision of this test method. The data in Tables 2 and 3 should not be applied to acceptance or rejection of material, as these data apply only to materials tested in the round robin and are unlikely to be rigorously representative of the other lots, formulations, conditions, material, or laboratories. Users of this test method should apply the principles outlined in Practice E 691 to generate data specific to their materials and laboratory, or between specific laboratories. The principles of 12.2 through 12.2.3 then would be valid for such data.

[8] Supporting data are available from ASTM Headquarters. Request RR. D 20-1199.

TABLE 2 Xylene Solubles by the Short Precipitation Method for Seven Laboratories and Five Materials

Material	Values Expressed in %				
	Average	S_r[A]	S_R[B]	r[C]	R[D]
PP	3.58	0.202	0.408	0.565	1.14
PP	5.62	0.490	0.729	1.37	2.04
PP	6.87	0.230	0.715	0.644	2.00
PP	15.0	0.354	0.799	0.993	2.24
PP	22.3	1.22	1.63	3.42	4.56

[A] S_r is the within-laboratory standard deviation for the indicated material. It is obtained by pooling the within-laboratory standard deviations of the test results from all of the participating laboratories.
[B] $S_r = [[s_1)^2 + (s_2)^2 + \ldots\ldots\ldots + (s_n)^2]/n]^{1/2}$
S_R is the between-laboratories reproducibility, expressed as standard deviation.
$S_R = [S_r^2 + S_L^2]^{1/2}$, where S_L is the standard deviation of laboratory means.
[C] r is the within-laboratory critical interval between two test results = $2.8 \times S_r$.
[D] R is the between-laboratories critical interval between two test results = $2.8 \times S_R$.

TABLE 3 Xylene Solubles by the Long Precipitation Method for Seven Laboratories and Five Materials

Material	Values Expressed in %				
	Average	S_r[A]	S_R[B]	r[C]	R[D]
PP	3.60	0.241	0.260	0.674	0.729
PP	5.43	0.247	0.412	0.691	1.15
PP	6.82	0.286	0.334	0.802	0.936
PP	14.4	0.474	0.910	1.33	2.55
PP	21.8	0.312	1.12	0.874	3.13

[A] S_r is the within-laboratory standard deviation for the indicated material. It is obtained by pooling with within-laboratory standard deviations of the test results from all of the participating laboratories.
[B] $S_r = [[s_1)^2 + (s_2)^2 + \ldots\ldots\ldots + (s_n)^2]/n]^{1/2}$
S_R is the between-laboratories reproducibility, expressed as standard deviation.
$S_R = [S_r^2 + S_L^2]^{1/2}$, where S_L is the standard deviation of laboratory means.
[C] r is the within-laboratory critical interval between two test results = $2.8 \times S_r$.
[D] R is the between-laboratories critical interval between two test results = $2.8 \times S_R$.

12.2 *Concept of "r" and "R" in Tables 2 and 3*—If S_r and S_R have been calculated from a large enough body of data, and for test results from testing one specimen for each test result, then perform the test as follows:

12.2.1 *Repeatability—"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. Two test results shall be judged not equivalent if they differ by more than the *"r"* value for the material.

12.2.2 *Reproducibility—"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, not necessarily on the same day. Two test results shall be judged not equivalent if they differ by more than the *"R"* value for that material.

12.2.3 Any judgment in accordance with 12.2.1 or 12.2.2 would have an approximate 95 % (0.95) probability of being correct.

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

13. Keywords

13.1 plastics; polypropylene; xylene solubles