Designation: D7029 – 09

Standard Test Method for Determination of Reactivity of Unsaturated Polyesters and Vinyl Esters at 180.0°F (82.2°C)[1]

This standard is issued under the fixed designation D7029; 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 standard provides a standardized test method for determining the gelation and exotherm curve of unsaturated polyester and vinyl ester resins. This method provides guidance for measurement of the "Standard 180°F (82.2°C) Exotherm Curve" along with information on variances of the measurement which may be required for special resins. This test method provides information concerning the reactivity of unsaturated polyester and vinyl ester resins as they go through polymerization after mixing with the initiator.

NOTE 1—There is no known ISO equivalent to this standard, although ISO 584 is similar.

1.2 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in nonconformance with the standard.

1.3 *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.*

2. Referenced Documents

2.1 *Society of Plastics Industry, Inc.:*

Handbook of Reinforced Plastics "Procedure for Running Exotherm Curves Using the Block Test Method"

2.2 *ISO Standard:*

ISO 584 Reinforced Plastics Based on Unsaturated Polyester Resins—Determination of Reactivity at 80°C[2]

3. Terminology

3.1 *Definitions:*

3.1.1 *gel time*—the period of time in minutes and seconds required for the recording pyrometer to go from a temperature below (usually 10 to 30°F or 5.5 to 16°C) bath temperature to 10°F (5.55°C) above the bath temperature, typically 150°F (65.5°C) to 190°F (78.8°C) for a bath at 180°F (82.2°C).

3.1.2 *cure time*—the period of time in minutes and seconds required for the recording pyrometer to go from a temperature below (usually 10 to 30°F or 5.5 to 16°C) bath temperature to the maximum temperature reading, typically 150°F (65.5°C) to the maximum temperature for a bath at 180°F (82.2°C).

3.1.3 *interval time*—the period of time in minutes and seconds required for the recording pyrometer to go from 10°F (5.5°C) above the bath temperature to the maximum temperature reading, typically 190°F (78.8°C) to the maximum temperature. Thus, interval time is cure time minus gel time.

3.1.4 *peak exotherm*—the maximum temperature reached during the testing.

3.1.5 *recording pyrometer*—a broad class of temperature measuring devices including thermocouples with the ability for continuous temperature recording.

3.1.6 *initiator*—a compound that generates free radicals to start the free radical polymerization of the unsaturated polyester and vinyl ester resins. It is typically a single peroxide, but a combination of initiators could be used.

4. Summary of Test Method

4.1 Polyester or vinyl ester resin is mixed with the initiator(s) in a beaker causing a polymerization of the resin to occur. Heat will accelerate the polymerization reaction. The exotherm generated by the resin as it cures is measured using a thermocouple. The curve is plotted and the time to reach various temperatures along with the peak temperature obtained (peak exotherm) is determined. The initiator normally employed to generate the test results is benzoyl peroxide, although the method may be used with other initiator systems.

4.2 The test method is useful in providing information about the heat generated during cure of the resin and the length of time the resin remains in the liquid state prior to polymerization into solid form.

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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 D20.18 on Reinforced Thermosetting Plastics.

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

5. Significance and Use

5.1 This test method is used to measure the reactivity of different lots of unsaturated polyester and vinyl ester resins. The information provided by this test can be used for assessing the predicted performance of a resin when used in elevated temperature as part of the process used to convert the resin into a finished product.

5.2 The method is used in research and development by companies that manufacture resins and for incoming quality control companies using these polymers as raw materials for production. The method is based on the methods which were previously outlined in the *Handbook of Reinforced Plastics*, "Procedure for Running Exotherm Curves Using the Block Test Method" published by the Society of the Plastics Industry.

6. Interferences

6.1 The results obtained can be influenced by the type of resin used, the age of the resin, the age of the initiator and the type of initiator used. Care shall be taken to assure that the chemicals used are stored and used in accordance with the manufacturers' guidelines.

6.2 Control of the bath temperature and the circulation within the bath can affect the results of the test. Care shall be taken to control the bath temperature and agitation to comply with the method instructions.

7. Apparatus

7.1 *Recording Pyrometer,* Iron Constantan, 60 in. (1.5 m) per hour charts speed or equivalent.

7.2 *Thermometer,* with divisions every 0.1°F (0.05°C) capable of reading a minimum of 180 ± 1°F (82.2 ± 0.5°C) or equivalent.

7.3 *Constant Temperature Water Bath,* or alternate media bath capable of being controlled to 180 ± 0.5°F (82.2 ± 0.2°C) with an agitation rate of 1 to 2 times the bath capacity per minute. The bath shall have a minimum capacity of 2.5 gal (8.8 L) an shall be fitted with a cover with access holes for the bath heater, thermometer, and test tubes in order to minimize evaporation of water.

7.4 *Borosilicate Glass Test Tubes,* of 19 mm diameter and 150 mm length with plain end and lip.

7.5 *"Type J" Thermocouple Needle,* made from 304 stainless steel, 6 in. (152 mm) in length, with an outside diameter of ⅛ in. (3.2 mm) connected to a "Type J" Jack Assembly or equivalent.

7.6 *"Type J" Double Conductor,* B&S Gauge wire with poly insulation and color coding (white for positive/red for negative) to connect "Type J" thermocouple needle to recording pyrometer or equivalent.

7.7 *Electronic Balance,* suitable for accurate weighing to 0.01 g and a minimum capacity of 200 g.

7.8 *Machined Centering Device,* for centering thermocouple needle within the resin sample. This device may be made from reinforced plastics, micarta, or other suitable material. See Fig. 1 for the set up of the device.

7.9 *Beaker (150 mL),* made of glass or plastic.

8. Reagents and Materials

8.1 *Styrene Monomer,* with 15 ± 5 ppm of Tertiary Butyl Catechol (TBC) Inhibitor.

8.2 *Initiator Type:*

8.2.1 *Type I*—98 % Benzoyl Peroxide crystals.

8.2.2 *Type II*—Benzoyl Peroxide paste/emulsion with a tolerance of ± 1.5 % of the specified concentration with a maximum of 18 % water. Example: 40 % benzoyl peroxide with a range of concentration from 38.5 to 41.5 %.

8.2.3 *Type III*—Initiator(s) mutually agreed upon by laboratories running the test.

8.3 *Unsaturated Polyester and Vinyl Ester Resin.*

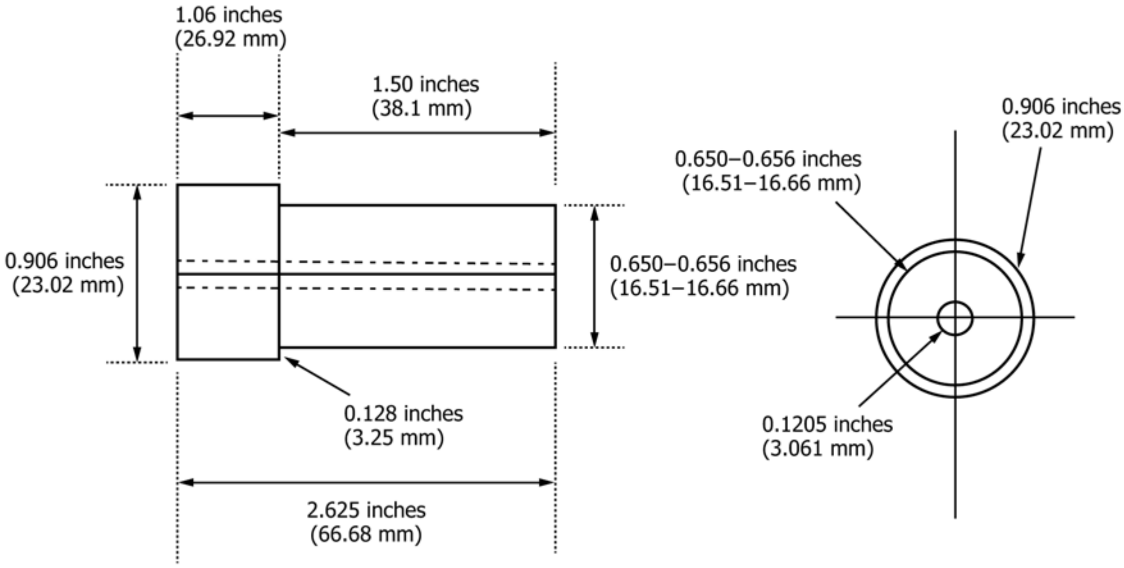

FIG. 1 Machine Centering Device for Thermocouple Assembly

8.4 *Silicone Grease.*

9. Hazards

9.1 Initiators such as benzoyl peroxide must be stored in accordance with manufacturers' guidelines. Failure to do so can result in the materials becoming unstable causing fire or explosions.

9.2 Directly mixing metals like cobalt and other chemical with the initiators can create explosive conditions.

10. Test Results

10.1 A single measurement of each property to be evaluated is considered one test result.

11. Preparation of Apparatus

11.1 Adjust the water bath to 180 ± 0.5°F (82.2 ± 0.25°C) using a calibrated thermometer.

11.2 Allow the water in the bath to equilibrate in temperature while circulating for a minimum of 60 min.

12. Calibration and Standardization

12.1 The thermometer and pyrometer utilized during the testing shall be calibrated against a known standard or be traceable to a certified source.

13. Conditioning

13.1 No special atmospheric conditioning is required for this test procedure.

13.2 A means must be provided, either by air temperature or hot plate, etc. to condition the resin to temperature prior to addition of initiator.

14. Procedure

14.1 Weigh 1.00 ± 0.02 g of active benzoyl peroxide into a 150 mL beaker. Add 1.00 g of the styrene monomer to the initiator and mix thoroughly.

NOTE 2—The above may be obtained by weighing 1 g of Type I benzoyl peroxide or by using 2 g of a 50 % Type II benzoyl peroxide or by adding an amount of an alternative concentration of paste/emulsion initiator that fulfills the necessary 1 % active initiator.

14.2 Place resin to be used in a suitable container and adjust the resin temperature to 77.0 ± 0.5°F (25 ± 0.25°C).

14.3 Add 100 ± 0.02 g of the temperature adjusted resin into the 150 mL beaker containing the initiator and styrene monomer, if used (for Type I and Type II initiators, Type III may not require any styrene), and mix thoroughly, being careful to entrap as little air as possible into the mixture.

14.4 Let beaker stand for 15 ± 5 min at approximately 77°F (25°C) prior to running the test.

14.5 Pour the initiated resin from the beaker into the test tube so that 3.00 ± 0.05 in. (76 ± 1 mm) of the resin is in the test tube.

14.6 Grease the thermocouple needle with a thin coat of silicone and insert the needle into the centering device. Insert the needle and centering device into the test tube so that it is centered side to side and so that the probe is 1.50 ± 0.05 in. (38 ± 1 mm) inches from the bottom of the test tube. See attached drawing of the centering device in Fig. 1.

14.7 Immerse the test tube in the 180°F (82.2°C) constant temperature bath so the level of liquid in the test tube is below the surface of the liquid in the bath and start the recording pyrometer.

14.8 When the peak exotherm temperature is reached, let the temperature begin to drop and remove the test tube from the bath. Remove the test probe from the resin and test tube.

15. Calculation or Interpretation of Results

15.1 Unless otherwise specified the following values shall be measured from the recording pyrometer:

15.1.1 *Gel Time*—150°F (65.5°C) to 190°F (78.8°C).

15.1.2 *Cure Time*—150°F (65.5°C) to the maximum temperature).

15.1.3 *Interval Time*—190°F (78.8°C) to the maximum temperature (Optional).

15.1.4 *Peak Exotherm Temperature.*

16. Report

16.1 The following shall be included in the report:

16.1.1 Equipment used:

16.1.1.1 Thermocouple type as well as whether it was grounded or ungrounded, and

16.1.1.2 Initiator type, brand, and amount used.

16.2 Using the recording pyrometer chart, measure and report the following:

16.2.1 Gel Time,

16.2.2 Cure Time,

16.2.3 Interval Time (Optional), and

16.2.4 Peak Exotherm temperature.

16.3 Report any Variance from the standard procedure. These variances may include:

16.3.1 *Initiator,* as designated by the laboratories running the tests,

16.3.2 *Bath Media,* as designated by the laboratories running the tests, and

16.3.3 *Bath Temperature,* as designated by the laboratories running the tests.

17. Precision and Bias

17.1 Table 1 is based on a round robin conducted on four materials (two resins with a short gel time and two resins with a long gel time) by six laboratories. Samples were prepared in accordance with the instructions in this method using the same type initiator. Evaluations of gel time, cure time, and peak exotherm were made. Each laboratory generated two test results for each material.**Warning—**The explanation of S_r, S_R, V_r and V_R are only intended to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 shall not be applied 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 lots, formulations, conditions, material, or laboratories. Users of this test method are encouraged to apply the

TABLE 1

Material	$\bar{X}$	Std dev	r	R	S_r[A]	S_R[B]	I_r[C]	I_R[D]
Gel Time in Minutes								
Resin 1 (Short Gel Time)	4.92	0.53	0.11	0.54	0.30	1.50	2.19 %	10.88 %
Resin 2 (Short Gel Time)	4.83	0.58	0.10	0.58	0.28	1.63	2.07 %	12.08 %
Resin 3 (Long Gel Time)	10.04	1.09	0.11	1.10	0.30	3.07	1.05 %	10.92 %
Resin 4 (Long Gel Time)	10.26	1.00	0.16	1.01	0.46	2.82	1.59 %	9.81 %
Cure Time in Minutes								
Resin 1 (Short Gel Time)	5.93	0.44	0.07	0.44	0.21	1.24	3.51 %	20.98 %
Resin 2 (Short Gel Time)	5.93	0.59	0.11	0.59	0.32	1.66	5.33 %	27.96 %
Resin 3 (Long Gel Time)	13.93	1.35	0.13	1.35	0.37	3.79	2.69 %	27.21 %
Resin 4 (Long Gel Time)	14.13	1.30	0.10	1.30	0.28	3.64	2.02 %	25.80 %
Exotherm Temperature in °F								
Resin 1 (Short Gel Time)	455.58	8.15	4.17	8.67	11.69	24.27	2.56 %	1.90 %
Resin 2 (Short Gel Time)	456.42	7.26	3.28	7.62	9.18	21.33	2.01 %	1.67 %
Resin 3 (Long Gel Time)	408.67	19.49	4.97	19.80	13.91	55.44	3.40 %	4.84 %
Resin 4 (Long Gel Time)	406.92	19.58	2.43	19.65	6.81	55.03	1.67 %	4.83 %

[A] S_r = 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:

$$S_r = [[(S_1)^2+(S_2)^2 \ldots+(S_n)^2]/n]^{1/2}$$

[B] S_R = between-laboratories reproducibility, expressed as standard deviation:

$$S_R = [S_r^2+S_L^2]^{1/2}$$

where:

S_L = standard deviation of laboratory means.

[C] V_r = within-laboratory coefficient of variation for the indicated material. It is obtained by first pooling the within-laboratory standard deviations of the test results from all of the participating laboratories:

$$S_r = \{[(S_1)^2+(S_2)^2 \ldots+(S_n)^2]^n\}^{1/2}$$

then:

V_r = (S_r divided by the overall average for the material) × 100, and
I_r = 2.8 times V_r.

[D] V_R = between-laboratories reproducibility, expressed as coefficient of variation:

$$S_R = [S_r^2+S_L^2]^{1/2}$$

where:

S_L = standard deviation of laboratory means.

then:

V_R = (S_R divided by the overall average for the material) × 100, and
I_R = 2.8 times V_R.

principles outlined in Practice E691 to generate data specific to their materials and laboratory (or between specific laboratories).

17.2 Concept of “*r*” and “*R*” in Table 1: If *r* and *R* have been calculated from a large enough body of data and for test results that were averages from testing of 2 specimens for each test result then:

17.2.1 *Repeatability*—Two results obtained within one laboratory shall be judged not equivalent if they differ by more than the “S_r” value or by the I_r percentage for that material. S_r is the critical value 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.

17.2.2 *Reproducibility*—Two test results obtained by different laboratories shall be judged not equivalent if they differ by more than the “S_R” value for that material. “S_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.

17.2.3 Any judgment in accordance with 17.2.1 or 17.2.2 would have an approximate 95 % probability of being correct.

17.3 There are no recognized standards by which to estimate the bias of this method.

18. Keywords

18.1 cure time; gel time; initiator; interval time; peak exotherm; resin; resin reactivity; SPI gel time; thermoset; unsaturated polyester; vinyl ester

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