Designation: D5028 – 09

Standard Test Method for Curing Properties of Pultrusion Resins by Thermal Analysis[1]

This standard is issued under the fixed designation D5028; 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 covers determination of curing parameters of pultrusions resins by differential scanning calorimetry.

1.2 This test method is applicable to pultrusion resin solutions with adequate initiator(s).

1.3 The normal operating temperature range is from 0 to 200°C.

NOTE 1—Resin systems that do not form an adequate baseline are not covered by this test method.

1.4 Computer or electronic based instruments or data treatment equivalent to this practice may also be used.

1.5 The values stated in SI units are to be regarded as standard.

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.* For specific hazard statements, see Note 1.

NOTE 2—There is no known ISO equivalent to this test method.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3418 Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry

D3918 Terminology Relating to Reinforced Plastic Pultruded Products

E473 Terminology Relating to Thermal Analysis and Rheology

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E2160 Test Method for Heat of Reaction of Thermally Reactive Materials by Differential Scanning Calorimetry

3. Terminology

3.1 *Definitions:*

3.1.1 *onset temperature*—an extrapolated point representing an intersection of the baseline and the front slope of the exothermic curing curve.

3.1.2 *peak temperature*—an extrapolated point representing an intersection of both front and rear slopes of the exothermic curing curve.

4. Summary of Test Method

4.1 The test method consists of heating of the test material at a controlled rate of temperature increase in a controlled atmosphere and continuously monitoring with a suitable sensing device the difference in heat input between a reference material and a test material due to changes of state in the material. A curing transition is marked by a release of energy by the specimen resulting in a corresponding exothermic curve.

NOTE 3—Toxic or corrosive effluents, or both, may be released when heating the material, and could be harmful to the personnel or to the apparatus.

5. Significance and Use

5.1 Differential scanning calorimeters are used to determine chemical reaction thermal profiles of materials. One such reaction is the curing of thermosetting resins.

5.2 This test method is useful for both specification acceptance and for research.

6. Apparatus

6.1 *Differential Scanning Calorimeter,* capable of heating a test specimen and a reference material at a controlled rate up to at least 20°C/min and of automatically recording the differential heat flow.

6.2 *Specimen Holders,* composed of clean aluminum or of other high thermal conductivity material.

[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.

Current edition approved Sept. 1, 2009. Published September 2009. Originally approved in 1989. Last previous edition approved in 2003 as D5028 - 96(2003) $^{\varepsilon 1}$. DOI: 10.1520/D5028-09.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

6.2.1 Specimen holders may be open, covered, or sealed type.

6.3 *Nitrogen,* or other inert purge gas supply.

6.4 *Flowmeter,* for purge gas.

6.5 *Recording Charts,* for temperature recording apparatus with suitable graduation for measurements of energy differential against temperature or time.

7. Technical Hazards

7.1 An increase or decrease in heating rate from those specified may alter the test results. This practice assumes linear temperature indication.

7.2 Since milligram quantities of sample are used, it is essential to ensure that samples are homogeneous and representative.

7.3 Sample sizes larger than those specified in the test method may alter the test results.

7.4 For comparison, the same heating rate, the same sample size and the same type of pan and lid shall be used.

7.5 For low viscosity resin systems, a sealed type of pan and lid shall be used to prevent excessive volatile component evaporation during the test.

8. Test Specimen

8.1 Thermoset resin system containing initiator(s) capable of curing in range from room temperature to 200°C.

8.2 Following the addition of initiator, the sample shall be held for a minimum of ½ h before commencing the test.

9. Calibration

9.1 Using the same heating rate to be used for samples, calibrate the apparatus with appropriate standard reference materials. For temperature range of this standard, the following material may be used (NIST or equivalent quality):

Standard	Melting Point, °C
Indium	156.4

10. Procedure

10.1 Weigh a sample of 5 to 10 mg.

10.1.1 Crimp a flat metal cover against the pan with the sample sandwiched between them to ensure good heat transfer. Take care to ensure that the cover contacts the resin surface. Place sample in the DSC cell.

10.1.2 Intimate thermal contact between the sample and clean thermocouple or other temperature probe is essential for reproducible results.

10.1.3 It is recommended to balance the energy flow into or out of the sample. Start the heating cycle when no movement of the recording pen is visible.

10.2 Select appropriate *x* and *y* axis sensitivities to yield an area of 30 to 60 cm^3 (5 to 10 $in.^2$) under the curing exotherm.

10.3 Purge the cell with nitrogen at 60 to 80 mL/min gas flow rate.

10.4 Perform and record the thermal cycle by heating the sample at a rate of 10°C/min under the nitrogen atmosphere from ambient to temperature high enough to achieve the entire exothermic curing curve information.

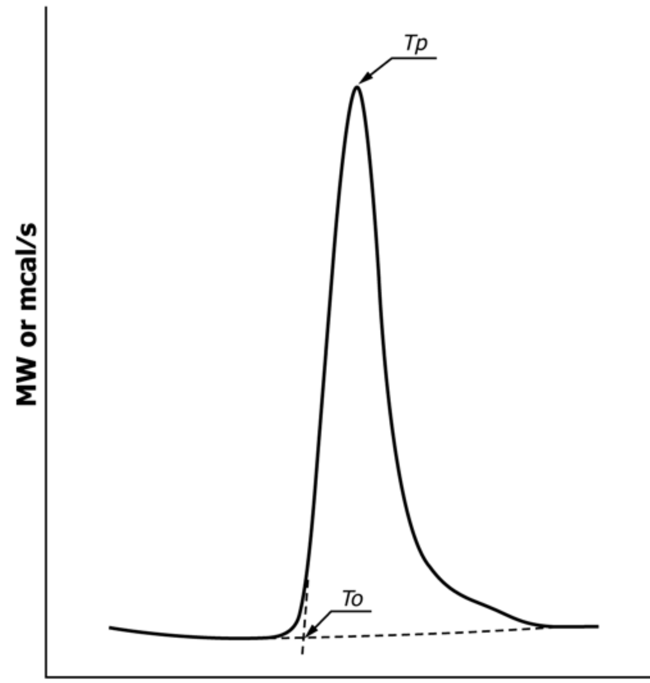

FIG. 1 Typical Exothermic Curing Curve

10.5 Measure the corrected temperatures for the desired points on the curves: T_o, T_p (see Fig. 1),

where:

T_o = extrapolated onset temperature, °C, and
T_p = extrapolated peak temperature,° C.

11. Report

11.1 Report the following information:

11.1.1 Complete identification and description of the material tested, including source, and manufacturer's code,

11.1.2 Description of instrument used for the test,

11.1.3 Statement of the mass, dimension, geometry, and materials of the sample holder, and the heating rate used,

11.1.4 Description of calibration procedure,

11.1.5 Identification of the sample atmosphere by gas flow rate, purity, and composition, and

11.1.6 Values of the transition measured using the temperature parameters (T_o, T_p) cited in Fig. 1.

12. Precision[3]

12.1 This precision data was generated as part of an industry round-robin between eight participating laboratories using resins from various suppliers' standard inventory.

12.2 *Repeatability (r)*—the critical difference within which two averages of three observations each, obtained on the same

[3] Supporting data are available from ASTM Headquarters. Request RR: D20 – 1160.

TABLE 1 DSC Indium Calibration Summary

Participant	Measured Indium Melting Point	Correction Factor	DSC Instrumentation
Ashland	157.8	–1.2	duPont 9900
Cargil	156.3	+0.3	Perkin Elmer DSC 4
Dow Chemical	158.8	–2.2	duPont 1090
Koppers	157.7	–1.1	Perkin Elmer DSC-2C
MMFG	156.4	+0.2	Omnitherm QC .25
OCF	156.0	+0.6	duPont 1090
PPG	157.0	–0.4	Perkin Elmer 7
R. D. Werner	155.6	+1.0	Omnitherm QC .25
Indium Standard	156.6	—	

material by a single operator using the same instrument, can be expected to lie 95 % of the time because of random variation within a laboratory.

12.2.1 The following criteria were established from tests of the resins indicated:

		Isophthalic Polyester A	Isophthalic Polyester B	Vinyl Ester
On-set Temperature,° C	Unfilled:	2.2	2.0	2.6
	Filled:	2.0	1.6	1.2
Peak Temperature,° C	Unfilled:	1.4	2.9	2.4
	Filled:	1.3	2.2	1.1

12.2.2 If the results and average working data on a given sample tested in the same laboratory differ by more than the values indicated in 12.2.1, the averages can be considered significantly different.

12.3 *Reproducibility (R)*—the critical difference within which two averages of three observations each, obtained by two different operators using different instruments in different laboratories, can be expected to lie 95 % of the time because of variation within and between laboratories.

12.3.1 The following criteria were established for the resins indicated:

		Isophthalic Polyester A	Isophthalic Polyester B	Vinyl Ester
On-set Temperature,° C	Unfilled:	3.8	3.4	3.1
	Filled:	2.6	4.6	2.3
Peak Temperature,° C	Unfilled:	2.8	5.2	3.9
	Filled:	2.7	3.9	4.3

12.3.2 If the results and average working data on a given sample test from different laboratories differ by more than the values indicated in 12.3.1, the averages can be considered significantly different.

TABLE 2 On-Set Temperature Precision Data Calculations Based on "Original" Test Values

Material	Mean Average, $\bar{X}$	Overall Relative Standard Deviation of Precision Test Method, V_R, %	Repeatability Interval, I_r	Repeatability Interval, I_R
1	93.07	0.815	2.148	4.381
2	92.47	0.751	1.967	4.171
3	95.32	0.729	1.967	4.370
4	96.35	0.582	1.585	5.697
5	102.82	0.878	2.558	4.222
6	102.41	0.400	1.160	4.590

TABLE 3 Peak Temperature Precision Data Calculations Based on "Adjusted" Test Values

Material	Mean Average, $\bar{X}$	Overall Relative Standard Deviation of Precision Test Method, V_R, %	Repeatability Interval, I_r	Repeatability Interval, I_R
1	92.72	0.818	2.148	3.784
2	92.12	0.754	1.967	2.635
3	94.97	0.731	1.967	3.354
4	96.00	0.584	1.585	4.587
5	102.47	0.882	2.558	3.068
6	102.06	0.401	1.160	2.270

TABLE 4 Peak Temperature Precision Data Calculations Based on "Original" Test Values

Material	Mean Average, $\bar{X}$	Overall Relative Standard Deviation of Precision Test Method, V_R, %	Repeatability Interval, I_r	Repeatability Interval, I_R
1	105.57	0.454	1.356	3.543
2	105.45	0.418	1.248	3.569
3	107.85	0.958	2.929	5.552
4	107.36	0.725	2.202	4.505
5	112.28	0.759	2.408	4.627
6	111.62	0.344	1.087	6.011

TABLE 5 Peak Temperature Precision Data Calculations Based on "Adjusted" Test Values

Material	Mean Average, $\bar{X}$	Overall Relative Standard Deviation of Precision Test Method, V_R, %	Repeatability Interval, I_r	Repeatability Interval, I_R
1	105.35	0.455	1.356	2.833
2	105.10	0.420	1.248	2.734
3	107.50	0.961	2.929	5.207
4	107.01	0.727	2.202	3.903
5	111.93	0.762	2.408	3.939
6	111.27	0.345	1.087	4.299