Designation: D4473 – 08 (Reapproved 2016)

Standard Test Method for Plastics: Dynamic Mechanical Properties: Cure Behavior[1]

This standard is issued under the fixed designation D4473; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This test method covers the use of dynamic-mechanical-oscillation instrumentation for gathering and reporting the thermal advancement of cure behavior of thermosetting resin. It may be used for determining the cure properties of both unsupported resins and resins supported on substrates subjected to various oscillatory deformations.

1.2 This test method is intended to provide a means for determining the cure behavior of supported and unsupported thermosetting resins over a range of temperatures by free vibration as well as resonant and nonresonant forced-vibration techniques, in accordance with Practice D4065. Plots of modulus, tan delta, and damping index as a function of time/temperature are indicative of the thermal advancement or cure characteristics of a resin.

1.3 This test method is valid for a wide range of frequencies, typically from 0.01 to 100 Hz. However, it is strongly recommended that low-frequency test conditions, generally below 1.5 Hz, be utilized as they generally will result in more definitive cure-behavior information.

1.4 This test method is intended for resin/substrate composites that have an uncured effective elastic modulus in shear greater than 0.5 MPa.

1.5 Apparent discrepancies may arise in results obtained under differing experimental conditions. These apparent differences from results observed in another study can usually be reconciled, without changing the observed data, by reporting in full (as described in this test method) the conditions under which the data were obtained.

1.6 Due to possible instrumentation compliance, especially in the compressive mode, the data generated may indicate relative and not necessarily absolute property values.

1.7 Test data obtained by this test method are relevant and appropriate for use in engineering design.

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

1.9 *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 precautionary statements are given in Note 5.

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4000 Classification System for Specifying Plastic Materials

D4065 Practice for Plastics: Dynamic Mechanical Properties: Determination and Report of Procedures

D4092 Terminology for Plastics: Dynamic Mechanical Properties

ASTM/IEEE SI–10 Standard for Use of the International System of Units (SI): The Modern Metric System

3. Terminology

3.1 *Definitions*—For definitions applicable to this test method refer to Terminology D4092.

4. Summary of Test Method

4.1 A known amount of thermosetting liquid resin or resin-impregnated substrate is placed in mechanical oscillation at either a fixed or natural resonant frequency or by free vibration and at either isothermal conditions, with a linear temperature increase or using a time-temperature relation simulating a processing condition. The elastic or loss modulus, or both, of the composite specimen are measured in shear or compression as a function of time. The point in time when tan delta is maximum, and the elastic modulus levels off after an increase, is calculated as the gel time of the resin under the conditions of the test.

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.10 on Mechanical Properties.

Current edition approved Nov. 1, 2016. Published November 2016. Originally approved in 1985. Last previous edition approved in 2008 as D4473 - 08. DOI: 10.1520/D4473-08R16.

[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.

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

NOTE 2—The particular method for measuring the elastic and loss moduli and tan delta depends upon the individual instrument's operating principles.

5. Significance and Use

5.1 This test method provides a simple means of characterizing the cure behavior of thermosetting resins using very small amounts of material (fewer than 3 to 5 g). The data obtained may be used for quality control, research and development, and establishment of optimum processing conditions.

5.2 Dynamic mechanical testing provides a sensitive method for determining cure characteristics by measuring the elastic and loss moduli as a function of temperature or time, or both. Plots of cure behavior and tan delta of a material versus time provide graphical representation indicative of cure behavior under a specified time-temperature profile.

5.3 This test method can be used to assess the following:

5.3.1 Cure behavior, including rate of cure, gel, and cure time.

5.3.2 Processing behavior, as well as changes as a function of time/temperature.

NOTE 3—The presence of the substrate prevents an absolute measure, but allows relative measures of flow behavior during cure.

5.3.3 The effects of processing treatment.

5.3.4 Relative resin behavioral properties, including cure behavior and damping.

5.3.5 The effects of substrate types on cure.

NOTE 4—Due to the rigidity of a supporting braid, the gel time obtained from dynamic mechanical traces will be longer than actual gel time of the unsupported resin measured at the same frequency. This difference will be greater for composites having greater support-to-polymer rigidity ratios.[3]

5.3.6 Effects of formulation additives that might affect processability or performance.

5.4 For many materials, there may be a specification that requires the use of this test method, but with some procedural modifications that take precedence when adhering to the specification. Therefore, it is advisable to refer to that material specification before using this test method. Table 1 of Classification System D4000 lists the ASTM materials standards that currently exist.

6. Interferences

6.1 Since small quantities of resin are used, it is essential that the specimens be representative of the polymeric material being tested.

6.2 The result is a response of the thermal advancement or cure behavior of the resin in combination with any substrate used to support the resin.

7. Apparatus

7.1 The function of the apparatus is to hold a neat (unmodified) resin or uncured supported composite formulation or coated substrate of known volume and dimensions. The material acts as the elastic and dissipative element in a mechanically driven oscillatory shear or dynamic compression system. These dynamic mechanical instruments operate in one or more of the following modes for measuring cure behavior in torsional shear or dynamic compression:

7.1.1 Forced, constant amplitude, fixed frequency,

7.1.2 Forced, constant amplitude, resonant oscillation,

7.1.3 Freely decaying oscillation.

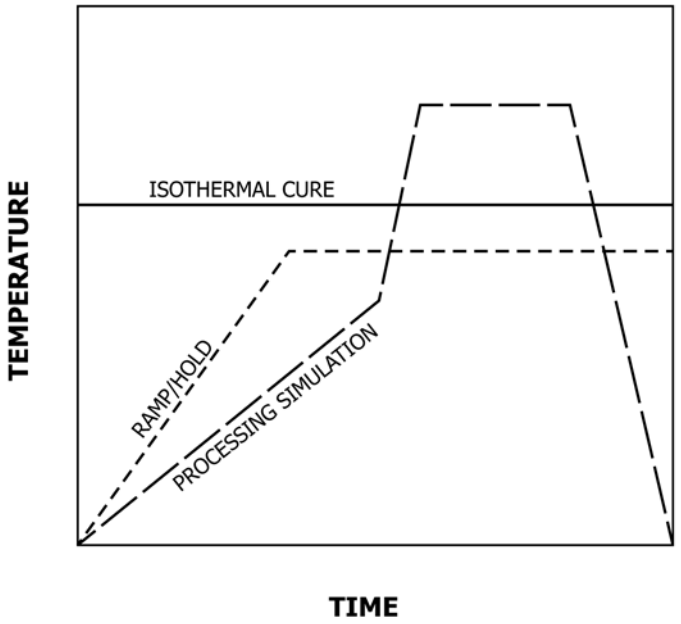

FIG. 1 Typical Temperature Profile

7.2 The apparatus shall consist of the following:

7.2.1 *Test Fixtures,* a choice of the following:

7.2.1.1 *Polished Cone and Plate (Having a Known Cone Angle)*—Usually a 25 or 50-mm diameter cone and plate or parallel plates are recommended for neat resins. Variations of this tooling, such as bottom plates with concentric overflow rims, may be used as necessary.

7.2.1.2 *Parallel Plates,* having either smooth, polished, or serrated surfaces are recommended for neat resins or prepregs having less than 6 % volatiles.

7.2.1.3 *Clamps*—A clamping arrangement that permits gripping of the composite sample.

7.2.2 *Oscillatory Deformation (Strain Device)*—A device for applying a continuous oscillatory deformation (strain) to the specimen. The deformation (strain) may be applied and then released, as in free-vibration devices, or continuously applied, as in forced-vibration devices (see Table 1 of Practice D4065).

7.2.3 *Detectors*—A device or devices for determining dependent and independent experimental parameters, such as force (stress or strain), frequency, and temperature. Temperature should be measurable with a precision of ±1°C, frequency to ±1 %, and force to ±1 %.

7.2.4 *Temperature Controller and Oven*—A device for controlling the temperature, either by heating (in steps or ramps), cooling (in steps or ramps), maintaining a constant specimen environment, or a combination thereof. Fig. 1 illustrates typical

[3] Hedvat, S., *Polymer Engineering and Science*, Vol 21, No. 3, February 1981.

time-temperature profiles. A temperature controller should be sufficiently stable to permit measurement of sample temperature to within 1°C.

7.3 *Nitrogen,* or other inert gas supply for purging purposes.

8. Test Specimens

8.1 The neat resin or the self-supporting composition, or both, should be representative of the polymeric material being tested.

8.2 Due to the various geometries that might be used for dynamic mechanical curing of thermosetting resins/composites, specimen size is not fixed by this test method. Cure rates may be influenced by specimen thickness, so equal volumes of material should be used for any series of comparisons.

8.3 For convenience, low-viscosity neat resins can be studied using a supporting substrate.

8.4 The substrate on which the resin is supported is normally in the form of a woven-glass cloth or tape or a braided-glass cord. The substrate should have negligible stiffness when compared to the cured resin sample in both a flexural and torsional mode of deformation. Other substrates can be used if their effect on cure mechanisms were of interest. The composition should be representative of the polymeric material being tested.

8.4.1 To standardize the pH of the supporting substrates, soak the cloth or braid overnight in distilled water and vacuum-dry. This will avoid any extraneous results with resins that are pH-sensitive.

9. Calibration

9.1 Calibrate the instrument using procedures recommended by the manufacturer for that specific make and model.

10. Procedure

NOTE 5—**Precaution:** Toxic or corrosive effluents, or both, may be released when heating the resin specimen to its cured state and could be harmful to personnel or to the instrumentation.

10.1 Apply the resin or uncured, self-supporting composite onto the test fixture. In the case of two-part room-temperature cure resins, mixing should be carried out in less than 1 % of the expected gel time.

10.2 Out-time effects and moisture-effect data must be recorded and reported.

10.3 *Procedure A—Unsupported Resin:*

10.3.1 Allow the sample to equilibrate to room temperature in a desiccator. In case of a solid sample, place it in an oven at 100°C for 5 to 10 min in order to soften. Use a vacuum oven to degas, if necessary. Use 50-mm diameter test plates for low minimum-viscosity systems and 25-mm diameter plates for higher minimum-viscosity materials.

10.3.2 For neat resins, be certain that there is sufficient material to cover the bottom plate uniformly.

10.3.3 Lower the upper test fixture so that it is touching the material to be cured.

10.3.3.1 The distance between the two parallel plates should be approximately 0.5 mm. However, when low viscosity materials are being evaluated using cone and plate test fixtures, the recommended minimum gap setting is equipment-dependent and reference should be made to the manufacturer's operational manual for correct gap setting.

10.3.3.2 Cone and plate experiments should be run only at one temperature. Any changes in the temperature setting will require adjusting the gap setting to the manufacturer's recommended value.

10.3.4 Conduct cure characterization of the submitted material in accordance with the desired time and temperature parameters recording the appropriate property values.

10.4 *Procedure B—Supported Compositions:*

10.4.1 For self-supporting compositions in prepreg-type form using cone and plate or parallel plate fixturing, be certain that there is sufficient material to fill the sample volume on the lower plate completely.

10.4.2 Insert the substrate between the plates of the test instrument. A sample disk (usually 25 mm in diameter) of the self-supporting composition can be die-cut, or several plies of prepreg can be compressed into a sheet (for example, for 3 min at 77°C at 75 atmospheres, 1000 psi) and then a disk die-cut. The orientation of unidirectional reinforcements may affect cure behavior and the orientation should be reported in 12.1.4.

10.4.3 For three to five plies, the recommended gap setting is 1 to 2 mm. This gap setting is arbitrary and dependent on the type of material and the number of plies being characterized. A gap setting of 0.5 mm would be minimum. Cone and plate test fixtures are not recommended for supported compositions.

10.4.4 For self-supporting substrates where either a bare substrate is to be impregnated with liquid resin (rectangular or cylindrical form) or where a similar prepreg-type specimen forms a rectangular specimen, clamp the substrate in place utilizing the instrument's grip system.

10.4.5 Conduct the cure characterization of the submitted material in accordance with the desired time and temperature parameters recording the appropriate property values.

10.5 *Procedure C—Dynamic Compression:*

10.5.1 Prepare the test specimen in accordance with the procedure described in 10.4.2 and 10.4.3.

10.5.2 Compress slightly the specimen disk and monitor and record the preload force by observing the normal force gage or indicator. Adjust the gap as necessary to accommodate any material expansion or contraction during the thermal advancement.

10.5.3 Conduct the cure characterization of the submitted material in accordance with the desired time and temperature parameters recording the appropriate property values.

10.6 Remove excess material by flushing or trimming the test fixtures, using a razor blade, spatula, knife, or hot soldering gun.

10.7 *Isothermal Curing at Elevated Temperature:*

10.7.1 In cases where the specimen can be introduced directly into the test chamber at elevated temperatures, preheat and stabilize the chamber to the desired temperature prior to introducing the test specimen.

10.7.2 Prevent the material from entering a variable tensile stress mode by adjusting the fixture to compensate for the contraction of the resin during curing.

10.7.3 *Ramped or Simulated Process Program Heating*—For materials that are to be cured starting at a low temperature and programmed for either a linear ramp or function, the material should be applied to the test tooling and the test chamber closed and heated at the desired rate. Although the temperature gradient is process- and product-dictated, a temperature increase of 0.5 (minimum) and a recommended range from 2 to 5°C should be monitored during this heat-up. The actual environmental chamber as well as the measured material temperature should be monitored, recorded, and reported.

NOTE 6—For an isothermal curing experiment at a temperature where the uncured resin is in a liquid state, the system may form branched molecules and gel with a dramatic increase in viscosity, and then vitrify to a glassy solid. In such cases, two peaks in the damping curve may be observed. The first peak has been associated with gelation and the second peak with vitrification. In other words, only a single peak is observed, that can be associated with either gelling or vitrification, depending on temperature, molecular weight, or other polymeric structural factors.

NOTE 7—The cured composite may be tested after cooling to room temperature to obtain dynamic mechanical properties using Practice D4065.

10.8 Maximum strain amplitude should be used to ensure adequate torque signal. For a neat resin, the strain amplitude may vary from 1 to 2 % and up to 50 % and still be within the linear viscoelastic region of the polymeric material being tested. For prepregs, a strain amplitude of less than 2 % is recommended, provided that the torque is adequate for the load range of the detector.

NOTE 8—The strain amplitude should be decreased as necessary with increasing torque and modulus, or the test should be stopped. This will prevent mechanical breakdown of the polymeric structure as it is being developed through crosslinking.

11. Calculation

11.1 The equations listed in Practice D4065 are used to calculate the following important rheological properties:

11.1.1 Storage (elastic) modulus in shear, G',

11.1.2 Loss (viscous) modulus in shear, G'',

11.1.3 Tan delta, d,

11.1.4 Complex modulus in shear, G^*, and

11.1.5 Complex viscosity, n^*.

11.2 The modulus, viscosity, and thermal advancement or cure behavior can be plotted as a function of either frequency, temperature, or time. Some recommended forms for data presentations are shown in Figs. 2 and 3.

11.3 The intersection of the elastic (G') and viscous (G'') moduli, where tan delta ($G''/G' = 1$) has been defined as an indication of the gel point of a thermosetting resin or composite prepreg system (see Fig. 4).[4]

11.4 For neat resins, the temperature corresponding to a complex viscosity, n^*, value of 100 Pa·s (1000 P) after the initial heating, flowing, and onset of the thermal advancement or cure, has been suggested as the dynamic gel temperature, DGT.

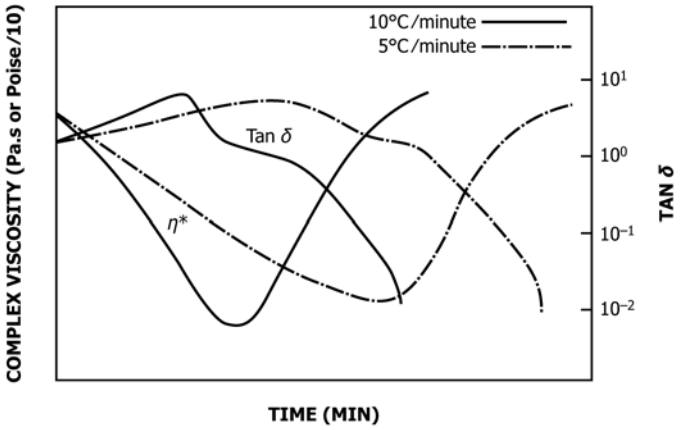

FIG. 2 Typical Cure Behavior at Different Thermal Gradients

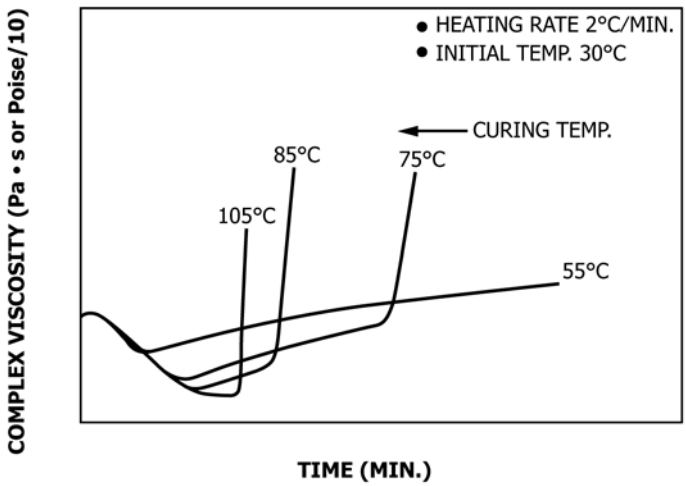

FIG. 3 Gel Point Identification of Cured Thermoset

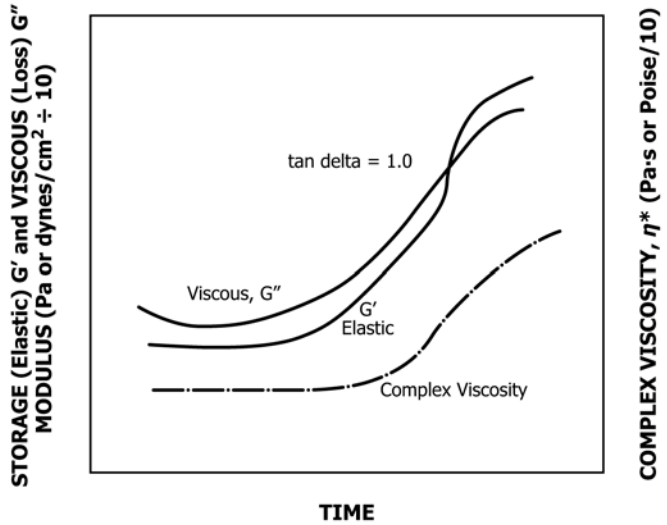

FIG. 4 Isothermal Cure Behavior After Initial Heating

[4] Maximovich, M. G., and Galeos, R. M., "Rheological Characterization of Advanced Composite Prepreg Materials," *1983 SAMPE Proceedings*, Vol 28, pp. 568 to 580.

12. Report

12.1 Report the following information:

12.1.1 Complete identification and description of the material tested, including the name, stock or code number, date made, form, source, etc.

12.1.2 Complete identification and description of the substrate (if applicable).

12.1.3 Description of the instrument used for the test.

12.1.4 Dimensions of the composite specimen and the gap setting. For supported materials, also report the number and the orientation of the prepreg plies.

12.1.5 Description of the calibration procedure.

12.1.6 Identification of the sample atmosphere by gas composition, purity, and gas flow rate used.

12.1.7 Details of conditioning the specimen prior to test.

12.1.8 The temperature or time/temperature profile used in the cure study and the time for the specimen to reach equilibrium, as applicable.

12.1.9 Table of data and results.

12.1.9.1 Tabulate the viscoelastic behavior, G', G'', and n^*, as a function of time or temperature. For example, report the time or temperature, or both, when the neat-resin viscosity has advanced, after initial flow through a minimum, upwards to 100 Pa·s (1000 P). (This is often referred to as the dynamic gel point of a neat resin.)

12.1.9.2 The minimum viscosity that is the lowest point on the viscosity curve under specified conditions.

12.1.9.3 For supported resins, the gel point has been identified as the crossover or intersection of G' and G'' (where tan delta = 1.0) after the viscosity has reached a minimum and has begun to develop its structure through thermal advancement or cure.

12.1.9.4 The onset of gelation is the time corresponding to the intersection of the tangent lines of the minimum viscosity and the subsequent rapid increase in viscosity due to thermal advancement.

NOTE 9—Moisture effects may cause dramatic changes in the slope or an anomaly in the viscosity curve at approximately 100°C.

12.1.10 Number of specimens tested.

12.1.11 A plot of the cure behavior versus time where tests are conducted at more than one temperature. This might include G'or G'' modulus, or both, viscosity, torque, etc.

12.1.12 Frequency of test or frequency range.

12.1.13 Date of test.

12.1.14 Maximum strain amplitude and frequency.

12.1.15 Equations used to calculate values.

13. Precision and Bias

13.1 A two-part epoxy (amine cured) system was investigated for its cure behavior in accordance with Test Method D4473. In one laboratory, two technicians conducted duplicate testing using 25 mm diameter parallel plates, a gap setting of 2 mm, and a testing frequency of 6 radians/s (almost 1 Hz).

The oscillatory strain was set initially at ten percent, although the auto-strain control did allow the strain to vary to ensure an adequate transducer torque signal. The isothermal cure was fixed at 65°C.

Technician	Time to reach selected complex viscosities	
	1E2 Pa-s	1E3 Pa-s
A-1	4.2 min	5.8 min
A-2	4.2 min	6.0 min
A-3	3.9 min	5.2 min
B-1	4.2 min	5.9 min
B-2	3.9 min	5.2 min
	Time to reach Gel Point (tan delta = 1.0)	Complex Viscosity at the Gel Point (tan delta = 1.0)
A-1	7.5 min	5.3 E3 Pa-s
A-2	7.6 min	4.5 E3 Pa-s
A-3	6.2 min	4.5 E3 Pa-s
B-1	7.5 min	5.1 E Pa-s
B-2	6.5 min	5.1 E Pa-s

14. Keywords

14.1 behavior; cure behavior; flow; rheological; thermosetting resins; viscosity