Designation: E3277 – 23

Standard Test Method for Determining the Liquid or Solid State of a Material by Rheometry[1]

This standard is issued under the fixed designation E3277; 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 Using rheometry, this test method determines, for regulatory purposes, whether a viscose viscous material is a liquid or a solid. Very small amounts of material (typical less than 3 g) may be used for this measurement.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4092 Terminology for Plastics: Dynamic Mechanical Properties

D4359 Test Method for Determining Whether a Material Is a Liquid or a Solid

D4473 Test Method for Plastics: Dynamic Mechanical Properties: Cure Behavior

E473 Terminology Relating to Thermal Analysis and Rheology

3. Terminology

3.1 *Definitions*—Technical terms used in this test method are defined in Terminologies D4092 and E473 including *dynamic mechanical analyzer, loss modulus, phase angle, rheometer, shear, storage modulus, strain, stress*, and *tan delta*.

3.1.1 *dissipative, adj—in dynamic mechanical analysis*, the irrecoverably loss of mechanical energy usually as heat.

3.1.2 *gel point, n*—the stage at which a liquid begins to exhibit pseudo-elastic properties.

3.1.3 *slip, wall, n*—in rheology, the lack of adhesion between the test specimen and the shearing surface.[3]

4. Summary of Test Method

4.1 Viscoelastic materials exhibit both solid-like and liquid-like characteristics. The loss modulus of a material is a measure of its liquid-like characteristic while the storage modulus of a material indicates its solid-like characteristics. When the loss modulus is greater than the storage modulus, a material is said to be predominantly a liquid. When the storage modulus is greater than the loss modulus, the material is said to be predominantly a solid. The ratio of loss modulus to storage modulus is known as tangent angle delta (tan δ).

4.2 Loss modulus and storage modulus of a material is measured using a cone-and-plate or parallel plate rheometer at ambient temperature conditions and tan δ is then calculated. Materials with a tan δ greater than unity (tan δ ≥ 1.0) are identified as liquids. Those materials with a tan δ less than unity are identified as solids.

5. Significance and Use

5.1 Shipping regulations often require the identification of a material as either a liquid or a solid. This test method may be used to make that determination for regulatory purposes. (See also Test Method D4359.)

5.2 For liquid thermosetting resin, as cure progresses, the liquid resin becomes a solid. A thermosetting resin is more easily worked or shaped while in the liquid-like form and becomes more difficult to do so as the cure advances. The point

[1] This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.08 on Rheology.

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[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.

[3] Bingham, E. C., *Fluidity and Plasticity*, McGraw-Hill, New York, NY, 1922, p. 231.

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

at which the solid-like character becomes dominant is called the gel point and is considered to be the end of the period where the thermosetting resin is workable. Gel point is identified as that point where tan δ = 1 as determined in Test Method D4473.

NOTE 1—Gel point at ambient temperature is seldom a useful parameter. Use of this test method at the more useful elevated temperatures requires capabilities readily available but outside of 7.2.6, 7.2.7, and Section 10.

5.3 This test method may be used in research, development, and for regulatory compliance.

6. Interferences

6.1 Since small quantities of material are used, it is essential that the specimen be representative of the sample being tested.

6.2 Wall slip may occur with a variety of materials to which this test method is applicable. When slip occurs, the measured rheological properties are significantly lower than their true values. Roughened measuring geometries are useful in these cases. The type of roughening shall be agreed upon by all interested parties.

7. Apparatus

7.1 A rheometer is a type of dynamic mechanical analyzer especially suited for testing liquid materials. The function of the rheometer apparatus is to hold a liquid test specimen of known volume and dimensions in which the material acts as the elastic and dissipative elements in a mechanically driven oscillatory shear system.

7.2 *Rheometer*—The essential instrumentation required providing the minimum rheological analytical capabilities for this test method include:

7.2.1 A *drive motor*, to apply force or displacement to the specimen in a periodic manner capable of frequencies of oscillation from 0.5 Hz to 2 Hz. This motor may also be capable of providing static force or displacement on the specimen.

7.2.2 A *coupling shaft*, or other means to transmit the force or displacement from the motor to the specimen.

7.2.3 A *fixture, geometry, or tool* to fix the specimen between the drive shaft and a stationary position.

7.2.3.1 Either roughened cone-and-plate geometries of diameter D having a known cone angle α (see Fig. 1a) or,

7.2.3.2 Roughened parallel plate geometries of known diameter D (see Fig. 1b).

NOTE 2—25 mm or 50 mm diameter cone-and-plate geometries have been found suitable for this test method. Other diameters may be used but shall be reported. The appropriate geometries shall be agreed upon by all interested parties.

7.2.3.3 The geometry surfaces are roughened in one of several ways. Type 1 geometries are supplied by a vendor with serrated surfaces specially designed to limit wall slip. In type 2 geometries, the surfaces of the geometries are roughened using 60 grit sandpaper. In type 3 geometries, 60 grit sandpaper is mounted on the two geometry surfaces either by self-adhesive or by double-sided tape. Type 4 geometries are unroughened.

7.2.4 Either a *force sensor* to measure the force developed by the specimen to within 1 %.

7.2.5 Or *position sensor* to measure the displacement of the test specimen to within 1 %.

7.2.6 A *temperature sensor* to provide an indicate of the specimen temperature over the range of 20 °C to 25 °C readable to within ±0.1 °C.

7.2.7 A *temperature controller* to maintain the temperature of the test specimen over the temperature range of 20 °C to 30 °C to within 0.5 °C.

7.2.8 A *stress or strain controller*, capable of executing a specific unidirectional or oscillatory stress or strain program between selected stress or strain limits to with 1 % or at an iso-stress or iso-strain constant to within 1 %.

7.2.9 A *data collection device*, to provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for this measurement are temperature, frequency, loss modulus and storage modulus.

7.2.10 Auxiliary instrumentation considered necessary or useful in conducting this test method includes:

7.2.10.1 *Cooling capability* to sustain an isothermal temperature in the range of 20 °C to 30 °C stable to with 0.5 °C.

7.2.10.2 *Data analysis* capability to provide storage modulus, loss modulus and tangent angle delta or other useful parameters derived from the measured signals of stress and strain.

8. Reagents and Materials

8.1 *Nitrogen* or other inert gas supply for purging purposes.

9. Calibration and Standardization

9.1 Calibrate the instrument using procedures recommended by the manufacturer as described in the operations manual.

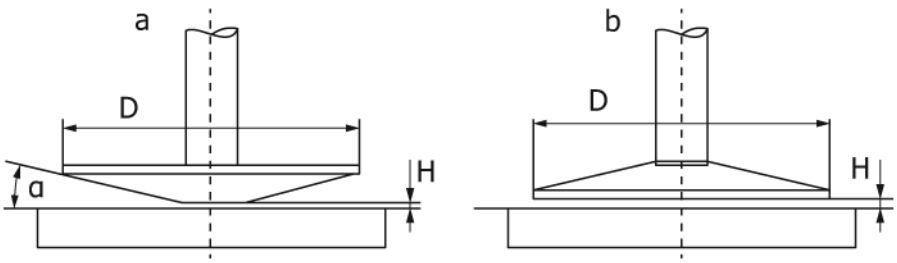

FIG. 1 Schematic Diagram of Cone-and-Plate (a) and Parallel Plate (b) Geometries

10. Procedure

10.1 Apply the test specimen onto the bottom plate of the test fixture. Be certain that there is sufficient material to cover the bottom plate uniformly.

10.2 Lower the upper test fixture (cone or parallel plate) so that it is touching the test specimen. The gap distance between the two plates or the tip of the cone and its plate in approximately 0.5 mm (see H in Fig. 1a or Fig. 1b).

NOTE 3—The recommended minimum gap setting may be equipment dependent and reference shall be made to the manufacturer's operations manual for the correct gap setting. The gap setting may also depend on the homogeneity of the material. The gap shall be greater than 10 times the size of the largest filler particle.

10.3 Ensure that the test specimen temperature is between 21 °C and 25 °C. Report the test temperature.

10.4 Initiate a rotational oscillatory motion to the upper plate or cone of 1 Hz and measure the loss modulus and storage modulus of the test specimen.

NOTE 4—Maximum strain amplitude shall be used to ensure adequate torque signal. The maximum strain amplitude is that which produces a 5 % or less (≤5 %) storage modulus change from that at 0.01 % strain. The strain amplitude may vary from 1 % up to 50 % and still be within the linear viscoelastic region.

10.5 Determine and report the tan δ value from storage shear modulus (G') and loss shear modulus (G") using Eq 1. If tan δ is equal to or greater than 1.0, report the material as a liquid. If the tan δ value is less than 1.0, report the material as a solid.

11. Calculation or Interpretation of Results

11.1

$$\tan\delta = G''/G' \quad (1)$$

where:

tan δ = tangent of the loss angle δ,
G'' = loss shear modulus,
G' = storage shear modulus, and
δ = angle between applied strain and resultant stress.

12. Report

12.1 The report shall include the following information:

12.1.1 A complete description of the apparatus including manufacturer, instrument model, and geometry description including texture type.

12.1.2 A complete description of the experimental parameters including test temperature and frequency, applied stress or strain.

12.1.3 The tan δ and identification of the test specimen as either liquid or solid.

12.1.4 The specific dated version of this test method used.

13. Precision and Bias

13.1 An interlaboratory study was conducted in 2022 on a sample of low loss and storage modulus material (toothpaste) with results from 6 laboratories using 2 instrument models from 2 vendors. All laboratories reported the test material to be a solid.

13.2 *Precision:*

13.2.1 The within-laboratory variability may be described using the repeatability value (r) obtained by multiplying the repeatability standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit. That is, two results from the same laboratory, performed by the same operator, using the same apparatus, closely spaced in time should be considered suspect (at the 95 % confidence level) if they differ by more than the repeatability value.

13.2.2 The between-laboratory variability may be described using the reproducibility value (R) obtained by multiplying the reproducibility standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limit. That is, results obtained from two laboratories, operators, apparatus or distant in time from each other should be considered suspect (at the 95 % confidence level) if they differ by more than the reproducibility value.

13.2.3 The tan δ within laboratory repeatability standard deviation was 0.030 on a mean value of 0.57 for a relative standard deviation (RSD) of 5.2 %.

13.2.4 The loss modulus within laboratory repeatability standard deviation was 48 Pa on a mean value of 286 Pa for a relative standard deviation of 16 %.

13.2.5 The storage modulus within laboratory repeatability standard deviation was 23 Pa on a mean value of 351 Pa for a relative standard deviation of 6.5 %.

13.2.6 The tan δ between laboratory reproducibility standard deviation was 0.39 on a mean value of 0.57 for a relative standard deviation of 69 %.

13.2.7 The loss modulus between laboratory reproducibility standard deviation was 165 Pa on a mean value of 286 Pa for a relative standard deviation of 58 %.

13.2.8 The storage modulus between laboratory reproducibility standard deviation was 98 Pa on a mean value of 351 Pa for a relative standard deviation 28 %.

13.3 *Bias:*

13.3.1 Bias is the difference between the mean value obtained and an acceptable reference value for the same material.

13.3.2 The developers of this test method are unaware of any suitable reference material close to the reference value of tan δ = 1 suitable as a reference material for this test. No bias is determined.

13.3.3 Liu and coworkers observed loss modulus of 660 Pa, a storage modulus of 1500 Pa, and a tan δ to be 0.12 for the commercial toothpaste used in this study.[4] Kim and coworkers observed loss modulus of 400 Pa and 800 Pa, storage modulus of 2000 and 3000, and the tan δ at 0.21 and 0.73 for several non-commercial toothpastes.[5]

14. Keywords

14.1 dynamic mechanical analysis; gel point; liquid; rheometry; solid

[4] Liu, Z., et al., "Toothpaste microstructure and rheological behaviors including aging and partical rejuvenation," Korea-Australia Rheology Journal, Vol 27, No. 3, 2015, p. 207-212.

[5] Kim, J.Y., et al., "Facile and effective approach enabling the prediction of the dispersibility of toothpastes with rheological parameters," *Bulletin of the Korean Chemical Society*, Vol 41, No. 12, 2020, p. 1211-1216.