Designation: E1824 – 13

Standard Test Method for Assignment of a Glass Transition Temperature Using Thermomechanical Analysis: Tension Method[1]

This standard is issued under the fixed designation E1824; 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 a procedure for the assignment of a glass transition temperature (T_g) of materials on heating using thermomechanical measurements in tension.

1.2 This test method may be used as a complement to Test Method E1545 and is applicable to amorphous or to partially crystalline materials in the form of films, fibers, wires, etc., that are sufficiently rigid to inhibit extension during loading at ambient temperature.

1.3 The generally applicable temperature range for this test method is −100 to 600°C. This temperature range may be altered depending upon the instrumentation used.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 There is no ISO method equivalent to this 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

E1142 Terminology Relating to Thermophysical Properties

E1545 Test Method for Assignment of the Glass Transition Temperature by Thermomechanical Analysis

E2602 Test Method for the Assignment of the Glass Transition Temperature by Modulated Temperature Differential Scanning Calorimetry

3. Terminology

3.1 *Definitions:*

3.1.1 The following terms are applicable to this test method and can be found in Terminology E473 and Terminology E1142: *thermomechanical analysis* (TMA), *thermodilatometry, glass transition,* and *glass transition temperature*.

4. Summary of Test Method

4.1 This test method uses thermomechanical analysis equipment (thermomechanical analyzer, dilatometer, or similar device) with the test specimen in tension to determine the change in dimension of a thin specimen observed when the material is subjected to a constant heating rate through the glass transition region. This change in dimension associated with the change from vitreous solid to amorphous liquid is observed as movement of a sensing probe in direct contact with the specimen and is recorded as a function of temperature. The intersection of the extrapolation of the slope of the probe displacement curve before and after the transition is used to determine a temperature that is assigned as the glass transition temperature.

5. Significance and Use

5.1 The glass transition is dependent on the thermal history, softening agents or additives of the material to be tested. For amorphous and semicrystalline materials the assignment of a glass transition temperature may lead to important information about thermal history, processing conditions, stability, progress of chemical reactions, and mechanical and electrical behavior.

5.2 Thermomechanical analysis provides a rapid means of detecting changes in hardness or linear dimensional change associated with the glass transition. Dimensional changes measured as a specimen is heated over the glass transition region may include the interaction of several effects: an increase in the coefficient of expansion, a decrease in the modulus, which under a constant stress leads to increased extension, stress relief leading to irreversible dimensional change (shrinkage in one dimension, expansion in another dimension), and physical aging effects which change the kinetics of the dimensional change.

[1] This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.10 on Fundamental, Statistical and Mechanical Properties.

Current edition approved Aug. 1, 2013. Published August 2013. Originally approved in 1996. Last previous edition approved in 2009 as E1824 – 09ε1. DOI: 10.1520/E1824-13.

[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.

5.3 This test method is useful for research and development, quality control, and specification acceptance testing; particularly of films and fibers.

6. Interferences

6.1 This test method may be used for materials having a glass transition at or below ambient temperature providing care is taken to avoid exposing the specimen to a tensile force prior to cooling the specimen below its glass transition. Applying a tensile load on a specimen that is above its glass transition will result in elongation of the specimen which may introduce orientation and residual stresses that will alter the specimen thermal history and may yield erroneous results during the heating cycle.

6.2 Specimens of thickness less than 0.2 mm may be difficult to handle.

6.3 Specimens of thickness greater than 5 mm may develop temperature nonuniformities of sufficient extent as to yield erroneously high values for an assigned glass transition temperature using this test method.

7. Apparatus

7.1 The essential equipment required to provide the minimum instrument capability for this test method includes:

7.1.1 A *Thermomechanical Analyzer* (TMA) or *Thermodilatometer*, consisting of:

7.1.1.1 *Rigid Specimen Holder,* of inert, low expansivity material (≤20 µm/m-°C), usually quartz, to center the specimen in the furnace and to fix the specimen to mechanical ground.

NOTE 1—Use of rigid specimen holders and tension probes constructed of lower thermal expansivity (≤20 µm/m-°C) materials or corrections for hardware expansivity may be necessary if very small changes in specimen dimensions are encountered with this test method.

7.1.1.2 *Rigid Tension Probe,* of inert, low expansivity material (≤ 5 µm/m-°C), usually quartz, which contacts the specimen with an applied in-plane tensile force.

7.1.1.3 *Sensing Element,* with a dynamic range of at least 5 mm, a linearity of 1 % or better, and sufficient sensitivity to measure the displacement of the rigid tension probe within ±1 µm resulting from changes in length of the specimen.

7.1.1.4 *Weight or Force Transducer,* to generate a constant force between 0 and 50 m*N* ± 2 % that is applied through the rigid tension probe to the specimen.

7.1.1.5 *Furnace and Temperature Controller,* capable of executing a temperature program of uniform controlled heating of a specimen at a constant rate of 5 ± 0.2°C/min between required temperature limits to ±0.5°C.

7.1.1.6 *Temperature Sensor,* that can be positioned reproducibly in close proximity to the specimen to measure its temperature between −100 and 600°C with a resolution of ±0.1°C.

7.1.1.7 *Means of Providing a Specimen Environment,* of an inert gas at a purge rate of 10 to 50 mL/min ± 5 %. The typical purge gas rate is usually given by the instrument manufacturer.

NOTE 2—Typically 99.99 % pure nitrogen, argon, or helium is employed when oxidation in air is a concern. Unless effects of moisture are to be studied, use of dry purge gas is recommended; especially for operation at subambient temperatures.

7.1.1.8 *Data Collection Device,* provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for thermomechanical analysis are dimension change, temperature and time.

7.1.2 *Rigid Specimen Clamps,* (clamps, grips, pins, or split shot) of inert, low expansivity material (≤ 20 µm/m-°C) that grip the specimen between the rigid specimen holder and the rigid tension probe without distortion (<1 %) or slippage (<1 %).

7.2 Auxiliary equipment considered useful in conducting this test method includes:

7.2.1 *Coolant System,* that can be coupled directly to the furnace/temperature controller to hasten recovery from elevated temperatures, to provide controlled cooling rates constant to ±1.0°C/min, and to sustain a subambient temperature to ±0.5°C.

7.2.2 *Calipers,* or other measuring device to determine specimen dimensions to ±0.01 mm.

7.2.3 *Balance,* to determine the specimen mass to ±0.1 mg.

8. Sampling

8.1 Analyze samples as received or after a prescribed pretreatment. If some treatment is applied to a specimen prior to analysis, note this treatment and any resulting changes in mass or appearance in the report. For samples with a glass transition below ambient, it may be desirable to form the glass with a known thermal history by using a controlled constant cooling rate to the starting temperature. Film samples may undergo stress relief related dimensional change that depends on whether the sample is prepared and measured parallel to the machine direction of manufacture or perpendicular to the machine direction.

9. Calibration

9.1 Perform temperature calibration in accordance with the apparatus manufacturer operator's manual using the same heating rate, purge, and temperature sensor position to be used with the test method.

10. Procedure

10.1 Attach a pair of rigid specimen clamps to a specimen with a minimum spacing of 5 mm between the contact points. Weigh the specimen and clamps and record this value.

NOTE 3—Use of between-clamp distances of less than 5 mm may impart erroneous results because of end effects introduced by the clamp pressure. Refer to the Precautions Section, if a thickness outside the range of 0.2 to 5 mm is to be used.

10.2 Suspend the specimen with clamps between the contact points of the specimen holder and the tension probe. BE SURE THE POSITION OF THE TEMPERATURE SENSOR IS UNCHANGED FROM THAT USED IN THE CALIBRATION PROCEDURE.

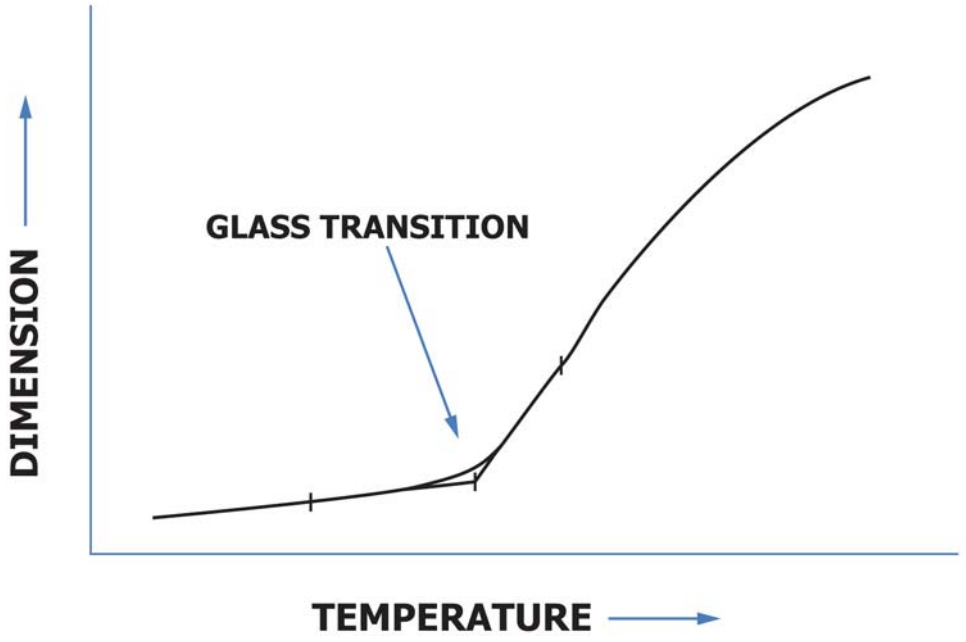

FIG. 1 Determination of T_g

10.3 Move the furnace to enclose the specimen and clamps. Start the inert gas purge and equilibrate the specimen and clamps at the desired starting temperature.

NOTE 4—Cool or heat the specimen, clamps and furnace to a temperature equivalent to at least 3 min of heating below the first temperature of interest to ensure stable heater control; for example, 15°C for a 5°C/min rate. The coolant used to lower the temperature should not come in contact with the specimen or clamps.

10.4 Apply a constant tensile force to the specimen in the range of either 5 to 10 m*N* (to observe shrinkage) or of 20 to 50 m*N* (to observe elongation).

NOTE 5—The observed inflection temperature will be dependent upon the applied stress. Therefore, the applied force should be adjusted for specimen cross-section area to ensure the same stress level is applied to all specimens.

10.5 Heat the specimen and clamps at a constant rate of 5°C/min over the desired temperature range.

NOTE 6—Other forces and heating rates may be used if applied both in the calibration and throughout the testing. The test conditions shall be noted in the report.

10.6 Note the occurrence of an abrupt change in slope (positive for shrinkage and negative for elongation) of the length versus temperature curve that indicates a transition of the material from one state to another.

10.7 Upon reaching the upper temperature limit of the heating program, remove the applied tensile force and restore the furnace, specimen, and clamps to ambient temperature.

10.8 Reweigh the specimen and clamps reporting any change in mass.

NOTE 7—Weighing of the specimen and clamps is required to determine whether changes such as loss of solvent or plasticizer which may alter the assigned glass transition temperature have occurred.

11. Calculation

11.1 Derive a glass transition temperature as follows using graphics or software:

11.1.1 Construct a tangent to the lower temperature portion of the thermal curve,

11.1.2 Construct a tangent to the steepest portion of the slope beyond the transition, and

11.1.3 The temperature at which these tangents intersect is the derived glass transition temperature, T_g'.

11.2 Apply any temperature correction determined from the instrument temperature calibration to T_g' to obtain the assigned glass transition temperature, T_g. (See Fig. 1.) Note, there are three cases illustrated, namely, a sample that exhibits shrinkage (over the T_g region under the conditions utilized), a sample that exhibits elongational reorientation, and a sample with no apparent stress-relied induced dimensional change. Because T_g is an assigned parameter its value may depend on experimental conditions, namely on the applied stress on the sample, and in the case of a film, the direction of the applied stress relative to the vector of the stress relief.

12. Report

12.1 Report the following information:

12.1.1 A complete identification and description of the material tested including specimen dimensions, clamp distance, and any pretreatment,

12.1.2 Description of the instrument used for the test including tensile force,

12.1.3 Test conditions including temperature program executed, purge gas composition and flow rate, and cooling medium if used,

12.1.4 Description of the temperature calibration procedure,

12.1.5 The thermomechanical analysis curves,

12.1.6 The assigned glass transition temperature, T_g, and
12.1.7 Any change in mass associated with the test.

13. Precision and Bias[3]

13.1 An interlaboratory test was conducted in 2007 on a polystyrene film. Ten laboratories participated in the test using two instrument models from a single manufacturer.

13.2 *Precision:*

13.2.1 Within laboratory variability may be describe using the repeatability value (r) obtained by multiplying the repeatability standard deviation by 2.8. The repeatability value estimates the 95 % confidence limits. That is, two results from the same laboratory should be considered suspect (at the 95 % confidence level) if they differ by more than the repeatability value.

13.2.1.1 The within laboratory repeatability standard deviation for polystyrene is 0.53°C with 28 [(n – 1) (p – 1)] degrees of experimental freedom (with 5 replicates (n) and 8 laboratories (p)).

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

13.2.2.1 The between laboratory reproducibility standard deviation for polystyrene was 1.2°C with 28 degrees of experimental freedom.

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 There is no accepted reference value for the glass transition by thermomechanical analysis in tension of this polystyrene material. No bias may be determined.

13.3.3 The overall mean value for the measurement of the glass transition on polystyrene was 106.9°C.

13.3.4 The glass transition temperature for this same material was assigned using an alternative technique of modulated temperature differential scanning calorimetry (Test Methods E1545 and E2602) in a limited interlaboratory test of five replicate determinations in two laboratories The mean value for the glass transition temperature was found be 103.2°C with a gauge R&R standard deviation of 0.92°C for the half temperature midpoint method.

14. Keywords

14.1 glass transition; glass transition temperature; T_g; tensile mode; thermomechanical analysis (TMA); thermodilatometry

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1037. Contact ASTM Customer Service at service@astm.org.