



# Standard Test Method for Assignment of the Glass Transition Temperature by Thermomechanical Analysis<sup>1</sup>

This standard is issued under the fixed designation E 1545; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers procedures for the assignment of the glass transition temperature of materials on heating using thermomechanical measurements under prescribed experimental conditions.

1.2 This test method is applicable to amorphous or to partially crystalline materials that are sufficiently rigid below the glass transition to inhibit indentation by the sensing probe.

1.3 The normal operating temperature range is from  $-100$  to  $600^{\circ}\text{C}$ . This temperature range may be extended depending upon the instrumentation used.

1.4 Computer- or electronic-based instruments, techniques, or data treatment equivalent to this test method may also be used.

NOTE 1—Users of this test method are advised that all such instruments or techniques may not be equivalent. It is the responsibility of the user of this test method to verify equivalency prior to use.

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

1.6 This test method is related to ISO 11359-2. ISO 11359-2 additionally covers the determination of coefficient of linear thermal expansion not covered by this test method.

1.7 *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 Section 7.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 832 Practice for Rubber Conditioning for Low-Temperature Testing<sup>2</sup>

E 473 Terminology Relating to Thermal Analysis<sup>3</sup>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>3</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E-37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Test Methods and Recommended Practices.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 09.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

E 831 Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis<sup>3</sup>

E 1142 Terminology Relating to Thermophysical Properties<sup>3</sup>

E 1356 Test Method for Glass Transition Temperatures by Differential Scanning Calorimetry or Differential Thermal Analysis<sup>3</sup>

E 1363 Test Method for Calibration of Thermomechanical Analyzers<sup>3</sup>

### 2.2 IIEPC Standard:

Test Method 2.4.24, Glass Transition Temperature TMA Method<sup>4</sup>

ISO 11359-2 Plastics—Thermomechanical Analysis (TMA) – Part 2: Determination of Coefficient of Linear Thermal Expansion and Glass Transition Temperature<sup>5</sup>

## 3. Terminology

3.1 *Definitions*—The following terms are applicable to this test method and can be found in Terminologies E 473 and E 1142: *thermomechanical analysis (TMA)*, *thermomechanical measurement*, *thermodilatometry*, *glass transition*, *glass transition temperature*, and *linear thermal expansion*.

## 4. Summary of Test Method

4.1 This test method uses thermomechanical analysis equipment (thermomechanical analyzer, dilatometer, or similar device) to assign the change in dimension of a specimen observed when the material is subjected to a constant heating rate through its glass transition. This change in dimension associated with the change from vitreous solid to amorphous liquid is observed as movement of the 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 the glass transition temperature.

## 5. Significance and Use

5.1 The glass transition is dependent on the thermal history of the material to be tested. For amorphous and semicrystalline materials the assignment of the glass transition temperature

<sup>4</sup> Available from The Institute for Interconnecting and Packaging Electronic Circuits, 7380 N. Lincoln Ave., Lincolnwood, IL 60646-1705.

<sup>5</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

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 expansion associated with the glass transition.

5.3 This test method is useful for research and development, quality control, and specification acceptance.

## 6. Apparatus

6.1 *Thermomechanical Analyzer (TMA)*—The essential instrumentation required to provide the minimum thermomechanical analytical capability for this test method includes the following:

6.1.1 A rigid specimen holder, composed of inert low expansivity material  $\leq 1 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ , to center the specimen in the furnace and to fix the specimen to mechanical ground.

6.1.2 A rigid circular expansion probe, 2 to 6 mm in diameter, composed of inert low expansivity material  $\leq 1 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ , that contacts the specimen with an applied compressive force.

6.1.3 A sensing element linear over a minimum 2-mm range to measure the displacement in length of the specimen.

6.1.4 A weight or force transducer to generate a constant force of 0 to 50 mN that is applied through the rigid compression probe to the specimen.

6.1.5 A furnace capable of providing uniform controlled heating (cooling) of a specimen to a constant temperature or at a constant rate over the temperature range of  $-100$  to  $600^\circ\text{C}$ .

6.1.6 A temperature controller capable of executing a specific temperature program by operating the furnace between selected temperature limits at a rate of temperature change of  $5 \pm 0.5^\circ\text{C}/\text{minute}$ .

6.1.7 A temperature sensor that can be attached to, in contact with, or reproducibly placed in close proximity to the specimen to provide an indication of the specimen/furnace temperature to  $\pm 0.1^\circ\text{C}$ .

6.1.8 A means of sustaining an environment around the specimen of a dry inert purge gas of 45 to 55 mL/minute.

NOTE 2—Typically, 99.9+ % pure nitrogen, argon or helium is used. Unless effects of moisture are to be studied, dry purge gas is recommended and is essential for operation at subambient temperatures.

6.1.9 A recording device, either digital or analog, capable of recording and displaying any fraction of the specimen dimension signal, including signal noise, on the Y-axis versus any fraction of the temperature signal, including noise, on the X-axis.

6.2 Micrometer or other measuring device to determine specimen dimensions of up to 8 mm with a precision of  $\pm 0.1$  mm.

## 7. Hazards

7.1 This test method may be used for amorphous and semicrystalline materials having a glass transition that is at or below room temperature providing care is taken to avoid contacting the specimen with a loaded probe prior to cooling the specimen below its glass transition. Applying a loaded probe to a specimen that is above its glass transition may cause partial penetration by the probe which can lead to probe

sticking upon cooling below the glass transition. This condition has been known to yield erroneous results during the heating cycle.

7.2 With some materials a transient may be observed between the pre-transition slope and the final slope (Run 1 of Fig. 1). This may occur due to settling, residual stresses within the specimen, or alteration of the specimen morphology. Refer to Note 6 for directions when this is encountered.

7.3 Specimens of thickness less than 0.2 mm may be very difficult to handle. Thin films (50 to 200  $\mu\text{m}$ ) on a substrate may be considered for this test method providing the substrate is mechanically stable in the temperature region of the film glass transition.

7.4 For specimens of thickness greater than 5 mm, temperature nonuniformities of sufficient extent can develop within the specimen as to yield erroneously high values of the glass transition temperature using this test method.

## 8. Sampling

8.1 Analyze samples as received or after pretreatment. If some treatment is applied to a specimen prior to analysis, note this treatment and any resulting change in mass in the report.

## 9. Calibration

9.1 Perform calibration in accordance with Test Method E 1363.

## 10. Procedure

10.1 Calibrate the thermomechanical analyzer in accordance with Test Method E 1363.

10.2 Place a preweighed specimen of 0.5 to 3-mm thickness on the specimen holder in line with the probe. BE SURE THE POSITIONING OF THE TEMPERATURE SENSOR IS UNCHANGED FROM THAT USED IN THE CALIBRATION PROCEDURE.

NOTE 3—Refer to Section 7 if thicknesses outside of this range are to be used.

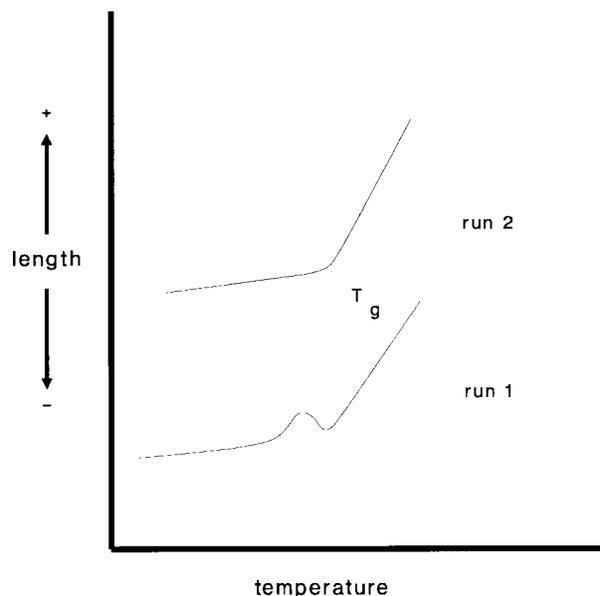


FIG. 1 Glass Transition Temperature from Expansion Mode

10.3 Move the furnace to enclose the specimen and holder. Start the dry inert gas purge before cooling or heating the specimen.

NOTE 4—If measurements are to be made at or below ambient temperature, cool the specimen 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 5°C/min. The refrigerant used for cooling should not come in direct contact with the specimen.

10.4 *Procedure A—Expansion Mode*—The transition temperature derived from this procedure is considered the glass transition temperature.

10.4.1 Lower the probe (4 to 6-mm diameter) into contact with the specimen and apply a force of 0 to 5 mN (or as recommended by the instrument manufacturer) to the probe.

10.4.2 Heat the specimen at a constant heating rate of 5°C/min over the desired temperature range.

NOTE 5—Other forces and heating rates may be used if applied both in the calibration and throughout the testing. The conditions used shall be noted in the report.

10.4.3 Note the occurrence of an abrupt positive change in the slope of the linear thermal expansion that indicates a transition of the material from one state to another (Run 2 of Fig. 1).

NOTE 6—If a sudden irreversible deflection is observed as in Run 1 of Fig. 1, stop the heating program 20°C above this temperature, remove any applied force from the probe, raise the probe from the specimen, and cool the specimen and furnace to the original start temperature. Conduct a second thermal cycle on the specimen beginning with 10.4.1.

10.4.4 Upon reaching the limit temperature of the heating program, remove any applied force from the probe, raise the probe from the specimen, and restore the furnace and specimen holder to room temperature.

10.5 *Procedure B—Penetration Mode*—The transition temperature derived from this procedure is referred to as the softening point,  $T_s$ . For most materials  $T_s$  is close to the  $T_g$  as measured in the expansion mode or as measured by differential scanning calorimetry. It is a common practice in many polymer laboratories to report  $T_s$  for  $T_g$ . The value of  $T_s$  may be affected by the applied force and the probe contact area. Hence, those values should also be reported when using this procedure.

10.5.1 Lower the probe (2 to 4-mm diameter) into contact with the specimen and apply a force of 20 to 50 mN to the probe.

10.5.2 Heat the specimen at a constant heating rate of 5°C/min over the desired temperature range.

NOTE 7—Other forces and heating rates may be used if applied both in the calibration and throughout the testing. The conditions used shall be noted in the report.

10.5.3 Note the occurrence of an abrupt negative change in the slope of the thermal curve which indicates a transition of the material from one state to another (Run 2 of Fig. 2).

NOTE 8—If a sudden irreversible deflection is observed as in Run 1 of Fig. 2, stop the heating program 20°C above this temperature, remove the applied force from the probe, raise the probe from the specimen, and cool the specimen and furnace to the original start temperature. Conduct a second thermal cycle on the specimen beginning with 10.5.1.

10.5.4 Upon reaching the limit temperature of the heating program, remove the applied force from the probe, raise the

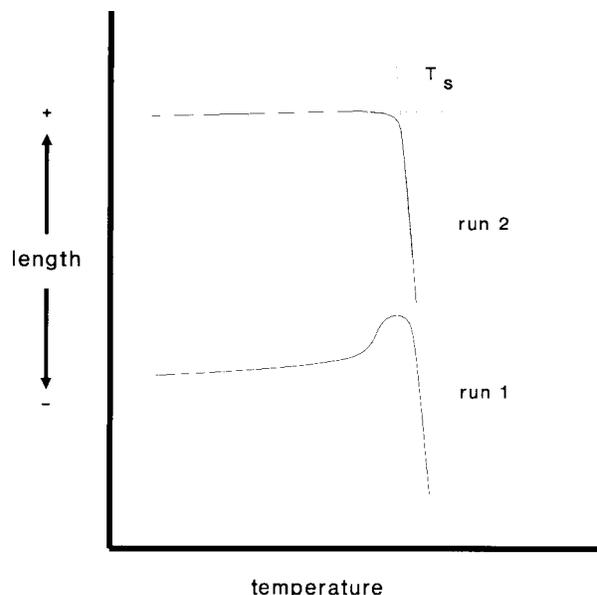


FIG. 2 Softening Point from Penetration Mode

probe from the specimen, and restore the furnace and specimen holder to room temperature.

10.6 Reweigh the specimen after the measurement and report any mass change along with any thermal pretreatment including any previous thermal cycles using either Procedure A or B.

NOTE 9—Weighing of the specimen is required to ensure whether changes such as loss of solvent or plasticizer that may have changed the observed glass transition temperature have occurred.

## 11. Calculation

11.1 Derive the glass transition temperature from Procedure A as follows using graphics or software:

11.1.1 Construct a tangent to the low-temperature thermal-expansion curve.

11.1.2 Construct a tangent to the thermal-expansion curve beyond the transition.

11.1.3 The temperature at which these tangents intersect is the observed glass transition temperature,  $T_g$ .

11.2 Derive the softening point from Procedure B as follows using graphics or software:

11.2.1 Construct a tangent to the low temperature portion of the thermal curve.

11.2.2 Construct a tangent to the steepest portion of the penetration slope beyond the transition.

11.2.3 The temperature at which these tangents intersect is the observed softening point,  $T_s$ .

11.3 Determine the corrected  $T_g$  or  $T_s$  by applying any temperature correction determined from the instrument temperature calibration to the observed values of  $T_g$  or  $T_s$ .

## 12. Report

12.1 Report the following information:

12.1.1 Complete identification and description of the material tested including dimensions and any pretreatment,

12.1.2 Description of the instrument used for the test including probe size, probe shape, and applied force,

- 12.1.3 Description of the temperature calibration procedure,
- 12.1.4 Purge gas, flow rate, and cooling medium if used,
- 12.1.5 The corrected glass transition temperature,  $T_g$ , or the corrected softening point,  $T_s$ ,
- 12.1.6 The thermomechanical measurement curves, and
- 12.1.7 Any change in mass during the test.
- 12.1.8 The specific dated version of this test method used.

### 13. Precision and Bias <sup>6</sup>

13.1 An interlaboratory study of the measurement of the glass transition temperature of an epoxy composite was conducted in 1993. Following temperature calibration using phenyl ether and indium melting temperatures, each of eight laboratories tested four specimens. Instruments from four manufacturers were used. The results were treated by Practice E 691.

13.2 *Precision*—Two values, each the mean of duplicate determination, should be considered suspect if they differ by

more than the 95 % confidence limits defined below:

- 13.2.1 Repeatability (within laboratory) =  $r = 3.6^\circ\text{C}$ .
- 13.2.2 Reproducibility (between laboratory) =  $R = 11.4^\circ\text{C}$ .
- 13.2.3 These limits are calculated from the respective standard deviations and are related by the factor 2.8.
- 13.2.4 Repeatability standard deviation =  $S_r = 1.3^\circ\text{C}$ .
- 13.2.5 Reproducibility standard deviation =  $S_R = 4.0^\circ\text{C}$ .

#### 13.3 Bias:

13.3.1 The mean glass transition ( $T_g$ ) of the epoxy composite was determined to be  $121.2 \pm 3.9^\circ\text{C}$  with 21 df.

13.3.2 The glass transition temperature ( $T_g$ ) of the epoxy composite used in this study was also determined by dynamic mechanical analysis (DMA) using this test method. The  $T_g$  by DMA was found to be  $120.8 \pm 4.2^\circ\text{C}$  with 18 df using a linear display of storage modulus.

### 14. Keywords

14.1 glass transition  $T_g$ ; linear thermal expansion; softening point  $T_s$ ; thermodilatometry; thermomechanical analysis (TMA)

<sup>6</sup> Available from ASTM Headquarters. Request RR: E37-1014.

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