Designation: E 1640 – 99

An American National Standard

Standard Test Method for Assignment of the Glass Transition Temperature By Dynamic Mechanical Analysis[1]

This standard is issued under the fixed designation E 1640; 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 the assignment of a glass transition temperature (Tg) of materials using dynamic mechanical analyzers.

1.2 This test method is applicable to thermoplastic polymers, thermoset polymers, and partially crystalline materials which are thermally stable in the glass transition region.

1.3 The applicable range of temperatures for this test method is dependent upon the instrumentation used, but, in order to encompass all materials, the minimum temperature should be about −150°C.

1.4 This test method is intended for materials having an elastic modulus in the range of 0.5 MPa to 100 GPa.

1.5 Electronic instrumentation or automated data analysis and data reduction systems or treatments equivalent to this test method may also be used.

NOTE 1—The user bears the responsibility for determining the precision, accuracy, and validity of the techniques and measurements made using dynamic mechanical analyzers in accordance with this standard. If disputes arise, only the manual procedures described in this standard are to be considered valid.

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:*

D 4065 Practice for Determining and Reporting Dynamic Mechanical Properties of Plastics[2]

D 4092 Terminology Relating to Dynamic Mechanical Measurements in Plastics[2]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

E 1142 Terminology Relating to Thermophysical Properties[3]

E 1356 Test Method for Glass Transition Temperatures by Differential Scanning Calorimetry or Differential Thermal Analysis[3]

E 1363 Test Method for Temperature Calibration of Thermomechanical Analyzers[3]

E 1545 Test Method for the Determination of Glass Transition Temperatures by Thermomechanical Analysis[3]

2.2 *Other Standard:*

SRM 18R-94 Recommended Method for Glass Transition Temperature (Tg) Determination by DMA of Oriented Fiber-Resin Composites [4]

3. Terminology

3.1 *Definition:*

3.1.1 Specific technical terms used in this document are defined in Terminology D 4092 and E 1142.

3.1.2 *dynamic mechanical analyzer*—any of various commercial or experimental devices used to study the viscoelastic response of a specimen under a forced or free resonant oscillatory load. The force may be applied in torsion, flexure, or a combination of tension and compression.

4. Summary of Test Method

4.1 A specimen of known geometry is placed in mechanical oscillation at either fixed or resonant frequency and changes in the viscoelastic response of the material are monitored as a function of temperature. Under ideal conditions, the glass transition region is marked by a rapid decrease in the storage modulus and a rapid increase in the loss modulus. The glass transition of the test specimen is indicated by the extrapolated onset of the decrease in storage modulus which marks the transition from a glassy to a rubbery solid.

5. Significance and Use

5.1 This test method can be used to locate the glass transition region and assign a glass transition temperature of amorphous and semi-crystalline materials.

5.2 Dynamic mechanical analyzers monitor changes in the viscoelastic properties of a material as a function of temperature and frequency, providing a means to quantify these changes. In ideal cases, the temperature of the onset of the

[1] 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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[2] *Annual Book of ASTM Standards*, Vol 08.02.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] Available from Cuppliers of Advanced Composite Materials Association, Arlington, VA.

decrease in storage modulus marks the glass transition.

5.3 A glass transition temperature (T_g) is useful in characterizing many important physical attributes of thermoplastic, thermosets (see SRM 18R-94), and semi-crystalline materials including their thermal history, processing conditions, physical stability, progress of chemical reactions, degree of cure, and both mechanical and electrical behavior. T_g may be determined by a variety of techniques and may vary in accordance with the technique.

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

6. Interferences

6.1 Because the specimen size will usually be small, it is essential that each specimen be homogeneous and/or representative of the material as a whole.

6.2 An increase or decrease in heating rates from those specified may alter results.

6.3 A transition temperature is a function of the experimental frequency, therefore the frequency of test must always be specified. (The transition temperature increases with increasing frequency.) Extrapolation to a common frequency may be accomplished using a predetermined frequency shift factor or assuming the frequency shift factor of about 8°C per decade of frequency.[5]

7. Apparatus

7.1 The function of the apparatus is to hold a specimen of uniform dimension so that the sample acts as the elastic and dissipative element in a mechanically oscillated system. Dynamic mechanical analyzers typically operate in one of several modes. See Table 1.

TABLE 1 Modes for Dynamic Mechanical Analyzers

Mode	Mechanical Response			
	Tension	Flexural	Torsional	Compression
Free/dec	...	...	X	...
Forced/res/CA	...	X	X	...
Forced/fix/CA	X	X	X	X
Forced/fix/CS	X	X	...	X

Free = free oscillation; dec = decaying amplitude; forced = forced oscillation; CA = constant amplitude; res = resonant frequency; fix = fixed frequency; CS = controlled stress.

7.2 The apparatus shall consist of the following:

7.2.1 *Clamps*, a clamping arrangement that permits gripping of the specimen. Samples may be mounted by clamping at both ends (most systems), one end (for example, torsional pendulum), or neither end (free bending between knife edges).

7.2.2 *Oscillatory Stress (Strain)*, for applying an oscillatory deformation (strain) or oscillatory stress to the specimen. The deformation may be applied and then released, as in freely vibrating devices, or continuously applied, as in forced vibration devices.

7.2.3 *Detector*, for determining the dependent and independent experimental parameters, such as force (or stress), displacement (or strain), frequency, and temperature. Temperatures should be measurable with an accuracy of ±0.5°C, force to ±1 %, and frequency to ±0.1 Hz.

7.2.4 *Temperature Controller and Oven*, for controlling the specimen temperature, either by heating, cooling (in steps or ramps), or by maintaining a constant experimental environment. The temperature programmer shall be sufficiently stable to permit measurement of specimen temperature to ±0.5°C. The precision of the required temperature measurement is ±1.0°C.

7.2.5 *Output Device*, capable of displaying the storage modulus (either linearly or logarithmically) on the *Y* axis increasing in the upward direction and temperature on the *X* axis increasing to the right.

NOTE 2—Some instruments suitable for this test may display only linear or logarithm storage modulus while others may display either linear and/or logarithm storage modulus. Care must be taken to use the same modulus scale when comparing unknown specimens, and in the comparison of results from one instrument to another.

7.3 *Nitrogen, Helium* or other gas supplied for purging purposes.

7.4 *Calipers* or other length measuring device capable of measuring dimensions (or length within)± 0.01 mm.

8. Precautions

8.1 Toxic and corrosive, or both, effluents may be released when heating some materials and could be harmful to personnel and to apparatus.

8.2 *Multiple Transitions*—Under some experimental conditions it is possible to have transitions secondary to the primary glass transition. Secondary transitions may be related to the glass transition of a second polymeric phase, melt processes, crystallization, chemical reactions, the motion of groups pendent to the main backbone or the crankshaft motion of the polymer backbone.

9. Samples

9.1 Samples may be any uniform size or shape, but are ordinarily analyzed in rectangular form. If some heat treatment is applied to the specimen to obtain this preferred analytical form, such treatment should be noted in the report.

9.2 Due to the numerous types of dynamic mechanical analyzers, sample size is not fixed by this method. In many cases, specimens measuring between $1 \times 5 \times 20$ mm and $1 \times 10 \times 50$ mm are suitable.

NOTE 3—It is important to select a specimen size appropriate for both the material and the testing apparatus. For example, thick samples may be required for low modulus materials while thin samples may be required for high modulus materials.

10. Calibration

10.1 Calibrate the storage modulus and temperature signals in accordance with manufacturer's recommended procedures and report the method used.

11. Procedure

11.1 Mount the specimen in accordance with the procedure recommended by the manufacturer.

11.2 Measure the length, width, and thickness of the specimen to an accuracy of ±0.01 mm.

[5] Ferry, D. "Viscoelastic Properties of Polymers," John Wiley & Sons, 1980.

11.3 Maximum strain amplitude should be within the linear viscoelastic range of the material. Strains of less than 1 % are recommended and should not exceed 5 %.

11.4 Conduct tests at a heating rate of 1°C/min and a frequency of 1 Hz. Other heating rates and frequencies may be used but shall be reported.

NOTE 4—The glass transition temperature measured by dynamic mechanical measurements is dependent upon heating rate and oscillatory frequency. The experimental heating rate and the frequency of oscillation should be slow enough to allow the entire specimen to reach satisfactory thermal and mechanical equilibration. When the heating rate or oscillatory rate is high, the experimental time scale is shortened, and the apparent T_g is raised. Changing the time scale by a factor of 10 will generally result in a shift of about 8°C for a typical amorphous material. The effect of these variables on the temperature of the tangent delta peak may be observed by running specimens at two or more rates and comparing the results (see appendix).

NOTE 5—Where possible in automated systems, a minimum of one data point should be collected for each °C increase in temperature. At low and high frequencies, use care in the selection of scanning rate and frequency rate; select test conditions and a data collection rate that will ensure adequate resolution of the mechanical response of the specimen. For example, select a heating rate that allows the specimen to complete at least one oscillation for each° C increase in temperature.

11.5 Measure and record the storage modulus, from 30°C below to 20°C above the suspected glass transition region.

12. Calculation

12.1 For the purpose of this test method the glass transition shall be taken as the extrapolated onset to the sigmoidal change in the storage modulus observed in going from the hard, brittle region to the soft, rubbery region of the material under test.

NOTE 6—Storage modulus may be displayed on a linear or logarithmic scale. The reported glass transition temperature will differ depending upon the scale chosen. The scale type (for example, linear or logarithmic) shall be reported and must be the same for all parties comparing results.

12.1.1 Construct a tangent to the storage modulus curve below the transition temperature.

12.1.2 Construct a tangent to the storage modulus curve at the inflection point approximately midway through the sigmoidal change associated with the transitions.

12.1.3 The temperature at which these tangent lines intersect is reported as the glass transition temperature, T_g (see Fig. 1).

NOTE 7—Under special circumstances agreeable to all parties, other temperatures taken from the storage modulus, loss modulus, or tangent delta curve may be taken to represent the temperature range over which the glass transition takes place. Among these alternative temperatures are the peak of the loss modulus (T_l) or tangent delta (T_t) curves as illustrated in Fig. 2 and Fig. 3, respectively. These temperatures are generally in the order $T_g < T_l < T_t$.

12.1.4 The value of T_g reported from this document shall be the mean value of duplicate determinations.

12.2 For fixed frequency measurements at 1 Hz.

12.2.1 Report the mean value of duplicate determinations as T_g.

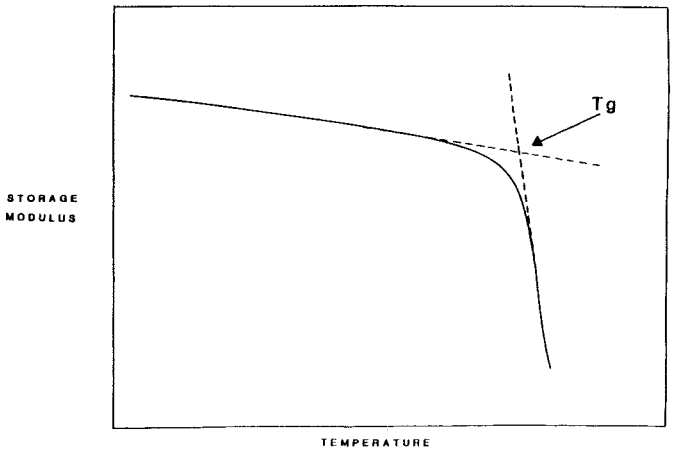

FIG. 1 Storage Modulus

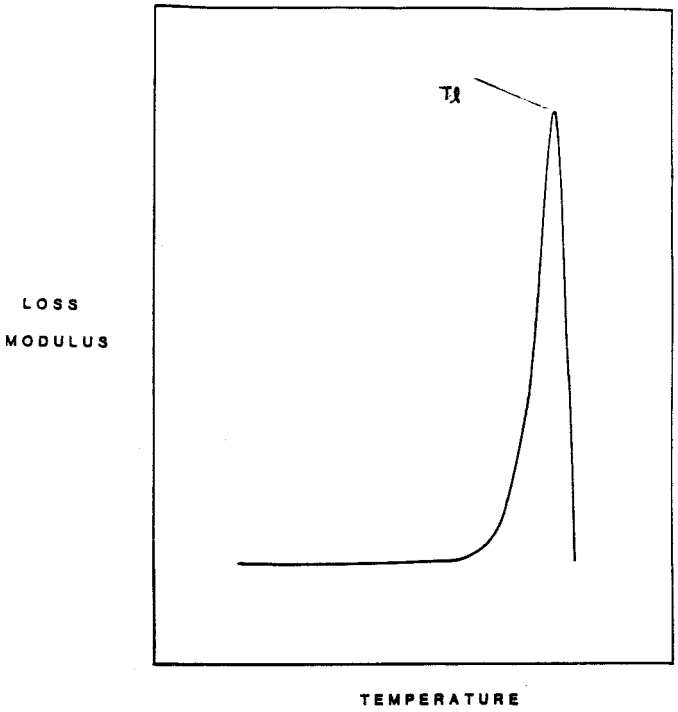

FIG. 2 Loss Modulus

12.3 For measurements made at frequencies other than 1 Hz.

12.3.1 Using a predetermined frequency shift factor (k) (see appendix), calculate the first approximation of the glass transition temperature (T_1') using equation 1.

$$T_l' = T + \frac{T^2}{k} \log \frac{F}{1\ \text{Hz}} \tag{1}$$

12.3.2 Calculate the glass transition temperature using equation 2:

$$T_1 = T + \frac{T\,T_1'}{k} \log \frac{F}{1\ \text{Hz}} \tag{2}$$

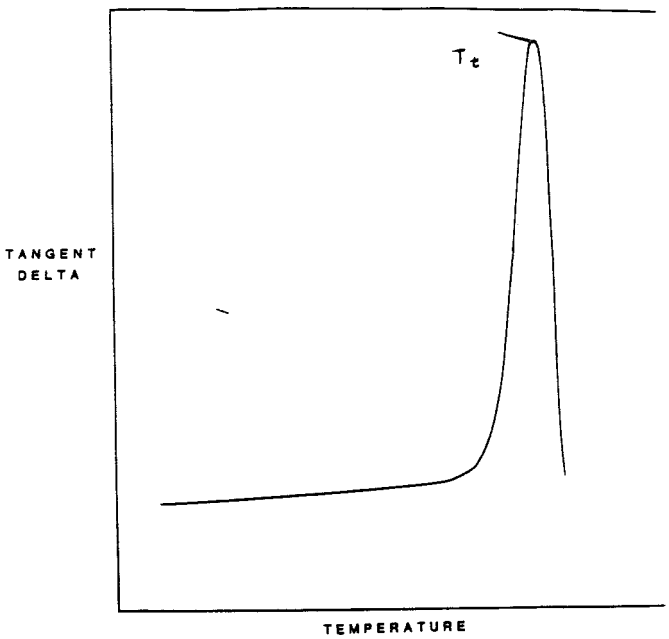

FIG. 3 Tangent Delta

where:

k = Predetermined Frequency Shift Factor (see Appendix X1.1)
F = Frequency of Measurement (Hz)
T = Glass Transition Temperature Observed at Frequency F (K)
T_1' = First Approximation for the Glass Transition Temperature at 1 Hz (K)
T_1 = Glass Transition Temperature at 1 Hz (K)

Example:

$k = -12{,}417K$
$F = 2$ Hz
$T = 100°C = 373K$

$$T' = 373K + \frac{(373K)\,(373K)}{-12{,}417K}\log 2 = 373K - 3.37K$$
$$= 369.62\ K$$

$$T = 373 + \frac{(373K)\,(369.62K)}{-12{,}417K}\log 2 = 373K - 3.34K$$
$$= 369.66\ K = 96.5°C$$

13. Report

13.1 The report shall include the following:

13.1.1 A complete identification and description of the material testing including dimensions and any pretreatment.

13.1.2 A description of the instrument used to perform the test.

13.1.3 A description of the temperature calibration procedure used.

13.1.4 Whether linear or logarithmic storage modulus was displayed.

13.1.5 The calculated glass transition temperature.

13.1.6 The frequency of test and any extrapolation procedures used to provide results comparable at 1 Hz.

13.1.7 The dynamic mechanical curves recorded.

14. Precision and Bias

14.1 An interlaboratory study of the measurement of the glass transition temperature of an epoxy composite was conducted in 1992. Following temperature calibration using a polystyrene thermoplastic polymer (a secondary reference material specifically prepared for this test program) each of 13 laboratories tested 4 test specimens. Seven laboratories used linear storage modulus while nine laboratories used logarithmic storage modulus. Instruments from five manufacturers were employed. The results were treated by Practice E 691 and are given in an ASTM Research Report [6].

14.2 *Precision*:

14.2.1 Using a linear presentation of storage modulus,

$$r = 95\ \%\ \text{repeatability limit (within laboratory)} = 4.1°C \quad (3)$$

$$R = 95\ \%\ \text{reproducibility limit (between laboratories)} = 12.3°C \quad (4)$$

14.2.1.1 Two values, each the mean of duplicate determinations, should be considered suspect if they differ by more than the limits described above. The respective standard deviations among test results, related to the above values by the factor 2.8, are:

$$s_r = \text{repeatability standard deviation} = 1.5°C \quad (5)$$

$$s_R = \text{reproducibility standard deviation} = 4.4°C \quad (6)$$

14.2.2 Using a logarithmic presentation of storage modulus,

$$r = 95\ \%\ \text{repeatability limit (within laboratory)} = 2.6°C \quad (7)$$

$$R = 95\ \%\ \text{reproducibility limit (between laboratories)} = 7.7°C \quad (8)$$

14.2.2.1 Two values, each the mean of duplicate determinations, should be considered suspect if they differ by more than the limits described above. The respective standard deviations among test results, related to the above numbers by the factor 2.8, are:

$$s_r = \text{repeatability standard deviation} = 0.9°C \quad (9)$$

$$s_R = \text{reproducibility standard deviation} = 2.7°C \quad (10)$$

14.3 *Bias*:

14.3.1 The glass transition temperatures (T_g) of the polystyrene calibrant and epoxy composite used in this study were assigned by thermomechanical analysis using Test Methods E 1363 and E 1545. T_g for the polystyrene was established to be 101.4 ± 1.8°C with 16 degrees of freedom (df) while $T_g$for the epoxy composite was established to be 121.2 ± 0.4°C with 21 df.

14.3.2 Using a linear presentation of storage modulus, the value for the epoxy composite glass transition by this dynamic mechanical test method was 120.8 ± 4.2°C with 18 degrees of freedom.

14.3.3 Using a logarithmic presentation of storage modulus, the value for the epoxy composite glass transition by this dynamic mechanical test method was 118.6 ± 2.6°C with 24 degrees of freedom.

NOTE 8—The glass transition derived from the linear presentation of storage modulus was 2.2°C lower for polystyrene and 2.3°C higher for the epoxy composite than those obtained for a logarithmic data presentation.

[6] A Research Report is available from ASTM. Request E37-1015.

15. Keywords

15.1 dynamic mechanical analysis; elastic modulus; glass transition; modulus; storage modulus; temperature; thermal analysis

APPENDIX

(Nonmandatory Information)

X1. Frequency Shift Factor

X1.1 The transition temperature is a function of experimental frequency with the transition temperature increasing with increasing frequency. This test method requires that results be reported at a frequency of 1 Hz. Experimental data collected at other frequencies may be extrapolated to 1 Hz through the use of a Frequency Shift Factor.

X1.2 *Determination of the Frequency Shift Factor:*

X1.3 Measure the transition temperature at two or more frequencies, according to the method.

NOTE X1.1—For best accuracy, the two test frequencies should be separated by a decade of frequency but be as close to 1 Hz as practical. For example, between 0.1 and 10 Hz.

X1.4 The Frequency Shift Factor is determined using equation A1:

$$k = \frac{T_1 T_2}{T_2 - T_1} \log \frac{F_1}{F_2} \quad \text{(X1.1)}$$

where:

k = Frequency Shift Factor (K)
F_1 = Frequency of Measurement 1 (Hz)
F_2 = Frequency of Measurement 2 (Hz)
T_1 = Transition Temperature at Frequency 1 (K)
T_2 = Transition Temperature at Frequency 2 (K)

Example:

$F_1 = 10$ Hz
$F_2 = 2$ Hz
$T_1 = 108°C = 381K$
$T_2 = 100°C = 373K$

$$k = \frac{(381K)\,(373K)}{(373K - 381K)} \log \frac{10\ \text{Hz}}{2\ \text{Hz}}$$

$$k = -12{,}417K$$

X1.5 The frequency shift factor is a function of the material and should be determined individually. The Frequency Shift Factors for many thermoplastics and thermosets are nominally 8°C per decade of frequency change. Values for elastomers are usually higher and may be as much as 40°C per decade of frequency change.