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Opening Discussion

This STP represents the ASTM symposium, Assignment of the Glass Transition, which celebrated the 20th anniversary of ASTM Technical Committee E–37's efforts at generating consensus standards for thermal measurements. Subcommittee E37.01 on Test Methods and Recommended Practices has 18 currently active task groups addressing a host of subjects including vapor pressure, temperature scale calibration, oxidative stability, heat flow, volatility, mass loss, and the glass transition. The two task groups of Subcommittee E37.03 on Nomenclature and Definitions continually review technical terms appropriate for use in thermal measurements. ASTM E–37 is responsible for 18 active standards including E 1356, Test Method for Determining Glass Transition Temperatures by Differential Scanning Calorimetry or Differential Thermal Analysis. A second procedure for determining the glass transition using thermomechanical analysis awaits Society approval.

Two additional ASTM standards under the jurisdiction of Technical Committee D–20 on Plastics allow for observation of glass transition temperatures in polymeric materials. They are: D 3418, Test Method for Transition Temperatures of Polymers by Thermal Analysis and D 4065, Practice for Determining and Reporting Dynamic Mechanical Properties of Plastics. Definitions for the glass transition and glass transition temperature may be found in five ASTM documents addressing terminology from Committees D–20, E–37, and also Committee F–17 on Plastic Piping Systems.

Glass transition and glass transition temperature are both used pervasively in the materials community. Underlying this usage is the implication that the glass transition is adequately understood and \( T_g \) is an unequivocal value. Survey a random selection of materials scientists and the majority, if not all, will be comfortable in their knowledge of the glass transition. Provide these same individuals with an amorphous specimen and ask them to report the glass transition temperature, and it will be accomplished with equal conviction of certainty. Review the reported values and it is likely that single temperatures of significantly varying values will have been provided. Why?

Let us begin our examination of the glass transition with a definition. A general definition is provided in ASTM E 1142, Terminology Relating to Thermophysical Properties.

\textbf{glass transition—}the reversible change in an amorphous material or in amorphous regions of a partially crystalline material, from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.

The remaining four documents including D 83, D 4092, E 375, and F 412 simply substitute "polymer" for "material" in this definition. A discussion is appended to these definitions:

\textsuperscript{1}Eastman Kodak Company, Rochester, NY 14650-2158; chairman of the symposium and editor of this STP.

\textsuperscript{2}Project TM-01-20-4 was approved as E 1545, Test Method for Test for Glass Transition Temperatures by Thermomechanical Analysis, in June 1993.
ASSIGNMENT OF THE GLASS TRANSITION

The glass transition generally occurs over a relatively narrow temperature region and is similar to the solidification of a liquid to a glassy state [it is not a phase transition]. Not only do hardness and brittleness undergo rapid changes in this temperature region, but other properties, such as, coefficient of thermal expansion and specific heat capacity, also change rapidly. This phenomenon sometimes is referred to as a second order transition, rubber transition, or rubbery transition. When more than one amorphous transition occurs in a material, the one associated with segmental motions of the backbone molecular chain, or accompanied by the largest change in properties is usually considered to be the glass transition.

This discussion is included in all of the ASTM definitions with the exception that “polymer” is substituted for “material” and the parenthetic expression in brackets is added to the definitions from D 20 and F 17.

Defining glass transition temperature within ASTM has not achieved quite the same extent of consensus. E 1142 provides:

**glass transition temperature**—a temperature chosen to represent the temperature range over which the glass transition takes place.

**DISCUSSION**—The glass transition temperature can be determined readily by observing the temperature region at which a significant change takes place in some specific electrical, mechanical, thermal, or other physical property. Moreover, the observed temperature can vary significantly depending on the property chosen for observation and on details of the experimental technique (for example, heating rate, frequency of test.) Therefore, the observed $T_g$ should be considered valid only for that particular technique and set of test conditions.

D 4092 and the other documents offer a somewhat different definition:

**glass transition temperature**—the approximate midpoint of the temperature range over which the glass transition takes place.

**NOTE**—The glass transition temperature can be determined readily only by observing the temperature at which a significant change takes place in a specific electrical, mechanical, or other physical property. Moreover, the observed temperature can vary significantly, depending on the specific property chosen for observation and on details of the experimental technique (for example, rate of heating, frequency). Therefore, the observed $T_g$ should be considered only an estimate. The most reliable estimates are normally obtained from the loss peak observed in dynamic mechanical tests or from dilatometric data.

This brief exercise in definitions has very pointedly identified many of the issues to be addressed at this symposium. The glass transition occurs over a temperature interval for which no single temperature is unique, but merely representative. Additionally, given the exact same material, the reported value of $T_g$ may differ if generated by a different measurement protocol. Hence the subject of this symposium, assignment of the glass transition, for we do not measure THE glass transition temperature but rather make measurements to observe the glass transition and then assign a temperature, $T_g$, to mark its occurrence.

Returning to the ASTM standard test methods for a moment, both E 1356 and D 3418 use differential scanning calorimetry (DSC) or differential thermal analysis (DTA) to observe
FIG 1.

Temperature

FIG 2.
the glass transition as an enthalpic step change in the baseline (Fig. 1). E 1356 allows use of either the extrapolated onset, \( T_o \), or the midpoint of the step change, \( T_m \), for \( T_g \). D 3418 indicates a preference for \( T_m \) to represent \( T_g \) as is widely practiced in the polymer community but does allow for use of \( T_g \) as an alternative. D 4065 is a general purpose dynamic mechanical analysis (DMA) method which uses the peak value of the loss modulus to represent the transition temperature regardless of its type. Since several decades of frequency could be used in this method and frequency shifts of 6° to 8°C per decade is possible, significantly different \( T_g \)'s may result from its use. The DMA method under consideration by E37.01.14 is very similar to D 4065 but prefers to represent \( T_g \) with the extrapolated onset of the drop in storage modulus. Display of the storage modulus on either a logarithmic or linear scale is allowed but slightly different temperatures will result. E37.01.20 has prepared a standard test method for ASTM approval that uses the compression mode of thermomechanical analysis (TMA) for identifying the glass transition. \( T_g \) is assigned as the extrapolated onset to the change in thermal expansivity or alternatively, as the extrapolated onset to softening under loading. Other measurements such as dielectric analysis are also suitable. E37.01.18 is currently laying the foundation for a possible future test method using dielectric measurements to observe the glass transition.

[An audience participation exercise, Glass Transition ? Yellow, was conducted using five tiles of different yellow hues. There is nothing sacred about the choice of yellow and is therefore repeated here using gray tiles of differing density. Each of the tiles was randomly selected and shown to the audience individually with the question, what color is this? The general response for each contained yellow in its color description. The tiles were then redisplayed together as a progression from reddish-yellow to greenish-yellow.]

Consider the tiles in Fig. 2a. What is the color of each? Each is a different shade of gray. If the tiles are now ordered in a progression from light to dark as in Fig. 2b, we have a transition that is a visual corollary to the glass transition. If we were to relate a level of heat capacity for each unit of density in these tiles, one could use the step change curve of Fig. 1 to depict this gray scale. \( T_o \) would be the point between tiles 1 and 2 and \( T_m \) would relate to tile 3.

Having "seen" a glass transition, all are entreated to seek an enhanced understanding of this phenomenon—the glass transition.