

Closing Discussion: Highlights and the Challenges that Remain

As editor, I will now attempt to summarize for you what I found to be some of the key concepts from these well prepared presentations and the numerous well founded audience discussions. It was particularly gratifying to experience the cross-fertilization of ideas offered by the physics/inorganic and the polymer/organic communities. For instance, the structural relaxation process introduced in Prof. Moynihan's lecture appears to substantiate the thermodynamic and kinetic aspects of the glass transition offered by Prof. Wunderlich. This leads us to the observation that:

the glass transition is the phenomenological passage between a glassy solid and a "melt" encountered through the promotion of or suppression of relaxation processes active in the time scales of the measurement used.

Conceptually then, the glass transition is a passage between short range vibrational processes in the glassy solid and long-range translational and rotational processes in the rubber/liquid state within a finite temperature interval. This may be observed by studying optical, electrical, mechanical, or thermal properties as a function of temperature. We are reminded that the glass transition is not reversible, but rather is bidirectional with hysteresis. The extent of this hysteresis is dependent upon the time scale of the measurement employed.

Despite the recognition that the glass transition requires a finite temperature interval over which to occur, there is a strong practical need to represent this interval with a singular temperature referred to as T_g . Confusion and discrepancies may, however, result from such practices because the temperature reported is somewhat arbitrary and strongly influenced by a host of extrinsic factors. Sound arguments of merit for assigning T_g as the onset, midpoint, endpoint, peak, or fictive temperature have been presented. Of these temperatures, the fictive temperature, although derived rather than directly measured, promises to be least impacted by many of the extrinsic factors influencing the temperatures where the glass transition is observed.

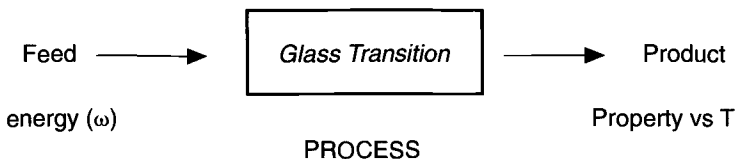
A number of recurring points about T_g were cited:

- A consistently assigned T_g will still vary because of differences in **heating rate** or **frequency of an oscillating load**. Frequency shifts are time-temperature superposable and are of the order of 6° to 8°C per decade. The frequency most often mentioned for T_g measurements was 1 Hz although comparisons of dynamic mechanical data with DSC data suggest that frequencies between 0.01 and 0.1 Hz most closely match the DSC midpoint value recorded at less than 20 K/min.

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

- **Aging effects** (enthalpic relaxation, densification, or free volume reduction) can influence the observed temperature, signal appearance (curve shape), or the ability to detect the glass transition, or a combination thereof.
- **Composition** (both chemical and physical) dependence of T_g and the temperature interval of the glass transition has been noted.
- Depending upon circumstances, certain **measurement techniques** may offer relatively better **sensitivity** to observe the glass transition. There does not appear to be a universally superior measurement method.
- Many of the techniques used to monitor the glass transition measure the specimen temperature indirectly. In order to achieve a reasonable **certainty of observed temperatures**, temperature calibration of the instrumentation at the measurement conditions to be used for measuring the glass transition is required.
- **Diluent/filler** presence in specimens usually affects the glass transition. **Moisture** is particularly troublesome in glass transition measurements, especially when sub-ambient temperatures are required as part of the measurement protocol. Unless water levels are of interest, every effort should be made to prevent moisture gain in a specimen prior to examining the glass transition.
- T_g may not necessarily represent the bulk material. Assigned values may differ within localized areas of a sample and may even be directionally different in oriented or structural forms.
- **Discrepancies or confusion** can and do exist in the open literature regarding T_g 's of materials. These are particularly problematic in digests, handbooks, or reviews where the measurement and material descriptions are typically not included.
- Measurement of **thin films** properties including the glass transition remains an analytical challenge. Acoustic wave microsensors were shown to be suitable for such purposes.
- Manufacturing and engineering applications of amorphous and semicrystalline materials require T_g to predict use temperature limits or to establish process conditions. These application needs underscore the need for a uniform, consistent approach to assigning the glass transition temperature, T_g .

What is the challenge we of the technical community face regarding the glass transition? Consider observance of the glass transition as a process:

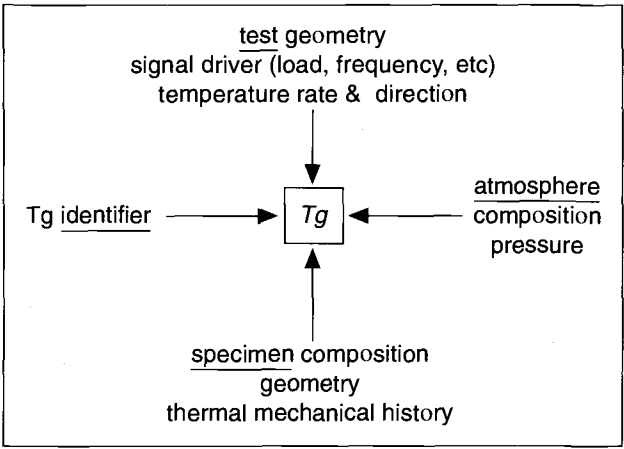


Energy is input to a material specimen as the process “feed.” The product of the process is a signal of the specimen response to the energy input. At some level of input the specimen undergoes a change in its response to the “feed” which signifies the occurrence of the glass transition. This change is neither discontinuous nor instantaneous. Two needs exist regarding this process: process understanding which would lead to a precise definition of the glass transition temperature and process representation which provides for assessment of the practical use of glasses as engineering materials. Both needs require a **unique identification** of the glass transition process. Providing this unique identification of the glass transition

which exists over a finite, but real temperature interval over which large changes occur is the **measurement challenge** facing us.

A recommendation has been offered that the glass transition be measured on cooling from the “melt” as the reference state. In practice most measurements of the glass transition are accomplished on heating because of generally better temperature control in equipment with heating, often, employing multiple temperature excursions through the glass transition to impose a reference thermal history. Although the recommended approach gives a more material specific assessment for academic purposes, the practiced approach may be more beneficial in applications where thermal history contributions are important or need to be understood.

In attempting to formulate a measurement concept for a unique identification of the glass transition, I am reminded of thermodynamics problems. It was always necessary to define the limits of the SYSTEM within which the problem was formulated and subsequently solved. The same holds for “assigning the glass transition.” Any measurement of T_g is a unique but meaningless outcome without a complete description of the system from which the unique identifier has been derived. This is illustrated in the schematic below where the system which yields a T_g is that encompassed by the large box. It includes not only the property whose change is used to identify the glass transition but also conditions of the test, specimen, and atmosphere.



Our goal must be to meet the measurement challenge for unique identification of the glass transition by achieving appropriate measurement protocols which will lead to reliable, reproducible ASSIGNMENTS of the glass transition as a singular temperature and to accurately communicate this assignment not simply as T_g but as

$$T_g + \text{SYSTEM!}$$