Glass Transition Measurement with DMA

Keywords: DMA, Glass Transition, PMMA, temperature sweep, viscoelasticity

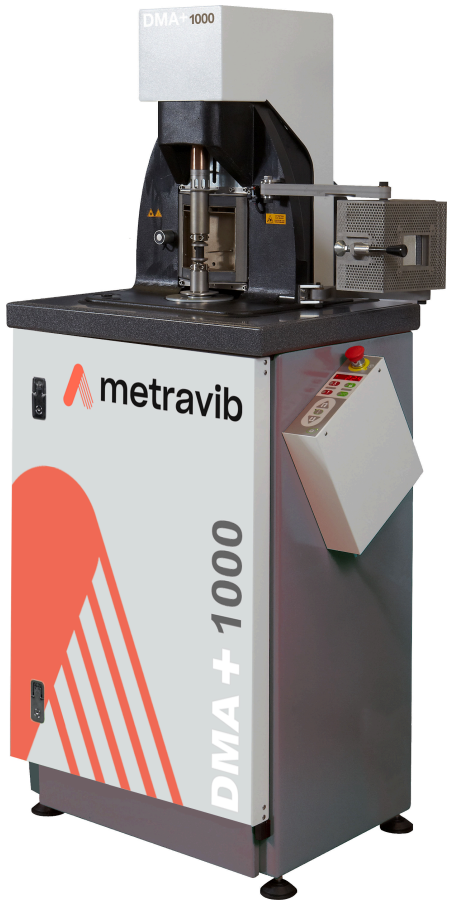

Figure 1. Metravib DMA+1000

Introduction

Glass Transition definition

The glass transition temperature (Tg), also called Tα, is a phenomenon that occurs for amorphous polymers. During that transition, the material changes from a glassy state to a rubbery state, the modulus decreases by 2 or 3 orders of magnitude and the viscous part increases (which leads to a Tan δ peak). At the molecular scale, during this thermodynamic transition, the initially static polymer chains acquire a certain mobility due the provided energy. The glass transition temperature depends on the relaxation time: characteristic time so that all the polymer chains have time to respond to dynamic mechanical excitation, a function of molecular mass.

Tg is a key characteristic of polymers which define their area of use, especially the temperature range. For example, above Tg, rubber tires are ductile and soft because those properties suit the best for car driving. On the other hand, other materials are designed to be used under their Tg, like polycarbonate glass.

The glass transition depends on the chemical state of the polymer and the molecular weight. The presence of some polar group or other ramifications can shift the Tg value. Moreover, some changes such as the crosslinking process, the crystallization and the addition of fillers also had a shifter effect on the Tg value. From that point of view, the Tg can also be considered as an indicator to express the quality of the material, or to rank materials for a specific use.

Other ways to measure Tg

Historically, Tg has been characterized by DSC (Differential Scanning Calorimetry), which is a thermo-analytical method monitoring the difference in heat flow between the material's specimen and a reference versus time or temperature. The thermomechanical analysis (TMA) is another method that is used to determine Tg. However, for around twenty years DMA analysis has been recognized as the most relevant method. Moreover, unlike DSC and TMA, DMA is sensitive to the excitation frequency: the higher the excitation frequency, the higher the Tg. The usual test to determine Tg via DMA is to perform a temperature ramp on a polymer applying a small sinusoidal deformation to measure the dynamic moduli E', E'', and Tan δ. Overall, Tg determination is relatively quick (usually between 1 and 3 hours), non destructive and requires relatively small specimens. Tests are also fast to prepare and easy to perform.

In this study, an optimized process to measure Tg is presented. The importance of the parameter choices on the outcome is highlighted. Then, different ways to measure Tg are introduced (Storage Modulus E', Loss Modulus E'' and Tan δ).

Materials & methods

PMMA materials were studied with a METRAVIB DMA+1000 in tension mode. The set of parameters are mentioned in Table 1. A strip of PMMA with the following dimensions was prepared:

- Height : 20 mm
- Width : 6 mm
- Thickness : 2 mm

The specimen is mounted in the tension specimen holder and the thermal probe is positioned as close as possible to the specimen (See Figure 2 below).

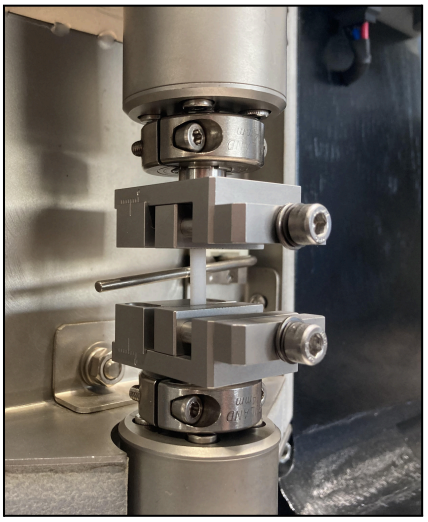

Figure 2. PMMA specimen fixed between the tension jaw of the specimen holder

A 10 µm sinusoidal waveform is applied on the specimen at 1 Hz frequency (see Figure 3) from room temperature to 180˚C at 2˚C/min.

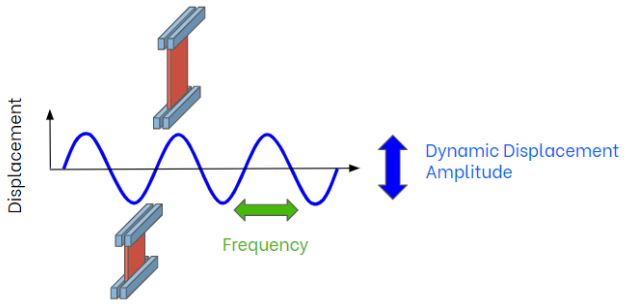

Figure 3. Graphical representation of the dynamic mechanical displacement applied to the specimen

Parameters	
Dynamic	10 µm
Frequency	1 Hz
Static	-
Temperature	From Room temperature to 180˚C at 2˚C/min

In order to stay in the material linear behavior, a low dynamic displacement of 10 µm was applied. Moreover, a dynamic displacement of 10 µm allows an optimal utilization of the DMA sensitivity. The 1 Hz frequency used in this start is a consensual value used by a large margin of DMA users (because it is supposed to be the closest to the DSC when looking at the E'' peak), along with 10 Hz.

A static strain, or preload strain is not applied in this test. Actually, this is an important choice because static strain in tension mode is usually recommended in order to avoid buckling effect. However applying a static stress or a static strain can also lead to a permanent deformation on the specimen. In this case, we have chosen not to apply it because the material studied is a tough PMMA material, the buckling effect risk is negligible, especially using a low dynamic displacement.

Results

The figures below show the viscoelastic properties as a function of the temperature. Figure 4 depicts the change of the elastic part (E') and the viscous part (E'') of the material between 20˚C and 180˚C. The DMA+1000 allows temperature dependent viscoelastic properties to be determined with excellent accuracy, while taking into account significant changes in properties. E' slightly decreases up to the glass transition and from this point an important loss of the modulus of 3 orders of magnitude is determined by the DMA. The behavior of the viscous part E'' is quite similar except that the initial value is one order of magnitude below. This is a typical result, most of the polymers are characterized by an elastic part more important than the viscous part. However, the value of E' and E'' are much closer around the glass transition because of the slow motion allowed to the polymer chains. Figure 5 shows Tan δ as a function of the temperature at 1 Hz from 20˚C to 180˚C. Here we remember that the Tan δ is the ratio between E'' and E', which is a

convenient way to present the balance between the elastic and the viscous properties.

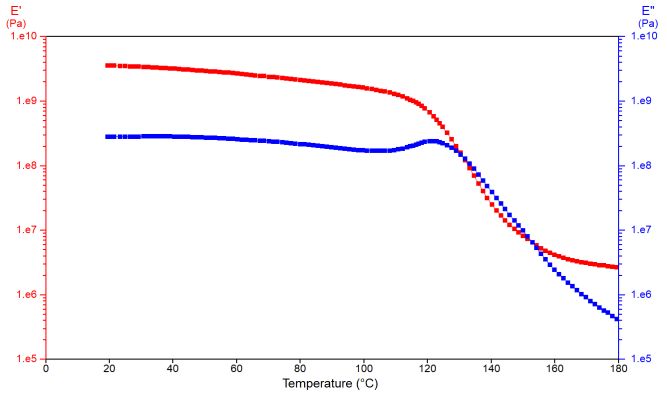

Figure 4. PMMA viscoelastic modulus E' and E'' as a function of the temperature (from 20˚C to 180˚C) at 1 Hz.

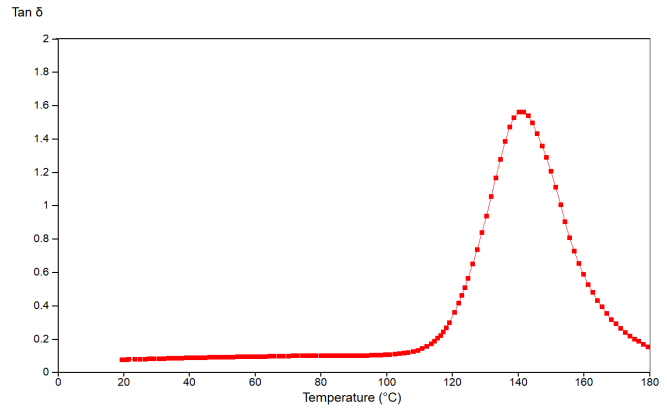

Figure 5. PMMA Tan δ as a function of the temperature (from 20˚C to 180˚C) at 1 Hz.

While it is often referred to as a single value, the glass transition actually occurs over a large range of temperatures. So the definition of Tg used usually depends on many different factors. Currently, 3 definitions are used to characterize the glass transition temperature value, and each leads to slightly different results.

Onset Tg: drop in E'

The value from E' is the lowest Tg measured by DMA and indicates the temperature at which the mechanical properties start to decrease. The method is to calculate the intercept from two tangents; the first one coming from the storage modulus below Tg and the second created from the lowest value of the derivative E' (dE'/dT˚C) (Figure 6). Applied to the results above, a Tg of 117˚C is determined.

Tg Loss: E'' peak

Figure 6 shows Tg being determined as the peak of E'' as a function of the temperature. Usually the loss modulus peak is determined at a higher temperature than the Tg value measured from E' and at a lower temperature than Tan δ peak. Unlike Tg determination from E', the peak of E'' is easier to determine and this leads to more accuracy on the Tg value. From a molecular point of view, the increase of E'' is explained by an increase of the dissipated energy due to a better mobility of the polymer chains. However E'' decreases quickly after because the material gets easier to deform.

Tan δ peak

Tan δ is both (1) the tangent of the phase angle between the applied force and the measured strain waves in the oscillation and (2) the ratio between E''and E'. Similarly to the

Tg determined via E'', the Tg determined from the Tan δ is the maximum value of the peak. This method is widely used by the scientific community, indicating the temperature at which the material reaches its maximum damping property.

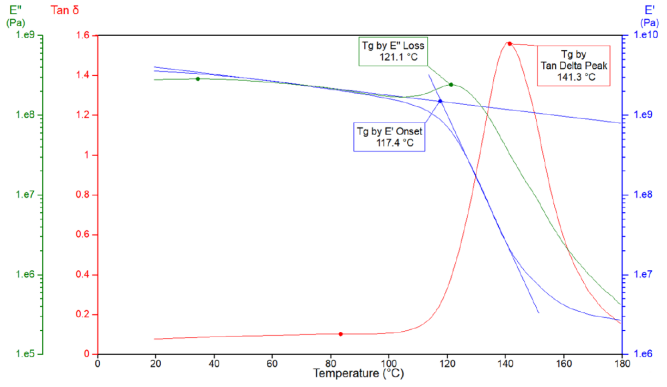

Figure 6. PMMA E', E'' and Tan δ as a function of the temperature (from 20°C to 180°C) at 1 Hz. Different ways to measure the Tg are highlighted.

Conclusions

The DMA proved to be the most prominent method to determine the Tg of polymer materials via temperature sweep measurement. Widely used by both the academic field and the industrial field, Tg determination from DMA does not require much time and rather a very small quantity of material. This study highlighted the glass transition definition and proposed a recommended testing parameters setup to get optimized Tg measurements. In a second part, 3 different methods to determine the glass transition from E', E'' and Tan δ were established.

References

1. https://www.metravib-materialtesting.com/material-testing-white-paper/

Standards

ISO 6721-11

ASTM E1640-13

AITM-0003

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More info: www.metravib-materialtesting.com