Detecting glass transitions in polymers using mechanical analysis

Introduction

Glass transition is a physical change between a metastable glassy state and a viscous or rubbery state upon temperature change. **It is of utmost interest for polymer processing and use**: polymers are often processed above the glass transition where they are less resistant to deformation; and for many applications they need to be kept below the glass transition to avoid softening.

Traditionally the glass transition is detected by measuring the change in heat capacity upon heating using calorimetry; however this change is small and often disturbed by other effects: polymer aging, heat transfer, etc.

A more straightforward approach consists in measuring the change in flexibility of a bar of polymer upon heating. This is achieved using a Dynamic Mechanical Analyser (DMA), which measures the storage modulus: it represents the degree of stiffness of the material.

Experimental details

- Method: ISO 6721-11:2012(E) [1]
- Instrument: *Mettler Toledo* DMA1
- Thermal profile: heating ramp at 3 K/min from 30 °C to 180 °C
- Sample holder: single-cantilever clamps, with a free length of 17.5 mm
- Sample: bar of poly(methyl methacrylate)
- Sample size: length 30 mm, width 7 mm, thickness 1.6 mm
- DMA oscillation: displacement control, amplitude 20 μm (i.e. 0.11 % strain), frequency 1 Hz
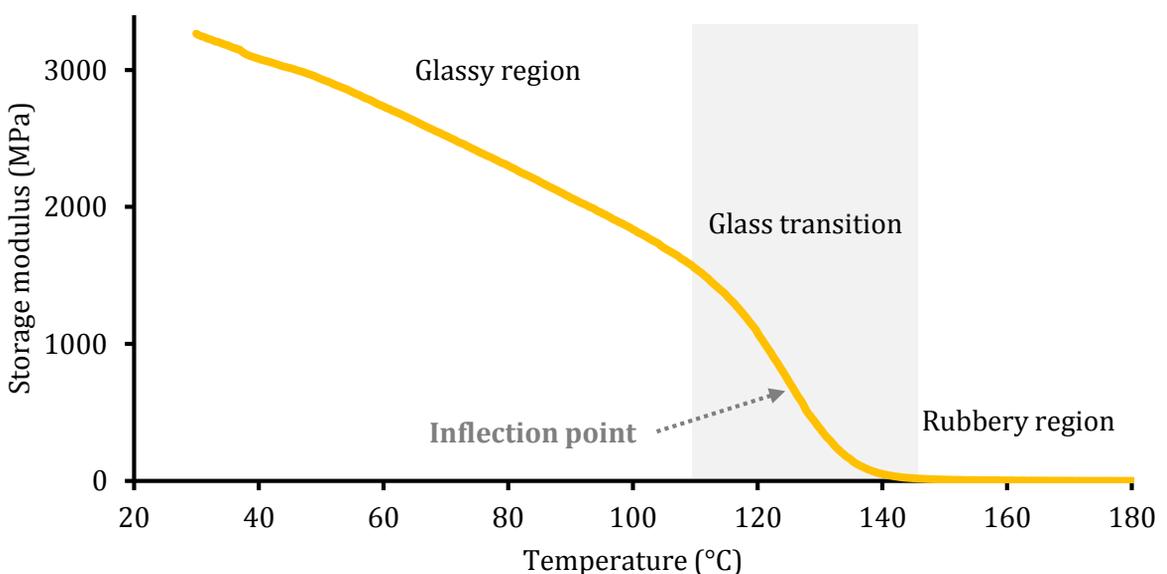

Variation with respect to the temperature of the storage modulus of a poly(methyl methacrylate) bar. Starting at high values, above 1 GPa, in the glassy region, it decreases suddenly from 120 °C to reach a few MPa in the rubbery region. That decrease is the glass transition, with an inflection point at 125.8 °C.

Results

As showed in the previous figure the glass transition occurs during a whole region, not to be reduced to a single temperature. However for the convenience of comparison it is usually described by the inflection point.

Besides the transition region may be shifted as the scanning rate used in the experiment varies: polymer chains indeed have more time to accommodate thermal changes if a slower ramp is used. The dependence of the inflexion point with the heating rate (chosen at 3, 5 and 10 K/min) is plotted on the right, with three tests for each rate. There seems to be sample-to-sample variation higher than variation with the scanning rate; a linear trend in that case, as advised by the standard method [1], does not appear to be significant.

A more meaningful approach is then to report the average of all those inflexion points: 126.5 ± 1.4 °C, at 95 % confidence.
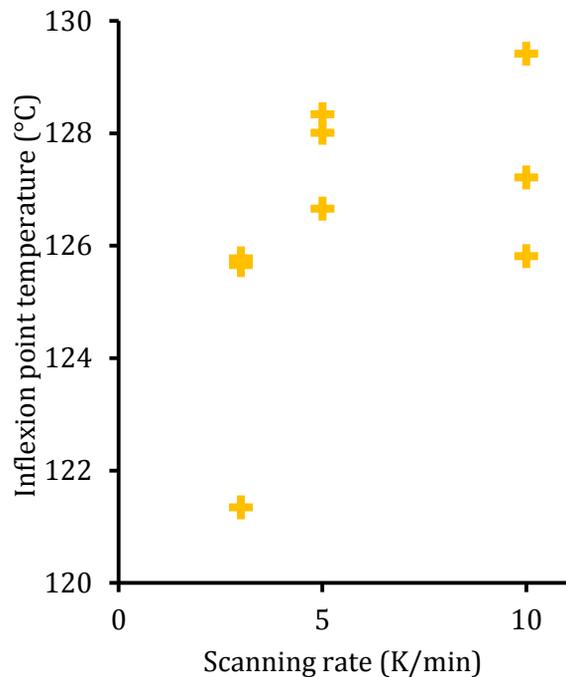
Conclusion

- Glass transition in polymers is detected by dynamic mechanical analysis, as it is accompanied by a change of flexibility.
- The main limitation associated with this analytical technique is the need of a bar or film of polymer, contrary to differential scanning calorimetry that also works with powders.
- It is crucial that the specimen is symmetrical with parallel faces and that its dimensions are accurately measured, as they are the main source of uncertainty on the modulus value.
- Various clamp assemblies can be used, depending of the flexibility and the thickness of the specimen: tension is best suited for films, compression for thick and soft specimens, three-point bending for stiff materials, etc.
- The DMA can operate within a large temperature range: from –160 °C to 500 °C, and in controlled humidity too.

[1] Plastics — Determination of dynamic mechanical properties, Part 11: Glass transition temperature, ISO 6721-11:2012(E)