Using mechanical analysis on polymer powder to detect the glass transition

Introduction

The glass transition in a polymer is a physical change between a metastable glassy state and a viscous 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 direct approach consists in measuring the change in flexibility during the glass transition on the polymer powder encapsulated in a metal frame, using Dynamic Mechanical Analysis (DMA).

Experimental details

- Method: ISO 6721-11:2012(E) [1]
- Instrument: *Mettler Toledo* DMA1
- Thermal profile: heating ramp at 3 K/min from 50 °C to 200 °C, after an initial heating and cooling to erase the thermal history
- Sample holder: single-cantilever clamps, with a free length of 10 mm
- Sample: powder pocket containing 5 mg of standard polystyrene powder
- Sample size: length 20 mm, width 5.45 mm, thickness 0.06 mm
- DMA oscillation: displacement control, amplitude 20 µm (i.e. 0.5 % strain), frequency 1 Hz
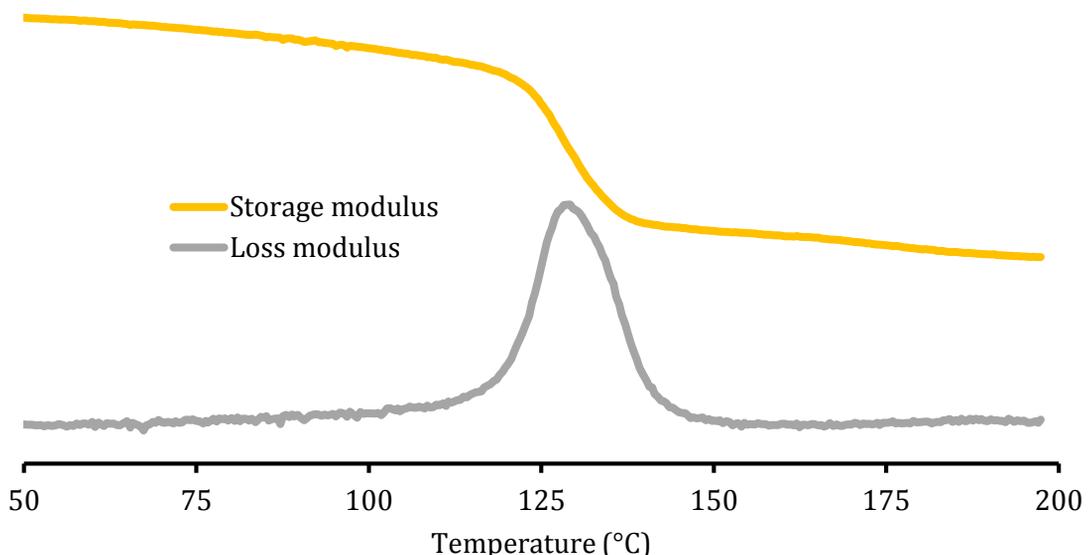
Variation with the temperature of the two DMA signals: storage and loss moduli, of polystyrene powder encapsulated in a powder pocket. At 130 °C the storage modulus shows a step decrease, indicating a decrease in stiffness, while the loss modulus shows a peak, indicating an increase in molecular motion; this double feature is typical of a glass transition.

Results

As showed in the previous figure the glass transition occurs during a whole region, but it is usually described by the inflection point in the storage modulus (T_1), the peak maximum in the loss modulus (T_2) or the peak maximum in the damping factor (T_3), the damping factor being the ratio between the loss and the storage moduli [1]. All of them are presented in the table below, based on three replicates, at three different heating rates.

Those characteristic temperatures depend on the heating rate: upon slower heating the glass transition is shifted towards lower temperatures, polymer chains having more time to accommodate thermal changes. It is advised to present the glass transition temperature observed at a moderate heating rate, i.e. 3 K/min, or to calculate the limit temperature at 0 K/min by linear regression from a set of three rates [1].

The glass transition measured by differential scanning calorimetry is 109.3 ± 0.7 °C (heating at 20 K/min after a cycle to erase the thermal history; three replicates of 5 mg). That value is not directly comparable with the ones given by DMA because the two techniques detect different phenomena associated with the same global effect known as glass transition.

Heating rate (K/min)	T_1 (°C)	T_2 (°C)	T_3 (°C)
10	144.8 ± 2.2	144.3 ± 3.0	144.8 ± 2.2
3	128.2 ± 2.7	128.7 ± 1.4	129.0 ± 0.4
1	121.2 ± 1.4	122.2 ± 1.4	123.0 ± 1.6
0 (linear regression)	119.4 ± 0.8	120.6 ± 0.7	121.2 ± 0.6

Conclusion

- Glass transition in polymers is detected by dynamic mechanical analysis, as it is accompanied by a change of flexibility.
- A small amount of polymer powder is needed, as for differential scanning calorimetry.
- The sensitivity of DMA is higher than that of calorimetry, which avoids erroneous curve interpretations that often come with that technique. The glass transition is even detectable for small amorphous fractions.
- The DMA can operate within a large temperature range: from –170 °C to 500 °C.

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