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CALIBRATION OF MICRO-THERMAL ANALYSIS FOR THE DETECTION OF GLASS TRANSITION TEMPERATURES AND MELTING POINTS

Repeatability and reproducibility

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Micro-thermal analysis (μTA^{TM}) is a technique in which thermal analysis is performed on surfaces of test specimens on a small (ca. 2×2 μm) scale. Like any thermal analysis technique, interpretation of results benefits from accurate temperature information and knowledge of the precision of the resultant measurement. However, temperature calibration for such methods is more challenging than with its macro relatives since the calibrant comes into direct contact with the AFM sensor. This paper describes suitable calibration procedures for different types of transitions namely for first order transitions (melting points) and for glass transition temperatures using organic chemicals and polymers.

Keywords: *calibration, glass transition, micro-thermal analysis*

Introduction

The scanning thermal microscope (SThM, μ-TA$^{®}$) combines the visualisation possibilities of the atomic force microscope (AFM) and its ability to image topography, phase shifts, friction, stiffness and adhesion with the characterisation capabilities of thermal analysis (thermal conductivity, micro-differential thermal analysis and micro-thermo mechanical analysis) in a single instrument [1–4]. The scanning mode may be used for the inspection of surfaces with respect to their thermal properties using a scanner fitted with a thermal sensor or probe (tip). A second mode gives the option to perform local thermo-mechanical and differential thermal analyses of discrete areas of a few square microns (L-TMA and L-DTA), currently a generally accepted method for the determination of T_g's of surfaces [1–4]. This development in sensor technology enables the exploration of thermal properties in a true micro-scale; on very small specimen areas as small as 2×2 μm. The sensor is a microscopically fine 5 μm diameter "V" shaped platinum wire loop, which can be heated in a controlled manner by passing a current through it. The temperature of the wire tip, and hence that of the specimen, can therefore be raised (or lowered) according to a linear program. The instantaneous temperature of the sample material in immediate contact with the tip can be measured, provided a suitable calibration of the temperature *vs.* electrical resistance characteristic of the probe has been carried out. However, a few aspects should be discussed a bit more in detail. The thermal probe acts both as a heater and a sensor of (1) the height of the sample surface (or more accurately the degree of bending of the probe cantilever) and (2) the electrical power required to maintain the temperature ramp. The former produces the L-TMA measurement and the latter gives the L-DTA signal. Any thermodynamic phase transition that produces a simultaneous change in mechanical properties (softening, expansion, melting) and thermal properties (heat of fusion, change of heat capacity) will be detected by both methods. A softening event is detected in the L-TMA measurement by a downward deflection in the sensor signal. The maximum depth of penetration and the rate of descent of the tip are controlled, respectively, by the initial probe force (imparted by the cantilever) and the change in viscosity of sample through the transition. During a transition, additional power is needed to maintain the linear heating program. When this signal is compared to that of a reference, a differential thermal analysis signal results. A melting transition is associated with an increase in power consumption. This signal, however, is also profoundly affected by any change in contact area between the tip and sample, such as that produced during a softening event. Any change in L-DTA signal through a glass transition (which produces only small changes in heat capacity) is almost entirely due to the increase in contact area. In this form of localised thermal analysis the glass transition temperature is, therefore, most often defined as the temperature at which the tip

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begins to penetrate into the sample due to the local softening.

In a conventional TMA experiment a probe is lowered onto the surface of a sample and the movement of the probe is measured as the sample is heated. With a load applied to the probe, a combination of modulus changes and expansion of the sample are observed. Depending upon the probe/sample contact area and the load applied, the glass transition can be detected either by a change in the rate of upward expansion or by a downward penetration of the probe. With large contact areas and low forces expansion is primarily observed, whereas, for small contact areas and high forces, penetration is the primary mechanism. The transition temperature value is often taken as the temperature at which the rate or direction of probe deflection changes suddenly. A TMA penetration-type probe is the closest macro–analogue to the case of a micro-thermal probe on a sample surface. For thermoplastic materials, expansion is detected prior to the T_g and penetration into the sample at the T_g, whereas for thermoset materials expansion is detected prior to and after the T_g, with penetration at the T_g. The location of this point is however rather connected to changes in melt viscosity and the thermo-mechanical response at a certain contact pressure than by the thermal effect itself. That makes a precise detection rather difficult and very depending on the molecular mass of the polymer sample since the melt viscosity scales with the molecular mass at a power between 3 and 5!

While many other techniques exist for studying the important and informative region of the glass transition, TMA offers advantages for certain types of study. The indentation and penetration probes for instance, can follow transitions in very thin films, such as lacquer coatings on metals.

Micro-thermal analysis is currently a quantitative tool for quality control of multi-layer films [5–7] but is more frequently used as a research tool in polymer science. Measuring the transition temperatures of polymeric samples is the most common use of µTA. Like all thermal analysis techniques, interpretation of results requires detailed temperature calibration procedures and an understanding of the precision of the temperature measurement. This is especially true since the accurate determination of glass transition temperatures on polymer surfaces or thin films is nowadays very much in focus in order to understand the basic behaviour of polymer chains at surfaces and interfaces but also the detailed structure of polymeric coatings.

Experimental

One set of calibration samples were selected from commercially available glassy polymers. Especially such polymers were selected which offer a substantial stability against degradation and therefore a qualification as calibration material (Table 1).

Additional to that another sample, a commercially available PS (Styron 634, Dow Chemical) with a broad molecular mass distribution (M_n=78 kg mol^{-1}, M_n/M_w=3.6) was inspected. The T_g of the samples was determined macroscopically between 50 and 200°C using a conventional DSC (Perkin-Elmer Pyris, heating speed 10 K min^{-1}, Table 1). The samples were prepared by compression moulding of 2 mm thick plates under nitrogen at 200°C *vs.* freshly cleaned float glass surfaces. The scanning thermal microscope (SThM) used in this study was a Micro-Thermal Analyzer (µTA^{TM} 2990) from TA Instruments/Veeco. Local thermal analysis was performed between 0 and 300°C using heating speeds of 10 K s^{-1}, 20 data points were collected per second. The probes have a spring constant of about 10 N m^{-1}. The contact surface area between probe and substrate (ca. 2–6 µm^2) was determined by inspection of the mark of the probe left on the substrate after a short contact on a PS surface (1–2 s) at 100°C. The experiments were performed at four different locations on a 100×100 µm^2 scan at least at three different areas and at each area at four different locations. A calibration for the inspection of crystalline materials has been performed according to known procedures; in this case already in references described samples were employed. The calibration of

Table 1 T_g calibration material chart

Material trade name and type	Glass transition temperature, T_g/°C	Colour
Makrolon (PC)	150	clear
Plexiglas (PMMA)	105	clear
Polystyrene (PS)	105	clear
Topas 6013 (COC)	140	clear
Udel P3500 (polysulfone)	185	yellow tint
Zeonex 480R (COP)	138	clear
Zeonor 1600 (COP)	163	clear

the thermal sensor was carried out following known procedures and will be discussed below.

Results and discussion

A good reference material has a number of desirable properties especially a well-documented value of phase transition, availability in a suitable form for analysis, homogeneity, stability and low toxicity. In traditional DTA and TMA, metals like indium, tin, and zinc meet these criteria. These metals are not suitable for temperature calibration in µTA, however, as they may irreversibly contaminate the platinum sensor. Organic calibration materials do not react with the platinum sensor and the sensor is easily cleaned at the end of an experiment by 'burning off' at 500–800°C in air. However, most of the low molecular crystalline compounds are not ordinarily suitable for use as µTA calibration materials in the fine powdered form in which they are received. Semicrystalline polymers such as PEO, PE, iPP, PCl, PA 6, PET and PTFE and paraffin's that form easily platelet shaped large crystals such as C24, C32, C36, C44 and C50, are currently used and recommended for the calibration of the µ-TA [8–13]. Additionally, polymers may have very high melting temperatures that provide a calibration range up to nearly 300°C, a range difficult to achieve with low molecular mass organic chemicals.

Most thermal analysts prefer a two-point calibration procedure. This is performed using a low temperature calibrant, such as C32 at 69°C and a high temperature one, such as PET at 250°C. A typical thermal curve for µTA of a sample of PET is shown in Fig. 1. The melting endotherm is seen near 250°C. In µTA, the sensor is located at the surface (i.e. outside) of the test specimen, as it is in DSC, and so the extrapolated onset is used to identify the melting temperature. The multiple measurements of the melting temperature are used to extract a mean temperature which is used to temperature calibrate the apparatus. The pooled standard deviation of the measurements gives an estimation of measurement precision. The within-laboratory precision of measurement is known as repeatability. Replicate measurements made on both organic crystals and polymeric films indicates that the standard deviation for melting temperature determine by the µTMA and the µDTA signal is about 2 K. In addition, the µTMA transition is about 3.5 K higher than the extrapolated onset temperature determined by µDTA. The precision of temperature measurement appears to be somewhat dependent upon heating rate at the very fast rates typically employed with µTA.

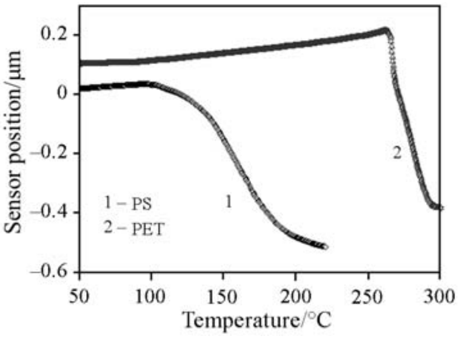

Fig. 1 Local thermal analysis of a semicrystalline polymer (PET) and of an amorphous polymer (PS). Displayed is the DTA signal, the changes of the sensor position with respect to temperature

The µDTA response signal may be used to identify the polymer melting transition temperature. This value is correlated with the melting onset temperature observed by DSC. As is observed with the organic materials, the µDTA response with polymers is a straight line with a correlation coefficient of 99.9% (Fig. 2). The line has the same slope as that observed with the organic chemicals but is somewhat offset to higher temperatures by a few degrees (~5 K). However, in most cases, this calibration procedure provides high reliability and accuracy for the detection of melting points of semicrystalline polymers; in case of detection of glass transition temperatures, an off-set of the detected T_g by 30–50 K is frequently observed [9, 14–19].

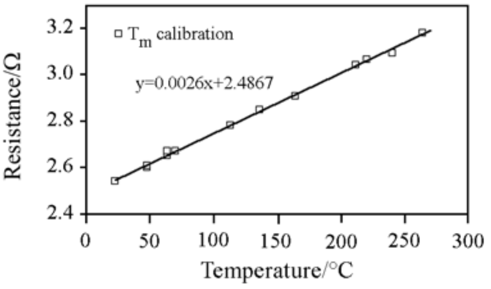

Fig. 2 Calibration of the sensor resistance using the melting points of organic substances and semicrystalline polymers

This phenomenon will be discussed in the following section in detail.

The discrepancy in detection in glass transition temperatures was observed earlier by Tillmann *et al.* [9] and was accounted to heat transfer effects between probe and specimen. A range of forces applied by the probe (50–500 nN) did not influence the measured value of T_g [14]. The dependence of the T_g in polymers on pressure is small [15] and has been reported as dT_g/dP 2.5×10^{-7} K Pa^{-1} for polystyrene [16], which translates into a change in T_g of less than (0.1 K over the range of forces applied by the probe tip. An increase in the thermal conductivity of the polymer film at T_g is an intuitively appealing origin for a delay in detection in time but literature data on the bulk thermal conductivity do not support this conclusion. Changes in bulk thermal conductivity of amorphous polymers at the T_g are relatively small. In fact, k decreases with increasing temperature above T_g for many polymers [17].

Heating rate effects are only partly responsible for the phenomenon of observing off-set glass transition temperatures as examined by Slough [18]. Zhang *et al.* observed a clear difference in the derivative power signals between an amorphous polymer (PLA) and a semicrystalline polymer (PEG) [19]. The glass transition is characterized by a small step in the power signal whereas the melting of polymers is connected with a relatively large downward peak at the T_m. Although the LTA traces recorded in this study were highly repeatable within a variation of about 1–3 K the off-set in detection of T_m was only 2–4 K whereas the off-set in detection of T_g was 12 K! This phenomenon consistently occurred with other polymers, Tillman *et al.* [6] observed differences in detection of the T_g between DSC and LTA in the order of 40–50 K whereas the difference in T_m were detected to be in the range of only 8 K! The transition reproducibility was found to decrease as the molecular size of the polymer samples increased.

Let us turn to the changes occurring while passing through the glass transition. During the glass transition, the shear modulus of the polymer decreases by 4 orders of magnitude, from 10^9 to 10^5 N m^{-2} [20]. The probe penetration is presumably the result of the film becoming rubbery at the glass transition temperature and unable to support the force applied by the probe at the point of contact. The rather large probe size used currently in the scanning thermal microscopy (ca. 2–5 μm^2) with a typical cantilever spring constant of 10 N m^{-1} [21] result in a contact force of ca. 5 μN and a contact pressure of ca. 1 MPa (depending on the set-point used). This may not be sufficient to cause an instant thermo-mechanical response, especially for samples with a high melt viscosity (Fig. 1).

LTA is essentially a combination of thermo-mechanical analysis and microindentation, whereby the penetration distance (P) by a probe of radius R under a force F is related to the shear modulus G by Eq. (1) [22]

$$P^3R = F^2 3/16G^2 \qquad (1)$$

Hence, the change in modulus associated with either the glass transition or the melting of the sample will be detected by an abrupt change in penetration distance.

Also, since the local thermal analysis uses rather high heating rates (5–20 K s^{-1}) a delay in time/temperature of thermo-mechanical effects may have to be expected especially for polymers with a low heat conductivity value [23]. Additional to that, changes of the contact area between probe and sample with increasing penetration depth during the local thermal analysis will lead to an influence onto the quality of the pure thermal signal, which has to be taken into account. The scan rate also has an effect on the detection of T_g similar to macroscopic experiments. As the heating rate is reduced the sensor deflection at T_g is increased, the signal to noise ratio is decreased and the transition temperature is shifted downward. However, the precision of temperature measurement appears to be somewhat dependent upon heating rate at the very fast rates typically employed with μTA. Heating rates between 10 and 25 K s^{-1} (i.e., 600 to 1500 K min^{-1}) give consistent results and are therefore recommended from the constructors of the instrument [23], while those at lower rates between 2 and 8 K s^{-1} (120 and 480 K min^{-1}) are described to display substantially poorer precision. This explains somewhat the shift of the transition temperatures upwards towards higher temperatures, than those detected by 'classical' DSC experiments (Table 1) and those calculated using the Flory–Fox equation with known parameters ($T_{g,\infty}$=104.9°C, K=1.14·10^5, γ=1.01) [24].

$$T_g = T_{g,\infty} - \frac{K}{M_n^{\gamma}} \qquad (2)$$

However, discrepancies in detection of T_g always exist and are rather addressed to the method of assignment of the T_g than to the actual location. The nature of polymeric motion changes greatly while crossing the T_g because the chain flexibility and mobility changes abruptly. Below T_g the polymer is glassy and the structure of the polymeric chain is more confined than the rubbery state above T_g.

In our method, while crossing over the T_g changes the slope of the sensor signal dramatically due to the change in mechanical properties of the material under investigation; the sensor starts to penetrate the viscoelastic fluid present at temperatures above T_g. Although the slope of the penetration is different for the samples with different M_w, (the experimental conditions (tip size, surface roughness, etc.) were kept constant, the location of the T_g is only influenced by the M_w following the known Flory–Fox-relation. However, if all polymers under investigation are well above the entanglement molecular mass and as such in other words true polymers [25], the temperature dependency of the viscosity above T_g follows in general similar trends with respect to the WLF equation.

The change in viscosity with respect to temperature can be calculated following the WLF equation:

$$\log\left(\frac{\eta}{\eta_{T_g}}\right) = -\frac{14.5(T - T_g)}{50.4 + (T - T_g)} \quad (3)$$

For a temperature 80 K above T_g $\log\eta$ is approx. 4.16, at temperatures only 10 K above T_g $\log\eta$ is approx. 10.6! This is clearly a large difference in melt viscosity and, hence detectability by means of TMA or µTMA and even nano-TMA will be greatly influenced.

An empirical relation between the location of the T_g and the T_m can be found in [26] as

$$T_g \sim 2/3 T_m \quad (4)$$

Therefore, the main difference in thermo-mechanical behaviour for glassy and for semicrystalline polymers is a direct consequence of the differences in melt viscosity after crossing from the solid to the visco-elastic state following Eqs (1), (3) and (4).

This does not mean at all that a precise determination of surface T_g's using LTA is not possible! It means only that, since the mechanical-rheological nature of the two transitions is that different, for the calibration of the detection of the two transitions calibration sets of samples representing the two different types of transitions, have to be used. The calibration of the sensor resistance using the glass transitions of the calibration materials as listed in Table 1 follows also a straight line (Fig. 3) similar to the calibration using the standards for the calibration of the determination of melting points (Fig. 2). The calibration curves for different types of transitions may be stored separately within the instrument, the appropriate calibration curve may then be selected to match the type of test specimen being examined.

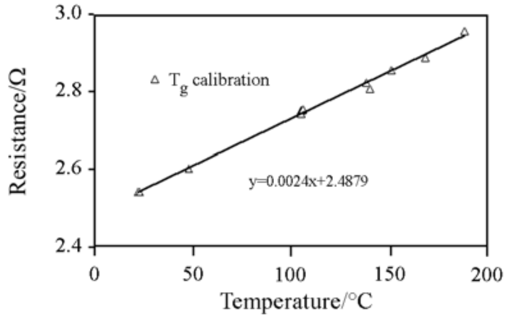

Fig. 3 Calibration of the sensor resistance using the glass transition temperatures points of different polymers (Table 1)

Conclusions

Separate µTA temperature calibration procedures are presented which are suitable either for the measurement of surface glass transition temperature or melting temperature. These procedures use calibrant materials that exhibit either reproducible glass transition or melting behaviour (Figs 2 and 3). For each class of material, the µTA response in the calibration function is linear with temperature. The selection of the point on the thermal curve for identification of the transition temperature leads to bias in the reported values. The bias between µDTA and µTMA values is about 3.5 K, the temperature precision of the detection of the transition temperature is about 3–5 K.

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