Erratum

Erratum and further comments on ''Temperature correction of dynamic mechanical and thermomechanical analysers during heating, cooling and isothermal experiments'' [Thermochim. Acta 346 (2000) 133–145][☆]

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Abstract

Comments and corrections are made on a report entitled ''temperature correction of dynamic mechanical and thermomechanical analysers during heating, cooling and isothermal experiments''. A few unnoticed mistakes that 'survived' the revision stages are corrected and the (new) equations are validated.

Keywords: Temperature; Differential scanning calorimetry; DMA

1. Introduction

The above paper, ''Temperature correction of dynamic mecahnical and thermomechanical analysers during heating, cooling and isothermal experiments'', by Alves and Mano [1], addressed an important topic in the context of the development and validation of thermal-differential scanning calorimetry (DSC), dynamic mechanical/thermomechanical analysis (DMA/TMA), etc. — data treatment procedures, for the correct assignment of materials' transition temperatures and the quantitative interpretation of their thermal and/or thermomechanical behavior.

Unfortunately, a few unnoticed mistakes were made in the writing of some of the most critical equations, which 'survived' the revision stages. The opportunity is now taken to correct those mistakes, to fully validate the resulting (new) equations, and to clarify the underlying concepts and the discussion of the original results. The whole of the original experimental findings, discussion and conclusions stand as valid.

As a matter of fact, the present note is much more than an erratum and really adds to the scope of the original paper, inasmuch as the equations and procedures are here fully put to the test against the very same experimental results [1].

2. Measured temperature offsets

One significant contribution of the paper [1] indeed is the experimental study of the sample's thermal

environment in a typical DMA, which clearly highlighted the influence that the type of test fixture does have, through the associated sample's position relative to the sensor (thermocouple), on the actual temperature readings, which therefore, requires different thermal calibrations (in heating, cooling and isothermal experiments), depending on the type of test and sample. This has so far been a much neglected, if not entirely overlooked, aspect in DMA/TMA experiment planning and data treatment procedures.

Three different test configurations (P1–P3) have been studied in detail, and their effect on the actual sample temperature readings quantified, by means of melting runs with a very pure (99.999%) metal (In) standard. The reader will readily recognize the importance and size of the effect (up to $11°C$ in temperature) and the striking similarities of P2 and P3 configurations. The large negative P2/P3 to P1 measured temperature difference(s) may also be readily associated, not simply to the (not so widely) different relative sample/thermocouple positions, but also (or perhaps mainly) to the more intense heat conduction losses through the metal platform and sample tube, in configuration P1. The original discussion could not delve into extensive detail, but it should be noted here that different temperature readings (offsets) should indeed be expected even when no purge gas actually flows through the measurement cell, for both temperature scanning and isothermal runs, because in any of the situations heat is actually flowing to the outer cell cooling block and mechanical mountings, through the (still or flowing) gas, probe and sample tube. As the associated thermal resistances are not negligible, thermal lags do result, thus requiring adequate temperature corrections to obtain real, meaningful, sample temperatures. It is thus important to note that the difference of $3.5°C$ obtained for the In melting onsets with configurations P1 and P2, at zero helium flow rate (Fig. 8 of [1]), are not necessarily due to errors (or extrapolation uncertainties), but may be physically meaningful.

Therefore, there will generally be two contributions to the thermal (temperature) lag of the sensor relative to the tested sample, namely (i) an isothermal, sensor and gas-dependent, lag and (ii) a scanning rate-dependent (also gas-dependent) lag. Changes in the nature and/or flow rate of the purge gas, and/or in the temperature program (in its nature and/or rate), will

thus always require specific temperature calibrations, to obtain accurate data. This is why the topic is of such critical importance, but despite continuing interest and relevant contributions [2–12], general, physically sound, quantitative solutions of the problem are still pursued [1,13–16], for various phenomena and measurement techniques.

As more or less universally accepted, the first (isothermal) contribution to the thermal lag may be evaluated by extrapolation from adequate runs (preferably the melting of very pure standard materials) at very slow scanning rates. This isothermal correction may itself be temperature-dependent, and thus require more elaborate quantitative formulation and experimental measurement, but in the context of the paper of [1], as customarily done in DMA work, a one-point (temperature) procedure is adopted to evaluate the thermal lags and perform the corresponding calibrations, for the selected programs and temperature scanning rates. Therefore, the isothermal correction, ΔT_0, is consistent with Eq. (4) of the original paper [1], i.e.

$$\Delta T_0 = T_{S,m}^0 - T_{r,m}, \tag{4a}$$

where (for In) $T_{r,m} = 156.6°C$.

3. The calibration on cooling — erratum of Eqs. (5), (6) and (8)–(10)

Eqs. (8)–(10) of the paper [1] were obtained from the expressions for the thermal lags during heating and cooling experiments (Eqs. (5) and (6)), ΔT^+ and ΔT^-, which account for the effect of the scanning rate. Eqs. (5) and (6) are, in fact, incorrect. The actual (physically operating, heat flux determining) thermal lags are, of course, the difference between the real temperatures of the sample, T_r, and the corresponding temperatures read by the thermocouple shifted according to the isothermal correction, i.e. $T_s^+ - (T_{s,m}^0 - T_{r,m})$. As a result

$$\Delta T^+ = T_r - T_s^+ + T_{s,m}^0 - T_{r,m} \tag{5}$$

and

$$\Delta T^- = T_r - T_s^- + T_{s,m}^0 - T_{r,m}, \tag{6}$$

which yield the new Eqs. (8–10):

$$T_s^- = 2(T_r + T_{s,m}^0 - T_{r,m}) - T_s^+, \tag{8}$$

$$T_r = \frac{T_s^- - 2(T_{s,m}^0 - T_{r,m}) - a_1^+/a_2^+}{2 - (1/a_2^+)} \qquad (9)$$

and

$$T_r = T_s^- - 2(T_{s,m}^0 - T_{r,m}) - (T_{r,m} - T_{s,m}^+). \qquad (10)$$

This formulation corresponds to an exact symmetry of $(T_s^+ - \Delta T_0)$ and $(T_s^- - \Delta T_0)$ relative to the real sample temperature, T_r, at each specified (heating and cooling) scanning rate, i.e. T_r is, as may be readily checked, the arithmetic average of the above shifted, true, sensor temperatures, in the absence of any extra thermal effects (like the dissipation of heats of reaction, crystallization or other material changes), which require separate quantification where necessary [13,15,16]. An alternative formulation is also possible, whereby the real sample temperatures on heating and cooling are symmetrical relative to a given true sensor temperature [13,15], but the numerical results turn out to be almost identical [13]. However, the former formulation, adopted in [1], is physically to be preferred [13], because it effectively guarantees exactly the same local heat flux value in both heating and cooling modes, as required by heat transfer theory and indeed implied in Eqs. (7) of [15] and [1].

In order to confirm the validity of the final equations, the data in Figs. 7 and 11 and Table 1 have been treated as indicated below. For a one-point calibration, $a_2^+ = 1$, and Eq. (10) may thus be used to calculate the

real values of T_{max} observed in the DMA experiments on cooling, while Eq. (5) will give the real sample temperatures on heating. We recall that the $T_{s,m}^+$ values are the observed melting temperatures of indium, at each of the (heating) scanning rates.

The calibrations on heating and cooling obtained with the above equations are shown in Fig. 1 of this note. The results of the calibration on heating are the same as those of Fig. 12 of [1]. They show a small (just over $1°C$) decrease of the glass transition (as measured in [1] from the maximum of tan δ) with the scanning rate. On the other hand, the results in cooling show a not so small, but smooth decrease of the glass transition with decreasing scanning rates. These variations (in both heating and cooling modes) may actually be somewhat amplified (the higher the scanning rate), if one accounts for the effect of the sample's thermal resistance, yielding higher (lower) than measured true sample temperatures on cooling (heating). Almost identical numerical results are obtained by the alternative method [15] referred to above.

According to the manufacturer of Perkin-Elmer DMA-7e, the temperature is measured with an error of $1°C$. The calibration performed according to the above equations has itself errors, that have been quantified in [15] and increase with the scanning rate in use. Despite the errors involved in the measurements, the predicted variations on heating and cooling (Fig. 1), suggest the applicability to dynamic
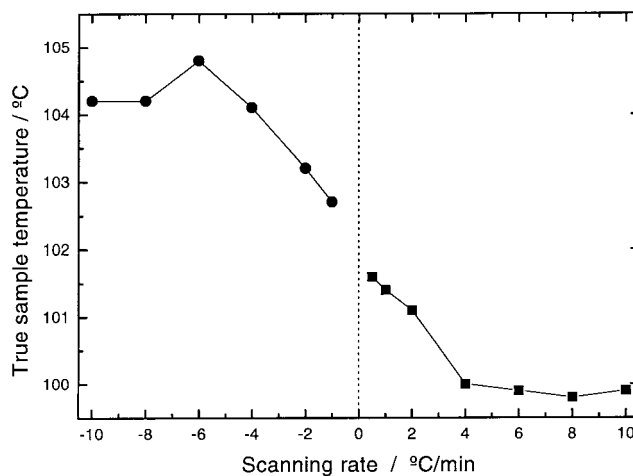

Fig. 1. Calibration on heating, according to Eq. (3) of [1], and on cooling, according to Eq. (10), for data shown on Fig. 12 and Table 1 of [1]. The isothermal correction was $\Delta T_0 = 2.8°C$ at $156.6°C$.

mechanical analysers of the proposed temperature calibration method.

4. Additional small corrections

As the reader may have already noted, two other small corrections are still due: (i) 'electromotive force' should replace 'electrical resistance' in the first line of page 137 and (ii) on page 143, the expression for the testing frequencies that ensure adequate resolution within ΔT is, of course, $\omega \gg \beta / \Delta T$.

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