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Temperature correction of dynamic mechanical and thermomechanical analysers during heating, cooling and isothermal experiments

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Abstract

In this work some procedures are outlined to improve the correction of the temperature axis in isochronal and isothermal experiments performed in DMA and TMA apparatus. For the case of experiments on heating, the influence of the position of the metallic standard used during the calibration procedures is found to have great importance, mainly due to the purge gas flux inside the furnace. New calibration routines are proposed, taking into account the mechanical mode used. The isothermal correction can be performed by extrapolating heating results for zero scanning rate or by running experiments at a very low heating rate. A method for correcting the temperature of experiments on cooling with data obtained from heating experiments is also proposed, provided that symmetry between heat fluxes of cooling and heating experiments exists. This method was confirmed by investigating the temperature position of the α-relaxation of a thermoset polymer, detected by DMA experiments on heating and cooling. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Temperature correction; Calibration; DMA; TMA; Glass transition; Polymer

1. Introduction

To characterise completely any material is necessary to measure its physical properties over a reasonable temperature range. Numerous thermal analysis techniques have been used, namely in polymeric systems, in order to study their thermal behaviour. In most of these methods the measurements are performed during a heating or cooling temperature program. Thus, one of the most important experimental requirements is the precise knowledge of the specimen temperature during the measurement of the physical variables. However, the sensor in the furnace is located close to, but separate (by a gas gap) from, the sample. Therefore, the difference between the real temperature of the sample and the temperature read by the sensor is seldom zero due to the existence of a thermal inertia between the sample and the sensor [1]. For any experimental condition it is thus important to undertake some appropriate measures which will allow one to know, at any time, the indicated sensor temperature, T_s, that corresponds to the real temperature of the sample, T_r.

The fusion of high purity standards, usually metals (or other first order transitions of organic materials), has been extensively applied in order to overcome this problem [1]. For example, in differential scanning calorimetry (DSC) and differential thermal analysis (DTA) techniques, the onset of the fusion peaks is compared with the corresponding melting point stan-

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dards. The same principle holds in dynamic (or thermal) mechanical analysis, where, the fusion of metals is monitored during heating by means of the penetration of a probe-tip through the sample (see later in this text). More sophisticated materials can be used in other techniques. To correct temperature in the thermogravimetry technique, for example, the ferromagnetic/paramagnetic transition of a ferromagnetic sample is used; the onset temperature corresponding to a small variation of mass of the standard detected under a magnetic field and during heating is compared with the expected Curie temperature [1].

Dynamic mechanical analysis (DMA) has been widely used in polymers in order to investigate the segmental mobility of the chains or their local non-cooperative motions and the general viscoelastic properties [2]. In this technique one measures the complex modulus ($E^* = E' + iE''$, $i = (-1)^{1/2}$) or the complex compliance ($D^* = D' - iD''$) whilst the sample is vibrating at a particular frequency, f. Many DMA experiments are performed in isothermal conditions where the complex modulus is monitored during a frequency scan. In this case, the data treatment and the interpretation of the results is relatively simple [2,3]. Similar experiments can be performed in a heating (or cooling) mode run, at a specific frequency, measuring the complex modulus or compliance as a function of temperature (isochronal experiment). In this way, characterisation of the material is less time consuming, which is an advantage. Moreover, in some cases, the various relaxational regions detected in a polymer may become more evident when the results are expressed as a function of temperature, relatively to those obtained in isothermal conditions and expressed as a function of frequency. This behaviour is also observed in other dynamic techniques. For instance, the isochronal dielectric results of the α-relaxation (assigned to the onset of the molecular motions during the glass transition) of PET were found to be much more defined than in the isothermal results [3].

In this work the temperature correction of isochronal DMA experiments will be discussed. As seen later in this text, it may also be necessary to calibrate the temperature in isothermal experiments (zero scanning rate).

Thermomechanical analysis (TMA) is also a very popular technique for the thermal characterisation of materials. It plays a major role in the plastic and rubber industries, as well as in the characterisation of many other materials, such as those encountered in the metal and ceramics industries. This technique follows the strain of the material, subjected to a static mechanical load, during a programmable temperature program or in isothermal conditions. A variety of information is obtained from TMA such as the assignment of transition temperatures (glass transition, melting temperatures, softening points) as well as some mechanical parameters of the sample. Under adequate experimental conditions, the commercial TMA instruments are also capable of performing linear or volume dilatometry. Note that many modern commercial DMA instruments are able to be used in a TMA mode, by applying a constant stress on the sample during heating. In such experiments the abscissa (temperature axis) also needs to be corrected.

The source of errors in the temperature reading of DMA or TMA experiments may have two different origins: first the intrinsic error associated with the reading of the thermocouple (isothermal correction) and finally the thermal lag due to the thermal resistance of the medium. The later reason is obviously temperature rate dependent and for an infinitely slow heating/cooling rate only the first error source persists if no gas flux exists within the furnace. In fact, as we will see later in this work, the isothermal correction of temperature depends on the gas flux, that may create a temperature gradient between the sample and the sensor.

In this work some new approaches on the experimental procedure of temperature calibration in DMA and TMA apparatus are discussed, including for the case of experiments on cooling. The experiments are performed in a dynamic mechanical analysis apparatus from Perkin–Elmer. Some dynamic–mechanical experiments carried out in the α-relaxation region of a thermoset polymer, using isothermal, heating and cooling temperature programs, are presented. The results are used to discuss the temperature calibration of the DMA apparatus in these situations.

2. Experimental

The dynamic mechanical apparatus used in this work was a DMA7e Perkin–Elmer analyser with controlled cooling accessory. Continuous flux of high purity helium (flow rate of ~65 $\mathrm{cm}^3\ \mathrm{min}^{-1}$) was used to improve heat transfer throughout the sample surroundings during the experiments.

The temperature calibration was undertaken using the DMA apparatus in a static mode (see next section). In all the experiments, a 3 mm spherical probe tip imposing a 10 mN static force into a small standard indium sample (from Goodfellow, 99.99999% purity) was monitored during heating at a specific rate, $dT/dt = \beta$. During each experimental batch only one indium sample was used, with ≈20 mg of mass and with a cubic geometry. A small aluminium plate (6.5 mm of diameter and 110 μm of thickness) was used as a base for the indium sample. After each of these experimental batch the sample was discarded.

The dynamic mechanical experiments were performed on a thermoset polymer synthesised from a polyester resin based on orthophthalic acid (Alpolic VUP 9731 from Hoechst). The thermoset curing was obtained by mixing a cobalt salt accelerator (2% vol) and an initiator (2% vol of benzoyl peroxide) in the resin between two plaques of glass; the curing time was ≈30 min at room temperature. Prior to any experiment the material was kept at 130°C for 30 min in order to complete the curing process.

Fig. 1 shows a DSC trace of the thermoset polymer (solid curve) obtained without previous ageing process in a Perkin–Elmer DSC7. The changing of the base line at ≈90°C corresponds to the glass transition of the material. This assignment was confirmed by the detection of the structural relaxation peak in the DSC trace just above T_g when the material was aged below T_g prior the DSC experiment (see dotted line in Fig. 1). The thermal stability of the polymer was studied by thermogravimetry. The experiment was carried out with a Perkin–Elmer TGA analyser (N_2 environment) at $\beta = 4°C\ min^{-1}$. The variation of the weight with temperature is shown in Fig. 2. One concludes that below 130°C no significant degradation occurs. Above 130°C the weight loss is found to decrease smoothly.

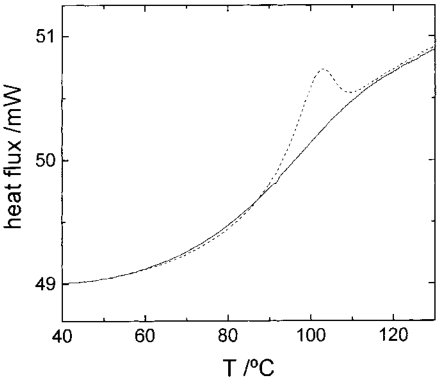

Fig. 1. DSC experiments on a 20.069 mg sample of the thermoset polymer obtained at $\beta = 10°C\ min^{-1}$. The solid curve corresponds to the result without previous ageing. The dotted line corresponds to the DSC result obtained after ageing the sample at 75°C during 16 h.

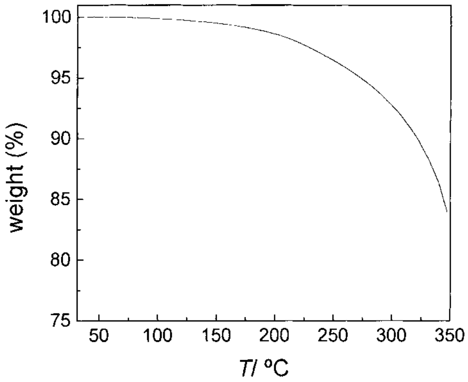

Fig. 2. TGA curve for the thermoset polymer (sample weight of 9.6 mg) obtained at $10°C\ min^{-1}$ under N_2 environment.

As it will be seen later, the decrease of the modulus of the polymer during the glass transition is much less than in amorphous conventional polymers. Moreover this material presents a negligible creep process below 130°C. The dynamic mechanical experiments proposed in this work require several measurements during heating, cooling and at isothermal conditions. The presented features of the polymer allow it to undergo those series of experiments. In fact only one sample was necessary to execute all tests. It must be stressed that it is not important for the goals of this work to completely characterise this material. The only requirements are the clear identification of the glass transition relaxation and the verification that the material shows adequate mechanical and thermal performances.

All experiments on the polymer were carried out with the three point bending mode. The rectangular sample, with dimensions of 1.45 mm × 5.47 mm × 18 mm, was cut from the original plaque. The sample was placed over a 15 mm bending platform and a 5 mm knife-edge probe tip provided the mechanical excitation: in all experiments a static stress of 2.4×10^5 Pa and a dynamic stress of 2.3×10^5 Pa were imposed to the sample. The amplitudes of these stresses were small enough to warrant the study of the sample in the linear viscoelastic regime.

Experiments were carried out at different scanning rates, from 0 to $\pm 10°\mathrm{C\ min}^{-1}$. For all isochronal runs the temperature read by the thermocouple was compared with the programmed temperature. It was observed that, even for the highest rates, the temperature control of the apparatus was maintained during the experiments, i.e., the experimental rate matched the programmed one.

3. Temperature calibration with metallic standards

For heating experiments one expects that the difference between T_s^+ (temperature read by the thermocouple in a heating experiment) and T_r (real temperature of the sample) must increase with increasing rate, β, because of the increase of the thermal inertia of the system.

The temperature correction in a DMA apparatus for one specific heating rate is usually achieved using high purity calibration standards (usually metals) with a well known melting temperature. Most commercial DMA or TMA are capable of performing linear thermodilatometry by the use of an expansion probe with the instrument. All experimental procedures for temperature calibration used in this work consists on using the DMA instrument in a penetration mode. The displacement of the spherical probe tip imposing a small stress into a small amount of a solid standard sample is monitored during heating. The onset of the probe displacement is then compared with the real melting temperature of the material. The assignment of the penetration onset temperature is shown in Fig. 3. A more extended explanation about this procedure can be consulted elsewhere [5,6].

Obviously, in this case only one temperature is corrected, unless one considers that the temperature difference $T_s^+ - T_r$ is constant throughout the temperature axis. This condition may be considered as acceptable if the standard melting temperature is near the temperature of the transition or phenomenon under study.

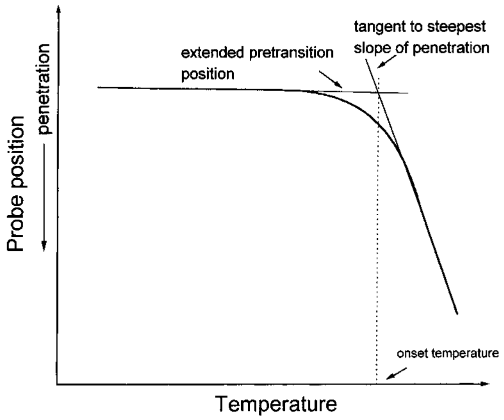

Fig. 3. Assignment of the onset temperature from a penetration thermal curve.

For a more reliable calibration, two standards may be used. In an experimental point of view, this procedure is performed the same as with the one-point calibration. The knowledge of two points in the T_r versus T_s^+ plot allows the construction of the following calibration line, which enables to access the real temperature of the sample when the sensor reads any temperature, T_s:

$$T_r = a_1^+ + a_2^+ T_s^+ \tag{1}$$

where a_1^+ and a_2^+ are dependent on β. Obviously, the experimental conditions used in the calibration (position of the thermocouple, heating rate, coolant, purge gas, purge gas flow rate) must be the same to that of the actual sample analysis procedure. It is also found that under the same conditions the values of the two calibration parameters may undergo small variations with time and for lengthy experiments a regular verification of the calibration is advisable.

The use of more than two standards can be useful whenever the experimental temperature range is very large. Considering a polynomial dependence of T_r on T_s^+ the calibration with n standards leads to the calibration equation:

$$T_r = \sum_{i=1}^{1<m\leq n} a_i^+ (T_s^+)^{i-1} \tag{2}$$

where the parameters a_i^+ are easily obtained by quadratic regression analysis. Note that if one assumes a linear response between the temperature and the electrical resistance read by the thermocouple a linear regression between T_r and T_s^+ should be used, whatever the number of standards used. In fact, it is usually observed that a plot of T_r versus T_s^+ for different standards obtained with the same heating rate follows a nearly linear relationship [7]. A list of recommended standards with melting temperatures from −38 to 1064°C are shown in Ref. [5].

The glass transition of common thermoplastic polymers, as well as in other materials, lies many times at temperatures between 70 and 200°C. Therefore, for many characterisation studies in a temperature range close to T_g the calibration with indium (real melting temperature, $T_{r,m} = 156.6°C$) should be sufficient. It should also be noticed that the accuracy of the temperature reading is about 1°C for the apparatus used in this work [6]. This error can be higher than the error assigned to the one standard choice.

The one standard calibration can be expressed according to Eq. (1) with $a_2^+ = 1$ and $a_1^+ = (T_{r,m} - T_{s,m}^+)$, where $T_{r,m}$ and $T_{s,m}^+$ are the real and observed melting temperatures of the standard:

$$T_r = T_s^+ + T_{r,m} - T_{s,m}^+ \quad (3)$$

As an example, two calibration experiments were performed, under the same conditions, with indium and tin ($T_{r,m} = 231.88°C$). The detected temperature onsets were 145.3 and 219.4°C, respectively. The calibration line corresponding to the choice of these two standards, according to Eq. (1), yield $a_1^+ = 9.04°C$ and $a_2^+ = 1.016$. The real temperatures of the sample at, for example, $T_s^+ = 70$ and 200°C are, respectively, 80.1 and 212.2°C. The same read temperatures, corrected only with the results from the indium standard, lead to 81.3 and 211.3°C, respectively. These results are only an indication of the differences that may be associated when the temperature correction is performed with one or two standards. One concludes that the one standard calibration may be performed only in restricted situations.

The difference between the real and observed temperatures may be a result of different factors. The most important are the inaccuracy of the thermocouple reading itself and the effect of the thermal resistance between the thermocouple and the sample. The last effect can be confirmed and studied by locating the standard sample in different positions inside the furnace, probing the temperature gradients inside closure. Such studies may be important since many DMA apparatus perform mechanical analysis under different modes, such as shear, torsion, flexure, compression or extension. For each of those modes different accessories must be used and the sample is fixed in different positions. Owing to that the sample may fell different thermal environments when tested with different mechanical modes, even under identical experimental conditions.

Using the three point bending mode the sample is placed over the edges of a platform. In tensile tests the film or fibre are hold between two clamps in which the bottom one is fixed. The usual suggested procedure for calibrate the temperature is to locate the sample in the centre of the three point bending platform (see Fig. 4) [6]. This procedure, that we call here P1, is proposed for any type of experiment [6].

In this work we want to take into account the effect of the type of mechanical mode used in the experiments on the temperature correction.

For the three point bending experiments, we propose that the standard sample should be placed in the centre of a stiff material piece with similar geometry to that of the sample under study and located, as the sample, over the edges of the bottom platform (see Fig. 4). The goal of this procedure is to probe, the better as possible, the thermal environment of the sample. We will call this procedure P2. In this case, the calibration is carried out with the sample closer to the thermocouple than in the P1 procedure. A similar procedure could be used for the case of the single or dual cantilever measuring systems. In this work a steel piece was used to hold the standards in three point bending experiments. However, we must be aware that the thermal conductivity of this material is much higher than of any polymer we may test. Therefore, it is predictable that during a heating/cooling experiment the temperature of the sample in our conditions is somewhat different to the temperature at the core of a polymeric sample in the same position. The use of a polymeric holder could be used to partially eliminate this effect. One could select a polymer whose T_g exceeds the melting temperature of the standard by at least 50°C. For example, if an indium standard is used one could try a polysulfone or a polyetherimide.

The temperature calibration for extension experiments may be executed with the standard at the top of the lower clamp and by fixing the spherical probe tip at

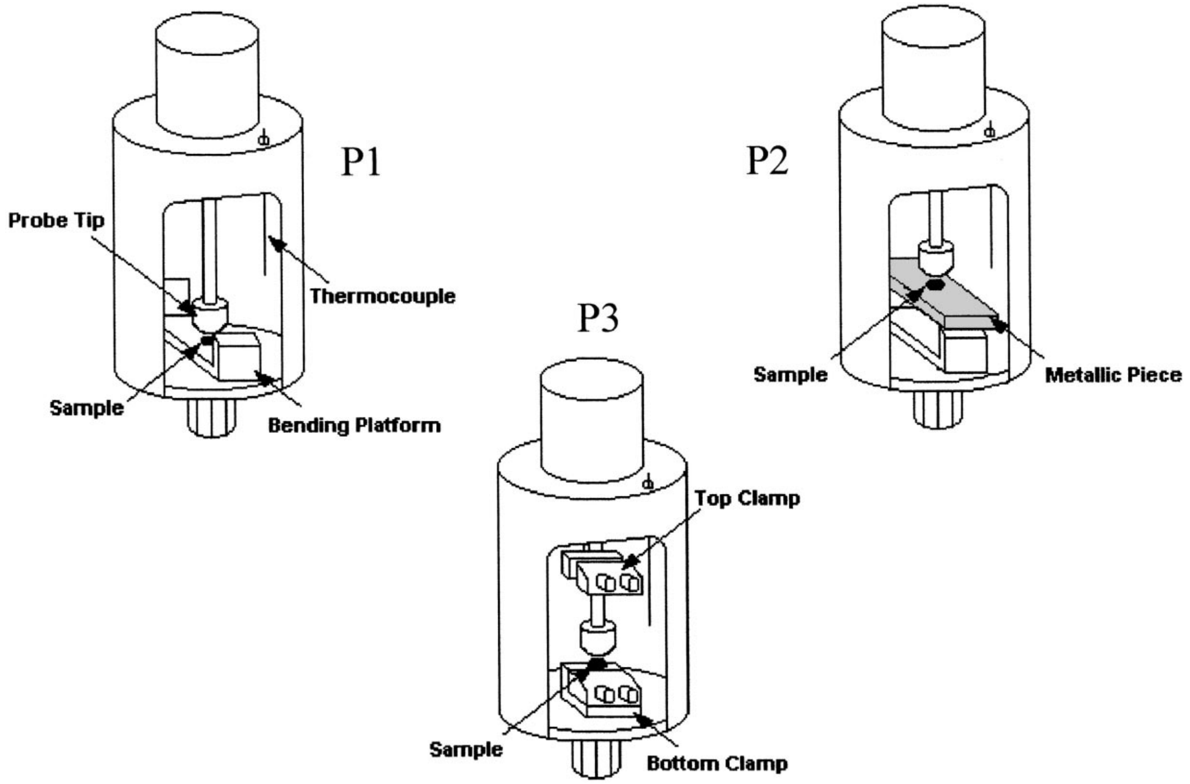

Fig. 4. Scheme of the different arrangements used in the DMA apparatus for temperature calibration, P1: calibration procedure usually suggested; P2: calibration procedure for flexural experiments; P3: calibration procedure for extension experiments.

the top clamp (see Fig. 4). This arrangement probes the temperature standard between the clamps, which is approximately the place of the sample during extension studies. This procedure is here named P3. Note that this procedure does not probe exactly the true temperature of the sample. In fact the sample is mounted vertically between the two clamps and therefore a temperature gradient must exist along the sample's length. In this case a more complete picture of this gradients should be needed in order to correct the read temperature in tensile experiments. In order to study this problem we could use a vertical holder, fixed at the bottom clamp, that allows the increasing of the standard's height to a desired position and the running of a penetration experiment at that point.

Three calibration runs, corresponding to the procedures mentioned above (P1, P2 and P3) were undertaken with the same indium sample and for $\beta = 4°\mathrm{C}\ \mathrm{min}^{-1}$. The results are shown in Fig. 5. One concludes that the onsets of the curves are very distinct, principally for the P1 procedure. The resemblance between the results for procedures P2 and P3 arises from the fact that the test specimen is located at a similar distance from the thermocouple. The results

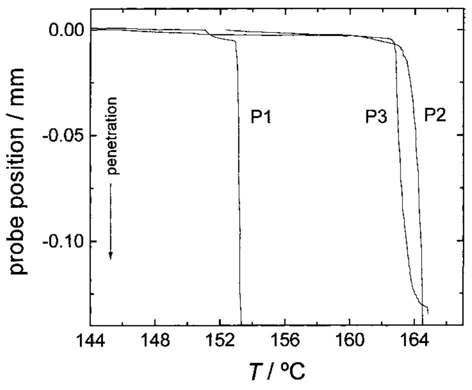

Fig. 5. Penetration thermal curves on indium obtained from procedures P1, P2 and P3 (see Fig. 4) at $\beta = 4°\mathrm{C}\ \mathrm{min}^{-1}$.

shown in Fig. 5 indicate that the calibration procedure must take into account the mechanical mode at which the samples will be studied. In this specific case, Fig. 5 demonstrates that the difference between the temperature corrections obtained by the usual method for calibrating any type of experiments (P1) and the corresponding proposed method for flexural experiments (P2) may be higher than 10°C.

The calibration must be performed at the same heating rate, β, of the experiment. As reported in a previous work, β has a strong influence on the temperature correction [8]. The effect of β on the penetration curves, as seen with the P1 and P2 calibrations, is shown in Fig. 6. The rate dependence of the onset temperature, obtained from the curves in Fig. 6, is shown in Fig. 7. In both procedures, the onset temperature increases with increasing β due to the increase of thermal inertia. On the other hand the onset difference between both procedures under the same rate is almost independent on β. Plots of that kind are useful because the extrapolation of the observed onsets for $\beta = 0$ allows the correction of temperature for isothermal experiments. This procedure will be called here *isothermal correction*.

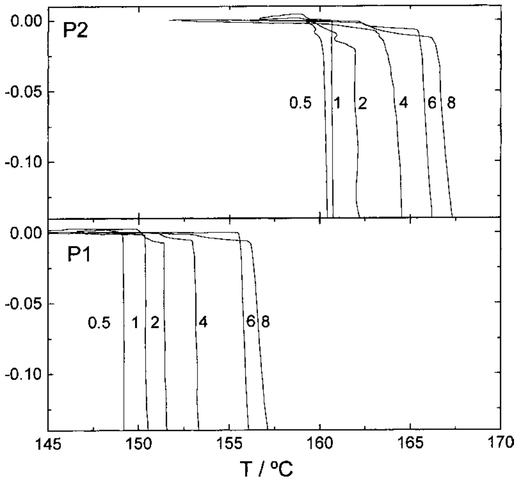

Fig. 6. Penetration thermal curves on the same indium sample obtained from procedures P1 and P2 at the indicated heating rates.

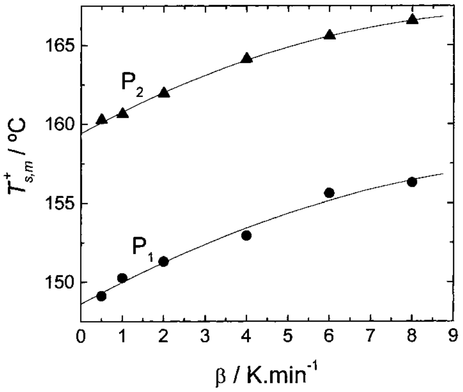

Fig. 7. Onset temperature as a function of heating rate, β, for the curves shown in Fig. 6 (circles: P1 procedure; triangles: P2 procedure). The solid lines are the quadratic fittings of the experimental results.

One should expect that the only source of errors in the isothermal correction is the inaccuracy of the thermocouple itself because both sample and thermocouple temperatures are thermally stable, i.e., both temperatures are not time dependent. From Fig. 7, however, one concludes that it is not the case in this study. In fact, the isothermal corrections of the P1 and P2 procedures are found to be different (the extrapolated onset to zero heating rate yield 148.6 and 159.4°C, respectively). The understanding of the origin of this difference is important because it directly affects the temperature calibration of isothermal experiments. One hypothesis is the effect of the helium flux that could create temperature gradients within the system, even during isothermal conditions. Therefore, since that in P1 and P2 procedures the samples are localised in different positions, the thermal environment between the thermocouple and the sample is different. This explanation can be easily verified by doing experiments with different values of helium flow rates.

Fig. 8 shows the differences between the onset temperatures found in the two methods P2 and P1, $\Delta T_{P2,P1}$, for three different flow rates. All experiments were carried out at $\beta = 4$°C min^{-1}. It is seen that the two onset temperature approaches as the flow rate decreases. One should expected that $\Delta T_{P2,P1}$ should tend to zero for the case of zero flow rate. The linear extrapolation of the data in Fig. 8 yield 3.5°C; the deviation from the expected value may due to the reduced number of data and their high distance to zero and the linear assumption of the relationship.

From the results shown in Fig. 8 one may thus conclude that the helium flux inside the furnace has a

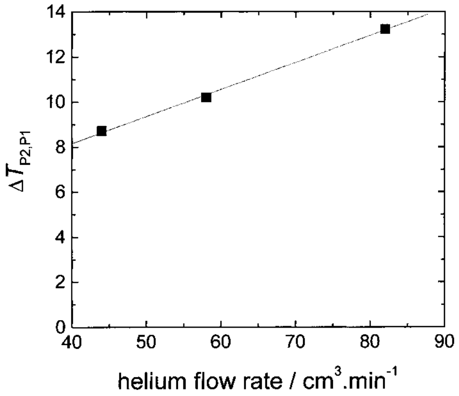

Fig. 8. Difference between the onset temperatures obtained with the P2 and P1 procedures, $\Delta T_{P2,P1}$, as a function of helium flow rate.

strong influence on the temperature calibration for isothermal experiments. Beyond this factor, as said before, the reading of the thermocouple itself may be inaccurate. Nevertheless, the isothermal correction takes automatically into account these two factors. The isothermal correction with, for example, one standard, may thus be written as follows:

$$T_r = T_s^0 + T_{r,m} - T_{s,m}^0 \qquad (4)$$

where T_s^0 is the thermocouple temperature read in the isothermal conditions and $T_{s,m}^0$ is the onset temperature of the standard when $\beta = 0$. $T_{s,m}^0$ can be determined, as seen before, by extrapolating the onset temperatures at different scanning rates for $\beta \to 0$. A good estimation of $T_{s,m}^0$ can be obtained by calculating the onset temperature of a calibration curve obtained at a very low scanning rate (say, $\beta < 0.5°\text{C min}^{-1}$).

The strong influence of the purge gas flow rate on the isothermal correction also explains the difference between the onset temperatures detected during procedures P1 and P2 for $\beta \neq 0$. This conclusion arises immediately from the parallelism found in both P1 and P2 calibration lines in Fig. 7.

4. Calibration of temperature on cooling in a DMA apparatus

In the previous section the temperature calibration was discussed for the case of DMA experiments carried out on heating or on isothermal conditions. There are, however, some DMA experiments that can be interesting to be done on cooling. For example, the study of the kinetics of crystallisation from the melt in non-isothermal or isothermal conditions can be undertaken by means of mechanical spectroscopy techniques [9,10]. Rheological studies also enables the study of the crystallisation process [11–14]. In that case the melt material can be subjected to different shear stresses, leading to different kinetic behaviours. This field of investigation is relevant in order to understand the solidification of polymeric materials during processing.

The dynamics of the glass transition can also be studied during cooling experiments. The advantage is that, in this case, the transition to the glassy state starts from the rubbery state, which is in thermodynamic equilibrium. Several studies showed that the viscoelastic response of the α-relaxation, as seen during heating experiments, depends on the thermal history of the material [15,16]. The differences are found in the ascending side of the tan δ peak. This behaviour occurs because the material is, at the beginning, in the metaestable glassy state.

It would be, then, interesting to analyse the possibility of correcting the temperature read by the thermocouple in cooling experiments. The direct approach used in the last section cannot be used for the cooling case. In fact, beyond experimental difficulties, the solidification of pure metals does not occur at a defined temperature, such as in melting, but rather depends, for example, on the cooling rate. This undercooling effect is due to the fact that the mechanism of crystallisation involves nucleus formation and growing, which have both a kinetic contribution.

In this work we propose an indirect method to surpass this problem. It is based on the assumption that the heat fluxes between the sample and the thermocouple during cooling are reverted, relatively to the heating experiment at the same rate, provided that the isothermal corrections are performed.

Consider ΔT^+ being the difference between the real temperature of the sample, T_r, and the temperature read by the thermocouple on heating, T_s^+, relatively to the same temperature reading at the isothermal condition, T_s^0:

$$\Delta T^+ = T_r - T_s^+ - T_s^0 \qquad (5)$$

On cooling, at the same rate, one also observes a thermal lag, ΔT^-, that should have an opposite sign of ΔT^+:

$$\Delta T^- = T_r - T_s^- - T_s^0 \tag{6}$$

where T_s^- is the read temperature on cooling.

The assumption that the thermal fluxes are reverted from heating to cooling should lead to the following symmetry effect:

$$\Delta T^- = -\Delta T^+ \tag{7}$$

The hypothesis of thermal fluxes reversion was suggested and tested before in three power compensated DSC [17]. Those studies were based on some symmetry arguments that were presented before [18]. Other authors, combining temperature calibrations on heating and DSC results on heating and cooling on a low molecular weight liquid crystal, suggested that, under a certain error, Eq. (7) is valid [19]. Of course, this condition may be device-dependent and it would be interesting to verify if it holds in a DMA apparatus.

Combining Eqs. (5)–(7) we have,

$$T_s^- = 2(T_r + T_s^0) - T_s^+ \tag{8}$$

This equation is valid for a particular scanning rate (the same for heating and cooling).

The knowledge, for example, of both a_1^+ and a_2^+ parameters obtained from calibration on heating with two standards (see Eq. (1)) enables to write the calibration line on cooling:

$$T_r = \frac{\left(T_s^- - 2T_s^0 - \dfrac{a_1^+}{a_2^+}\right)}{(2-1)/a_2^+} \tag{9}$$

Eq. (9) relates the real sample temperature with the read temperature on cooling by using calibration data obtained from heating experiment. A similar methodology was used in temperature calibration of a DSC equipment on cooling [19].

The calibration line on heating, for the case of using only one standard (see Eq. (3)), leads to the following calibration line on cooling for the same scanning rate:

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

In conclusion, the calibration of temperature on cooling can be easily achieved with the results of the calibration on heating, provided that the symmetry between temperature lags, shown in Eq. (7), is valid.

In the following section this condition will be analysed by investigating the viscoelastic response in the α-relaxation region of the poliester thermoset (presented in the experimental section) detected by means of heating, cooling and isothermal experiments. Only one temperature standard will be used in these studies. Similar conclusions could be achieved with two-point calibrations which is, in fact, deemed the preferred approach for assuming high-quality temperature measurement.

It is important to notice that conclusions about the proposed procedures for calibration of temperature, either in isothermal, heating and cooling modes, can be, in principle, applied in other DMA and TMA apparatus or, even, with appropriate modifications, in other thermal analysis systems, such as some rheometers. Although the instrumentation used was that of a vertical configuration, the same approaches may be applicable to the horizontal ‘pushrod dilatometers’ such as the one referred in Ref. [20]. The main conclusions may also contribute for further developments in the calibration of DSC equipments on cooling.

5. Analysis of dynamic-mechanical results and discussion

The α-relaxation usually observed in polymers corresponds to the glass relaxation process and is due to the micro-Brownian cooperative reorientations of the polymeric segments. We will assume in this section that the location in the real temperature axis of the α-relaxation of the studied thermoset polymer (see experimental section) is not dependent on the testing mode: isothermal or isochronal (heating or cooling). Note that the usual frequencies used in isochronal DMA studies are above the ‘equivalent frequency’ of the heating process itself (for instance, usual DSC experiments probes the chain dynamics of the sample at frequencies around 10^{-2} Hz [21]). Therefore, the temperature of maximum tan δ of the α-relaxation, $T_{\max}$, is above the calorimetric glass transition temperature and $T_{\max}$ should not be affected by the structural relaxation of the glassy material. This means that the dynamic-mechanical response of the material in this temperature range (near the temperature of maximum tan δ) is only temperature and frequency

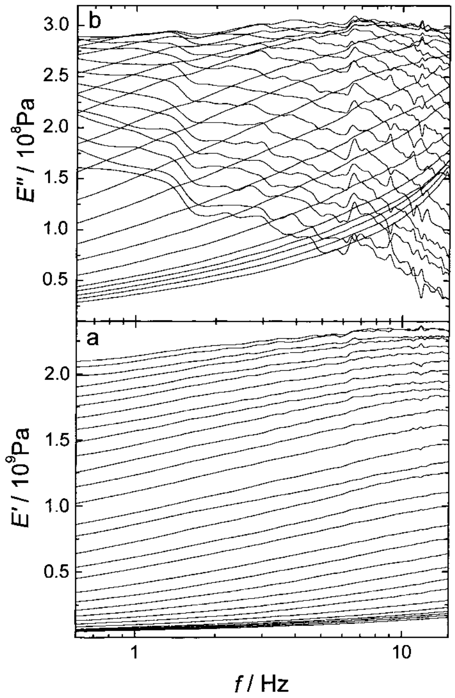

Fig. 9. Dynamic mechanical results (a: storage modulus, E'; b: loss modulus, E'') of the thermoset polymer obtained at isothermal conditions trough the frequency range 0.6–15 Hz. The experimental temperature varied between 30 and 132°C.

dependent (not temperature rate dependent) and thus can be used as a probe in order to validate the calibration procedure on cooling explained before. The same methodology was recently used in the comparison between isothermal and isochronal dielectric experiments on PET [4].

Fig. 9 shows the viscoelastic response of the polymer (storage modulus, E', and loss modulus, E'') for isothermal experiments obtained at different temperatures, between 30 and 132°C. The frequency range used in those experiments was 0.6–15 Hz. Before those experiments, the polymer sample was kept above T_g, inside the furnace, for about 15 min to erase any thermal or mechanical history. Between each isothermal stage the polymer rested for about 10 min such that its temperature is stabilised. Therefore, one may consider that the temperature of each experiment can be corrected with the isothermal correction.

The isothermal results shown in Fig. 9 were treated in order to allow the representation of the data as a function of temperature, at a fixed frequency. Figs. 10 and 11 show the experimental isothermal temperature dependence on the storage modulus and the loss factor, tan δ, for $f = 1$ Hz (solid points). Note that no correction was applied to the temperature axis.

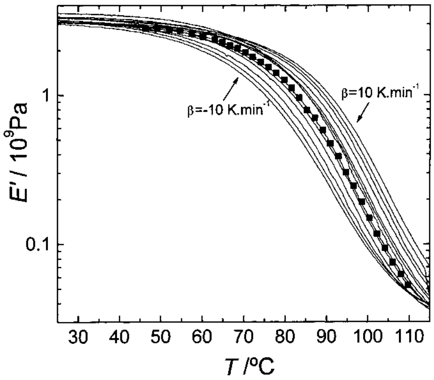

Fig. 10. Storage modulus of the thermoset polymer obtained at isochronal conditions ($f = 1$ Hz and β from -10 to $+10$°C min^{-1}) in the temperature range 20–117°C (solid lines). The lines shift to higher temperatures with increasing β. Squares: isothermal results at 1 Hz taken from the results shown in Fig. 9.

Figs. 10 and 11 also show the same plot for results obtained with the same sample during heating and cooling experiments. Those experiments were carried out with $f = 1$ Hz and the used rates were ±10, ±8, ±6, ±4, ±2, ±1 and +0.5°C min^{-1}. The temperature axis is also shown without calibration. It is clear from the figures that the α-relaxation shifts to higher temperatures with increasing rate. This is consistent with the temperature calibration results shown in Fig. 7. As

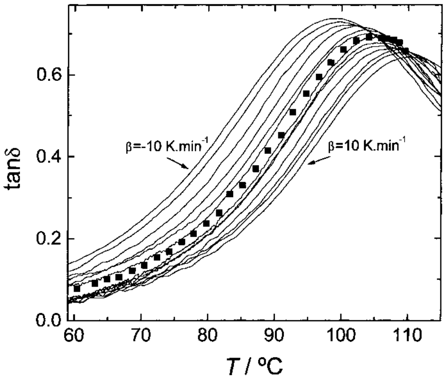

Fig. 11. Temperature dependence of the loss factor for the same experiments shown in Fig. 10.

expected, the isothermal results are found to have approximately an intermediate behaviour to the cooling and heating results obtained at low rates. It must be also referred that the non-isothermal results shown in Figs. 10 and 11 are representative of many more experiments obtained with different types of cycles. The general features of the results were found to be reproducible.

The maximum of tan δ for each run decreases with increasing rate. This behaviour may be ascribed to the intrinsic smearing of the temperature dependence of the mechanical response due to the heating process. In fact, during dynamic experiments on heating, if the information needs to be resolved within temperature intervals ΔT, one must used frequencies $\omega \gg \beta\Delta T$ [22]. This effect was not observed in dielectric relaxation results, due to the high frequency range which are usually used [4]. However, this effect may be important in DMA experiments, where the frequencies are much lower. Similar shift of temperature and variation of the maximum of tan δ were also observed in our laboratory on other systems, such as in DMA flexural experiments on a semicrystalline PET film. The decrease of the maximum of tan δ with increasing β in DMA studies on a PVC sample was already mentioned, without further explanations [23].

As explained before we will consider that the maximum of tan δ, for example, always occurs at the same sample temperature, for a fixed frequency, regardless the rate of the experiment. Therefore, the correction of the experimental temperatures of maximum tan δ, $T_{\max}$, obtained at different heating rates, according to the temperature calibration using standards, should yield the same value.

Fig. 12 shows the dependence of experimental $T_{\max}$ on β (squares). These values are also summarised in Table 1. The correction of the experimental values obtained on heating and on isothermal conditions was executed using the onset values of indium shown in Fig. 7 (P2 procedure). Extrapolation of the data shown in Fig. 7 allowed to correct the $T_{\max}$ values for $\beta = 0$ and 10°C min^{-1}. The corrected $T_{\max}$ values are shown in Fig. 12 (circles). It is clear that for $\beta > 0$ the corrected $T_{\max}$ values smoothly decreases with increasing β. This is an indication that other effects should be taken into account when one uses metallic standards for calibration. Besides experimental errors, the decrease of the corrected $T_{\max}$ may be related with the same effect responsible for the variation of the maximum of tan δ, explained before. Nevertheless, the corrected values shown in Fig. 12 are an indication that the calibration procedure on heating may be used within an error of ±1°C. This temperature difference is close to the temperature fluctuation of the onset temperatures measured in many repeated calibration experiments with indium. An extensive study in this context showed, at the 95% confidence level, a repeatability of 1.44°C [24]. This scatter was found to be greater in other TMA results on several polymers studied in 15 different laboratories [25].

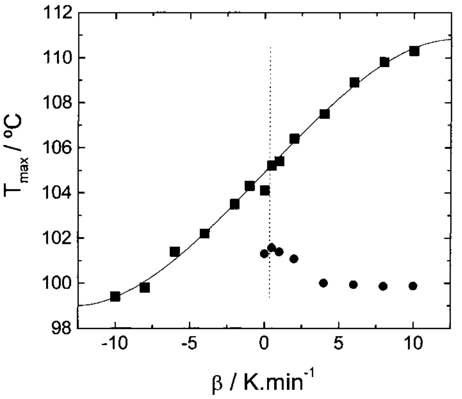

Fig. 12. Squares: temperature of maximum loss factor (tan δ) as a function of the scanning rate (values taken from data shown in Fig. 11). Circles: corrected $T_{\max}$ values for the isothermal and heating experiments according to the calibration line shown in Fig. 7 (P2 procedure). Solid line: fitting of the $T_{\max}$ values obtained from the isochronal experiments as a function of the scanning rate to the polynomial function shown in the text, leading to $T^{+}_{\max} = 104.9 + 0.6931\,\beta - 0.00141\,\beta^3$.

The comparison between heating and cooling results shown in Fig. 12 can validate, or not, the

Table 1
Scanning rate dependence on the temperature of maximum tan δ found in cooling ($T^{-}_{\max}$) and heating ($T^{+}_{\max}$) experiments (values taken from Fig. 11)

β/°C min^{-1}	$T^{+}_{\max}$/°C	$T^{-}_{\max}$/°C	$(T^{+}_{\max} + T^{-}_{\max})/2$
1	105.4	104.3	104.85
2	106.4	103.5	104.95
4	107.5	102.2	104.85
6	108.9	101.4	105.15
8	109.8	99.8	104.80
10	110.3	99.4	104.85

procedure for the calibration on cooling suggested in the previous section.

The symmetry assumption, implicit in Eq. (7), can be confirmed if the values of $T^+_{\max}$ and $T^-_{\max}$ (temperatures of maximum tan δ as seen during heating and cooling experiments, respectively) at a same rate, are always at the same distance from a temperature $T^0_{\max}$ (temperature of maximum tan δ at $\beta \to 0$). Table 1 presents the average values of $T^+_{\max}$ and $T^-_{\max}$ as a function of β. These mean values are an estimation of $T^0_{\max}$ if Eq. (7) is valid. One observes that all those values are very similar within a temperature range of 104.9 ± 0.3°C. This is a clear indication that, in this case, the symmetry between heat fluxes is valid. Therefore, the procedure proposed for the temperature calibration on cooling is able to be used.

The estimated $T^0_{\max}$, as seen from cooling and heating experiments, was 104.9. This value is different from the one observed in the isothermal results ($T^0_{\max} = 104.1$). The isothermal and isochronal experiments were performed with the same sample but at different times. This reason may be the cause of the difference between the zero maximum temperatures which is less than 1°C. This observation supports the resolution of the temperature read by the equipment suggested before. It is also interesting to note that $T^+_{\max} = 105.2$°C for the experiment at $\beta = 0.5$°C min^{-1}. This value is only 0.3°C above the result obtained for the case of $\beta \to 0$ and indicates that calibration experiments at $\beta < 0.5$°C min^{-1} may be used in isothermal corrections.

The solid line in Fig. 12 is the fitting of the $T^+_{\max}$ versus β data (for $\beta \neq 0$) to the three-order polynomial law $104.9 + a\beta + b\beta^3$. This function has a symmetric character around $T^+_{\max} = 104.9$, that is, $T_{\max}(\beta) - 104.9 = -(T_{\max}(-\beta) - 104.9)$. The adjustable parameters (a and b) do not have any physical meaning but the good agreement between the fitted curve and the experimental data strengthens the hypothesis of heat fluxes symmetry. Moreover, the obtained curve could be used for interpolating expected results.

6. Conclusions

In this study some approaches for correcting the temperature axis of DMA experiments were analysed and improved. From the obtained results we can draw the following conclusions:

1. Calibration of temperature on heating and isothermal experiments may be carried out with metallic standards within an error of 1°C, provided that the location of the standards is consistent with the location of the sample under study. Two methods of correcting temperature are proposed, for the case of flexural and extension DMA experiments. The temperature correction was found to depend strongly on the purge gas flow rate.
2. Isothermal correction may be performed by extrapolating the calibration results on heating for zero scanning rate. A good approximation may be achieved by performing a unique experiment at a very low scanning rate ($\beta \leq 0.5$°C min^{-1}).
3. The increase of the scanning rate decreases the maximum of the tan δ of the α-relaxation in polymers. In this context, isothermal results are found to be consistent with the isochronal results. The temperature dependence of the elastic modulus obtained in isothermal results also presents an intermediate behaviour to that of experiments performed on heating and cooling.
4. For the case of the equipment used in this work, the symmetry between heat fluxes on heating and cooling experiments (at the same rate) was observed. This information can lead to the development of an usable and acceptable method for the temperature calibration on cooling, by using the results of the calibration experiments on heating.

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