Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 37–49

TEMPERATURE CALIBRATION IN DIELECTRIC MEASUREMENTS

J. F. Mano[1*], *S. Lanceros-Méndez*[2], *A. M. Nunes*[3] *and M. Dionísio*[3]

[1]Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
[2]Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710 Braga Codex, Portugal
[3]Departamento de Química, Centro de Química Fina e Biotecnologia, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2825-114 Monte de Caparica, Portugal

(Received March 1, 2001)

Abstract

Dielectric experiments are often performed in non-isothermal conditions. Thus, there is a difference between the temperature of the sample and the sensor temperature. In this work we propose and compare three temperature calibration methods based on the detection of transitions or relaxations: i) the melting of high-purity metallic standards (indium and tin), ii) the 2nd order phase transition of a ferroelectric crystal (TGS); iii) the α-relaxation of an amorphous polymer (poly(carbonate)). The results obtained from the three different methods were used to construct a calibration curve for a given heating rate.

Keywords: dielectric, metallic standards, polymer, temperature correction, TGS, TSC

Introduction

Dielectric relaxation spectroscopy or dielectric thermal analysis (DETA) has been widely used to investigate the electric polarization and conduction processes in a variety of materials such as polymers, crystals, organic substances or ceramics. DETA provides information about the motional processes at a molecular level associated to relaxations/transitions throughout a large frequency range: combined modern dielectric spectrometers are able to cover a very broad frequency range from the millihertz up to the microwave region. Moreover, this technique also provides direct practical relevant information concerning, among others, insulation properties, piezoelectric, pyroelectric and ferroelectric behaviour and microwave adsorption characteristics.

Most of the DETA experiments are performed in isothermal conditions, where the complex permittivity ($\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$) is measured over a frequency scan. In this case, the treatment of the experimental data and the theoretical interpretation of

---

[*] Author for correspondence: E-mail: jmano@dep.uminho.pt

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

the results are relatively simple; this is due to the fact that the characteristic time of the processes (or its distribution) is kept constant during the experiment. Similar experiments can be performed in a heating/cooling mode experiment at a specific frequency, measuring the real permittivity $\varepsilon'(T)$ and the loss tangent $\tan\delta(T)=\varepsilon''(T)/\varepsilon'(T)$ as a function of temperature (isochronal experiments). This type of experiments may be more suitable in some situations such as:

- To identify quickly the relaxational spectrum of a material in a routine procedure of identification or in quality control. In general, the regions of relaxation may become more evident when the results are expressed as a function of the temperature, relatively to those obtained in isothermal conditions and expressed as a function of frequency (see [1] for a poly(ester) and references therein).
- To investigate the thermodynamic transitions in materials. In this case, only one temperature scan is needed because the general features of a pure thermodynamic transition do not depend on frequency.
- To monitor reactions (polymerisation or curing, for example) or crystallisation in non-isothermal conditions.

The isochronal experiments can be performed even when the complex permittivity is needed at different frequencies and temperatures. It is possible to program isochronal experiments where ε^* is measured at different frequencies settled prior to the experiment. Some commercial equipment enables such kind of experimental procedure. If the frequencies are high enough (typically above 500 Hz) and a relatively short number of frequencies is used (below 10) we can obtain reliable values at low temperature rates (~1°C min^{-1}).

In the non-isothermal method the sample is not in thermal equilibrium and the existence of a thermal lag between the sample temperature and the temperature of the thermocouple must be considered. In fact, this has been a major problem in many thermal analysis techniques (see discussion in [2]) because the thermocouple that measures the temperature of the sample is seldom in direct contact with the sample. Therefore, it is expected that, at a given time, the temperature of the sample is not equal to the temperature read by the sensor. For the required experimental condition it is thus important to undertake some appropriate measures which will allow one to know, at any moment of the experiment the correspondence of the indicated sensor temperature T_s to the real temperature of the sample T_r.

In this paper we propose and compare three different methods that may be used to correct the temperature axis of isochronal dielectric experiments. All these methods use systems that have a relaxation or transition that is well characterised in terms of its positions in the temperature axis. The method has been used to construct the temperature calibration curve of a Polymer Laboratories apparatus (PL) for a given heating rate.

Experimental

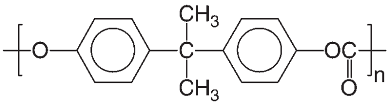
Materials

The two metallic standards were used in this work were indium (99.99999% purity) and tin (99.9999% purity), from Goodfellow. These metals exhibit melting temperatures of 156.6 and 231.4°C, respectively.

Tri-glycine sulfate (TGS, $(NH_2CH_2COOH)_3{\cdot}H_2SO_4$) exhibits ferroelectric properties at room temperature with the 2nd order ferroelectric phase transition at 49°C. TGS crystals were grown by a slow cooling technique – from 45°C to room temperature at a rate of 0.25°C/day – from a water solution. Glycine and sulphuric acid were from Aldrich Chemicals.

The polymer used was a commercial poly(carbonate) (Goodfellow, code number CT301300/1) in the form of an extruded isotropic film (0.1 mm thickness).

The structure of the studied poly(carbonate) is:



This material has a calorimetric glass transition around 150°C. Due to possible crystallisation the film was subjected to a thermal treatment at ca 200°C for more than 1 h. After this treatment, successive temperature scans of the film in the PL equipment (see below) up to 220°C did not show differences in the obtained traces.

Equipments

The dielectric relaxation experiments were carried out with two different apparatus:

Polymer Laboratories equipment (PL)

The Polymer Laboratories DETA apparatus consists in a General Radio 1693 digital RLC bridge, a dielectric spectrometer head, a temperature controller unit (Model 706) and a controlling computer with PL software. The two components of permittivity (ε' and ε'') are obtained by measuring the capacity and the loss tangent (tanδ) on the DETA bridge.

The dielectric spectrometer cell consists of a lower base with provision for mounting the sample, and a furnace chamber (internal dimensions: 6 cm diameter and 6 cm high). The temperature is measured by a small 100 ohm platinum resistance Thermometer (PT100) placed at ca 5 mm below the bottom electrode.

Measurements were performed over the frequency range 100 Hz to 100 kHz in constant heating mode at temperature rates between 0.2 and 8°C min^{-1} in the temperature range 25 to 250°C. Prior to the experiments the usual calibration routines of internal reference resistors and removal of stray effects due to leads and cell were performed.

Novocontrol equipment (NC)

This equipment consists of a Hewlett-Packard impedance analyser HP 4284A, covering a frequency range from 20 Hz to 1 MHz, a BDS 1200 sample cell, and a temperature control module (QUATRO Cryosystem from Novocontrol GmbH) which allows for isothermal and ramp temperature experiments.

The poly(carbonate) (PC) film was studied in this equipment. For the experiments in the NC equipment, the PC film was sputtered on both sides with a gold layer to enhance the electrical contact. The film was kept between two gold-plated electrodes (diameter 20 mm) of the sample cell, which is mounted into a BDS 1100 cryostat and exposed to a heated gas stream evaporated from a liquid nitrogen dewar. The temperature in the cryostat is measured by a platinum PT100-type sensor which is fit into the lower electrode.

The parallel capacitance (proportional to the real part of the complex permittivity, ε') and the loss tangent ($\tan\delta=\varepsilon''/\varepsilon'$) were measured both in isothermal and ramp temperature tests.

Results and discussion

Fusion of high-purity metallic standards

The fusion of high-purity metallic standards has been extensively applied in the temperature calibration of several thermal analysis techniques [2]. For example, in differential scanning calorimetry (DSC) and differential thermal analysis (DTA) techniques, the onsets of the fusion peaks of these materials are compared with the corresponding melting point. 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 [2]. It should be mentioned that temperature calibration of dielectric measurements in dynamic scanning mode using indium has been already reported [3].

Owing to the electrical conductivity of such materials, they cannot be employed directly to calibrate the temperature axis of DETA equipments. In this work we propose the use of metallic standards in a special arrangement that undergoes some modification when the metal melts.

We have designed the following experiment. A piece of the metallic standard (~10 mg) with a flat cylindrical geometry (~100 μm high) is placed between two poly(imide) sheets (15×15 mm and 200 μm thick). Poly(imide) is a very stable polymer that does not present appreciable dielectric changes in the temperature range under consideration. This set-up is then placed between two steel discs of 24 mm diameter. This assembly is mounted between the electrode plaques of the PL equipment. The mobile top electrode is moved down until some pressure is created, assuring a good physical contact through all elements. The top electrode is then fixed in order to maintain the distance between the electrodes during the experiment (situation I in Fig. 1). The initial temperature is set well below the melting temperature, enabling the heating rate to stabilize before the melting.

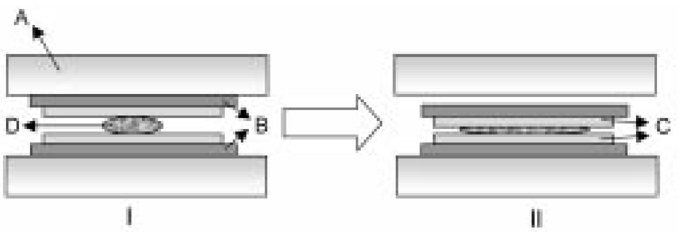


Fig. 1 Scheme of the set-up for the temperature calibration of the PL equipment using metallic standards. A – electrodes of the PL equipment, B – metallic plaques, C – polyimide films, D – metallic sample

During heating, the metal melts at a certain temperature. At this moment the top steel disc (B in Fig. 1) separates from the top electrode by gravity and a new empty layer between B and the top electrode is formed (situation II in Fig. 1). The signal of the apparatus will be modified due to this geometric change.

Two examples of such experiments, with indium (T_m=156.6°C) and tin (T_m= 231.4°C) are shown in Figs 2a and 2b, respectively. The melting temperature read by the

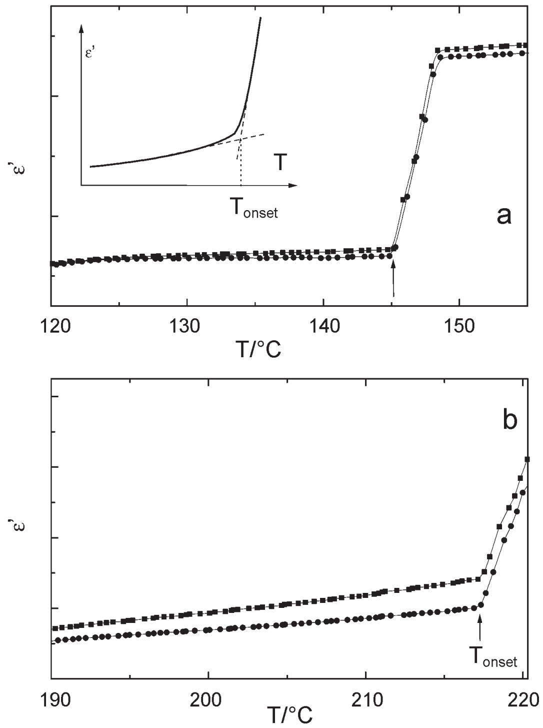


Fig 2 Storage permittivity during a temperature scan in the PL equipment with indium (a) and tin (b), according to the set-up of Fig. 1, at 1°C min^{-1} and measured at two frequencies (squares: 500 Hz, circles: 1000 Hz). Inset in Fig. 2a: method for obtain the onset temperature, T_{onset}

thermocouple is calculated by the onset temperature, T_{onset}, as explained in the inset of Fig. 2a. In this case we obtain T_{onset}=145.2±0.2°C for indium and T_{onset}=215.5±0.2°C for tin. The onsets were found to be independent of the frequency used, due to the fact that melting is a pure 1st order thermodynamic transition.

The gradual increase in ε' observed in Fig. 2 above T_{onset} is due to the progressive melting of the metals associated with their thermal resistance.

A variety of metals and even organic compounds may be used in this method, provided that the theoretical melt temperature is well known and that the melt is sufficiently fluid. A list of recommended standards with melting temperatures from –38 to 1064°C is presented in [4].

Transitions in crystals

Chemically and crystallographically, TGS is not by far the simplest ferroelectric known, but its phenomenological behaviour is very simple. It represents, in fact, one of the most typical examples of a ferroelectric, the behaviour of which fits quite perfectly the description given by the thermodynamic theory for 2nd order phase transitions, with the Curie temperature at 49°C [5]. In the vicinity of the transition temperature the dielectric constant along the ferroelectric b-axis shows a pronounced anomaly. The dielectric constant follows a Curie–Weiss law and the Curie-Weiss temperature agrees practically with the Curie temperature [5]. For the dielectric measurements, samples in the shape of thin slices (d≈1.5 mm) were oriented perpendicularly to the polar b-axis and silver painting served as electrodes. The temperature dependence of $\varepsilon'(T)$ and $\tan\delta(T)$ were measured at several velocities ranging from 0.2 to 8°C min^{-1} in the PL equipment described above. One can thus compare the temperature of the maximum in ε' with the true transition temperature.

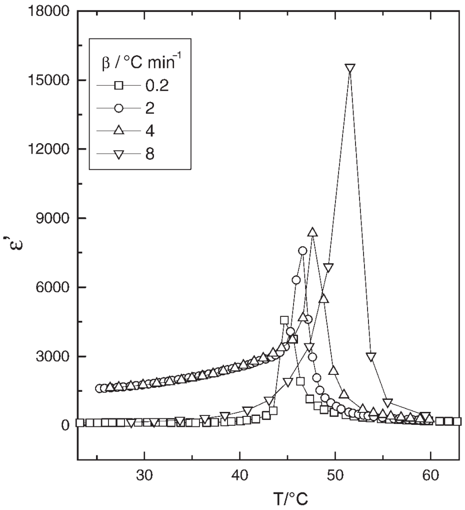


Fig. 3 Storage permittivity of TGS measured at 1 kHz in the PL equipment at different scanning rates (in the legend)

In Fig. 3 the ε' *vs.* T results obtained for TGS at different rates are shown in the region of the ferroelectric transition. The peaks are well defined, enabling the determination of the transition temperature as read by the sensor $-T_s$.

The differences observed 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 former effect should be scanning rate independent, whereas the second factor depends on the scanning rate ($\beta=dT/dt$): as β increases the sensor temperature gradually separates from the real temperature (or, at least, from the temperature read at low scanning rates). This effect is shown in Fig. 3 where T_s is found to increase with increasing β.

Due to the fact that the sensor is located outside the capacitor plates, several factors contribute to the thermal resistance associated with the dependence of T_s on β: the ceramic wrapping the thermocouple, the air gap between the sensor and the capacitor, the capacitor plates, and even the own thermal resistance of the sample. As we shall see later, the last factor is very small if we measure thin films, which is not the case in this particular system.

In Fig. 4 the sensor temperature at maximum of ε' is plotted *vs.* the heating rate. The plot shows that a linear relationship is maintained between these two variables (the linear fitting yields R=0.997, Fig. 4). The slope of the fitting is related, among other factors, with the thermal resistance between the thermocouple and the sample. The slope should increase as the thermal resistance increases. For this particular case,

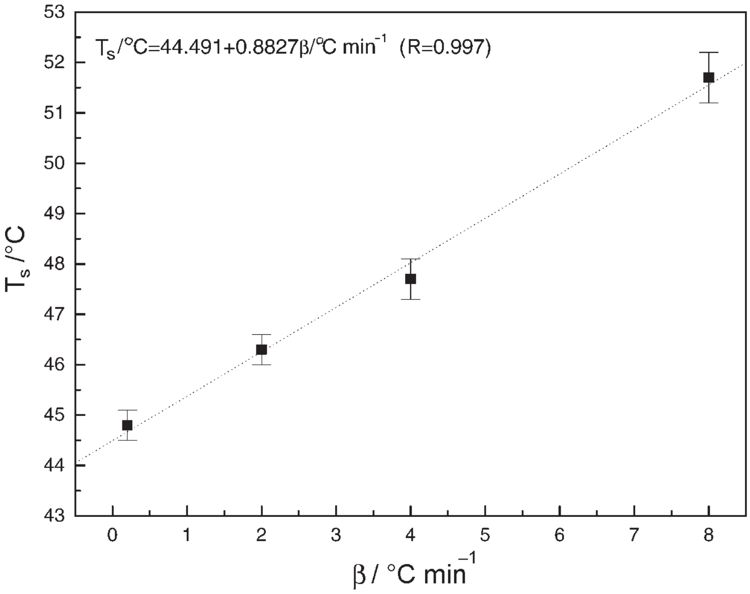


Fig. 4 Maximum of the storage permittivity as a function of the heating rate for TGS (data extracted from Fig. 3)

the results suggest that the calibration must be carried at the same heating rate of the experiments.

The plot in Fig. 4 also enables to correct the temperature for isothermal experiments. The procedure is to use the intercept of the fitting curve as the sensor temperature, i.e., an isothermal situation can be predicted by observing the calibration curve in Fig. 4 for the case $\beta \rightarrow 0$. Note that the intercept (44.49°C) is different from the expected value for the studied transition. This difference may be due to two different reasons: i) the sensor is not well calibrated or ii) the existence of heat fluxes inside the furnace. Those fluxes may exist even in isothermal conditions because there are still a hot and a cold thermal sources coupled to the furnace that originates temperature gradients inside the chamber.

It is interesting to note that due to the fact that the studied phase transition occurring in TGS is a second order thermodynamic transition, showing no thermal hysteresis, we could use this material to correct the temperature axis in dielectric equipment under cooling conditions.

α-Relaxation in amorphous polymers

The α-relaxation usually observed in amorphous polymers corresponds to the dynamic glass transition 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 corrected temperature axis of the α-relaxation of a stable amorphous polymer is not dependent on the testing mode: isothermal or isochronal (heating or cooling). The usual frequencies used in isochronal DETA studies are well 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 [6]). Therefore, the temperature of maximum tanδ 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. Moreover the applied frequencies used are high enough so that the temperature dependence of the response is not smeared out by the heating process; i.e. if the permittivity must be resolved within a temperature interval ΔT, we assure that we have $\omega >> \beta/\Delta T$. For all these reasons, we may expect that the dynamic-dielectrical response of the material in this temperature range (near the temperature of maximum tanδ) is only temperature and frequency dependent (not heating rate dependent) and can be used as a probe to the calibration procedure like the two systems described before. The same idea was discussed in the comparison between isothermal and isochronal dielectric experiments on polyethylene terephthalate [1].

In this work we used poly(carbonate) (PC), an amorphous thermoplastic. We focus on the tanδ data due to the fact that this quantity is not dependent on the geometry of the sample. Therefore, the comparison between results obtained in different apparatus, and/or where the comparison of results when the measurement of the thickness of the samples may be difficult, is better achieved by using tanδ instead of the loss permittivity, ε''.

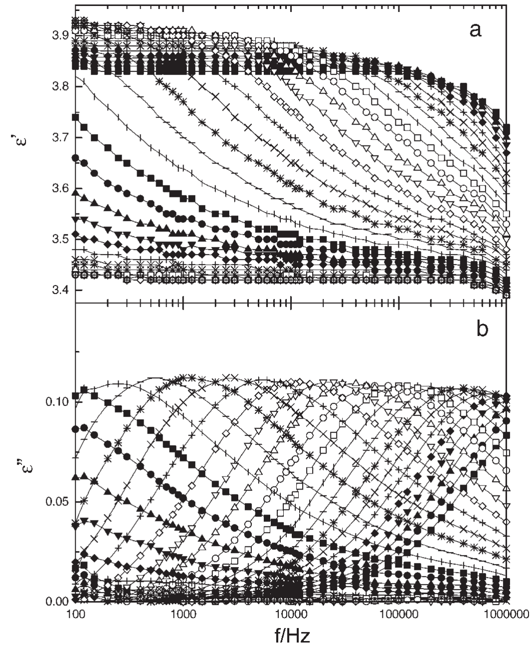


Fig. 5 Isothermal frequency scans in the NC equipment, from 100 Hz to 1 MHz, on the polycarbonate film at different temperatures, from 200 to 130°C (every 2°C). a – storage permittivity, b – loss permittivity

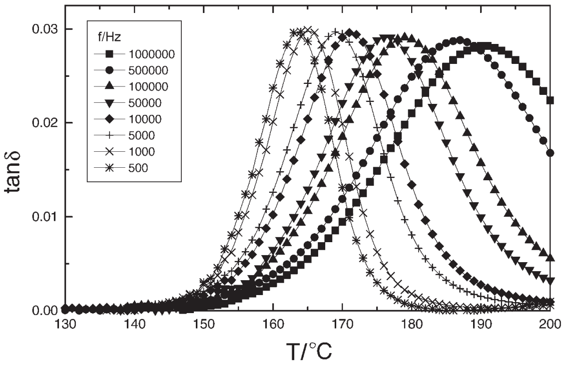


Fig. 6 Loss tangent obtained isothermally, as a function of temperature for different frequencies (see legend)

We will assume that the thermocouple of the NC equipment is well calibrated: this could be verified by running the experiments with the first method (metallic standards) at a very low heating rate (<0.5°C min^{-1}). In fact, the use of this method requires that the dielectric property of the polymeric standard is well characterized as a function of temperature.

In a first set of experiments, PC was investigated in the NC equipment in isothermal conditions. This will assure that the sensor temperature is the same as the sample temperature. The sample was annealed at 220°C prior to the experiments. A frequency scan from 20 Hz to 1 MHz was made every 1°C in decreasing temperature from 200 to 130°C. The system was kept at each temperature during a time necessary to warrant that the temperature was constant within ±0.05°C. The isothermal experiments are shown in Fig. 5, in temperature intervals of 2°C.

In Fig. 6 the tanδ values obtained in the isothermal experiments are plotted *vs.* temperature for 500 Hz, 1 kHz, 5 kHz, 10 kHz, 50 kHz, 100 kHz, 500 kHz and 1 MHz. It is important to stress that we assumed the thermocouple in the NC equipment to be well calibrated. Therefore, the temperature axis in Fig. 6 corresponds also to the temperature of the sample. We can, thus, use this poly(carbonate) film to calibrate the temperature of our PL equipment. For example, we have a maximum of tanδ at 165°C for the frequency of 1 kHz (Fig. 6).

Isochronal experiments were also carried out in the NC equipment at 1 kHz and scanning rates of –8, –4, –2, –1, +1, +2, +4 and +8°C min^{-1}. The negative sign in the heating rate means that the experiments began at 200°C and the sample was cooled down to 130°C at that rate. The opposite procedure was applied in the heating experiments (positive sign). The results for the loss tangent are shown in Fig. 7 together with the isothermal data. It can be seen that all points overlap, indicating that the results of the experiments apparently do not depend on the scanning rate. This behaviour is different from the results obtained in the PL equipment (Fig. 3), where the temperature location of the processes strongly depends on the scanning rate. This difference can be explained by the fact that in the NC equipment the thermocouple contacts directly with the upper part of the lower electrode, i.e., it is very close to the sample. Therefore the thermal resistance between both is very small. Moreover, the thermal resistance of the sample is also small because the film is very thin.

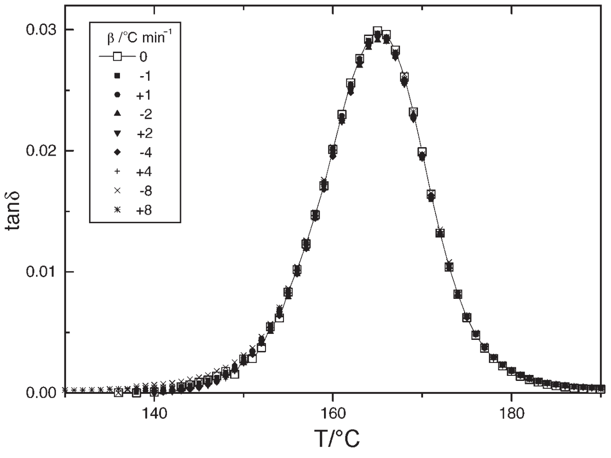


Fig. 7 Loss tangent of polycarbonate measured in the NC equipment at 1 kHz at different scanning rates (see legend). For comparison purposes the isothermal results are included (open squares)

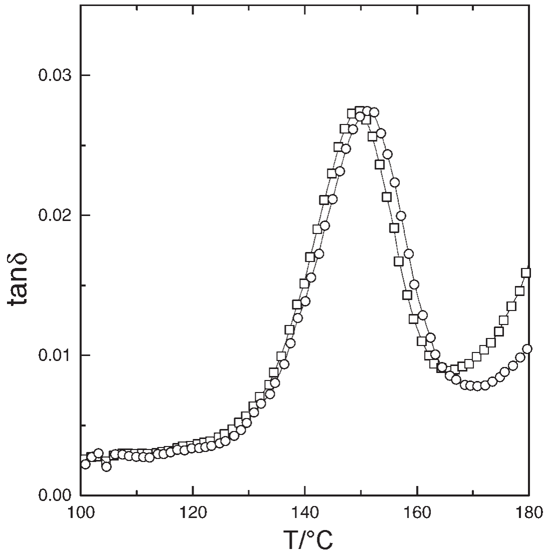


Fig. 8 Isochronal results of polycarbonate measured in the PL equipment at 1°C min^{-1} for two frequencies: squares – 500 Hz; circles – 1 kHz

The same polycarbonate was studied in the PL equipment at 1°C min^{-1} and several frequencies between 100 Hz and 100 kHz. In Fig. 8 the tanδ is plot *vs.* frequency for 500 and 1000 Hz. The maximum of the tanδ is, in this case, located at 151.3°C for the frequency of 1 kHz, which is different from the results shown in Fig. 6. This indicates that, when the sensor reads 151.3°C, the sample is at 165°C.

Concluding remarks

In the three previous sections, three methods for correcting the temperature axis of dielectric spectroscopy equipments (DETA) were suggested: the fusion of metallic standards, the 2nd order ferroelectric transition of a crystal and the α-relaxation of an amorphous polymer. The systems used for the calibration covered a wide range of temperatures.

It is interesting to group the results in order to construct a calibration curve that allow, for this particular case, to correct the temperature axis of the PL equipment for experiments carried out, for example, at 1°C min^{-1}.

We can use directly the information obtained from the experiments with the metallic standards and with the poly(carbonate), because the experiments were performed in the PL apparatus at 1°C min^{-1}. We can also use the results obtained with the crystalline system (TGS), interpolating the results shown in Fig. 4 in order to obtain the sensor temperature at the maximum of ε' for a heating rate of 1°C min^{-1}.

The calibration curve is shown in Fig. 9. It should be stressed that this calibration curve is only valid for the PL equipment with the used thermocouple and the described set-up. A good linear relationship is observed between the sensor temperature and the corresponding real temperature of the sample. For example, for other thermal analysis techniques, such as DSC, it is often observed that a plot of T_r *vs.* T_s for different standards obtained with the same heating rate follows a nearly linear relationship [7].

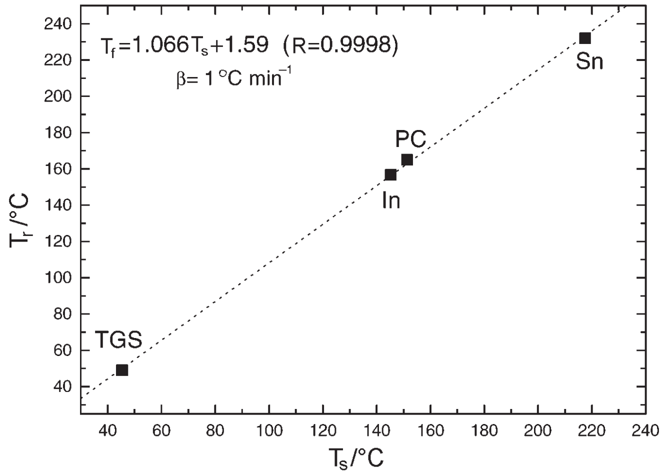


Fig. 9 Calibration curve for the PL equipment at 1°C min^{-1} (real temperature of the samples, T_r, as a function of the read temperature of the sensor, T_s) constructed with the results obtained by the three methods proposed in the work (R=0.9998)

It must be noticed that the temperature range of the calibration curve shown in Fig. 9 could be extended by using different crystals, amorphous polymers and metals.

The methods presented in this work could be used, with simple modifications, to correct the temperature in other equipments such as those used to carry out transient experiments either in isothermal conditions or during temperature sweeps. The later experimental protocol is usually associated with the so-called thermally stimulated currents technique (TSC).

* * *

Financial support for this work was provided by Fundação para a Ciência e Tecnologia (Portugal) through the projects PRAXIS/P/CTM/14171/1998 and PRAXIS/P/QUI/10071/1998.

The authors wish to thank Dr. G. Arunmozhi from the Dept. de Física da Universidade do Minho for kindly supplying the TGS crystal.

References

1 M. Dionísio, N. M. Alves and J. F. Mano, Polymer, 40 (1999) 2675.

2 T. Hatakeyama and F. X. Quinn, ‘Thermal Analysis, Fundamentals and Applications to Polymer Science’, John Wiley & Sons, Chichester 1994.

3 A. Bizet, N. Nakamura, Y. Teramoto and T. Hatakeyama, Thermochim. Acta, 237 (1994) 147.
4 C. M. Earnest and R. J. Seyler, J. Testing and Evaluation, 20 (1992) 430.
5 F. Jona and G. Shirane, Ferroelectric Crystals, Dover Publications, Inc. New York 1993, p. 28.
6 E. Donth, 'Relaxation and Thermodynamics in Polymers; Glass transition', Akademie Verlag, Berlin 1993.
7 G. W. H. Höhne, W. Hemminger and H. J. Flammersheim, in: 'Differential Scanning Calorimetry', Springer, Berlin 1996.