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TOPEM, A NEW TEMPERATURE MODULATED DSC TECHNIQUE
Application to the glass transition of polymers

Iria Fraga[1], *S. Montserrat*[2] *and J. M. Hutchinson*[2*]

[1]TERBIPROMAT, Facultade de Física, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain
[2]Departament de Màquines i Motors Tèrmics, ETSEIAT, Universitat Politècnica de Catalunya, 08222 Terrassa, Spain

TOPEM is a new temperature modulated DSC technique, introduced by Mettler-Toledo in late 2005, in which stochastic temperature modulations are superimposed on the underlying rate of a conventional DSC scan. These modulations consist of temperature pulses, of fixed magnitude and alternating sign, with random durations within limits specified by the user. The resulting heat flow signal is analysed by a parameter estimation method which yields a so-called 'quasi-static' specific heat capacity and a 'dynamic' specific heat capacity over a range of frequencies. In a single scan it is thus possible to distinguish frequency-dependent phenomena from frequency-independent phenomena. Its application to the glass transition is examined here.

Keywords: *DSC, glass transition, TMDSC*

Introduction

Differential Scanning Calorimetry (DSC) is one of the most widely used thermal analysis techniques for the study of transitions and relaxation processes in polymers and other materials. For example, a simple search in the Web of Knowledge database using the keyword 'DSC' yields nearly 30.000 references for a technique that was introduced about 40 years ago. More recently, somewhat less than 15 years ago, a new technique was commercialised in which a periodic temperature modulation of small amplitude is superimposed on the underlying rate of conventional DSC. Several versions of this exist in the market, including Modulated DSC (MDSC, from TA Instruments) and Alternating DSC (ADSC, from Mettler-Toledo), and they are usually referred to generically as Temperature Modulated DSC techniques (TMDSC).

Despite their differences, all are fundamentally based upon the same principle, which involves a Fourier Transformation of the modulated heating rate and heat flow signals, from which one can obtain certain information additional to that available from conventional DSC. In particular, TMDSC permits the evaluation of two different kinds of heat capacity: (*i*) the 'thermal' heat capacity from the underlying heating or cooling rate, which is identical to that available from conventional DSC at the same rate, and (*ii*) the 'dynamic' heat capacity from the amplitudes of the heating rate and heat flow modulations, which is dependent on the frequency of the modulations. Thus, in a single experiment it is possible to determine the response of the polymer on two different time/frequency/rate scales, which has been shown to offer advantages in a number of different areas [e.g. 1–4], and in particular in its application to cross-linking reactions [5–12] and the glass transition [13–18].

Nevertheless, the impact of TMDSC does not appear to have been as dramatic as it could have been. A search in the Web of Knowledge database using the combination of keywords 'TMDSC or MDSC or ADSC' yields fewer than 600 references, a strike rate considerably less than that for 'DSC' above. More pertinently, a search using the keyword 'TMDSC' shows that the number of citations peaked in the year 2001 and is now declining. One possible reason for this is that, despite the advantages afforded by TMDSC in various areas, and particularly in those specifically mentioned above, it is not a particularly convenient technique to use. Perhaps of major importance here, at least in respect of ADSC, is that it requires a minimum of two separate scans, a 'blank' and a 'sample', for any given set of experimental parameters, which results in a very time-consuming procedure if one wishes to study, for example, the frequency dependence of a certain phenomenon. Thus any technique that could overcome this drawback would be welcome, and this is just what TOPEM can offer.

Instead of being based upon a periodic modulation of the heating rate, as is the situation with TMDSC techniques, TOPEM uses a stochastic modulation of the heating or cooling rate by means of random pulses of temperature. This stochastic perturbation introduces a broad frequency spectrum in the response, while a novel data analysis procedure, based

* Author for correspondence: hutchinson@mmt.upc.edu

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

upon a 'parameter estimation method' widely used in other technologies, allows the evaluation of a so-called 'quasi-static' heat capacity and the separation of correlated and non-correlated components of the heat flow with respect to the heating rate, which are related to the reversing and non-reversing heat flows in the usual TMDSC terminology. In particular, the broad frequency response implies that TOPEM is apparently able to determine the complex heat capacity over a range of frequencies in a single scan. In the present paper we examine this aspect of TOPEM performance, by applying it to the glass transition region of a polymer and comparing the results with those obtained by ADSC.

Experimental

Materials

The glassy polymer selected for this study is polycarbonate. In order to obtain samples of different masses for comparison of their response, 5 mm diameter discs of different thicknesses were machined from a 40 mm diameter extruded rod of Lexan (GE Plastics) following the procedure described in detail elsewhere [19]. The surfaces of these discs were carefully polished with P#1200 silicon carbide paper to give good thermal contact with the aluminium crucibles of the DSC. Sample masses from about 4 mg to about 40 mg were used.

Methods

Temperature modulated DSC method

The calorimeter used is a DSC823^e from Mettler-Toledo equipped with sample robot and Julabo FT400 intracooler, and with STAR^e software for control of the experimental conditions and for data analysis. It can be used as conventional DSC, as ADSC or as TOPEM; the difference lies only in the software. In TOPEM mode, it is necessary to specify some experimental parameters: the temperature range for the scan, which here was from 180 to 80°C in order to cover the glass transition interval (T_g≈145°C); the underlying rate, which here is almost invariably cooling in order to avoid problems associated with structural relaxation, and which ranges from –2 to –0.02 K min^{-1}; the amplitude of the temperature pulse, which can be as small as ±0.001 K but here takes values of ±0.5, ±0.25 and ±0.1 K; the switching time range, which limits the duration of the pulses, and has a minimum of 15 s and a maximum of 30 s or any longer time as considered appropriate. Most TOPEM experiments (and in particular for all the results reported here except those at the two slowest cooling rates, –0.2 and –0.02 K min^{-1}, for which a larger sample mass was used) were conducted with a sample mass of approximately 20 mg, the recommended value, and a switching time range of 15 to 30 s, the default values. Nevertheless, smaller sample masses and wider switching time ranges were also used to investigate whether or not these had any effect.

For comparison with the TOPEM results, some ADSC experiments were also performed over the same temperature interval and for a range of frequencies, by using periods from 30 to 960 s, always with an amplitude of ±0.5 K. To accommodate this range of periods, the underlying cooling rate was decreased as the period increased, from –1 K min^{-1} for a period of 30 s to –0.0625 K min^{-1} for a period of 960 s. At the same time, the sample mass was increased from about 8 mg to about 40 mg in order to maintain a measurable heat flow.

Data analysis

The TOPEM experiment gives the heat flow signal which results from the stochastic temperature pulses. To calculate the response function for the system, there must be a region of the data in which there is no transition; it is for this reason that the cooling curves here start at 180°C, well above the nominal glass transition which is centred at about 145°C. The TOPEM evaluation is made within a calculation window, the width of which is set by the user. It is recommended that it be less than or equal to one third of the width of the transition interval, with larger windows giving better signals, and has a default value of 120 s. Once the calculation window has been selected, the TOPEM evaluation yields the curve of c_{p0}, the 'quasi-static' specific heat capacity. Figure 1 illustrates this with the original heat flow modulations from which the c_{p0} curve shown has been obtained.

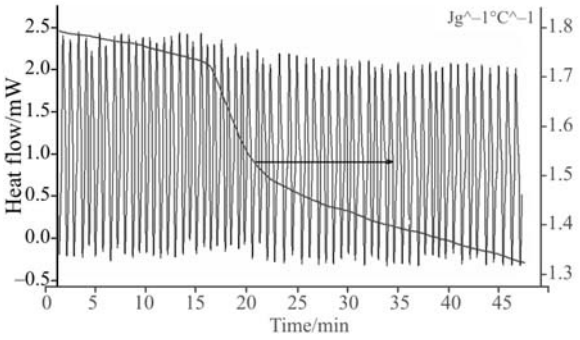

Fig. 1 Heat flow response to stochastic temperature pulses of magnitude ±0.25 K during cooling of polycarbonate at –2 K min^{-1} from 180 to 80°C with switching time range of 15–30 s, from which the 'quasi-static' specific heat capacity curve shown is derived. Left-hand axis refers to the randomly alternating heat flow signal; right-hand axis refers to the sigmoidal-shaped specific heat capacity curve

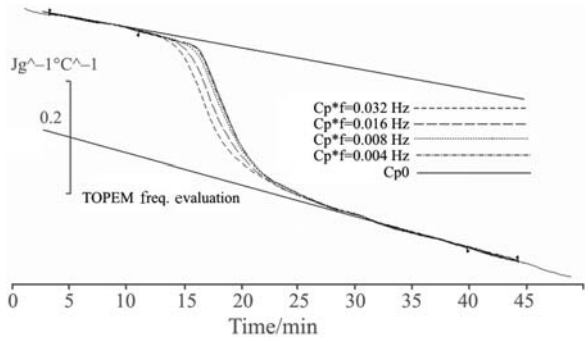

Fig. 2 Quasi-static specific heat capacity from Fig. 1 (full line) with asymptotes defined by transition interval selected. Lines show the frequency evaluation at selected frequencies of 32, 16, 8 and 4 mHz, as indicated. The curve for 4 mHz is barely visible as it is superposed almost exactly onto the quasi-static specific heat capacity curve

The next step in the procedure is to select the transition interval limits between which the frequency evaluation is to be made. Once this interval has been selected, the software defines the asymptotes to the liquid-like and glassy regions of the c_{p0} curve, as shown in Fig. 2. The user can adjust these asymptotes by moving the two flags in each of the liquid-like and glassy regions. Finally, the user selects the particular frequencies desired and TOPEM calculates the complex specific heat capacity corresponding to each selected frequency, also illustrated in Fig. 2 for frequencies of 32, 16, 8 and 4 mHz. It can be seen that the effect of increasing frequency is to reduce the time (increase the temperature) at which the complex specific heat capacity displays its transition.

The ADSC experiments were analysed in the usual way in order to obtain the complex specific heat capacity curves as a function of temperature. The quantitative effects of the various experimental and calculation parameters for TOPEM and the comparison of TOPEM with ADSC are examined by calculating the mid-point temperature, T_{mid}, of the glass transition in each case, defined as the temperature at which the curve passes mid-way between the liquid-like and glassy asymptotes. Since this evaluation depends to some extent on the way in which the asymptotes are drawn, unique asymptotes in the liquid-like and glassy regions were used for any given set of experiments.

Results and discussion

General appearance

Figure 2 shows quite clearly that the TOPEM experiment and evaluation leads to a set of complex specific heat capacity curves at different frequencies. From these it would be possible to determine, for example, an activation energy from the temperature shift of the curves as a function of the frequency; this is discussed in more detail in a later section. From a practical point of view, this ability of TOPEM to extract multi-frequency information from a single experiment is of great importance. In particular, it means that thermal events that depend on the frequency, such as the glass transition, can be separated by this criterion from those that are not frequency-dependent, such as crystallization and melting. This can be a very useful attribute in situations in which it is difficult to identify unequivocally a certain transition.

Amplitude of temperature pulse

The temperature pulse should be sufficiently small such that the sample response remains essentially linear. In ADSC the amplitude of the modulation is commonly taken to be ±0.5 K, and so here we investigate the effect of pulse magnitudes of ±0.5, ±0.25 and ±0.1 K. Figure 3 shows the results for TOPEM experiments using an underlying cooling rate of –0.5 K min^{-1} and with a switching time range of 15–30 s. The evaluation was made for a calculation window width of 480 s (to maintain the same width of 4 K as with 120 s for a cooling rate of –2 K min^{-1}) and the frequencies selected were 32, 16, 8, 4, 2 and 1 mHz. When the results are plotted in the form of log(frequency) *vs.* reciprocal T_{mid}, as in Fig. 3, the data should fall on a straight line if the temperature dependence of the relaxation times is Arrhenius, or on a curve with slight downward curvature for a Vogel-Tammann-Fulcher (VTF) type of temperature dependence. In fact, for the rather small interval of T_{mid} (about 5 K) involved in these experiments covering a range of frequencies from 32 to 1 mHz, it would

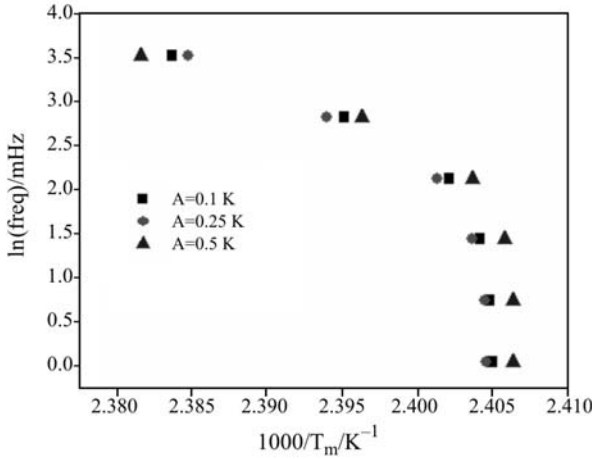

Fig. 3 Log(frequency) *vs.* reciprocal mid-point temperature for TOPEM experiments with underlying rate –0.5 K min^{-1}, switching time range 15–30 s and pulse amplitudes of ±0.5, ±0.25 and ±0.1 K

be difficult to distinguish the curvature of a VTF dependence, and hence we would anticipate an essentially linear variation in Fig. 3. The very marked curvature that is seen instead should not be confused with a VTF temperature dependence, but results from an aspect of the TOPEM analysis that is discussed in a later section.

On the other hand, it can be seen, as would be expected for pulses small enough that the sample response remains linear, that over the whole range of frequencies there is no systematic effect of the magnitude of the pulse on T_{mid}. The same result has been obtained for other cooling rates of –1.0, –1.5 and –2.0 K min^{-1}, from which we conclude that, at least for investigating the glass transition, it is acceptable to use pulse amplitudes of up to ±0.5 K.

Underlying cooling rate

TOPEM experiments were made with cooling rates from –2.0 to –0.02 K min^{-1} and with an amplitude of ±0.5 K and a switching time range from 15 to 30 s. As intimated in the Experimental section above, while a sample mass of approximately 21 mg was used for the majority of TOPEM experiments, a larger sample mass of approximately 37 mg was used for experiments with cooling rates of –0.2 and –0.02 K min^{-1}. When the curves are evaluated with a calculation window width of 4 K and for frequencies from 32 to 1 mHz, the relationship between log(frequency) and reciprocal T_{mid} is as shown by the filled points in Fig. 4. Here it can be seen that there is no obvious systematic effect of the cooling rate on the frequency dependence of T_{mid}, though there is rather more scatter in the data than is seen in Fig. 3, and resulting particularly from the data for the cooling rate of –0.02 K min^{-1}. This result, that there is no effect of cooling rate on the frequency dependence of T_{mid}, is as would be expected by analogy with the frequency dependence of the complex heat capacity obtained from ADSC. In that case, provided that the thermal and dynamic glass transitions are sufficiently separated on the temperature scale, then the dynamic glass transition is not influenced by the underlying cooling rate [13, 16, 20]. However, there is again a very marked downward curvature of the TOPEM data noticeable in Fig. 4, which in fact leads to a region, for frequencies less than about 4 mHz, where T_{mid} is virtually independent of the frequency.

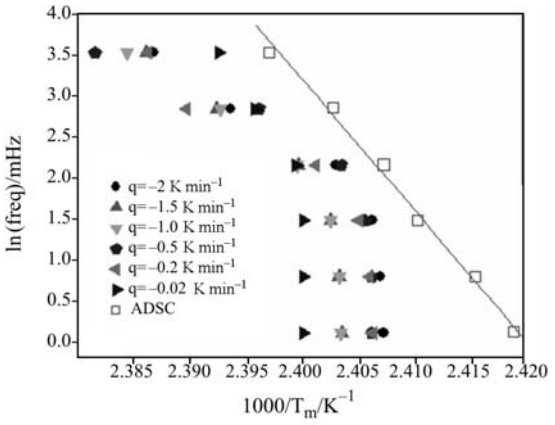

Fig. 4 Filled points: log(frequency) *vs.* reciprocal mid-point temperature for TOPEM experiments with amplitude ±0.5 K, switching time range 15–30 s, calculation window width of 4 K, and underlying rates from –2.0 to –0.02 K min^{-1}. Open squares: ADSC results for periods from 30 to 960 s

Width of calculation window

For any given TOPEM experiment it is possible to evaluate the data using different calculation window widths. For example, Fig. 5 shows the effect of increasing the window width from 60 to 240 s for an experiment with the parameters defined in the figure caption. It can be seen that there is a small but systematic decrease in T_{mid} as the window width increases. We recall that the recommendation is that the window width be less than one third of the transition interval, which in the present case can be estimated from Fig. 2 to be about 15 min time interval at a cooling rate of –2 K min^{-1}, which equates to a temperature interval of 30 K. The maximum window width in Fig. 5 is 240 s for a cooling rate of –1 K min^{-1}, which equates to 4 K, or less than one sixth of the transition interval. Thus, even though the window widths fall within the limits recommended, there is a clear effect of this on the mid-point temperature.

The converse of this can be seen if a much slower cooling rate is used, –0.02 K min^{-1}, for which a wide range of window widths can be investigated while maintaining a small value for the maximum

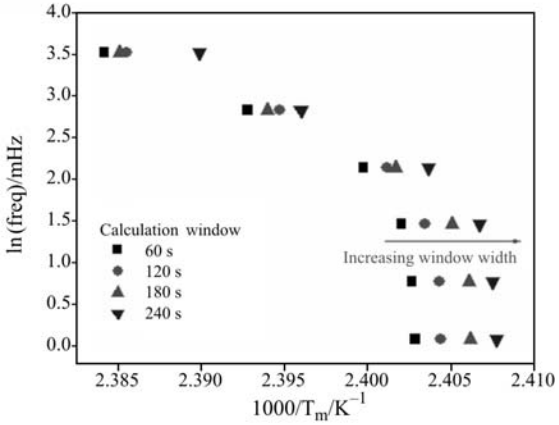

Fig. 5 Effect of width of calculation window on plot of log(frequency) *vs.* reciprocal mid-point temperature. Underlying cooling rate –1.0 K min^{-1}, amplitude of pulse ±0.5 K, switching time range 15–30 s

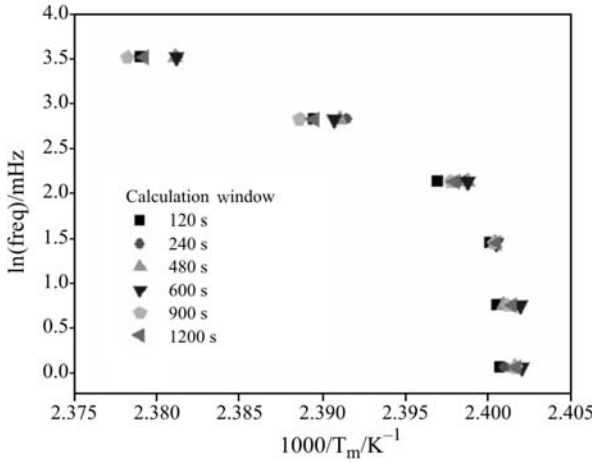

Fig. 6 Effect of width of calculation window on plot of log(frequency) *vs.* reciprocal mid-point temperature. Underlying cooling rate –0.02 K min^{-1}, amplitude of pulse ±0.5 K, switching time range 15–30 s

window width. The results are shown in Fig. 6. Here, the window widths from 120 to 1200 s correspond to temperature intervals of only 0.04 to 0.4 K, much smaller than those in Fig. 5, and the effect is that the window width now has no influence on T_{mid}. Similar results were obtained for a cooling rate of –0.2 K min^{-1}, for which T_{mid} was independent of window width except for a width of 1200 s, equivalent to a temperature interval of 4 K, for which the mid-point temperature was displaced significantly to lower temperatures. We conclude from this that the recommended restriction on the window width is not strict enough, and that it should be equivalent to less than about one tenth, rather than a third, of the transition interval.

Other parameters (sample mass, switching time range)

The recommended sample mass for use in TOPEM is 20 mg. However, for the two slowest cooling rates used here, namely –0.2 and –0.02 K min^{-1}, and by analogy with the experimental procedure adopted for the ADSC measurements as a function of increasing period (and hence decreasing underlying cooling rate), a larger sample mass of 37 mg was used. In order to check that the sample mass does not have an effect on the TOPEM results, though, the same experiment involving cooling at –0.5 K min^{-1} from 180 to 80°C with a pulse amplitude of ±0.5 K was made with two different sample masses of 21 and 8 mg. The mid-point temperature T_{mid} in the first case is 142.6°C and in the second case is 142.5°C, which represents an insignificant difference. On the other hand, there is a more significant effect in the frequency evaluation, whereby the complex specific heat capacity curves at the selected frequencies are displaced further to higher temperatures the larger is the sample mass, with a difference of about 1°C between the T_{mid} values for the sample masses of 8 and 21 mg for the highest frequency of 33 mHz. On the 1000/T_{mid} scale this corresponds to a difference of about 0.006 K^{-1}, which is somewhat larger than the typical scatter in values such as is seen in Fig. 3. This probably contributes to the observation that the scatter is greater in Fig. 4, where a different sample mass was used for the slowest cooling rates, than it is in Fig. 3, but does not detract from general trend of T_{mid} reaching a limiting value at low frequencies.

To investigate the effect of switching time range, experiments were performed with an underlying cooling rate of –0.2 K min^{-1}, a pulse amplitude of ±0.5 K, and switching time ranges of 15–30, 15–200 and 15–900 s. For consistency, the same calculation window of 1200 s, equivalent to 4 K of temperature interval, was used, being necessarily greater than the longest possible switching time. It transpires that there is no systematic variation in T_{mid} with switching time range, all the results displaying the same trend such as that shown in Figs 3 to 6, and having a scatter of the same order as that shown in Fig. 3 with respect to the effect of the amplitude of the temperature pulse.

Frequency dependence

We return to the observation, made above, that the plots of log(frequency) as a function of reciprocal temperature indicate that T_{mid} becomes independent of frequency for frequencies less than approximately 4 mHz. This can be seen also very clearly when the individual curves of $c_p(\omega)$ for the selected frequencies are all included on the same plot as c_{p0}. For example, if the frequency analysis of Fig. 2 is extended to include frequencies of 2 and 1 mHz, the $c_p(\omega)$ curves for these frequencies are indistinguishable from that for 4 mHz, and the curves for all frequencies less than or equal to 4 mHz are superposed onto the curve for c_{p0}, the quasi-static specific heat capacity, which indicates that 4 mHz appears as a kind of limiting frequency for TOPEM. The results shown in Figs 3 to 6 indicate that this limit is reached whatever are the experimental or calculation parameters, and hence that it must be intrinsic to the TOPEM experiment.

One possible explanation is that it arises because c_{p0} is calculated from the temperature pulses, which are applied with a certain heating or cooling rate. These rates can be estimated from the temperature programmes, and it transpires that they are approximately ±8 K min^{-1}. According to the relationship between rate (q) and frequency (f) that can be derived from the temperature fluctuation model of the glass transition [21, 22]:

$$2\pi f = |q|/a\delta T \quad (1)$$

where $a\delta T$ is a parameter that depends on the glassy material, it is possible to determine the frequency corresponding to the pulse heating and cooling rates. Taking values of x=0.46 and 0.456<β<0.6 for the non-linearity and non-exponentiality parameters, respectively, for polycarbonate [19], and using our earlier theoretical results given in Table 2 of [23], we find $a\delta T$<8.32 K, and hence the frequency corresponding to 8 K min^{-1} to have a minimum value of about 2.5 mHz. This is remarkably close to the limiting value of 4 mHz found above, and suggests that this limit is determined by the way in which the pulses are imposed.

This appears also to have an effect on the calculation of the frequency dependence of T_{mid}. The comparison of such data obtained by TOPEM with those obtained by ADSC is shown in Fig. 4. The ADSC data, shown as the open squares, display a linear dependence, from which a reduced activation energy of 160 kK is found. This compares well with the literature value of 150 kK [24]. The TOPEM data, on the other hand, not only show the marked curvature and limiting frequency mentioned above, but also yield T_{mid} values significantly larger than those from ADSC. We believe that this could result from the assignment of c_{p0} as a 'quasi-static' specific heat capacity, equivalent to $c_p(\omega)$ as $\omega \rightarrow 0$, whereas it is in fact equivalent to $c_p(\omega)$ as $\omega \rightarrow 4$ mHz.

Conclusions

TOPEM is a modulated DSC technique that permits the simultaneous evaluation of the dynamic response of a sample over a range of frequencies. This has obvious advantages in respect of simplifying data acquisition and in separating frequency-dependent phenomena from those that do not depend on frequency. However, it appears that the so-called 'quasi-static' specific heat capacity, c_{p0}, is not really equivalent to the dynamic specific heat capacity $c_p(\omega)$ as $\omega \rightarrow 0$, but in fact corresponds to a limiting frequency of about 4 mHz. It is suggested that this limit is related to the heating and cooling rates of the stochastic temperature pulses. Comparison of the frequency dependence of the dynamic glass transition as determined by TOPEM with that found by ADSC indicates differences that are attributed to the same effect.

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