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Thermal expansivity of polystyrene determined by multi-frequency dilatometry

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Abstract

Thermal expansibility and heat capacity of solids in general are linked by the first Grüneisen parameter. While the thermal expansion results from molecular motion in an anharminic potential, contribution to the heat capacity results from all kinds of motion. Similar to the temperature modulated DSC, thermal expansion can be measured by modulated temperature dilatometry (MT-DIL). One component corresponding to the reversing dilatation contributes to both the total and the modulated dimension change, while the non-reversing gives a characteristic easily distinguishable spike.

In the present work a multi-frequency temperature modulated program was applied in push-rod dilatometer to measure a coefficient of thermal expansion (CTE) of polystyrene in the temperature range up to glass transition. At the temperature just below glass transition, the frequency dependence of CTE is observed, similar to the heat capacity behavior by MT-DSC.

Keywords: Thermal expansibility; Polystyrene; Multi-frequency dilatometry

1. Introduction

Calorimetry is the standard method for characterizing glass transitions through the observation of the changes in specific heat. However, this method is limited by the fact that a slower heating or cooling rate leads to a smaller heat flow and thus a smaller signal from the calorimeter. If one would like to study glass transition kinetics over a wide range of experimental time scales, a slow measurement technique must be used. One possibility is the modulated temperature technique [1], adapted for a conventional differential scanning calorimeter (DSC) [2] (further indicated by prefix MT). The advantage of modulated temperature appears in increased sensitivity, better resolution, and improved ability to resolve overlapping transitions with extremely slow heating rate. Since the introduction of MT-DSC, numerous techniques applying modulation temperature were developed using other than a sine temperature profile and a variety of data analysis methods [3,4]. Of special interest is the multi-frequency modulation with a complex sawtooth [5], and a step-isothermal profile [6], which permit the measurement of an apparent heat capacity as a function of frequency in a single experiment. These methods have been used to explore the frequency dependence of the heat capacity in the glass transition region of polystyrene [7] (Fig. 1). At the nearly same time, modulated temperature programs have been used in thermogravimetry (TMG) [8] and thermomechanical analysis (TMA) [9,10]. While the DSC measures the change in enthalpy of a material upon the temperature program, TMA monitors the change in volume or corresponding length with temperature under controlled mechanical load. The signal strength is independent of scanning rate. One can therefore carry out experiments on long time scales. In principle, TMA

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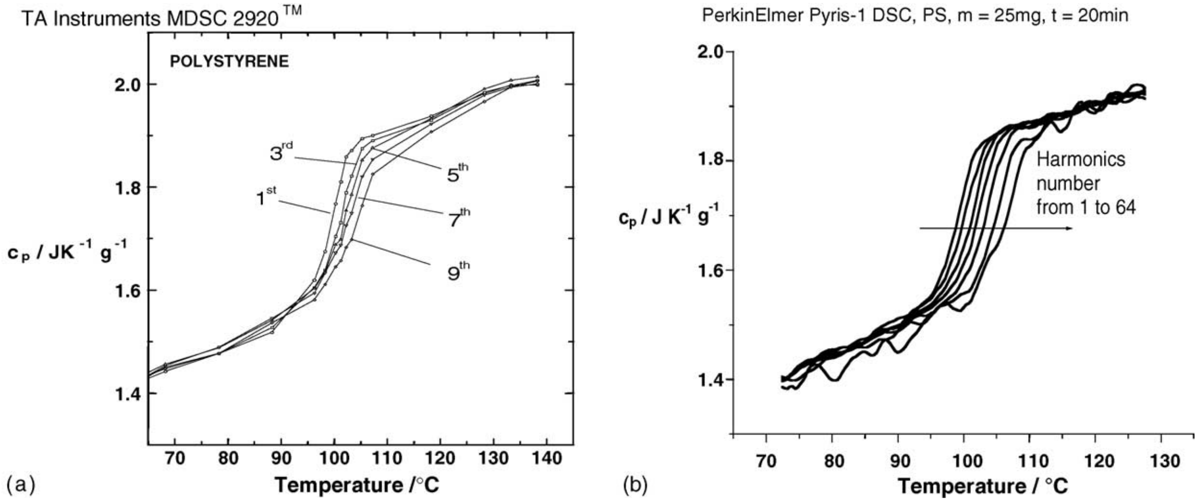

Fig. 1. Apparent specific heat capacity of PS vs. temperature in the glass transition region, plotted for different harmonics of the four-frequency sawtooth with corresponding periods: 420, 140, 84, 60, and 46.7 s (a), and for seven harmonics extracted from response on step-isothermal modulation numbered as 2^x ($0 \le x \le 6$) (from Ref. [7]).

is very close to the dilatometry (DIL). In dilatometry, the dimension of a substance is measured as a function of temperature under negligible load. For solids and liquids, volume expansion is proportional to its specific heat at constant pressure, therefore TMA and DIL are widely used as complementary methods to DSC.

As reported earlier [11], in the MT-TMA experiment the sample temperature comprises an experimental error due to physical size of the sample and heat transfer. The calibration procedure was applied [12].

In the present work, a linear coefficient of thermal expansion (CTE), α, of polystyrene was measured by push-rod dilatometer as a function of applied frequencies. To obtain true value of CTE as a function of frequency, the correction of the sample temperature is applied. The result obtained in the temperature range of the glass transition of polystyrene is compared with the same experiment carried out on CuZn alloy in the region of structural order–disorder transition.

2. Experimental

A sample was prepared from polystyrene PS 280,000 MW in the form of rod 30 mm in length and 3 mm in diameter under pressure of 30 atm at the temperature of 220 °C. After shaping the sample was cooled at a rate of 1 K/min to the ambient temperature.

A multi-frequency experiment was carried out using a home made push-rod dilatometer described elsewhere [13]. The modulated temperature profile by IR radiant heating was applied. The program consists of a linear ramp at a rate of 0.25 K/min modulated by multi-frequency heating with corresponding periods of 8, 4, 2, 1 min. A heating power was adjusted to obtain modulated temperature of the sample not higher than 2 °C. The displacement sensor was chosen with minimal tracking force from commercially available. Thus, BROWN & SHARPE TESA SA type was chosen which has tracking force from 0.3 to 0.6 N. It was experimentally found that with increasing frequency, the measured temperature

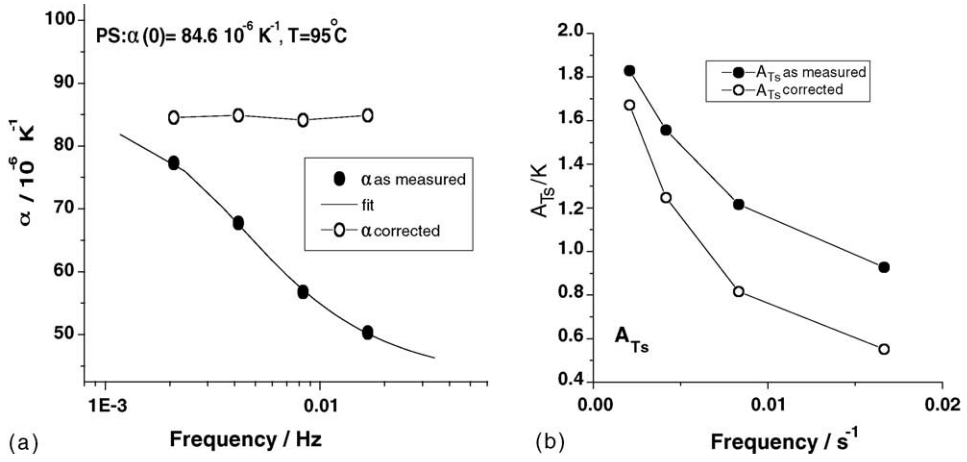

Fig. 2. Frequency correction of the coefficient of thermal expansion α (a). The measured and corrected temperature of the sample (b).

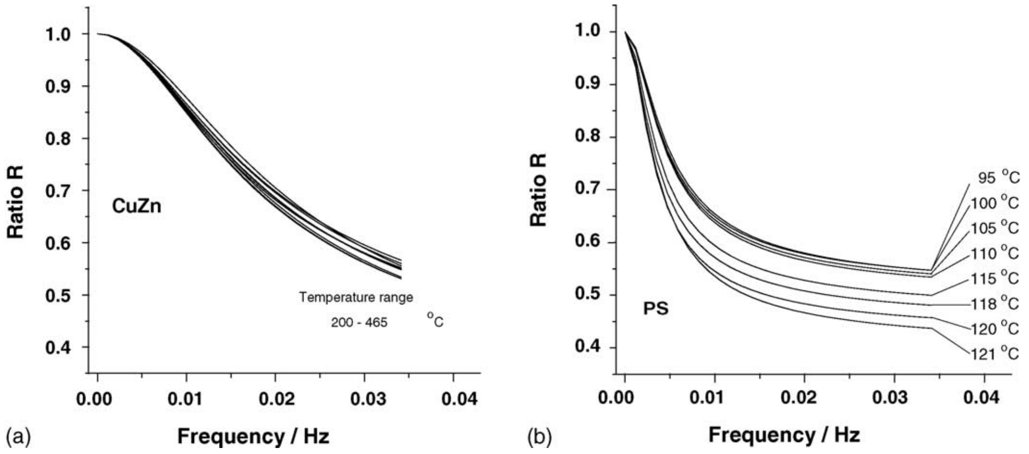

Fig. 3. The ratio $R(\omega) = A_{\mathrm{Ts}}\mathrm{corr}/A_{\mathrm{Ts}}\mathrm{meas} = \alpha(\omega)/\alpha(0)$: obtained for CuZn alloy in the temperature range of the structural order–disorder transition (a), and for polystyrene in the range of glass transition (b).

does not correspond to the true sample temperature. Considering the thermal path between the sample, thermocouple and heating source, similar to MT-TMA, it was necessary to employ the correction temperature algorithm for higher frequencies.

2.1. Temperature correction procedure

The first stage of the correction is shown in Fig. 2. The coefficient of thermal expansion, α, as measured, without correction, is obtained from the ratio $\alpha = A_{\mathrm{DIL}}/A_{\mathrm{Ts}} \cdot L_0$, where A_{Ts} and A_{DIL} denote amplitudes of modulated temperature and corresponding dilatation, respectively, and L_0 is the initial length of the sample (solid cycles in Fig. 2a). Amplitudes of the modulated temperature and corresponding dilatation at different frequencies are obtained by Fourier analysis. Then the fit to the function

$$\alpha(\omega) = \frac{\alpha(0)}{\sqrt{1+(\omega\tau)^2}} + C$$

was made to obtain "zero" frequency CTE-$\alpha(0)$ (solid line in Fig. 2a). At the temperature of 95 °C, the value of CTE, $\alpha(0) = 84.6 \times 10^{-6}\,\mathrm{K}^{-1}$ was obtained. Using this value, the measured temperature (solid cycles in Fig. 2b) was corrected by $A_{\mathrm{Ts}}\mathrm{corr} = A_{\mathrm{DIL}}/\alpha(0) \cdot L_0$, (open cycles in Fig. 2b). This procedure is valid upon assumption that dilatation of the sample is a function of temperature only, independent of frequency.

A corrected temperature, which can be taken as the real temperature, is lower than a measured one. It has been found, that a temperature of the thermocouple is higher mainly with increasing frequency, due to a thermal resistance between sample and thermocouple, and also that a thermocouple is exposed to the IR radiation.

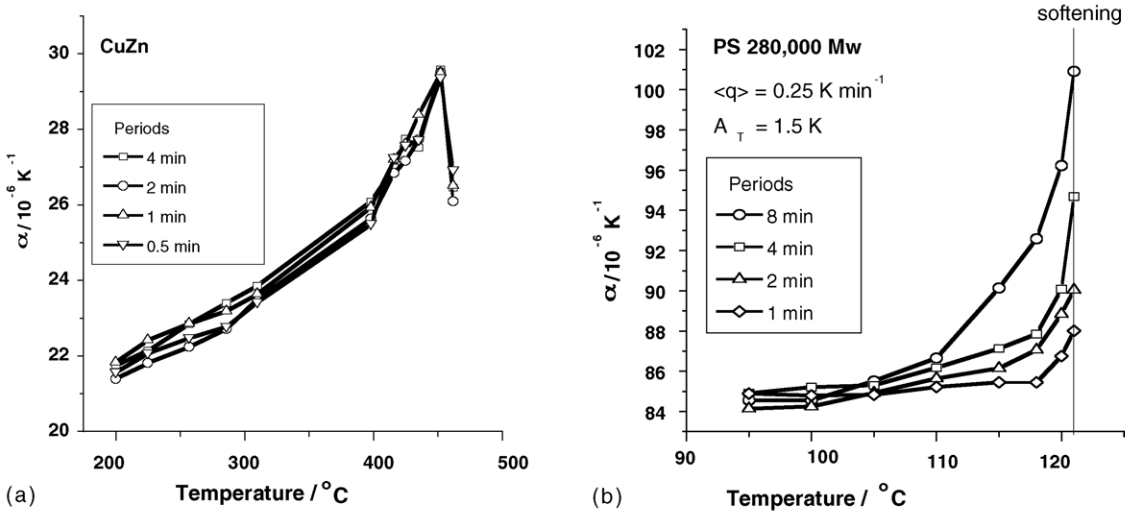

Fig. 4. The frequency dependence CTE: of CuZn alloy at the temperature range of the structural order–disorder transition obtained by the described method for periods indicated (a), of polystyrene vs. temperature in the glass transition region, plotted for four harmonics of the four-frequencies for periods indicated (b).

From the other side, it was practically found, that the ratio of a corrected, A_{Ts}corr, and measured, A_{Ts}meas, temperatures:

$$R(\omega) = \frac{A_{\mathrm{Ts}}\mathrm{corr}}{A_{\mathrm{Ts}}\mathrm{meas}} = \frac{\alpha(\omega)}{\alpha(0)}$$

can be used to characterize thermal properties of the experimental system. Thermal conditions do not change in the temperature range of interest, except the heat capacity of the sample. However, changes of the heat capacity with temperature have negligible impact in comparison with the measured temperature, and finally, on a behavior of $R(\omega)$. DTA only or heat flow can detect these changes in temperature, which have to be of two orders more sensitive than an absolute temperature measurement. One can see, that the ratio R is equal also to $\alpha(\omega)/\alpha(0)$, and may be more suitable to use for subsequent computation. This assumption of the proposed procedure was verified by experiment with a CuZn alloy, which has well known order–disorder transition at around 450 °C, with characteristic maximum of the specific heat capacity, c_p, and the coefficient, α. As we measured, the ratio, $R(\omega)$, is nearly the same in a measured temperature range for this material, and does not indicate on any transition, as it is illustrated in Fig. 3a. In contrast, the ratio function, $R(\omega)$, from experimental data of polystyrene, indicates difference between ranges below and in the glass transition (Fig. 3b). Curves, $R(\omega)$, corresponding to temperature T, equal 95, 100, 105, and 110 °C are nearly overlaid. Starting from 115 °C, curves are different with increasing frequency. This effect can be explained by anomaly of CTE for polymer only.

In the second stage of the proposed procedure, CTE is calculated from experimental data, A_{DIL}meas and A_{Ts}meas, and then are corrected by the ratio function, $R_{\mathrm{T}}(\omega)$, obtained at temperature, T, below expected transition:

$$\alpha(\omega) = \frac{A_{\mathrm{DIL}}\mathrm{meas}}{A_{\mathrm{Ts}}\mathrm{meas} \cdot R_{\mathrm{T}}(\omega) \cdot L}$$

For CuZn alloy, the ratio function was used from temperature 200 °C, $R_{200}(\omega)$. To analysis CTE of polymer, the $R_{95}(\omega)$ function was used. Results of this procedure are illustrated in Fig. 4.

3. Results

Using the above-described procedure, we have obtained a CTE at critical temperatures for the two considered materials: the first is structural order–disorder transition in CuZn alloy, and the second, a phenomenon of a glass transition in polystyrene. The result is illustrated in Fig. 4.

As it is shown, the CTE of CuZn brass is frequency independent. At the temperature of structural order–disorder transition the maximum of CTE is observed. With this transition it also maximum of heat capacity revealed by DSC is associated. Characteristic for two component alloys, this type of second order transition is characterized by short time relaxation (in the scale of the experiment time).

In contrast, a glass transition in polystyrene is the process for which an equilibrium state is reached after a long time when temperature is changing. More concisely, the process is heating-cooling rate dependent, so the transition is observed at different temperatures. As previously described [7], the apparent heat capacity of polystyrene depends on frequency. Comparing results, depicted in Fig. 3, with dilatometic experiments ones in Fig. 4b, the CTE is frequency sensitive in the same ratio as specific heat capacity obtained from MTDSC measurement – for higher frequencies the transition is observed at higher temperature. One can also see in Fig. 4b, that there are data only up to the temperature of 121 °C. Above this temperature the softening of the sample is observed. The push-rod indents into the sample and further test became impossible.

4. Conclusions

The frequency-dependent of the thermal expansivity of polystyrene in the temperature region of the glass transition is observed. The result is in agreement with obtained previously by MT-TMA. The correction procedure of the measured temperature eliminates instrumental effects and the observation of kinetic phenomena of the glass transition in polystyrene by DIL measurement is possible.

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