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Thermochimica Acta 432 (2005) 212–215

thermochimica acta

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Simultaneous measurement of thermal expansion and heat capacity using temperature modulation technique

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Received 19 October 2004; received in revised form 11 April 2005; accepted 12 April 2005

Abstract

An instrument for simultaneous measurement of thermal expansion and heat capacity was developed using temperature modulation technique. The instrument was designed for thin films in order to avoid temperature distribution in the sample. Electric capacitance was measured to obtain temperature dependence of the sample thickness. The instrument was applied to the glass transition of polystyrene and it was confirmed that reliable comparison between the dilatometric and calorimetric results could be made.

Keywords: Simultaneous measurement; Dilatometry; Calorimetry; Temperature modulation; Glass transition; Polystyrene

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1. Introduction

It is widely recognized that simultaneous measurement is very important for reliable comparison of the results from different types of experiments. Particularly in the case of polymeric materials, simultaneous measurement is essential not only for measurement under the same condition but also for the same thermal history. In this work, an instrument for simultaneous measurement of the thermal expansion and the heat capacity of the polymer film was developed. It is aimed to apply this instrument to glass transition of polymers. Both the thermal expansion coefficient and the heat-capacity exhibit characteristic changes around the glass transition temperature. Detailed and reliable comparison of those thermodynamic quantities will provide useful information for both the basic studies to construct a proper model for the glass transition and the practical technology to produce high performance materials with critically controlled processing.

We used the temperature modulation technique in the instrument. The temperature modulation technique has been utilized in various types of instruments [1]. Temperature modulated differential scanning calorimeter (TM-DSC) is the most widely used instrument [2–4]. Many authors using TM-DSC have pointed out the benefits of the temperature modulation technique, such as separation of the heat flow to the reversing and non-reversing components [5,6], kinetic information obtained from the complex heat capacity [7–9], and time-dependent measurement in the quasi-isothermal mode [10]. The instrument developed in this work provides these benefits as well as TM-DSC.

For the temperature modulation, particularly at high frequencies, the sample has to be thin to avoid temperature distribution. In order to measure the volume change of the thin sample we employed a method to measure the electric capacitance, which depends on the sample thickness, instead of direct measurement of the volume. This method has been used in the studies of glass transition [11,12].

2. Experimental

Atactic polystyrene (at-PS) ($\mathrm{Mw} = 2.8 \times 10^5$) was used as the sample. Pellets of at-PS were pressed on a hot plate to form a disk of 1.5 mm thickness. The disk was further pressed between two glass plates at 230 °C for 12 h in a vacuum chamber. The final film of 70 μm thickness was used as the sample.

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doi:10.1016/j.tca.2005.04.008

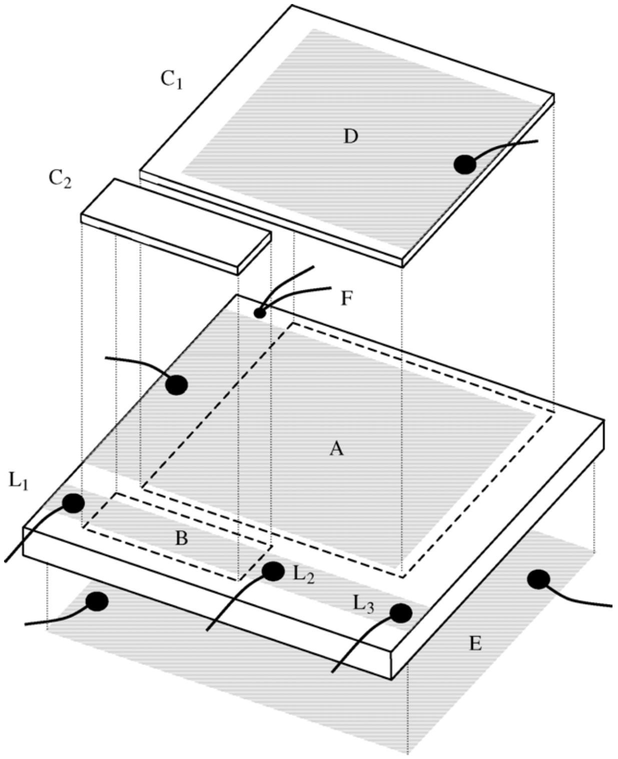

Fig. 1. Structure of the detector for the dilatometry and calorimetry measurement. The base plate is a cover glass for the optical microscope. A: aluminum film; B: copper film; C$_1$ and C$_2$: at-PS films; D: aluminum film; E: copper film; F: thermocouple. Black circles show the connecting points of the lead wires.

Fig. 1 shows the structure of the detector containing the sample. A cover glass for the optical microscope (40 mm × 50 mm, 0.15 mm thick) was used as the base plate. Aluminum film A of 150 nm thickness and copper film B of 250 nm thickness were made by vacuum deposition on the top surface of the base plate. A and B were used as the lower electrode for electric capacitance measurement and temperature detector for calorimetry, respectively. Temperature change was detected as the change in the electric resistance of the copper film. The sample films C$_1$ and C$_2$ cut from the same sheet were put on A and B, respectively. The detector with the films was kept at 150 °C for 8 h in the vacuum chamber to make the films be in good contact with A and B. Then aluminum film D of 150 nm thickness was made by vacuum deposition on the top surface of C$_1$ as the upper electrode for the electric capacitance measurement. The effective area of the capacitor was 600 mm^2. On the bottom surface of the base plate, copper film E of 150 nm thickness was vacuum deposited as the heater for temperature modulation. Black circles show the points where electric lead wires were connected. Temperature of the sample (temperature averaged over one modulation period) was measured by the thermocouple F. The sensor between L$_1$ and L$_2$ was covered by the sample. Measurement of the resistance change of the part L$_1$–L$_2$ can be regarded as ac calorimetry with finite heat drain to the surroundings. On the other hand, measurement of difference between resistance change of the copper films L$_1$–L$_2$ and L$_2$–L$_3$ can work as differential type measurement.

The electric capacitance was measured by an impedance analyzer (HP4294). Frequency of the electric field was 100 kHz, which was sufficiently high to avoid non-negligible effects from dispersion phenomena. Assuming that change in the area of the electrodes with temperature is negligible the next equation is obtained.

$$\frac{1}{C_{\mathrm{el}}}\frac{\partial C_{\mathrm{el}}}{\partial T} = \frac{1}{L}\frac{\partial L}{\partial T} = -(1+3\eta_0)\alpha_{\mathrm{L}} \tag{1}$$

where C_{el}, T, L and α_{L} are the electric capacitance, temperature, thickness of the sample and the linear thermal expansion coefficient, respectively. η_0 is the coefficient derived from the Clausius–Mossoti's relation.

$$\eta_0 = \frac{(\varepsilon_\infty + 2)(\varepsilon_\infty - 1)}{3\varepsilon_\infty} \tag{2}$$

where ε_∞ is the dielectric coefficient at a frequency much higher than the dispersion frequency of the sample. Since η_0 of polystyrene is estimated to be 1.0 using the value $\varepsilon_\infty = 2.8$ at frequencies higher than 1 kHz [13] $(1+3\eta_0)$ of Eq. (1) is estimated to be 4.0. The literature value for the linear expansion coefficient at temperature higher than the glass transition region was $2.0 \times 10^{-4}\,\mathrm{K}^{-1}$ [14]. Experimentally, we obtained $9.0 \times 10^{-4}\,\mathrm{K}^{-1}$ for the value of $\frac{1}{C_{\mathrm{el}}}\frac{\partial C_{\mathrm{el}}}{\partial T}$, the left-hand side of Eq. (1) at temperatures lower than the glass transition region as will be shown below. From these values $(1+3\eta_0)$ is estimated to be 4.5, which is close to the value calculated from the value of η_0. Therefore, we used Eq. (1) with $\eta_0 = 1.0$ to calculate the linear expansion coefficient from the electric capacitance. Since time-dependent temperature profile is used, it is convenient to rewrite Eq. (1) as the next equation.

$$\frac{1}{C_{\mathrm{el}}}\frac{\partial C_{\mathrm{el}}/\partial t}{\partial T/\partial t} = -(1+3\eta_0)\alpha_{\mathrm{L}} \tag{3}$$

For the steady heating, Eq. (3) gives *total* linear expansion coefficient corresponding to the total heat flow divided by the underlying heating rate in TM-DSC. For the cyclic temperature profile, Eq. (3) gives the complex linear expansion coefficient.

The detector was placed in a cell whose temperature was controlled linearly with time. Preliminary measurement was made between 60 °C and 120 °C with the underlying heating rate of 0.5 K/min and the modulation period of 10 s. The amplitude of the temperature modulation was 0.6 K at the room temperature, but it slightly decreased with increasing temperature because the amplitude of the output voltage of the power supplier for the modulation heater was fixed.

3. Results and discussion

Fig. 2 shows the raw data of the electric capacitance on the heating process plotted against time (lower axis) and temperature (upper axis). The curve is broadened in the vertical

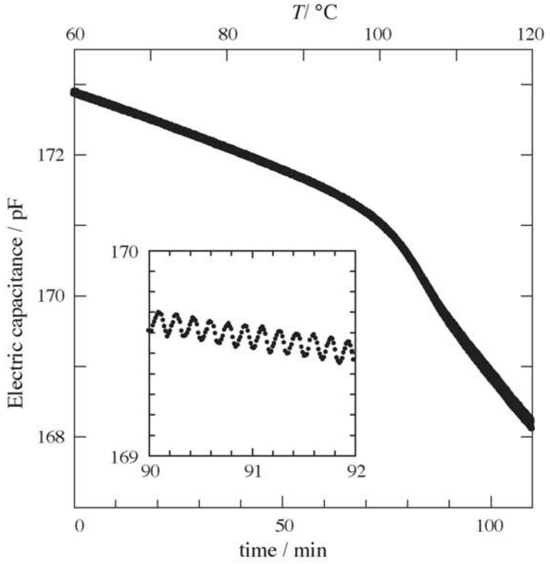

Fig. 2. Raw data of the electric capacitance on the heating process. An extension of the time range between 90 min and 92 min is inserted in the graph.

direction because of the response to the temperature modulation as can be seen in the inserted extension. The electric capacitance averaged over one modulation period decreased almost linearly to temperature up to ca. 90 °C. Then, the slope became steeper with increasing temperature from 90 °C to 110 °C, which corresponds to the glass transition. At temperatures higher than 110 °C, the electric capacitance decreased linearly again but more quickly. It can be seen that the amplitude of the capacitance modulation was larger at $T > T_g$ than $T < T_g$. These behaviors were consistent with temperature dependence of the volume around T_g. The extended figure exhibits that the electric capacitance changed sinusoidally with time at the modulation period. Judging from these results, it can be said that the thermal expansion could be measured successfully by the instrument developed in this work.

Fig. 3 shows temperature dependence of the total linear expansion coefficient $\bar{\alpha}_L$. Stepwise change in $\bar{\alpha}_L$ was observed in both the heating and cooling processes. The value of 6.0×10^{-5} at $T < T_g$ agreed well with the literature value [14]. The curve of the heating process exhibited a peak just above T_g. This peak can be attributed to the volume recovery after irreversible volume relaxation at $T < T_g$. Calorimetric results were not good enough to be compared with the results of Fig. 3 possibly because heat capacity change at T_g is much smaller than that of the linear expansion coefficient. Fig. 4 shows temperature dependence of the absolute value of the complex linear expansion coefficient α_L^* (thick curve) and the complex heat capacity C^* (thin curve) measured simultaneously with each other. The results are scaled by the amount of the step-like change at the glass transition temperature and the value at $T < T_g$ are subtracted. α_L^* and C^* traces agreed well with each other in both the heating and cooling processes. Signal to noise ratio was better in α_L^*. The peak of the volume recovery was not observed in the complex linear expansion coefficient as expected. This shows that the separation of the total linear expansion coefficient to the reversing and non-reversing linear expansion coefficient will be possible similarly to TM-DSC measurement. In Fig. 4, the heating traces are not identical with the cooling traces. This suggests that the relaxation effects during cooling and heating below T_g were not negligible being consistent with the results of Fig. 3.

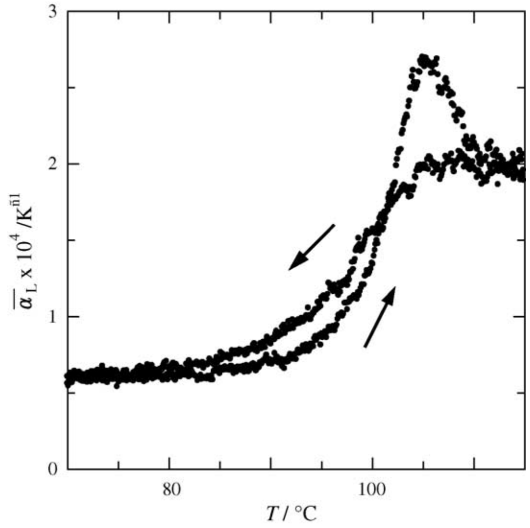

Fig. 3. Temperature dependence of the total linear expansion coefficient $\bar{\alpha}_L$.

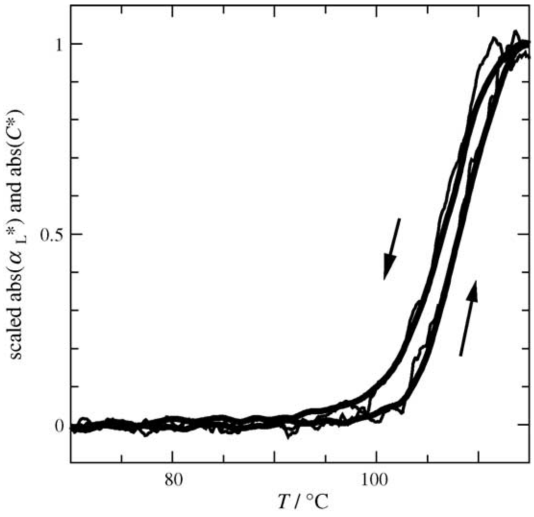

Fig. 4. Temperature dependence of the absolute value of the complex linear expansion coefficient α_L^* (thick curves) and the complex heat capacity C^* (thin curves).

4. Conclusion

An instrument for simultaneous measurement of the dilatometry and the calorimetry was developed. The linear expansion coefficient was calculated from the results of electric capacitance measurement. The linear expansion coefficient was successfully obtained and comparison with the results from the simultaneous calorimetric measurement could be made reliably. It is aimed to apply this new instrument to detailed comparison of thermal history dependence of the linear expansion coefficient and the heat capacity.

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