

# Aging effects on the thermal expansion coefficient and the heat capacity of glassy polystyrene studied with simultaneous measurement using temperature modulation technique

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## Abstract

Aging effects on the glassy polystyrene were studied with simultaneous measurement of the complex thermal expansion coefficient and the complex heat capacity. Aging period was changed from 10 to 100 h at 90 °C. It was found that the stepwise change in the real part of the complex thermal expansion coefficient and the peak of the imaginary part occurred at lower temperature than those of the complex heat capacity in all cases. As the aging period increased the stepwise change in the real part shifted to the higher temperature and sharpened. A qualitative model based on the energy landscape picture is proposed.

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*Keywords:* Thermal expansion coefficient; Heat capacity; Simultaneous measurement; Temperature modulation technique

## 1. Introduction

Aging of glassy materials just below the glass transition temperature has been studied extensively [1]. Aging effects appear as change in temperature dependence of material properties such as volume, thermal expansion coefficient, heat capacity, dielectric coefficient and so on. Temperature dependence of these properties changes with the aging condition such as temperature and time. Comparison of the aging effects on different properties will provide useful information to understand the aging phenomena and the slow dynamics characterizing the glass transition. However, reliable comparison is often difficult because the material properties are sensitive to the thermal history. If two kinds of properties are measured independently non-negligible difference in the aging condition and/or the heating/cooling rate before and after the aging are difficult to be avoided. Such difference in the experimental condition makes the comparison less reliable.

In order to solve this problem an instrument for simultaneous measurement of the thermal expansion coefficient and the heat capacity has been developed in the authors' laboratory [2]. Since this instrument uses the temperature modulation technique it will be called temperature modulated expansion and

heat capacity (Ex-HC) meter below. A simultaneous measurement of the thermal expansion coefficient, the heat capacity and the compressibility has been carried out by Takahara et al. [3]. They used an adiabatic type instrument. The adiabatic technique and the temperature modulation technique are complementary to each other. Our study is aimed to investigate the aging effects. As mentioned above the heating and cooling processes as well as the isothermal aging can affect the sample properties. In order to minimize the effects from the heating and cooling processes the heating and cooling rate should be high. The temperature modulation technique is more suitable to achieve the high heating/cooling rate than the adiabatic technique because the sample dimension of our instrument is much smaller than that of the adiabatic instrument.

The temperature modulated Ex-HC meter provides the complex thermal expansion coefficient and the complex heat capacity. The complex heat capacity has been measured with the temperature modulated differential scanning calorimeter (TMDSC) in the studies of the melting [4], the crystallization [5] and the glass transition [6,7] of polymers. The complex thermal expansion coefficient  $\alpha^*$  is defined similarly to the complex heat capacity as given by the next equation.

$$\alpha^* = \frac{1}{V} \frac{A_V}{A_T} \quad (1)$$

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where  $V$  is the volume of the sample.  $A_V$  and  $A_T$  are the complex amplitude of the sinusoidal modulation of the volume and the temperature, respectively. In this work the thickness of the sample was measured with the capacitive dilatometry which is a technique to evaluate the sample thickness from the electric capacitance [8,9]. Thermal expansion coefficient has been measured with temperature modulation by Price using TMA [10–12] and by Kamasa et al. using an instrument for a rod shaped sample [13–16]. Since the capacitive dilatometry can measure the thickness change of a thin sample it fits the temperature modulation technique particularly at high frequencies.

## 2. Experimental

The sample was atactic polystyrene (at-PS) of  $M_w = 2.8 \times 10^5$ . Pellets of at-PS were heated in air on a hot plate and pressed just after passing the glass transition temperature to form a disk of 1.5 mm thickness in less than 10 s. The disk was further pressed at 230 °C between two glass plates for 12 h in a vacuum chamber. The final film of 66  $\mu\text{m}$  thickness was used as the sample.

The design of the detector was modified from the previous one [2] as shown in Fig. 1. A glass plate of 0.15 mm thickness was used as the base plate. A and B are the samples cut from the same sheet. C and D are aluminum films of 150 nm thickness made with vacuum deposition on the top surface of the base plate. C and D are the detector for the calorimetry and the lower electrode for the electric capacitance measurement, respectively. A and B were put on C and D, respectively, and the detector was kept at

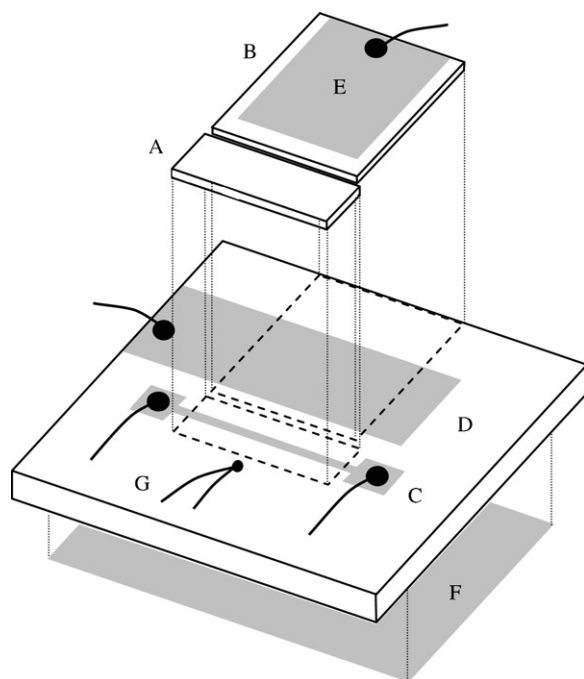


Fig. 1. A diagram of the sample and the detector. (A, B) samples for the calorimetry and the capacitive dilatometry, respectively, (C) thermometer for the temperature modulation, (D, E) the lower and the upper electrode for capacitance measurement, respectively, (F) heater for the temperature modulation, (G) thermocouple.

150 °C for 8 h in the vacuum chamber to make the samples be in good contact with the aluminum films. Then aluminum film E of 150 nm thickness was made by vacuum deposition on the top surface of B as the upper electrode for the electric capacitance measurement. The effective area of the capacitor was 450 mm<sup>2</sup>. On the bottom surface of the base plate, aluminum film F of 150 nm thickness was vacuum deposited as the heater for the temperature modulation. Black circles show the points where electric lead wires were connected. The thermocouple G was used to measure the temperature averaged over one modulation period. The detector was placed in a cell whose temperature was controlled linearly with time. The temperature on the sample surface of the previous detector was not sufficiently uniform for detailed comparison of the thermal expansion coefficient and the heat capacity. In the present instrument the temperature distribution was within  $\pm 0.2$  K which was achieved with making the area of the samples smaller and optimizing the geometric arrangement on the base plate.

The electric capacitance was measured with an impedance analyzer (HP4294). Frequency of the electric field was 100 kHz, which was sufficiently high to avoid non-negligible effects from dispersion phenomena. The method to calculate the sample thickness from the electric capacitance was described in reference [1]. The thermal expansion coefficient attributed to the linear heating, which will be called total thermal expansion coefficient below, was calculated from the volume averaged over one modulation period and the temperature measured with the thermocouple G. The complex thermal expansion coefficient was calculated from the complex amplitude of the periodic change of the thickness and the complex amplitude of the temperature modulation measured with the detector C.

The complex heat capacity was calculated as follows. Assuming that the heat drain from the sample surface to the air is proportional to the sample temperature the next mathematical model was obtained.

$$C^* \frac{dT_{ac}}{dt} = K_h P - K_d T_{ac} \quad (2)$$

where  $C^*$ ,  $T_{ac}$ ,  $t$  and  $P$  are the complex heat capacity of the sample, the periodic component of the temperature, time and the periodic component of the power of the heater F in Fig. 1, respectively.  $K_h$  and  $K_d$  are coefficients of correction for the heater power and the heat drain.  $P$  was calculated from the voltage of the power supplier and the electric current passing the heater. Correction with  $K_h$  was necessary because the power supplied to the sample was not exactly equal to  $P$  because of the heat diffusion through the base plate. It was assumed that  $C^* = C_{liq}^* + C_{gl}^*$  where  $C_{liq}^*$  was the liquid component or the configurational component and  $C_{gl}^*$  was the glass component. Eq. (2) became

$$C_{liq}^* = |K_h| \left( \frac{\exp(i\theta_h) P}{i\omega T_{ac}} - \frac{i\omega C_{gl}^* + K_d}{i\omega |K_h|} \right) \quad (3)$$

where  $\theta_h$  is the phase of  $K_h$ . It was further assumed that the second term in the parentheses could be expressed by a linear

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