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Development of the light heating dynamic DSC¹

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Abstract

The dynamic DSC is a recently developed technique for simultaneous measurement of DSC and AC calorimetry (ACC). Thermal information which cannot be obtained by DSC or ACC alone can be obtained by comparing the results of DSC and ACC. Commercial apparatus are not always suitable for such comparison because of the low frequency and the large amplitude of the sinusoidal modulation. In this study the light heating technique used in ACC was employed to generate the sinusoidal modulation. The frequency and the amplitude achieved were, respectively, ten times and one-tenth those of the commercial apparatus. Results obtained from polyethylene by light heating dynamic DSC are presented.

Keywords: DSC; ACC; Dynamic DSC; Light heating; Sinusoidal modulation

1. Introduction

Dynamic DSC (DDSC) is a recently developed technique for simultaneous measurement of DSC and AC calorimetry (ACC). The benefits of the new technique have been reported [1–3]. It has been recognized that the results of DSC and ACC are not identical in the temperature range of phase transitions [4,5], glass transitions [6] etc. This suggests that comparison of the results of DSC and ACC will provide information about these phenomena which cannot be obtained from DSC or ACC alone. For an accurate comparison, the states of the samples of DSC and ACC measurements must be identical. This requires simultaneous measurement of DSC and ACC.

The DDSC apparatus is commercially available. This commercial DDSC apparatus provides an easy way to use the new and powerful technique of thermal analysis. How-

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ever, the commercial apparatus has some limitations attributed to the method to add the capability of ACC to the conventional DSC apparatus. In this report we first consider the limitations of the commercial apparatus. Then a new type of the DDSC apparatus is introduced and the results obtained are explained.

2. Limitations of the commercial apparatus

The commercial apparatus uses the hardware of the conventional heat flux type DSC as it is sold. The control software of the heat bath temperature T_b is modified to generate the temperature profile $T_b = at + T_0 \sin(2\pi\nu t)$ [1–3], where the first term on the right hand side is the same as the steady heating of conventional DSC along with time t at a heating rate a . The second term is superimposed for ACC; T_0 and ν are the amplitude and frequency of the sinusoidal temperature profile, respectively. Since the size of the sample chamber is large, the sinusoidal component of the temperature profile has low frequency (ca. 0.01 Hz) and large amplitude (ca. 1 K).

The DSC and ACC results are obtained by calculating the average and Fourier component of the frequency ν of the output of DDSC, respectively. Such calculations contain an integral over a time range t_i equal to a multiple of $1/\nu$. The temperature of the sample moves within a temperature range ΔT during the time range of the integral. The calculated DSC and ACC results are taken as the values at the average temperature over the integral time. Thus the temperature dependence of the calculated DSC and ACC results are smeared by ΔT . ΔT becomes larger with t_i and T_0 . The low frequency and large am-

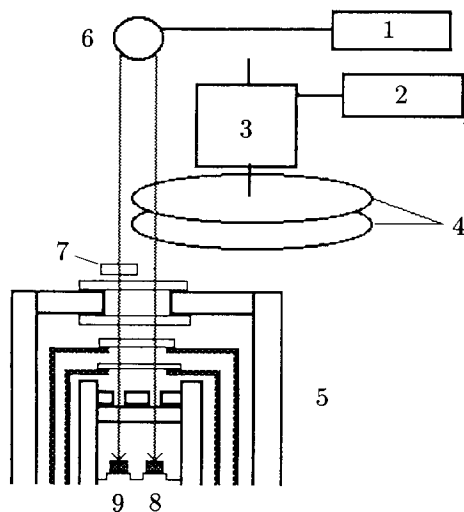


Fig. 1. A diagram of the light heating system. 1, stabilized power supply; 2, pulse generator; 3, stepping motor; 4, polarizers; 5, sample chamber; 6, light source; 7, light intensity attenuator; 8, sample; 9, reference material.

plitude of the sinusoidal component of T_b result in a large ΔT , that is, significant smearing effects. This is the main limitation of the commercial DDSC apparatus.

3. Experimental

In order to overcome the limitations of the commercial DDSC apparatus we combined the light heating system used in ACC to a heat flux type DSC, Rigaku DSC 8230. The light heating system is shown in Fig. 1. The light from the light source passes through the intensity modulators composed of two polarizers; one is rotating and the other is fixed. The modulated light is incident only to the sample and the light of a constant intensity is incident to the reference material for temperature balance. A distinctive feature of this method is the direct sinusoidal heat flow to the sample without heat conduction in the sample chamber. The direct sinusoidal heat flow enables high frequency and small amplitude of the sinusoidal modulation. According to the modes of the sinusoidal modulation our apparatus and the commercial one may be called direct modulation type and heat bath modulation type, respectively.

A diagram of the whole system of our light heating DDSC is shown in Fig. 2. The output signal from the DSC apparatus surrounded by broken lines in Fig. 2 is read by a personal computer with the temperature data. The output signal before the average and Fourier integral is shown in Fig. 3 which shows the data obtained around the melting transition of polyethylene. The frequency of the light heating and the heating rate of the sample chamber were 0.25 Hz and 1°C min^{-1} , respectively. The amplitude of the sinusoidal temperature modulation was less than 0.1°C . The frequency and amplitude arc, respectively, much higher and smaller than those of the commercial apparatus.

The average and Fourier integral calculations were carried out by the personal computer in the following way. The average of the observed signal over two heating periods was calculated. The average values, called the DC component in the following, agree with the DSC results. The ACC signal was obtained by subtracting the DC component

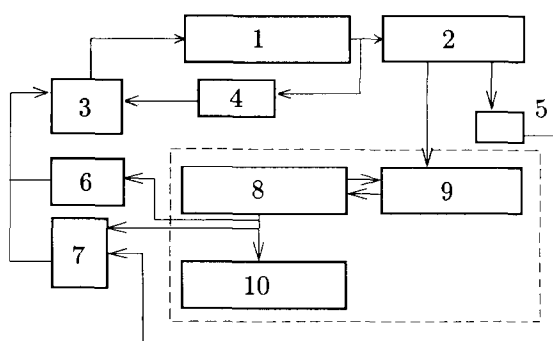


Fig. 2. A diagram of the light heating DDSC. 1, pulse generator; 2, light heating system; 3, personal computer; 4, frequency divider; 5, reference detector for the modulated light; 6, digital V meter; 7, data logger; 8, DSC controller; 9, DSC furnace; 10, pen recorder. The DSC apparatus is surrounded by broken lines.

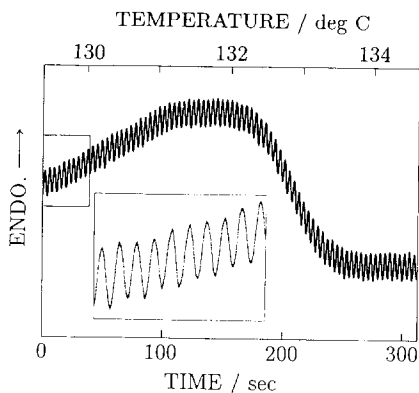


Fig. 3. Output signal from the DSC apparatus obtained around the melting transition of polyethylene. The frequency of the modulation and the heating rate of the sample chamber are 0.25 Hz and $1^{\circ}\text{C min}^{-1}$, respectively. The part in the box is expanded.

from the observed signal; actually the curve obtained by spline approximation to the calculated DC component was subtracted. The Fourier integral of the ACC signal was calculated and the inverse of the value obtained was regarded as the ACC result. The ACC result is called the AC component in the following. It should be noted that the AC component is expressed by a complex number having amplitude and phase angle.

A preliminary measurement was made for a laminated sample of polyethylene and polystyrene films. Polystyrene was used to determine the fitting parameters for the DC component and the amplitude of the AC component as described in the next section. A polyethylene film, $30\ \mu\text{m}$ thick, was laminated on a polystyrene film, $150\ \mu\text{m}$ thick, with a polyimide film, $8\ \mu\text{m}$ thick, between the polyethylene and polystyrene films to avoid mixing of the two materials. The upper surface of the polyethylene film and the lower surface of the polystyrene film were covered with the polyimide films. The top surface of the whole sample was covered with carbon powder for light absorption. Before starting the measurement, the sample was heated to 200°C for 10 min. Then the sample was cooled down to the starting temperature by $-1^{\circ}\text{C min}^{-1}$. The frequency of the sinusoidal modulation was 0.25 Hz and heating rate of the sample chamber was $1^{\circ}\text{C min}^{-1}$.

4. Results and discussion

Fig. 4 shows the result obtained from the laminated sample in the heating process. Fig. 4a shows the whole temperature range measured and Fig. 4b shows the details around the melting temperature of polyethylene. In Fig. 4 the DC component, the amplitude and phase angle of the AC component are shown with solid circles, open circles and open triangles, respectively. The values of the DC component calculated using the method in the previous section were not suitable for comparison with the amplitude of the AC component because of the slope of the base line of the DC component and disagreement be-

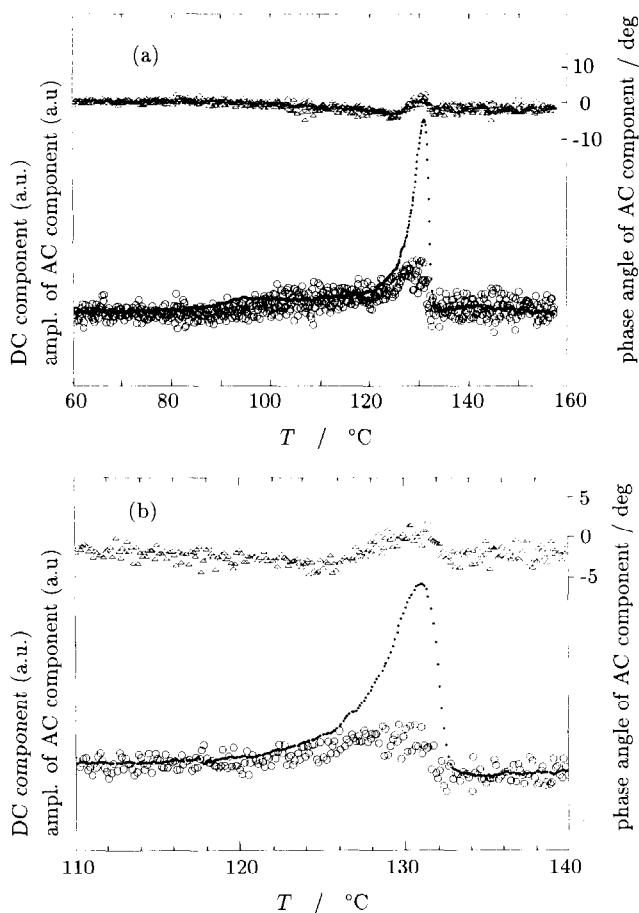


Fig. 4. Results obtained from the laminated sample of polyethylene and polystyrene. The frequency of the modulation and the heating rate of the sample chamber are 0.25 Hz and $1^{\circ}\text{C min}^{-1}$, respectively. (a) Shows the whole temperature range measured and (b) shows details around the melting temperature of polyethylene. In both figures solid circles, open circles and open triangles are the DC component, the amplitude of the AC component and the phase angle of the AC component, respectively.

tween the scale factors of the DC component and the amplitude of the AC component. In Fig. 4 the DC component was plotted after the following correction for good comparison.

$$\text{DC}_{\text{corr}}(T) = p \left(\text{DC}(T) - \frac{(T_2 - T)\text{DC}(T_1) + (T - T_1)\text{DC}(T_2)}{T_2 - T_1} \right) + \frac{(T_2 - T)|\text{AC}|(T_1) + (T - T_1)|\text{AC}|(T_2)}{T_2 - T_1}$$

where $DC_{\text{cor}}(T)$ and $DC(T)$ are the corrected and uncorrected values of the DC component at temperature T , respectively. T_1 and T_2 are the observed temperatures averaged over the ranges lower than 70°C and higher than 140°C, respectively. $DC(T_n)$ and $|AC|(T_n)$ ($n = 1$ or 2) are the averaged values of $DC(T)$ and the amplitude of the AC component over the temperature range corresponding to T_n , respectively. The parameter p is for the correction of the scale factor. The value of p was determined to fit the corrected DC component to the amplitude of the AC component between 105°C and 115°C. If the values of $DC(T)$ in this temperature range were close to the values of the second term on the right-hand side of the above equation the value of p could not be determined successfully. The second term on the right-hand side of the above equation expresses a linear change from $DC(T_1)$ to $DC(T_2)$. Polystyrene was used to make a step like increase of the DC component at the glass transition temperature to avoid the linear change of $DC(T)$.

In the following, results which cannot be obtained by DSC alone are explained. The DC component increases gradually towards the melting peak. One cannot determine only from the DC component whether the increase is due to the latent heat of melting or increase of the heat capacity. Since the amplitude of the AC component increases with the DC component up to 124°C we can say that the increase up to 124°C is due to the increase of the heat capacity. The DC component and the amplitude of the AC component do not agree with each other between 124°C and 133°C. An ACC study of the first order phase transition [4] showed that the contribution of the latent heat became smaller as the frequency of the sinusoidal heating became larger. This suggests that the melting transition occurs between 124°C and 133°C. The phase angle of the AC component decreases towards 124°C. This shift of the phase angle corresponds to the shift of the phase angle at a dispersion frequency of DMA measurement, that is, the correlation time of the motion responsible for the increase of the heat capacity is of the order of 4 s, the period of the sinusoidal modulation. Behavior of the phase angle in the melting transition region is different from that in other temperature regions. It is necessary to take account of the temperature distribution in the sample to explain the behavior of the phase angle in this temperature range.

If the frequency of the sinusoidal modulation is high enough, the contribution of the latent heat at phase transition temperatures will be completely excluded from both the amplitude and the phase angle of the AC component [4]. Although it was not checked whether 0.25 Hz is high enough in this case, the large difference between the DC component and the amplitude of the AC component suggests that the contribution of the latent heat is rather small. The temperature dependence of the difference between the DC component and the amplitude of the AC component gives the distribution profile of the melting points of the polyethylene crystals. Such a profile of the melting point distribution may be obtained by the commercial apparatus if the frequency of the sinusoidal modulation of the commercial apparatus is high enough. However, it will not be satisfactory because of the large smearing effects.

In some reports it has been pointed out that the curve of the temperature modulation at the phase transition temperatures is significantly distorted from the sinusoidal curve [8–10]. However, in Fig. 3 the temperature modulation in the melting transition region is not distorted. In the case of Fig. 3 the amplitude of the temperature modulation is much

smaller than the width of the distribution of the melting point. This is essentially different from the cases of very sharp distribution of the melting point as metals and the large amplitude of the temperature modulation of the commercial apparatus.

Our measurement is still qualitative at the present stage. Quantitative measurement will be reported in a future paper with an improved apparatus. Differential measurement of the AC component will be carried out with the improved apparatus. Quantitative measurements have been reported using the commercial apparatus. However, it should be noted that the phase angle of the complex heat capacity is a new quantity and there is no standard materials for calibration of the apparatus. As explained above, the phase angle gives useful information on the correlation time of the motion in the sample. Standardization of the phase angle is required for future DDSC studies. To use standard materials, machine constants have to be determined. The light heating DDSC has a simple thermal system compared with the commercial apparatus. The light heating DDSC will be calibrated easily for quantitative measurement of the phase angle.

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