

THERMAL ANALYSIS OF POLYMER SAMPLES BY THE ROUND ROBIN METHOD. PART III. HEAT CAPACITY MEASUREMENT BY DSC

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ABSTRACT

The results of the round robin test (RRT) on the heat capacity (C_p) measurement by differential scanning calorimetry were analysed. The C_p of polystyrene sheet was measured at around the glass transition temperature region (from 335 to 395 K). Five organizations participated and three kinds of apparatuses were used, namely three power-compensation DSCs and two different kinds of heat-flux DSCs (quantitative DTAs). The experimental procedure was followed precisely before the DSC measurement was performed. The results obtained in each of the five organizations were within 3% deviation of the mean values in the whole temperature range. It was noted that the results obtained by power-compensation DSC corresponded well with those obtained by heat-flux DSC. It was found that the sample weight affected the C_p values.

INTRODUCTION

In previous studies [1–3], we reported the results of the round robin test (RRT) of polymers concerning the transition temperatures [1,3] and the heats of transitions [2]. The RRT participants and almost all the organizations that contributed to the results were familiar with the above measurements [1–3]. However, although heat capacity (C_p) measurement by differential scanning calorimetry (DSC) is as an established technique [4–8] in various fields of scientific research [9–13], only five organizations reported the result of C_p measurement in the RRT. This fact suggested that this method may not be widely accepted as a standard application of thermal analysis.

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In the RRT of the thermal analysis of polymers [1–3], C_p measurement of polystyrene film was one of the objectives, as the thermal analysis survey suggested a widespread demand for C_p data [3]. The results obtained from the RRT indicated the reliability of this method and we can expect future applications in various fields.

EXPERIMENTAL

Sample

Polystyrene (high impact type) sheet was used. The sample was the same as reported previously [1–3].

Apparatus

The apparatus used in the above C_p measurement consisted of 3 power-compensation differential scanning calorimeters (DSCs) and 2 heat-flux DSCs (quantitatively differential thermal analysers (q-DTAs), made by two different companies.

Procedure

It was recommended that the participants of the RRT carry out the following procedure:

1. Choose a pair of aluminum sample containers having similar weight.
2. Set the apparatus at the initial temperature of 335 K (T_i) and at the end temperature of 395 K (T_e).
3. Maintain T_i for 1 min and obtain the straight line I as shown in Fig. 1.
4. Scan at the heating rate of 5 or 10 K min⁻¹ and obtain curve II shown as in Fig. 1.

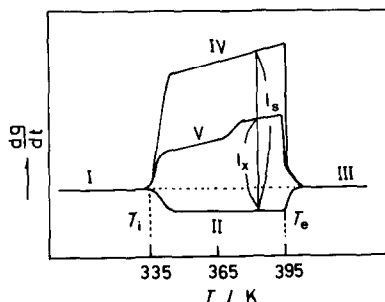


Fig. 1. Schematic DSC curves for C_p calculation.

5. Maintain at T_e for 1 min and obtain the straight line III as shown in Fig. 1.
 6. Adjust the slope controller of the apparatus in order that line I meets line III on the same line as shown in Fig. 1.
 7. If (6) is not attained, adjust again until condition 6 is satisfied.
 8. Once the above conditions have been satisfied, they should be maintained.
 9. Weigh 10–30 mg of the synthetic material, Al_2O_3 (standard sapphire) with a precision of 0.01 mg.
 10. Scan (curve IV).
 11. Weigh the sample (approximately 10 mg) with a precision of 0.01 mg.
 12. In order to eliminate the thermal history of the sample, heat the sample at rate of 20 K min^{-1} to 395 K and maintain this temperature for 10 min. Then cool the sample at rate of 20 K min^{-1} to 335 K and maintain for 10 min (this procedure is the same as that used in the glass transition measurement [1]).
 13. Measure the sample under the same conditions as (10) (curve V).
 14. If the three curves II, IV and V are not in accordance at T_i and T_e , adjust the apparatus and repeat again.
 15. Calculate C_p using the following equation

$$C_{px} = (l_x/l_s) \times (M'_s/M_x) C'_{ps} \quad (1)$$
- where C_{px} is the heat capacity of the sample, C_{ps} is that of the standard material, M_x is the weight of the sample and M_s is that of the standard. l_x and l_s are shown in Fig. 1.
16. When the calculation is made, C_p data obtained from T_i to $T_i + 10$ should be omitted.

RESULTS AND DISCUSSIONS

Table 1 shows the C_p values obtained by the five participants. Figure 2 shows the relationship between C_p and temperature. As shown in Table 1 and Fig. 1, the data from two of the participating organizations agreed completely. The mean value (C_p) and the standard deviation (σ_n) showed that the data from the five organizations agreed fairly well. It should be noted that the results obtained by the qualitative DTA's and those obtained by the heat-compensation DSC's agreed well. In the previous studies, almost all C_p data were measured using a heat-compensation DSC [8–10]. It was considered that a heat-flux DSC equipped a large heater took a longer time to attain the isothermal state (T_i or T_e in Fig. 1). In fact, a participating organization that used a heat-flux DSC reported that the base-line fluctuated slightly after maintaining at T_e . Because of this, the organization estimated a straight line in order to obtain line III. It was also pointed out that there was difficulty in attaining condition 6 in the experimental procedure. Several

TABLE 1

Heat capacities of polystyrene

T (K)	C_p (kJ kg ⁻¹ K ⁻¹)						Average	σ_n
	A	B	D	E	F			
345	1.508	1.441	1.479	1.414	1.502	1.469	0.036	
350	1.541	1.470	1.501	1.423	1.531	1.493	0.043	
355	1.568	1.506	1.526	1.452	1.578	1.526	0.045	
360	1.603	1.552	1.563	1.493	1.645	1.571	0.051	
365	1.681	1.638	1.652	1.597	1.788	1.671	0.064	
370	1.841	1.811	1.819	1.769	1.942	1.836	0.057	
375	1.899	1.873	1.858	1.800	1.909	1.868	0.038	
380	1.902	1.868	1.845	1.800	1.925	1.868	0.044	
385	1.925	1.868	1.854	1.793	1.928	1.874	0.050	
390	—	1.913	1.871	1.800	1.949	1.883	0.055	
395	—	1.937	1.879	1.828	1.960	1.901	0.051	
w_s (mg)	10.52	10.246	8.89	4.7	28.96			
Symbol	○	■	●	△	▲			
Apparatus ^a	II	I	I	II	I			

^a I, heat-compensation DSC; II, heat-flux DSC.

organizations estimated the straight line from T_i to T_e , and also estimated l_x and l_s values.

The weight of the sample of each organization ranged between 5 and 20 mg (see Table 1), despite the fact that the instructions indicated that a weight of approximately 10 mg should be used. The sample weight seemed to affect the C_p value. Figure 3 shows the relationship between the sample weight and C_p values at 345 K (the glassy state) and at 380 K (the molten state). Regardless of the kinds of apparatus, C_p values increased as the sample weight increased. If we consider the DSC thermal balance of the

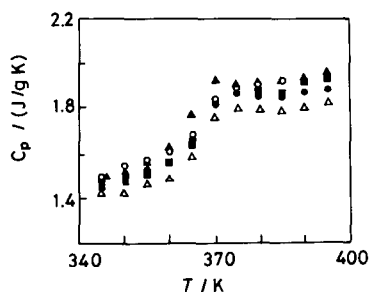


Fig. 2. Relationship between C_p and temperature. ■, ●, ▲, heat-compensation DSC; ○, △, heat-flux DSC.

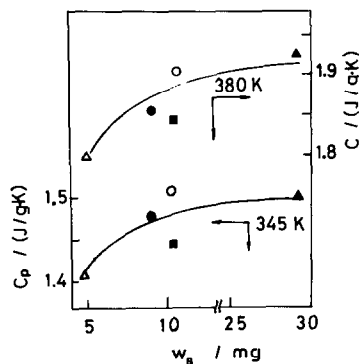


Fig. 3. Relationship between C_p and sample weight.

sample side and that of the reference side, the following equation is obtained [5].

$$\left[M_x C_p + (W_s - W_r) C_{sp} + (H_s - H_r) \right] (dT/dt) = d(q_s - q_r)/dt - (f_s - f_r) \quad (2)$$

where W_s is the weight of the sample, C_{sp} is the heat capacity of the materials of the sample, H_s is the effective heat capacity of the sample holder, q_s is the heat transferred to the sample side, f_s is the heat transferred per unit time to the exterior from the sample holder, W_r is the weight of another sample put into the reference holder, H_r is the effective heat capacity of the reference holder, q_r is the heat transferred to the reference holder and f_r is the heat transferred per unit time to the exterior from the reference holder.

In order to obtain C_p values using eqn. (1), we assumed that $H_s = H_r$ and $W_s = W_r$. Therefore, eqn. (2) was simplified to yield

$$M_x C_p (dT/dt) = d(q_s - q_r)/dt - (f_s - f_r) \quad (3)$$

The fact that C_p depended on M_x suggested that eqn. (3) was not satisfied. The values of q_s and f_s might be responsible for this discrepancy.

CONCLUSION

It should be noted that the data obtained by the five organizations agreed to within 3% deviation, even though, as mentioned above, the experimental conditions did not completely coincide. This suggested that C_p measurement using DSC will be more frequently used in various applications in the future. At the same time, further investigation concerning the factors affecting the C_p measurement by DSC may be necessary in order to establish the applicability of this method.

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