

THERMAL ANALYSIS OF POLYMER SAMPLES BY ROUND ROBIN METHOD PART II. FACTORS AFFECTING HEATS OF TRANSITION

TATSUKO HATAKEYAMA and HISAAKI KANETSUNA *

Research Institute for Polymers and Textiles, 1-1-4 Higashi, Tsukuba, Ibaraki 305 (Japan)

(Received 8 April 1988)

ABSTRACT

The results of a round robin test (RRT) of heats of melting (ΔH_m) and heats of crystallization (ΔH_c) of polymers have been analysed. Fourteen laboratories participated in the RRT. Three kinds of polymer were tested: two samples of polyethylene (pellets and film), with the same origin but a different thermal history; two samples of poly(ethylene terephthalate) fibre; and poly(ether ether ketone) pellets. Eight types of differential scanning calorimeter (DSC) were used. Seven of these were power-compensate type DSCs and seven were heat-flux type DSCs (quantitative DTAs). The standard deviations of ΔH_m and ΔH_c were correlated with various factors. In particular, the heats of transition of all samples were directly correlated with the temperature width between the measured onset and end temperatures of transition. Variation in the values of heats of transition obtained could be mainly attributed to variation of the measured onset temperature of melting or the measured end temperature of crystallization. Two experimental procedures are suggested as a means of decreasing this variation.

INTRODUCTION

Thermal data on polymeric materials are required in various fields, including research and development, production, and trading. A survey on the present and future application of thermal data on polymeric materials in Japan was carried out across 46 organizations (27 private enterprises, 5 universities and 14 public institutions) [1]. The results of this survey indicated that these organizations normally measured not only the temperatures of melting, glass transition and decomposition, but also, frequently, heat of melting (ΔH_m), heat capacity (C_p) and heat conductivity (λ).

A round robin test (RRT) performed in 1985 involved 22 organizations (13 private enterprises, 3 universities and 6 public institutions) [1]. There were four programmes of enquiry: thermogravimetry; measurement of tem-

* Present address: Tokyo Kasei University, 1-18-1, Kaga, Itabashi-ku, Tokyo 173, Japan.

peratures of melting, crystallization and glass transition by differential thermal analysis (DTA) and differential scanning calorimetry (DSC); determination of heat of melting and crystallization by DSC; and heat capacity measurement by DSC. The RRT examined 11 polymer samples and 15 metals and inorganic compounds [1,2].

This paper describes the results of the RRT relating to heat of melting (ΔH_m) and heat of crystallization (ΔH_c) of polymers. Factors affecting the variation of the enthalpy values are considered, and several experimental procedures for the measurement of ΔH_m and ΔH_c are suggested as means of decreasing the variation of the values obtained.

EXPERIMENTAL

Sample

ΔH_m and ΔH_c were measured for samples of polyethylene (PE), poly(ethylene terephthalate) (PET) and poly(ether ether ketone) (PEEK). Detailed characteristics of the samples are listed in Table 1. The samples were chosen to meet the following requirements: (i) a wide range of melting temperatures across the various polymers (PE, PET, PEEK); (ii) instances of the same kind of polymer with different shapes and thermal histories (PE pellets and fibre, PET fibre); and (iii) a variety of shapes (pellets, film and fibre). The samples were packed into the sample pan, after having been cut to suitable sizes as recommended by ASTM [3].

Apparatus

One Du Pont 940 DSC, four Perkin-Elmer DSC II, three Rigaku TG-DSC, one Rigaku DSC 8230B, two Seiko Denshi SSC 50 (DSC20), one

TABLE 1

Samples used in the RRT for the examination of enthalpies of melting (ΔH_m) and crystallization (ΔH_c)

Sample	Shape	Commercial name	Measurement
Polyethylene PE	pellets	Yukalon EY-40L	ΔH_m (Runs 1 and 2) ΔH_c
	film	Yukalon EY-40L	ΔH_m (Run 1)
Poly(ethylene terephthalate) PET	fibre A	Torey T-210 (75d)	ΔH_m (Run 1)
	fibre B	Torey T-702c (1500d)	ΔH_m (Run 1)
Poly(ether ether ketone) PEEK	pellets	^a	ΔH_m (Runs 1 and 2)

^a Requested not to publish the commercial name.

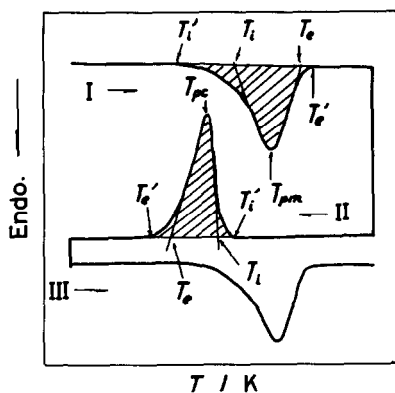


Fig. 1. Schematic heating and cooling curves of polymers: (I) first heating run; (II) first cooling run; (III) second heating run.

Seiko Denshi SSC 560S, a Shimadzu DSC-40M and one Shimadzu DSC-30 were used. This apparatus can be categorized as seven power-compensate type DSCs and seven heat-flux type DSCs (quantitative DTAs).

Procedure

Figure 1 shows schematic DSC curves of heating and cooling runs. When measuring ΔH_m for PE (pellets) and PEEK (pellets), participants were required to report first (curve I) and second (curve III) runs. ΔH_m values for PE (film) and PET (fibre) were determined at the first run only. For the ΔH calculation, participants were asked to use standard metals (purity greater than 99.99%), rather than the standards which were normally used in each laboratory. They were required to follow almost the same procedure as is described in ASTM. The following methods for determining the shadowed

TABLE 2

Mean values and standard deviations of ΔH_m and ΔH_c for the samples used in the RRT

Run	ΔH_m (kJ kg ⁻¹)						ΔH_c (kJ kg ⁻¹)		
	PE		PET	PEEK		PE	PEEK		
	Pellets	Film	Fibre	Pellets		Pellets	Pellets		
			A	B					
Run	1	2	1	1	1	2	1	1	
<i>n</i>	12	12	12	12	12	12	12	12	
\bar{x}	167.0	192.3	173.1	50.8	57.2	31.7	32.3	176.8	38.4
σ_n	17.4	16.4	14.0	7.0	4.6	10.0	12.3	26.5	8.7
x_{min}	133.2	154.9	164.2	34.0	50.2	14.0	14.0	132.7	21.8
x_{max}	196.5	225.2	204.6	61.9	66.7	43.6	51.4	219.1	51.2

TABLE 3

The number of data located within $\bar{x} \pm 4 \text{ kJ kg}^{-1}$ and $\bar{x} \pm 8 \text{ kJ kg}^{-1}$ ^a

Sample	Run	$\Delta H_m \text{ (kJ kg}^{-1}\text{)}$		$\Delta H_c \text{ (kJ kg}^{-1}\text{)}$	
		$\bar{x} \pm 4$	$\bar{x} \pm 8$	$\bar{x} \pm 4$	$\bar{x} \pm 8$
PE pellets	1	3/11	4/11	0/12	1/12
	2	4/12	6/12		
PE film	1	3/12	6/12		
	1	8/12	9/12		
PET fibre A	1	9/12	11/12		
	1	5/12	6/12	6/12	7/12
PEEK pellets	1	5/12	6/12		
	2	1/12	5/12		

^a The denominator indicates the total number of reported data.

area shown in Fig. 1 were suggested: (i) cutting and weighing the copied graph; (ii) using a computer according to the Simpson method; and (iii) using a planimeter.

RESULTS

Table 2 shows the mean value (\bar{x}) of ΔH_m and ΔH_c , the number of data (n), the standard deviation σ_n , and the maximum (x_{\max}) and minimum (x_{\min}) values reported, for all the samples examined in the RRT.

Table 3 shows the number of reported values which were located within $\bar{x} \pm 4 \text{ kJ kg}^{-1}$ and the number located within the extended allowance of $\bar{x} \pm 8 \text{ kJ kg}^{-1}$.

DISCUSSION

It is generally thought that, among various factors affecting the values of ΔH_m , the shape of the sample may be a major factor. However, our data suggest that there is no general correlation between σ_n and the shape of the samples. As shown in Table 2, for example, in the first run σ_n obtained for PE film was slightly lower than for PE pellets, and σ_n for PE pellets in the second run was lower than that for PE pellets in the first run. This is to be expected if we consider the thermal conductivity between the surface of the sample and the bottom of the aluminium pan. On the other hand, σ_n for PEEK was smaller in the first run than in the second run. In this case, the crystallization process of PEEK may have affected the melting in the second run. The values of ΔH_c scatter particularly widely, as indicated in Table 3. From these results, it is difficult to think of the shape of the sample as being a major factor affecting ΔH_m or ΔH_c values.

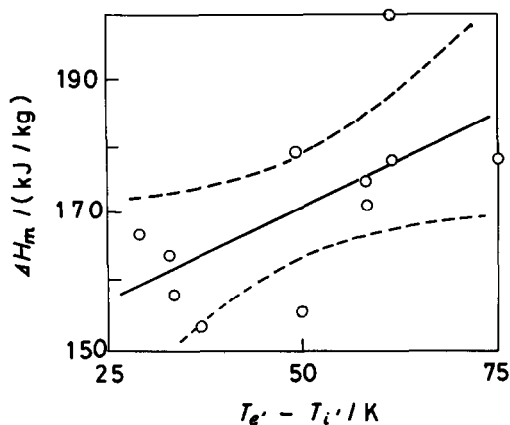


Fig. 2. Relationship between ΔH_m and $(T_e' - T_i')$ of polyethylene film at first run.

The thermal history, which might also influence σ_n , showed no particular tendency to affect the ΔH_m values obtained. The thermal history is necessarily related to the characteristics of each sample, and especially to stability against molecular rearrangement during heating. Well-annealed samples, such as the PET fibre sample, showed very small σ_n values. In particular, the smallest value of σ_n observed was for the PET fibre B sample, which was drawn and annealed according to the automobile tyre code. This suggests that the stability of the higher order structure of polymers decreases σ_n . In contrast, the shape of the sample scarcely affected σ_n .

Other factors which have been considered to affect σ_n of ΔH_m —type of apparatus, weight of the sample, and so on—were also examined. However, the only correlation with a reliability of 95% found was for the temperature width between the onset temperature T_i' and the end temperature T_e' . When we examined the original data reported, it was found that the value of ΔH_m depended on differences among participants. Some participants tended to report larger values of ΔH_m than others, irrespective of samples. Moreover, participants who reported a large ΔH_m value necessarily read T_i' at a temperature lower than the mean value of T_i' . This suggests that ΔH_m correlated directly with the large temperature width between T_e' and T_i' .

Figures 2–8 show the relationship between the ΔH_m values for the samples and the temperature width $T_e' - T_i'$. The dotted line shows a reliability of 95%. As these figures demonstrate, the correlation was good. All the ΔH_m and ΔH_c values were also correlated with $T_e' - T_i'$ within 95% reliability.

ΔH_m and ΔH_c can be written as follows

$$\Delta H_m \text{ or } \Delta H_c = a + b(T_e' - T_i') \quad (1)$$

Table 4 shows the constants a and b for all samples tested in the RRT.

To obtain a smaller σ_n for ΔH_m , all participants should read T_i' at almost the same point on the base line. Since T_e' of melting was observed at almost

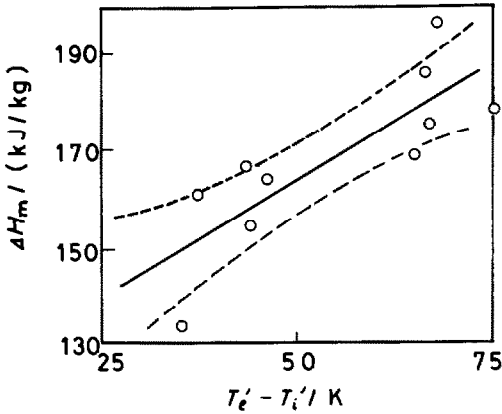


Fig. 3. Relationship between ΔH_m and $(T_e' - T_i')$ of polyethylene pellets at first run.

the same temperature for all data, the variation was considered to be caused by scattering of T_i' . In the case of ΔH_c , T_e' varied widely among laboratories. The above results indicate that it is difficult to distinguish the endothermic deviation from the base line. Moreover, we must take into consideration the fact that the base line of each DSC curve is not always straight, owing to the structure of the sample cell and other factors. If the base line is not a straight line, and the area is calculated by the method shown in Fig. 1, ΔH_m values necessarily scatter.

It is important to adjust the apparatus in order to obtain a straight base line across the temperature range of measurement. When the base line is curved even after careful adjustment, two methods can be considered as a means of solving the problem. (i) A DSC curve obtained by using vacant sample pans under the same conditions can be used as the base line. (ii) By following the procedure of heat capacity measurement, ΔH_m and ΔH_c

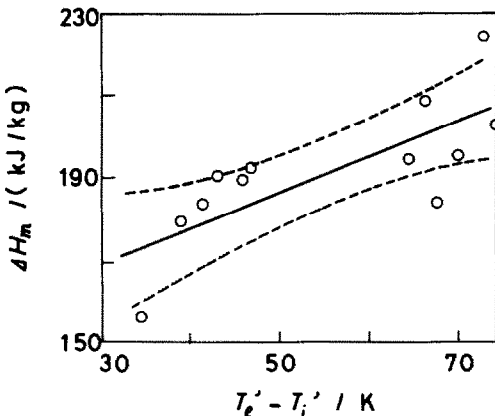


Fig. 4. Relationship between ΔH_m and $(T_e' - T_i')$ of polyethylene pellets at second run.

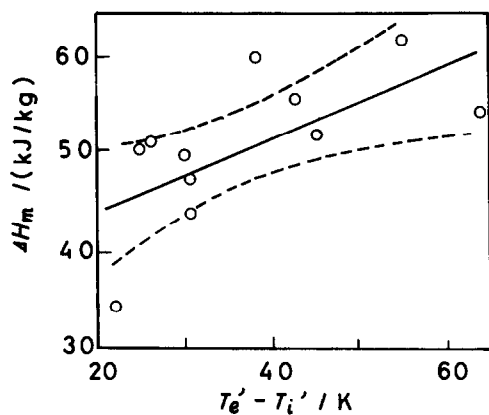


Fig. 5. Relationship between ΔH_m and $(T_e' - T_i')$ of poly(ethylene terephthalate) fibre A at first run.

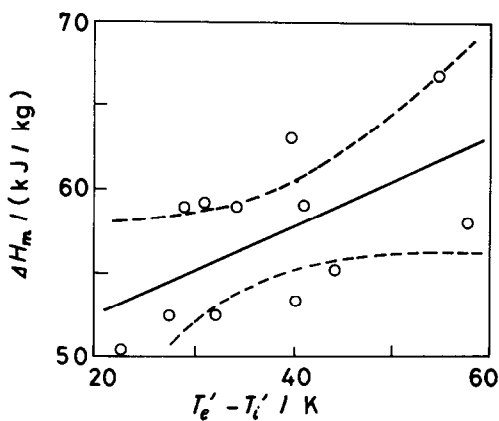


Fig. 6. Relationship between ΔH_m and $(T_e' - T_i')$ of poly(ethylene terephthalate) fibre B at first run.

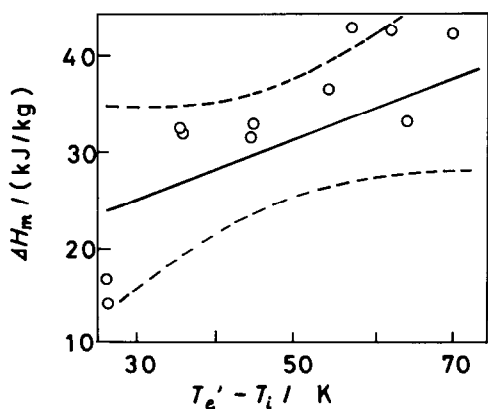


Fig. 7. Relationship between ΔH_m and $(T_e' - T_i')$ of poly(ether ether ketone) at first run.

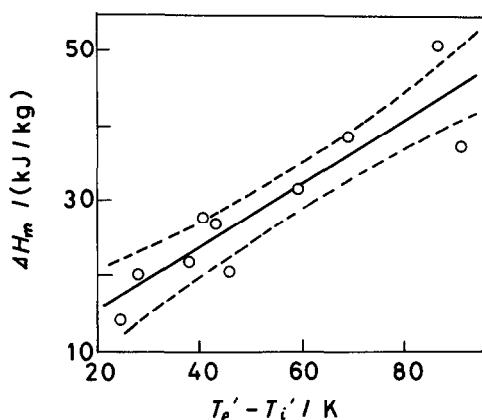


Fig. 8. Relationship between ΔH_m and $(T_e' - T_i')$ of poly(ether ether ketone) at second run.

TABLE 4

Constants a and b in eqn. (1) for the samples used in the RRT

	Sample	Run	a (kJ kg ⁻¹)	b (kJ kg ⁻¹)
ΔH_m	PE pellets	1	115.1	0.97
		2	144.3	0.86
	PET film	1	142.1	0.63
		PET fibre A	1	36.7
	PET fibre B	1	47.1	0.26
	PEEK pellets	1	16.3	0.31
2		6.1	0.45	
ΔH_c	PE pellets	1	142.8	1.00
	PEEK pellets	1	27.6	0.29

values can be calculated from the change in relationship between the heat capacity and the temperature [4]. The second procedure is probably the most reliable, and the report of the RRT concerning C_p measurement suggests the future application of C_p in the determination of enthalpy values.

ACKNOWLEDGEMENTS

The authors are grateful to the participants in the RRT and to the members of the RRT committee, Dr. T. Ozawa (Electrotechnical Laboratory), Prof. S. Nakamura (Kanagawa University), Mr. M. Momomota (Rigaku Corporation), Dr. S. Ichihara (Mitsubishi Petrochemical Co. Ltd.) and Dr. M. Todoki (Torey Research Center) for their helpful discussions. The RRT was financially supported by the Machinery Industry Promotion Funds of the Japan Motorcycle Racing Organization.

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