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THERMAL ANALYSIS OF POLYMER SAMPLES BY A ROUND-ROBIN METHOD
IV. ANALYSIS OF FACTORS AFFECTING THE REPRODUCIBILITY OF TRANSITION TEMPERATURE MEASUREMENTS

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ABSTRACT

The scattering of the data concerning the transition temperatures of polymers and standard reference materials obtained by a round-robin method were analyzed, and the following conclusions were drawn.

(1) In, Sn, Pb and Zn, having a purity of above 99.99%, are useful for standard reference materials of temperature in DSC and DTA measurements. Powdered In and Sn from among the ICTA certified reference materials for DTA, GM-758, are also adequate. However, KNO_3, $KClO_4$ and Ag_2SO_4 from GM-758 are not as suitable because some participants of the round robin tests reported abnormal values.

(2) Both the calibration of the temperature scale of the apparatus with standard reference materials and the temperature correction after measurement are necessary to decrease the scattering of the transition temperature data.

(3) Time is required to attain a steady state of heating from the non-steady state of heating caused by transition. This time constant depends on the type of apparatus. The time constant affects the extrapolated end temperature of melting of polymers having a sharp peak.

(4) The differences in the scattering of the data reported by each participant is fairly large. However, the scattering does not depend on the type of apparatus. It is assumed that the difference in the scattering of the data is caused by the different specimen handling techniques.

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INTRODUCTION

As reported previously [1], the reproducibility of the data in the thermal analysis of polymers has been examined by a round-robin method. Its outlines and the reproducibility of transition temperatures measured by differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are described in the previous paper [1].

DSC and DTA are very frequently used to observe the transition behaviour of polymers. However, there are some problems associated with obtaining better agreement in the transition temperature data measured by different persons and with different apparatus. The major problems in the transition temperature measurements by DSC and DTA are considered to be as follows.

(1) Selection of the standard reference materials for temperature calibration.

(2) Usefulness of temperature calibration and correction.

(3) Influence of the type of apparatus used.

(4) Scattering of the data measured by different persons and with different types of apparatus.

In this paper, the results of the analyses of these problems are reported.

EXPERIMENTAL

Samples

Indium wire (In), tin plate (Sn), lead pellets (Pb), zinc wire (Zn), each having a purity above 99.99%, and the ICTA certified reference materials for DTA, GM-758, were examined for their potential as standard reference materials for temperature calibration and correction of DSC and DTA curves. GM-758 is composed of indium, tin, KNO_3, $KClO_3$ and Ag_2SO_4, all in powdered form. The melting temperatures of these metals are 429.6 K for In, 505.1 K for Sn, 600.6 K for Pb and 692.7 K for Zn. The equilibrium transition temperatures of inorganic non-metallic substances cited in the ICTA certificate are 400.9 K for KNO_3, 572.7 K for $KClO_4$ and 703.2 K for Ag_2SO_4.

The polymer samples were high density polyethylene (PE), pellets and film, two poly(ethylene terephthalate) (PET), fibers, poly(ether ether ketone) (PEEK), pellets, polystyrene (PS), sheet, and poly(ether sulfone) (PES), pellets. Detailed descriptions of these polymer samples are in the previous paper [1]. The polymer samples were cut to the appropriate size according to the method recommended by ASTM D3418-82.

Apparatus

The apparatus used in melting, crystallization and glass transition measurements were 13 power-compensate-type DSCs consisting of three types of instrument, and 8 heat-flux-type DSCs, quantitative differential thermal analyzers, (q-DTAs), consisting of five types of instrument.

Treatment of the data

The temperature scales of the apparatus were calibrated and the obtained data were corrected according to the methods conventionally used in each laboratory with the same heating rates used for the measurements of the samples.

Conditions of measurements

For PE and PEEK pellets, melting of as-received samples, crystallization and re-melting were measured. For PE film and two PET fibers, only melting of as-received samples was measured. The heating rate was 10 K min^{-1} and the cooling rate was 5 K min^{-1}. The sample weight was about 5 mg for each sample.

The glass transition was measured for PS sheet and PES pellet. The samples were previously heated to about 50 K above their glass transition temperatures and then quenched to the glassy state in the sample pan. The heating rate used for measurements of the glass transition was 20 K min^{-1}. The sample weight was 5–10 mg.

For four high purity metals and two powdered metals included in GM-758, melting of as-received samples and re-melting after crystallization in the sample pan were measured. For three powdered inorganic materials in GM-758, only the transition of as-received samples was measured.

Temperatures used in the analysis of the reported data

The characteristic temperatures representing melting, crystallization and glass transition behavior measured by DSC and DTA were defined in the previous paper [1]. Among them, the following are used for analysis in this paper.

(1) Melting and transition of standard reference materials and polymers:
T_{im} extrapolated onset temperature
T_{pm} melting peak temperature
T_{em} extrapolated end temperature

(2) Glass transition of polymers:
T_{ig} extrapolated onset temperature
T_{mg} midpoint temperature
T_{eg} extrapolated end temperature

Usually, the melting and transition temperatures of very pure low molecular weight materials correspond to the extrapolated onset temperature of the peak in the DSC curve. Therefore, T_{im} values were used for the standard reference materials. As the scattering of T_{im}, T_{pm}, T_{em}, T_{ig}, T_{mg} and T_{eg}, especially T_{pm} and T_{mg}, are smaller than the onset or end temperatures of melting and glass transition of polymers [1], those temperatures were used for analysis. The temperatures related to crystallization behaviour were not analyzed because the standard reference materials for temperature calibration and correction in the cooling experiments of DSC and DTA are not yet established and, therefore, the temperature calibration in the cooling process was not examined in the round-robin tests.

RESULTS AND DISCUSSION

Melting or transition temperatures of standard reference materials

Table 1 shows mean values $\langle T_{\mathrm{im}} \rangle$ and standard deviations $\sigma_n = (\Sigma(T_{\mathrm{im}} - \langle T_{\mathrm{im}} \rangle)/n)^{1/2}$, of T_{im} of high purity metals, and their melting temperatures, T_{m}. There is a slight difference between the $\langle T_{\mathrm{im}} \rangle$ and T_{m} of Zn. The difference is larger for the 2nd run than for the 1st run. The σ_n values become larger when T_{m} is high. For Sn and Pb, the σ_n values for the 2nd run are smaller than those for the 1st. For Zn, σ_n and $T_{\mathrm{m}} - \langle T_{\mathrm{im}} \rangle$ for the 2nd run are larger than those for the 1st. The reason is not obvious. One of the possible explanations is the decrease in the purity of Zn caused by dissolving aluminum from the sample pan when the Zn is molten. If this is true, the reliability of the data from the 2nd Zn run is lower than that of the 1st. Therefore, for Zn, data from only the 1st run were used hereafter.

Most participants of the round-robin tests used In, or In and Sn to calibrate the temperature scale of their apparatus. Therefore, many appara-

TABLE 1

T_{m}, $\langle T_{\mathrm{im}} \rangle$ and σ_n of high purity metals

Sample	T_{m}	I [a]		II [b]	
		$\langle T_{\mathrm{im}} \rangle$ (K)	σ_n (K)	$\langle T_{\mathrm{im}} \rangle$ (K)	σ_n (K)
In wire	429.6	429.3	0.82	429.3	0.82
Sn plate	505.1	504.7	0.89	504.6	0.85
Pb pellets	600.6	600.6	2.02	600.1	1.05
Zn wire	692.7	691.3	3.23	689.9	3.82

[a] First run.

[b] Second run.

TABLE 2

T_m or T_{eq}, $\langle T_{im} \rangle$ and σ_n (K) of GM-758

Sample	T_m or T_{eq}	I [a]		II [b]		$\langle T_{im} \rangle$ [c]	σ_n [c]
		$\langle T_{im} \rangle$	σ_n	$\langle T_{im} \rangle$	σ_n		
In	429.6	429.3	0.85	429.3	0.89	–	–
Sn	505.1	504.6	1.07	504.8	1.17	–	–
KNO_3	400.9	402.4	1.48	–	–	402.6	1.04
$KClO_4$	572.7	573.9	1.60	–	–	574.0	1.08
Ag_2SO_4	703.2	699.9	1.89	–	–	700.4	0.77

[a] First run.
[b] Second run.
[c] Corrected values.

tuses were not calibrated at the T_m of Zn. This is a possible reason why σ_n and $T_m - \langle T_{im} \rangle$ for Zn are large.

Table 2 shows similar data for GM-758. The temperatures shown in Table 2 are melting temperatures, T_m, for In and Sn, and solid state transition temperatures, T_{eq}, for other samples. The equilibrium transition temperatures cited in the ICTA certificate were used here. For In and Sn, the data of the 1st and 2nd runs are shown. The $\langle T_{im} \rangle$ values of In and Sn agree well with those shown in Table 1. However, the σ_n values are slightly larger.

For KNO_3, $KClO_4$ and Ag_2SO_4, only the 1st run was done. The values under c in Table 2 are the mean values of the corrected temperatures and their standard deviations. The method of correction will be described later. For these three materials, the σ_n values are larger than those of In, Sn and Pb. The differences between T_{eq} and $\langle T_{im} \rangle$ are also large. Furthermore, for KNO_3, two participants reported abnormally high T_{im} values (606 and 607.7 K). For $KClO_4$, one reported a T_{im} value of 650 K. Another participant could not observe the transition of $KClO_4$. For Ag_2SO_4, two participants reported abnormal values (928.8 and 933 K). These discrepancies are undesirable in standard reference materials. Of course, these abnormal values were excluded in the calculation of $\langle T_{im} \rangle$ and σ_n.

The transition temperatures of KNO_3, $KClO_4$ and Ag_2SO_4 are near to the melting temperatures of In, Pb and Zn respectively. The σ_n and $|T_m - \langle T_{im} \rangle|$ values of In and Pb are smaller than those of KNO_3 and $KClO_4$. Therefore, as standard reference materials, In and Pb are better than KNO_3 and $KClO_4$. Zn is also better than Ag_2SO_4 because two participants reported abnormal values for the transition temperature of Ag_2SO_4. The σ_n value of Zn is larger than that of Ag_2SO_4. The reason will be clarified in the following section. More accurate values for the transition temperatures of these three inorganic materials are needed because the $|T_{eq} - \langle T_{im} \rangle|$ values are large.

Calibration and correction of temperature scale

According to the methods conventionally used in each laboratory, the temperature scale of the apparatus was calibrated and the data were corrected. It is assumed that the reported data can be classified into the following four cases.

(1) All data were corrected or else the temperature scale of the apparatus was calibrated between the melting points of In and Zn.

(2) The polymer data were corrected. Other samples were treated as standard materials and their data were not corrected.

(3) The data from the polymers and the inorganic non-metallic materials were corrected, only the metals being treated as standard materials.

(4) None of the data were corrected, or, the temperature scale of the apparatus was calibrated for different temperature regions or at only two points, because of the non-linearity of the temperature scale of the apparatus.

The T_{im} of metals and inorganic materials, the T_{pm} of the 2nd runs of PE and PEEK, and the T_{mg} of PES were used to analyze the calibration and correction conditions of the data reported from each laboratory. In this section, these temperatures are represented by T_{a}, i.e. $T_{\mathrm{a}} = T_{\mathrm{im}}$ for metals and inorganic materials, $T_{\mathrm{a}} = T_{\mathrm{pm}}$ for PE and PEEK, and $T_{\mathrm{a}} = T_{\mathrm{mg}}$ for PES. If the apparatus is designed so that heat flows from the bottom to the top of the sample pan during heating experiments and a temperature sensor is placed under the sample pan, the T_{im} values of very pure low molecular weight materials correspond to the 1st order transition temperature [2]. Therefore, the T_{im} values of metals and inorganic materials were used for analysis. The σ_n values of T_{pm} are smaller than those of T_{im} and T_{em} for polymers. The σ_n value of $\mathrm{T_{mg}}$ is also smaller than the σ_n values of T_{ig} and T_{eg}. This is the reason why the T_{pm} and T_{mg} of polymers were used for analysis. $T_{\mathrm{m}} - T_{\mathrm{a}}$ values of metals and $\langle T_{\mathrm{a}} \rangle - T_{\mathrm{a}}$ values of other samples were plotted against T_{a} for each participant, where $\langle T_{\mathrm{a}} \rangle$ represents the mean value of T_{a}. Figure 1 shows five examples of these plots. A, G, Y, L and S are symbols denoting each of five participants.

Participant A reported that his apparatus was calibrated with melting temperatures of In, Sn, Pb and Zn. Therefore A in Fig. 1 corresponds to case 1. It is supported that G corresponds to case 2 though there is some uncertainty because his data are widely scattered. Y reported that his apparatus is calibrated with In, Sn and Pb. It is thought that the data of Y correspond to case 3. L calibrated his apparatus with H_2O, In and Sn, and reported all data without correction. S calibrated with In and Pb, and reported all data without correction. Therefore, the data of L and S correspond to case 4.

For each participant, $T_{\mathrm{m}} - T_{\mathrm{a}}$ and $\langle T_{\mathrm{a}} \rangle - T_{\mathrm{a}}$ were plotted against T_{a}, and smoothed curves were drawn for the plots of $T_{\mathrm{m}} - T_{\mathrm{a}}$ and T_{a}. These curves

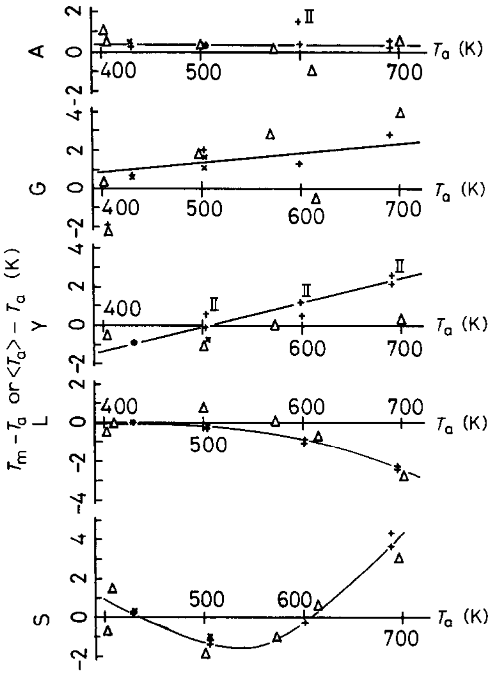

Fig. 1. $T_m - T_a$ and $\langle T_a \rangle - T_a$ plotted against T_a. A, G, Y, L and S represent different participants. +, High purity metals; ×, metals from GM-758; △, inorganic materials from GM-758 and polymers. For metals and inorganic materials, $T_a = T_{im}$, and $T_a = T_{pm}$ for PE and PEEK, and $T_a = T_{mg}$ for PES. Data marked with II are those of the 2nd run.

were used to correct the reported data of polymers and inorganic materials if the data were not thought to be corrected. The data under c in Table 2 are $\langle T_{im} \rangle$ and σ_n after correction. σ_n is small for all samples. Not only temperature scale calibration of the apparatus, but also correction using $T_m - T_a$ versus T_a plots of high purity metals are effective in decreasing σ_n. However, there are still differences between T_{eq} and the corrected $\langle T_{im} \rangle$ values. More accurate T_{eq} data are needed in order to use these materials for calibration and correction.

The correction curves of many participants, except those falling in case 1, deviate widely from zero in the high temperature region. This is the reason why the σ_n value of Zn is large. For Ag_2SO_4, some participants reported corrected values. Therefore, the σ_n value of Ag_2SO_4 before correction is smaller than that of Zn.

Effects of temperature correction on the transition temperatures of polymers

Table 3 shows the mean values and the σ_n values of T_{im}, T_{pm} and T_{em}, and their corrected values, for the 1st and 2nd runs of PE and PEEK pellets. The σ_n values of the 2nd runs are similar to or smaller than those of the 1st

TABLE 3

Effect of temperature correction for PE and PEEK pellets

Sample		$\langle T_{im} \rangle$ (K)	σ_n (K)	$\langle T_{pm} \rangle$ (K)	σ_n (K)	$\langle T_{em} \rangle$ (K)	σ_n (K)
PE	I	395.5	2.1	404.1	2.1	408.0	2.0
	I_c	395.6	1.7	404.2	1.9	408.2	2.1
	II	396.8	2.2	406.5	1.3	410.0	2.0
	II_c	396.9	1.8	406.7	1.1	410.1	2.0
PEEK	I	595.7	3.4	612.6	2.1	620.9	2.3
	I_c	595.7	3.2	612.7	1.7	621.1	2.0
	II	600.5	2.2	613.9	1.5	619.2	1.8
	II_c	600.9	2.0	614.1	1.1	619.5	1.3

I, 1st run; II, 2nd run.
Subscript c, corrected values.

runs. The thermal contact between sample and sample pan is better for the 2nd run than for the 1st run, and so σ_n for the 2nd run became smaller. The σ_n values of T_{im} and T_{em} are larger than that of T_{pm}. In some cases, the non-linearity of the baseline would increase the extrapolation error. This would be a reason why the σ_n values of T_{im} and T_{em} are large. Temperature correction decreases the σ_n, except for the T_{em} of PE. Temperature correction is useful to decrease the scattering of the data. The reason why the σ_n value of the T_{em} of PE does not decrease is described later.

Table 4 shows the mean values and the σ_n values of the reported and corrected T_{ig}, T_{mg} and T_{eg} values of PS and PES. The σ_n of T_{eg} are large. The σ_n values of the corrected temperatures are similar to or slightly smaller than those of the reported data.

Table 5 shows the mean values and the σ_n values of the reported and corrected T_{im}, T_{pm} and T_{em} of the as-received PE film, and PET fibers A and B. Correction decreases σ_n except for the T_{em} of PE film.

The σ_n values of as-received samples (the 1st run of PE and PEEK pellets, PE film and two PET fibers) are similar to or slightly larger than those of the 2nd run of PE and PEEK pellets. It is thought that thermal contact

TABLE 4

Effect of temperature correction for PS and PES

		$\langle T_{ig} \rangle$ (K)	σ_n (K)	$\langle T_{mg} \rangle$ (K)	σ_n (K)	$\langle T_{eg} \rangle$ (K)	σ_n (K)
PS		364.9	2.1	368.9	1.7	376.4	4.5
	c	365.0	1.8	369.0	1.7	376.6	4.3
PES		495.2	3.0	499.8	2.0	509.6	7.6
	c	495.4	2.8	500.0	1.9	509.8	7.6

c, Corrected values.

TABLE 5

Effect of temperature correction for PE film and PET fiber A and B

		$\langle T_{im}\rangle$ (K)	σ_n (K)	$\langle T_{pm}\rangle$ (K)	σ_n (K)	$\langle T_{em}\rangle$ (K)	σ_n (K)
PE film		395.2	2.6	403.7	1.6	407.0	2.5
	c	395.3	2.1	403.8	1.4	407.1	2.6
PET fiber A		518.0	6.1	528.2	2.9	532.6	2.0
	c	518.1	5.9	528.3	2.8	532.7	1.9
PET fiber B		520.2	2.2	525.9	2.4	532.2	1.7
	c	520.3	2.1	526.1	2.2	532.3	1.6

c, Corrected values.

between as-received samples and the sample pan is poor and, therefore, the σ_n values of as-received samples are large. In any case, the σ_n values of corrected data are similar to or slightly smaller than those of reported data.

Influence of the type of apparatus

For metals, $(T_{em} - T_{pm})$ and $(T_{pm} - T_{im})$, and their mean values, $\langle T_{em} - T_{pm}\rangle$ and $\langle T_{pm} - T_{im}\rangle$, were calculated for each participant. $(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle$ against $(T_{pm} - T_{im})/\langle T_{pm} - T_{im}\rangle$ of Sn plate and powder were plotted for each participant (Fig. 2).

Mean values of the ratios for metals, $\langle (T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle\rangle$ and $\langle (T_{pm} - T_{im})/\langle T_{pm} - T_{im}\rangle\rangle$, were calculated and plotted in Fig. 3 for each participant.

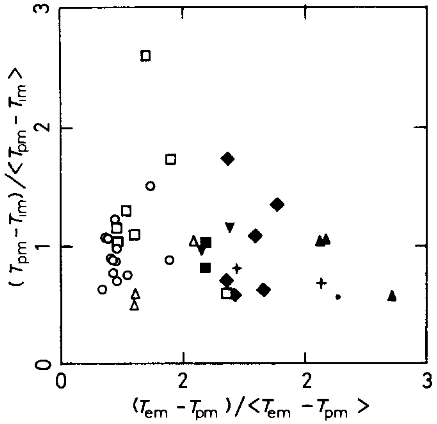

Fig. 2. $(T_{pm} - T_{im})/\langle T_{pm} - T_{im}\rangle$ vs. $(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle$ of Sn plate and powder. Different symbols show different manufacturers of apparatuses. Open symbols (○, □, △) correspond to power-compensate-type DSCs, and filled symbols (■, ▲, ▼, ◆) and crosses (+) show heat-flux-type DSCs and DTAs respectively.

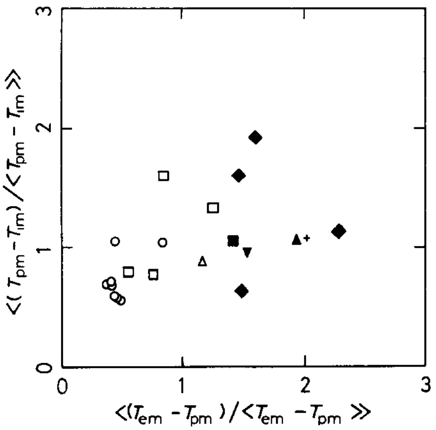

Fig. 3. $\langle(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle\rangle$ vs. $\langle(T_{pm} - T_{im})/\langle T_{pm} - T_{im}\rangle\rangle$ of metals. Symbols are as in Fig. 2.

From Figs. 2 and 3, it is obvious that the ratios $(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle$ for power-compensate-type DSCs are smaller than those for heat-flux-type DSCs and DTAs.

$(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle$ is related to the time constant of the apparatus from the non-steady heating state caused by the 1st order transition to the steady heating state. Figures 2 and 3 show that the time constant of power-compensate-type DSCs is smaller than that of heat-flux-type DSCs

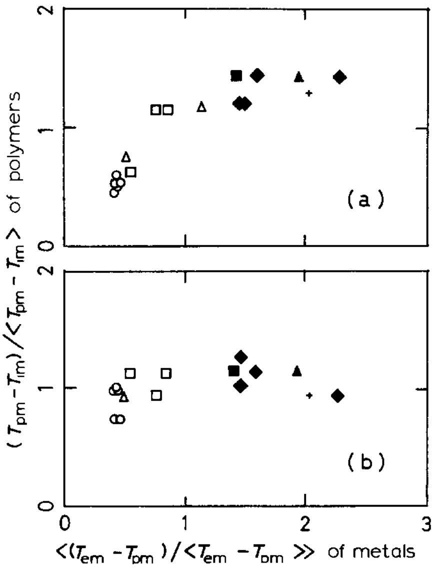

Fig. 4. $\langle(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle\rangle$ of metals vs. $(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle$ of the 2nd run of PE (a) and PEEK (b). Symbols are as in Fig. 2.

and DTAs. The time constants are varied by the design of the sample holder, but the difference among the types of apparatus is not clear even though the time constants of power-compensate-type DSCs are smaller than those of heat-flux-type DSCs or DTAs.

$(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle$ ratios of PE and PEEK were plotted against $\langle(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle\rangle$ ratios of metals in Fig. 4. For $(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle$ of PEEK, the differences between the types of apparatus are small. For the data of PE obtained by power-compensate-type DSC, there is a correlation between the $(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle$ of PE and the $\langle(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle\rangle$ of metals. As the latent heat of PE is large and melting is sharp, T_{em} values of PE are affected by the time constant of the apparatus [2]. This is the reason why there is a correlation between the $(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle$ of PE and the $\langle(T_{em} - T_{pm})/\langle T_{em} - T_{pm}\rangle\rangle$ of metals and why the σ_n of T_{em} for the 2nd run of PE is larger than that of PEEK.

The scattering of the data of each participant

Samples other than metals are classified into two groups: group 1 consists of three inorganic materials in GM-758, the 2nd runs of PE and PEEK, PS and PES; group 2 consists of the 1st runs of PE and PEEK pellets, PE film, and PET fibers A and B. The T_{im} of inorganic materials, the T_{pm} of crystalline polymers and the T_{mg} of glassy polymers were used to analyze the scattering of the data of each participant. These temperatures and their

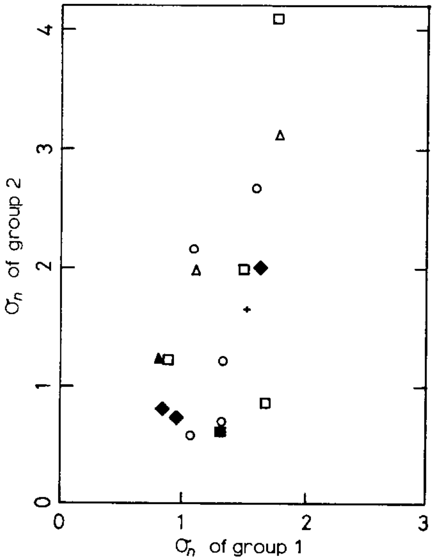

Fig. 5. Standard deviations σ_n of temperatures before correction of each participant for sample groups 1 and 2 (as-received samples). Symbols are as in Fig. 2.

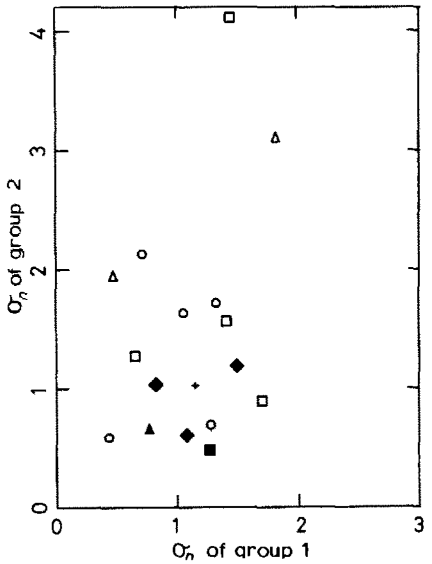

Fig. 6. σ_n of temperatures after correction of each participant for sample groups 1 and 2. Symbols are as in Fig. 2.

mean values are represented by T and $\langle T \rangle$, respectively, in this section. $T - \langle T \rangle$ values were calculated for each sample and each participant. Then, the standard deviations σ_n of $T - \langle T \rangle$ of each group were calculated for each participant. The σ_n values were calculated for the data before and after temperature correction.

The σ_n values of group 1 were plotted against those of group 2 in Fig. 5 (before correction) and Fig. 6 (after correction). The scattering of the data of group 1 is smaller than that of group 2 (group 2 consists of as-received samples). Furthermore, temperature correction decreases the scattering of data. However, there are fairly large differences between the σ_n values of each participant even if the temperatures were corrected. It is thought that the manner of handling the samples when they were packed into the sample pan, and, therefore, the thermal contacts between sample and sample pan and between sample pan and sample holder were different for each participant. This is the main reason for the difference between the σ_n value of each participant. It seems that the difference in the types of apparatuses used by each participant does not affect the value of σ_n.

CONCLUSIONS

From the results shown above, the following conclusions can be drawn.

(1) In, Sn, Pb and Zn, with purity above 99.99%, are useful standard reference materials for temperature calibration of DSC and DTA measure-

ments. Powdered In and Sn in GM-758 are also appropriate. KNO_3, $KClO_3$ and Ag_2SO_4 in GM-758 are not as suitable.

(2) Not only the calibration of the temperature scale of the apparatus with standard reference materials, but also the temperature correction after calibration are needed to decrease the scattering of the data.

(3) Time constants are different for different types of apparatus. The time required to attain the steady heating state from the non-steady heating state caused by the transition is longer for heat-flux-type DSC and DTA than for power-compensated-type DSC. The time constant depends on the design of the sample holder and does not depend on the types of apparatus. The difference in time constants affects the T_{em} of the polymers which have sharp melting peaks.

(4) The differences in the scattering of temperature data reported by each participant are fairly large. However, the scattering does not depend on the type of apparatus. The differences in the scattering are caused by the differences in the handling of the samples and, therefore, by the differences in the thermal contact between sample and sample pan and between sample pan and sample holder.

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REFERENCES

1 S. Nakamura, M. Todoki, K. Nakamura and H. Kanetsuna, Thermochim. Acta, 136 (1988) 163.

2 S. Ichihara, T. Takahama and H. Nakagawa, Netsusokutei, 5 (1978) 2.