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Standardization Workshop

INDUSTRIAL STANDARDIZATION OF THERMAL ANALYSIS IN JAPAN*

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To satisfy the needs for industrial standards for thermal analysis in the Japanese polymer industry, round-robin tests of differential scanning calorimetry (DSC), thermogravimetry (TG), thermomechanical analysis (TMA) and thermodilatometry (TD) have been carried out recently. The results are discussed in this short review.

The DSC applications tested were not only for determination of transition temperature but also for measurements of the transition heat and heat capacity. The TG task group did not aim at long-term thermal endurance studies, but relative thermal stability in molding and estimation of filler content, residual solvent content, etc. TMA was found to be a useful tool for measuring softening temperature and heat distortion temperature, especially for high-temperature engineering plastics, instead of the Vicat test which has temperature limitations. For temperature calibration of DSC and TG, ICTA-NIST certified reference materials were used together with other potential temperature standards; some inorganic substances and alloys were not found to be preferable to pure metals. For TMA and TD metal plates were found to be very useful for temperature calibration. Analysis of the round-robin test results also clarified present status of practical applications of thermal analysis, such as reproducibility and causes of errors.

Keywords: DSC, industrial standardization, TD, TG, TMA

Introduction

For the last hundred years thermal analysis has developed steadily, and its development can be classified into five directions. The first direction is an increase in the variety of techniques, and recent progress in spectroscopic thermal analysis by utilizing Fourier transformation is a typical case. The second is in the

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expansion of applied fields, e.g., from clay minerals in the beginning to food, pharmaceuticals and thin films of electronic materials in recent years. Sophisticated applications, such as kinetic analysis, purity determination, heat capacity measurement etc., and automation with a computer and a robotic system are two other directions of development. Finally I should point out the diffusion from basic research through R and D to manufacturing processes and quality control, then eventually to industrial standardization.

A typical example of this diffusion was observed in the polymer industry in Japan. The needs for industrial standardization of thermal analysis in the Japanese polymer industry were investigated by questionnaire, and results are summarized in Table 1 [1–3]. Following these results, task groups were set up for round-robin tests of differential scanning calorimetry (DSC), thermo-gravimetry (TG), thermomechanical analysis (TMA) and thermodilatometry (TD).

The DSC application tested by the task group was not only the determination of transition temperature, but also measurements of transition heat and heat capacity. The TG task group did not aim at long-term thermal endurance but relative thermal stability in molding and estimation of filler content, residual solvent content, etc. TMA was found to be a useful tool for measuring softening temperature and heat distortion temperature, especially for high-temperature engineering plastics, instead of the Vicat test which has temperature limitations. Reproducible results were also obtained by the round-robin test using TD.

For temperature calibration of DSC and TG, ICTA-NIST certified reference materials (CRM) [4] were used together with pure metals; some inorganic substances and metal alloys among the certified reference materials were unsatisfactory. For TMA and TG, pure metal plates were found to be very useful for calibration, and fused quartz was used for base line calibration of TD.

Analysis of the round-robin test results also revealed the current situation in the practical applications of thermal analysis, such as reproducibility and causes of errors. These results are also described.

Round-robin tests

Research projects, number of participating laboratories, types of the apparatus, samples, materials for calibration and established Japanese Industrial Standards (JIS) are given in Table 2 with published references. For each project task group was organized, and results were analysed and discussed in a small committee.

Transition temperatures

The melting temperature of PE, PET and PEEK was measured; crystallization temperatures were also measured for the last two, while PS and PES were used for glass transition temperature measurement. PE, PET and PEEK were chosen for their wide melting temperature range. PE was used also to observe the effect of sample shape. The effect of thermal history was observed for two types of PET fibres of different thermal history.

Table 1 Needs of industrial standardization of thermal analysis in Japanese polymer industries

		T_m	T_c	T_g	ΔH_m	c_p	λ	T_{dec}	H.R.*
(1)	Often	28	17	24	13	6	9	21	24
Application	Occasionally	10	8	12	13	12	7	10	5
state	At planning stage	2	5	3	4	6	4	2	2
	Interested	2	4	2	6	10	13	3	3
	Not interested	0	2	0	2	2	1	0	0
(2)	Quality control	11	7	4	2	0	1	3	8
Purpose of	Marketing	7	1	3	1	2	0	1	5
testing	For catalogue or quality indication	4	2	4	0	3	5	2	9
	Data for enineering Data for planning	19	15	20	16	10	15	16	19
	Reserach	28	25	32	29	25	18	29	26
	Others**	4	2	2	2	1	1	3	2
(3)	Necessary for development of new materials	18	19	23	11	13	10	17	19
Importance of testing	Necessary for testing of industrial products	9	5	10	3	5	7	8	8
	Necessary for general purpose	5	3	2	10	11	11	3	1
	Not necessary	0	0	0	0	0	0	0	0
	Others	0	0	0	0	0	2	0	0
(4)	DTA	16	9	10	2	–	–	15	4
Testing	DSC	29	24	28	26	16	2	9	6
method	Dilatometry	2	1	2	–	–	–	–	2
	Polarizing microscope	9	1	2	–	–		–	–
	Capillary tube	2	3	2	–	–	–	–	3
	TMA	6	2	16	–	–	–	1	9
	TG	–	–	–	–	–	–	28	112
	EGA	–	–	–	–	–	–	3	3

* H.R. = heat resistance. **E.g. requested by other organization.

Table 2 Round-robin tests for industrial standardization of polymers in Japan

Reserach project	T_m,T_c and T_g	ΔH_m and ΔH_c	c_p	TG	TMA	TD
Participants	21	14	5	10	15	5
Types of apparatus*	5 types hfDSC 3 types pcDSC	7 hfDSC 7 pcDSC	2 hfDSC 3 pcDSC	5 TG 3 TG-DTA 2 TG-DSC	TMA	TMA
Samples**	PE pellet & film PET fibers PEEK pellet PS sheet PES pellet	PE pellet & film PET fibers PEEK pellet	PS sheet	PE film PES pellet EP resins POM	POM (500 μm) PC (500 μm) PAR (100 μm) PEEK (200 μm) PET (40 μm) PPS (130 μm)	PE block EP block PI block & film [Al]
Materials for temperature calibration	ICTA-NIST CRM GM-758 In wire Sn plate Pb pellet Zn wire	ditto		ICTA-NIST CRM GM-761 Ni wire	In (500 μm) Sn (300 μm) Sn (350 μm) Pb (300 μm) Pb (500 μm) Zn (300 μm)	Woods metal (200 μm) In (200 μm) Sn (200 μm)
Materials for other calibrations		In Sn Pb Zn (for heat)	Sapphire (for heat capacity)			Quartz glass (for base line)
JIS	K 7121	K 7122	K 7123	K 7120	K 7196	K 7197
References	5, 6	7	8	9	10	11, 12

* hfDSC= heat flux DSC; pcDSC=power compensation DSC.

**Abbreviations for polymeric samples are the same as ISO 1043-1-1987, and PAR is polyarylate.

For temperature calibration, ICTA-NIST CRM GM-758 [4] were used together with high-purity (over 99.99%) metals, viz. indium wire, tin plate, lead pellets and zinc wire.

For measurement of melting temperature and crystallization temperature, the heating rate and cooling rate were respectively 10 and 5 deg·min^{-1}, and the sample mass was about 5 mg, while the heating rate and the sample mass were respectively 20 deg·min^{-1} and 5–10 mg to increase sensitivity in the measurement of glass transition temperature.

Because polymers melt and crystallize in a wide temperature range in contrast with pure low-molecular-mass substances, the onset temperature, T_{im}', the extrapolated onset temperature, T_{im}, the peak temperature, T_{pm} the extrapolated end temperature, T_{em} and the end temperature, T_{em}' were measured [4]; the first and the final ones are the temperature at which the DSC curve deviates from and returns to the base line, while the second and the fourth ones are the temperatures at which the extrapolated base line intersects the tangents drawn at the maximum slopes of the peak.

For amorphous polymers, namely PS and PES, the following temperatures in the glass transition region were observed: the onset temperature, T_{ig}', the extrapolated onset temperature, T_{ig}, the midpoint temperature, T_{mg}, the extrapolated end temperature, T_{eg} and the end temperature, T_{eg}'. The first and the final temperatures are the temperatures at which the curve deviates from and returns to the base line, and the second and the fourth temperatures are the temperatures at which the extrapolated base lines intersect the tangent drawn at the point of the maximum slope. T_{mg} is the temperature at the midpoint of the two base lines [4].

Among the DSC used, a few simultaneous DSC-TG instruments were included.

Assessment of errors in practical measurements

Because temperature calibration was achieved by various methods conventionally used in the participating laboratories, the following results and discussion relate to data obtained by the usual procedure, so that they reflect the results obtained in practical measurements.

Data obtained for T_{im}' were scattered widely, but the standard deviation for T_{em}' was relatively small (3–5 K). The standard deviations for the other three were less than 3.0 K except T_{im} for one variety of PET fibre (6.1 K) and for PEEK (3.4 K). To observe the thermal characteristics of the polymer itself, the sample should be heated at a constant rate up to an appropriate temperature above its melting temperature to erase the previous thermal history. After this preliminary thermal cycle, the standard deviation of T_{pm} for PE is decreased, and the other temperatures do not change appreciably, while the degree of scatter for all temperatures decreases appreciably. For PEEK, the peak becomes somewhat sharper, but the standard deviations and the ranges of T_{im}' and T_{im} increase.

For the crystallization of PE, the standard deviations of T_{im}, T_{pm} and T_{em} are smaller than for melting, but those of PEEK are all somewhat larger than for melting.

Similarly for the glass transition, small standard deviations (<3.1 K) were observed for T_{ig} and T_m, but those of the other temperatures were relatively large.

Factors affecting reproducibility

In the above measurements, temperature calibration was made by a method conventionally used in each laboratory, so that the methods may change from laboratory to laboratory. To investigate this point, CRM GM-758 and the pure metals were used. Because these are standards or potential standards not for cooling but for heating, only the data measured by heating are discussed below.

Inorganic substances in GM-758, i.e. potassium nitrate, potassium perchlorate and silver sulfate were revealed to be inappropriate for the following reasons. A few participants observed abnormally high temperatures for all three substances for some unknown reason, and one participant could not observe the crystalline transition of potassium perchlorate. Even omitting these data, the standard deviations of the extrapolated onset temperature for these substances are larger than those for the pure metals, and differences between the measured temperature and the reported equilibrium transition temperature are large.

For each participant the difference between T_{im} and the equilibrium melting temperature for the pure metals is plotted against T_{im} . Smooth curves were drawn from the plots, and the curves reflect differences in the above-mentioned temperature calibration. Because these curves are deviations from the equilibrium temperature, the reported temperatures for the polymers and the inorganic substances are corrected using these curves, if there is any deviation.

The standard deviations of the corrected data of T_{im}, T_{pm} and T_{em} for all polymer samples are similar to or slightly smaller than those of the reported uncorrected data. Similarly the correction decreases the standard deviation of the glass transition temperatures. It was also revealed that the standard deviations of the data for the second run were smaller than those of the first run for the as-received PE and PEEK, presumably because the thermal contact between the sample and the sample pan became better due to melting in the first run.

The effect of the above-mentioned correction on the variance of the data was elucidated in a different way. For each participant and sample, the deviation of the temperature from the average was obtained and the standard deviation of this deviation was calculated for each participant. In Figs 1 and 2 the deviations for T_{im} of the inorganic substances in the CRM and T_{pm} of the second run of PE and PEEK (group 1) are compared with those for T_{pm} of the first run of PE pellet, PEEK pellet, PE film and PET fibres and T_{gm} of PS and PES (group 2). Using the correction the points in the figures shift to the origin, and this fact illustrates the effect of the correction.

Furthermore, the standard deviations for group 1 are much smaller than those for group 2. This is presumably due to differences in sample handling and hence

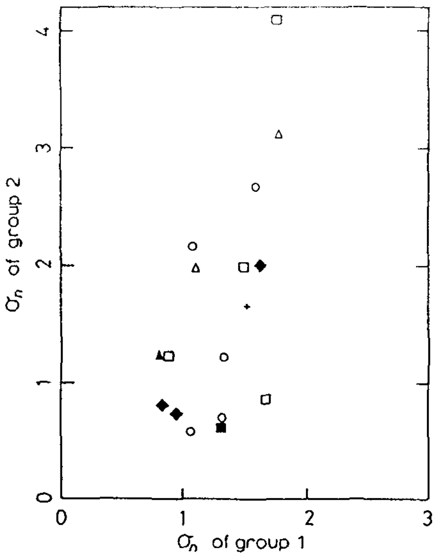

Fig. 1 Standard deviations σ_n of temperature measurements of each participant for sample group 1 and group 2 (before correction). Filled symbols and a cross are heat-flux DSC, and open symbols are power-compensation DSC

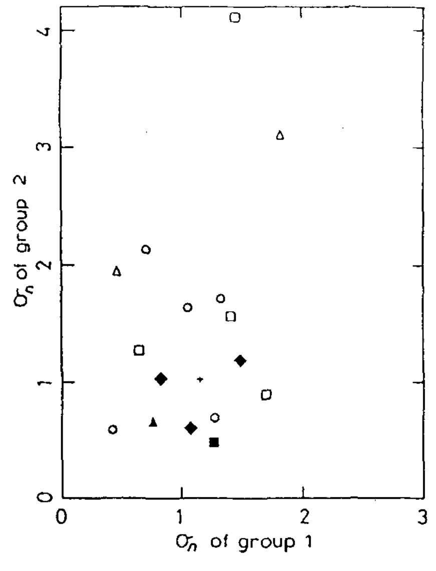

Fig. 2 Standard deviations σ_n of temperature measurements of each participant for sample group 1 and group 2 (after correction). Symbols are as in Fig. 1

the thermal contact between the sample pan and the sample holder among the participants, and this difference has more influence on the samples in group 2 than those in group 1.

Both types of DSC apparatus were used in this round robin test, namely power-compensation DSC and heat-flux DSC. The difference in the data between the two types of apparatus was examined. For each peak, the difference between T_{im} and T_{pm}, $(T_{pm}-T_{im})$, was obtained and this was divided by the difference averaged among the same sample, $<T_{pm}-T_{im}>$, for the purpose of normalization to eliminate the influence of the differences in the melting behaviour among the samples. A similar calculation was also made for the difference between T_{pm} and T_{em}.

In Fig. 3 the former normalized difference, $(T_{pm}-T_{im})/<T_{pm}-T_{im}>$ is plotted *vs.* the latter normalized difference, $(T_{em}-T_{pm})/<T_{em}-T_{pm}>$ for Sn powder and plate. Separation occurs between the power-compensation DSC and the heat-flux DSC in the abscissa, while it does not occur in the ordinate. Similar plots were made for the normalized difference averaged among the metal samples, and a more clear separation was observed.

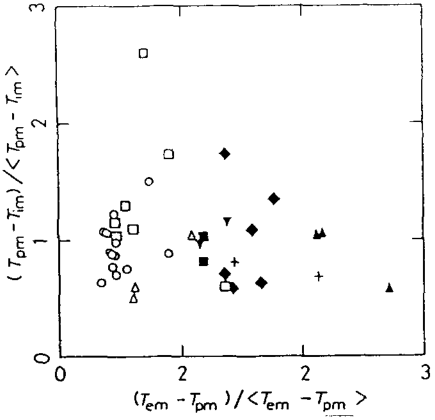

Fig. 3 $(T_{pm}-T_{im})/<T_{pm}-T_{im}>$ *vs.* $(T_{em}-T_{pm})/<T_{em}-T_{pm}>$ of Sn plate and powder. Symbols are as in Fig. 1

Because these plots were made only for the pure metals, the ordinate, $(T_{pm}-T_{im})/<T_{pm}-T_{im}>$, is related to the heat transfer coefficient between the sample and the heater in the heat-flux DSC and to the heat transfer coefficient between the sample and the microheater or the temperature sensor in the power-compensation DSC [13, 14]. The abscissa, $(T_{em}-T_{pm})/<T_{em}-T_{pm}>$, is related to the time constant of the apparatus recovering from non-steady state caused by the melting to the steady state (the base line) [13, 15]. It can be concluded from the above facts that the difference in heat transfer coefficient between both types of DSC is negligibly small, but the time constant differs appreciably between the two types.

From the above separation, the author infers that the geometry and the materials of the sample pan, the sample holder and their surroundings are similar to each other for both types of DSC, so that the heat transfer coefficient are also similar. Because temperature control of the sample is made with the microheater and the sensor independently of the reference material in power-compensation DSC, the non-steady state is limited around the sample, and its volume and hence its heat capacity is small, so that the time constant is small [13, 15]. On the other hand, the temperature control is made for both the sample and the reference material with the common heater and sensor in heat-flux DSC (and DTA), so that the non-steady state occurs in a large volume, and hence the time constant is larger than that of the power-compensation DSC [13].

For the second run of PE and PEEK, the latter normalized differences are plotted against the latter normalized differences of the metals in Fig. 4. As seen in the figure, the normalized differences for PEEK are quite similar to each other and independent of those for the pure metals, while correlation is observed in their small value for PE. This fact was inferred by the sharp melting of PE.

Heat of transition

The samples are the same crystalline polymers used for the above melting temperature measurements, and temperature calibration is also the same as mentioned above. For calibration of heat, only indium of over 99.99% purity was used by almost all participants, but two participants used tin, lead and zinc of over 99.99% purity together with the indium standard. Only the first heating was recommended for zinc because of possible contamination by aluminium from the sample pan. The heat of crystallization and the heat of melting in the second heating were measured only for PE pellet and PEEK. The rates of heating and cooling were 10 and 5 deg·min^{-1}, respectively.

The reproducibility of the measurements was examined by calculating the standard deviation of the reported data.

Percentages of the standard deviation are listed in Table 3. The shape of the sample seems to have little influence on the reproducibility, because the standard deviation for the first heating is smaller than for the second run for PEEK. Comparing the results of both PET samples of different thermal history, we can examine its effect on the reproducibility, but it was not found. Other factors, such as type of the apparatus, the sample mass etc., were examined, but their effects were not detected with over 95% reliability by statistical analysis. Only one factor affecting the reproducibility is the temperature width from T_{im}' to T_{em}', and it was detected with over 95% reliability.

One typical example of the correlation between the reported heat and the temperature width is shown in Fig. 5, where the results with the largest standard deviation are shown. A similar linear correlation is also clearly seen in the other results. This is due to base line drawing in the melting temperature range, because

Table 3 Averages and standard deviations of heats of melting and crystallizaton

	Heat of melting/kJ·kg^{-1}							Heat of crystallization/kJ·kg^{-1}	
	PE			PET		PEEK		PE	PEEK
	Pellet		Film	Fiber		Pellet		Pellet	Pellet
				A	B				
Run	1	2	1	1	1	1	2	1	1
Participants	12	12	12	12	12	12	12	12	12
Average	167.0	192.3	173.1	50.8	57.2	31.7	32.3	176.8	38.4
Standard deviation	17.4	16.4	14.0	7.0	4.6	10.0	12.3	26.5	8.7
Standard deviation /%	10.4	8.5	8.1	13.8	8.0	31.5	38.0	15.0	22.7

it was recommended that the linear line should be drawn connecting the base lines at T_{im}' and T_{em}'. For the heat of melting, the larger reported heat tends to correspond to the lower reported T_{im}' while the variance of the reported T_{em}' is small. Therefore, the observed low reproducibility is caused by difficulties in recogni-

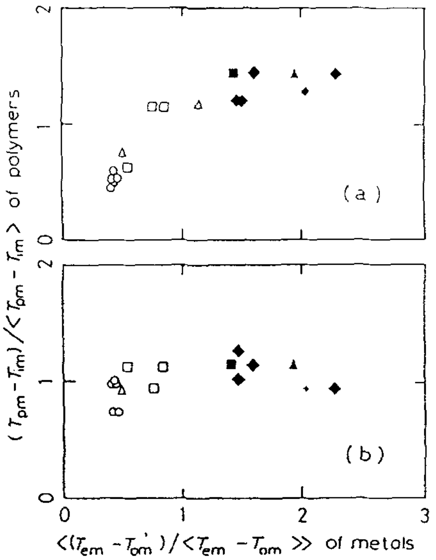

Fig. 4 $<(T_{em}-T_{pm})>/<T_{em}-T_{pm}>$ of metals *vs.* those of the 2nd run of PE (a) and PEEK (b). Symbols are as in Fig. 1

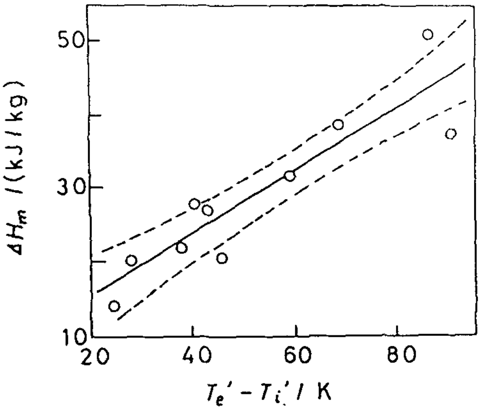

Fig. 5 Relation between heat of melting and difference between onset temperature and end temperature for the 2nd run of PEEK

tion of the endothermic deviation from the base line. For the heat of crystallization, the reported T_{cm}' is also scattered.

To improve the reproducibility, adjustment of the apparatus should be recommended to obtain a straight base line. Another way is to use a base line obtained with an empty pan. The method of heat capacity measurement described later is also applicable to the transition region, and by integrating the obtained apparent heat capacity we can get the temperature dependence of the apparent enthalpy, which shows a step change at the transition. The heat of transition can be estimated by the difference between the extrapolated linear change of the equilibrium enthalpy at the extrapolated onset transition temperature [15].

Heat capacity

Only five laboratories participated in this round robin test, presumably due to the low popularity of this method and also due to the relatively low needs for the measurement. The usual method was applied to PS in a temperature range including the glass transition.

One of the remarkable results found by this round-robin test was that both types of DSC can be used for this purpose in spite of the larger thermal response time of the heat-flux DSC, although one participant using a heat-flux DSC had difficulties with the instability of the horizontal isothermal base line. Some participants found disagreement between two isothermal base lines and connected them with a straight line.

Nevertheless the reproducibility is very good. In the glass transition region, the standard deviation is less than 4% at its maximum, and in the other temperature region it is less than 3%. However, sample mass dependence was found as

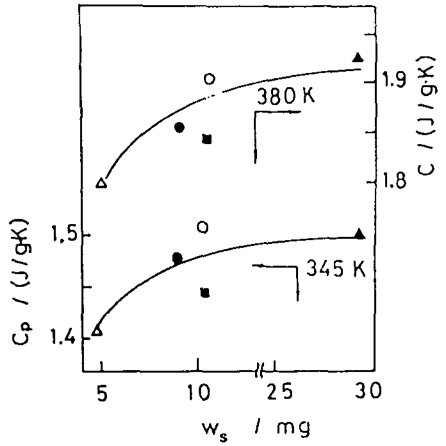

Fig. 6 Relation between measured heat capacity and sample mass

seen in Fig. 6, though approximately 10 mg was recommended for the sample mass. Therefore samples of more than 10 mg are essential.

Thermogravimetry

The samples used were PE films, PES pellet, two kinds of polyacetal (POM) and two kinds of bulk epoxide (EP) resins. PE and PES are the same as mentioned before. Polyacetals were selected because of thermal decomposition during fabrication.

All TG runs were carried out at 10 deg·min^{-1} under nitrogen or argon gas flow except for the epoxide resins, for which TG was carried out under air flow to estimate the contents of filler and glass fibre. The polymeric specimens were 10 mg finely cut samples, while the metallic samples for calibration were cut sheets or cut wires.

Temperature calibration

Temperature calibration was made with ICTA-NIST CRM GM-761 and nickel wire of over 99.997% purity. However some participants could not observe the Curie point at the first run. The following procedure was recommended. The sample is set in a thermobalance and a permanent magnet or an electromagnet is advanced toward the thermobalance until an appreciable apparent mass change is observed. Then the run is started, and the Curie point can be detected by a stepwise change in the apparent mass.

Reproducibility in the Curie point measurement of the nickels is very good, and nickel from the CRMs or nickel of high purity is excellent for this purpose. Among others, Trafoperm from the CRMs is also very good, and the standard deviations of the three characteristic temperatures described below are in a range of 3–5 K. When calibration in a high temperature range is needed, it is very useful.

Thermogravimetry of polymers

Reproducibility in the mass loss measurements is very good. The standard deviations of these measurements are 2% for PE and one kind of polyacetal. The data of two participants deviated greatly for some unknown reason, and by omitting these data the standard deviations are improved to 0.5%, which seems to be the intrinsic precision in TG. The standard deviations for another kind of polyacetal and two epoxide resins are also very good (2%). However, the reproducibility of PES is not so good as the others. The decomposition of this material proceeds gradually in a wide temperature range, and the final decomposition temperature, T_3, scatters very much. These seem to be the reasons for the low reproducibility. One plausible cause for the scattering of the mass loss data is insufficient exchange of the atmosphere, and control of the atmosphere is very important to obtain high reproducibility and reliability. Naturally a similar tendency was observed for the measurements of the residue.

To characterize the thermal stability, three temperatures are measured, and they are the same as measured in the Curie point measurements. They are the initial decomposition temperature, T_1, at which the tangent at the maximum slope intersects the horizontal zero line, the mid-point temperature, T_2, which corresponds to the mid-point of the mass loss, and the final decomposition temperature, T_3, at which the above tangent intersects the extrapolated quasi-horizontal line after the decomposition. The reproducibility of these temperature measurements is not so good as the mass loss measurements. The highest reproducibility was found for PE, and the standard deviations for T_1, T_2 and T_3 are less than 6 K. For the polyacetals and PES the standard deviations for T_1 and T_2 are in the range 9–23 K and fairly good. For the epoxide resins the standard deviations are 23–70 K, and some participants observed a one-step decomposition, while others observed a two-step mass loss. This discrepancy seems to be due to difference in the procedure, such as subdivision of the specimen. The worst reproducibility was that for PES as mentioned above.

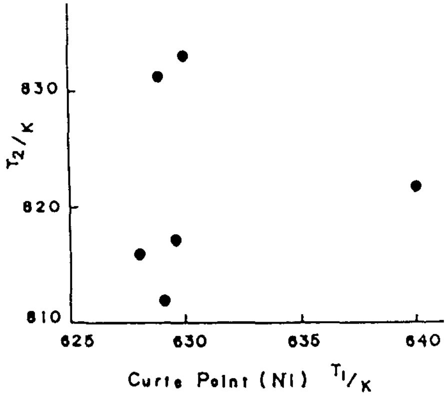

Fig. 7 Correlation between measured Curie point of Ni and mid-point temperature of PES

The correlation between the observed decomposition temperatures and the reported Curie temperatures was examined. One example is shown in Fig. 7, and there is no clear correlation. Compared with the reproducibility of the Curie point measurements, the scattering of the decomposition temperatures is very large. Similar results were also obtained for the other polymeric samples. Therefore, the main causes for the low reproducibility is not in the temperature measurement but in the procedure, such as sample subdivision, sample packing etc., and in the experimental conditions, such as control of atmosphere. To achieve good reproducibility, keen attention should be paid to these points.

Thermomechanical analysis

This round-robin test was carried out to establish a test method for evaluating the thermomechanical stability of so-called engineering plastics. Therefore, the samples used were different from those in the above round-robin test; they were sheets of polyoxymethylene (POM; 500 µm thick), polycarbonate (PC; 500 µm), polyarylate (PAR; 100 µm), poly(ether ether ketone) (PEEK; 200 µm), poly(ethylene terephthalate) (PET; 40 µm), and poly(phenylene sulfide) (PPS; 130 µm). Because temperature standards for TMA have not yet been established, pure metal plates were used instead; indium (99.99% purity, 500 µm thick), tin (99.9%, 300 and 350 µm), lead (99.9%, 300 and 500 µm) and zinc (99.99% 300 µm).

All TMA runs were carried out at 5 deg$\cdot$min^{-1} under a flow of inert gas, by penetration mode; the loads were 10 gf, 50 gf and 100 gf for the polymers and 50 gf for the metals, and the probe tip diameter was 0.5, 1.0, 1.1 or 1.2 mm.

Temperature calibration

A sharp change was observed at the melting of the metals. Thus pure metal plates were revealed to be very good useful temperature standards. The temperature at which the horizontal base line intersects the tangent at the maximum slope of the change was measured as the melting temperature and used for the calibration. The same temperature was measured also for the polymeric samples, and the measured temperature was corrected with the nearest lower and higher melting temperatures of the metals measured with the same TMA apparatus.

The repeatability of the measured melting temperatures of the metals by the same participant is very good; the maximum range in the repeated runs is 4 K and most ranges were less than 2 K. However, the reproducibility or scattering of the data among the participating laboratories is relatively large; differences between the melting temperature and the reported one scattered from +0.6 K to + 9.6 K at best (In) and from −10.4 K to +10.6 K at worst (Sn). This low reproducibility in the measured melting temperature shows a need for temperature standards and correction of data by calibration.

Softening temperature of polymers

Repeatability of the measured softening temperature is generally good with a few exceptions. However, to achieve high reproducibility, the above-mentioned correction of the data is essential; for example the standard deviation decreased markedly on applying this correction. The ranges and the standard deviations of the corrected data are 3.2–22 K and 1.3–8 K, respectively.

The probe tip diameter has no influence on the measurement. The load does not have a definite effect on the measured temperature, and the difference in the measured temperature between 50 gf and 100 gf is smaller than that between 10 gf and 50 gf. Therefore 50 gf was recommended for the load.

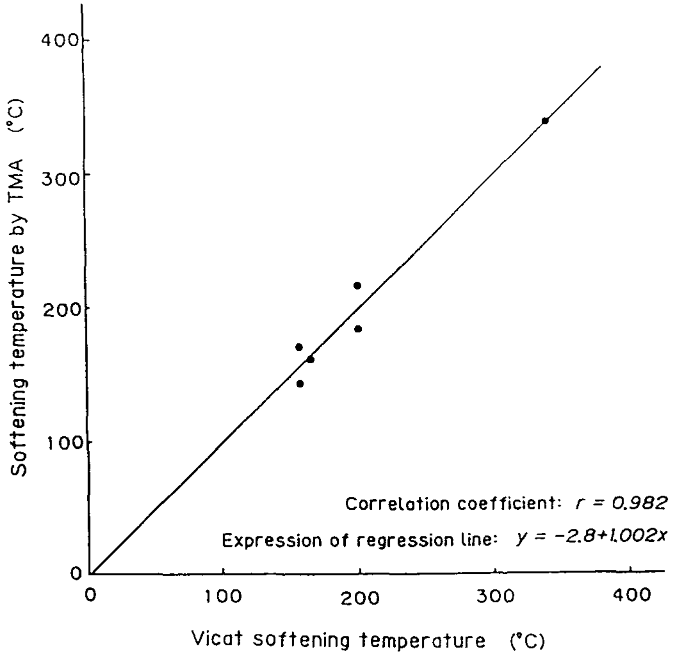

Fig. 8 Correlation between Vicat softening temperature and softening temperature determined by TMA

The corrected softening temperatures by TMA were related to those by the conventional Vicat test in Fig. 8 for POM, PC, PAR and PEEK; two-step softening was observed for PC and PAR, and the melting temperature of PEEK was plotted in this figure. As is seen, a clear correlation was obtained, and it was concluded that TMA can be applied to the estimation of softening temperature of thermoplastics satisfactorily, using pure metals as temperature standards.

Thermodilatometry

TMA was applied to thermodilatometry; block specimens were measured in the compression mode with constant weights of 20 gf·cm^{-2} and 40 gf·cm^{-2}, and polyimide film was measured with a 2 gf tensile load. All runs were in inert gas atmosphere and at heating rates of 2.5 and 5 deg·min^{-1}.

Calibration

Temperature calibration was made with the pure metals in Table 2 sandwiched between PI blocks. Deviations of the measured temperatures from the equilibrium were −1.5 K– +4.0 K for Woods metal, −3 K– +6 K for In and −1.5 K– +8.0 K for Sn. These were used for temperature correction, and these metals were shown to be useful for temperature calibration of thermodilatometry as well as for TMA. Blank tests were also carried out with quartz glass as the specimen to check drift of the base line on heating, and the results were used for correction of the base line drift.

Measurement of polymers

Because residual stress has an influence on the measurements, all polymeric samples were annealed at the maximum measuring temperature for two days to eliminate the residual stress from molding, and this procedure is also effective for dehumidification. The results were analysed by variance analysis, and it was found that neither heating rate nor load influenced the data. Differences among the participants were detected at the 99% or 95% confidence level, but the difference in thermal expansion coefficient was in a range from +2% to +7%, and the results are satisfactory after correction of the data, as shown in Fig. 9.

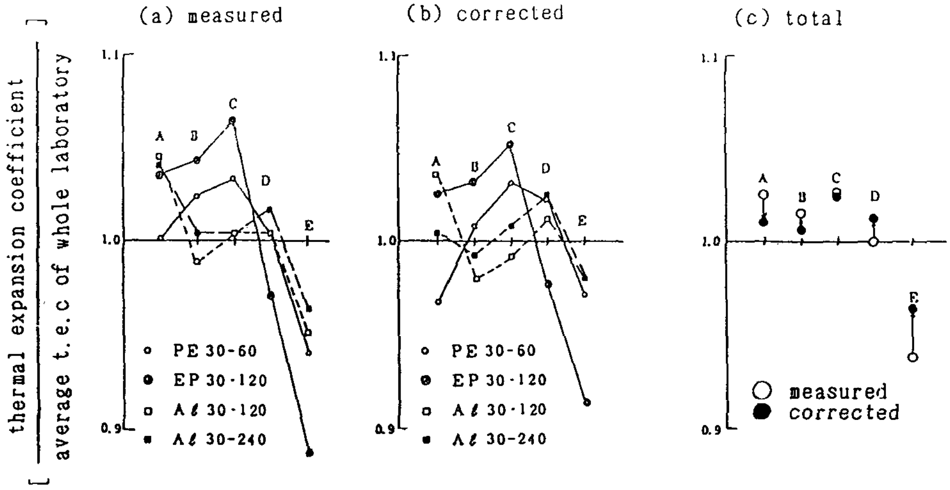

Fig. 9 Thermodilatometry results. The symbols on the abscissa (A–E) indicate the participants, and the ranges shown are the temperature range of measurements

Other activities

On the basis of the above round-robin test results, other standardization programmes were established in Japan, for instance, determination of the transformation temperature of shape memory alloys and thermodilatometry of ceramic materials. Similar activities are also in progress in other countries as presented in the standardization workshop of the 10th ICTA Congress.

In the International Standardization Organization (ISO), a series of thermoanalytical standardizations of polymeric materials, such as described in this review, are now in progress, and round-robin tests will be organized in the future. They will reveal the current situation in thermal analysis on an international basis.

It should also be noted that a round-robin test of evolved gas analysis is now proceeding in Japan, and the purpose is to establish a test method for estimating the activation energy or temperature dependence of long-term thermal endurance life of electrical insulating materials. This method was proposed to the International Electrotechnical Commission (IEC).

Concluding remarks

The round-robin tests revealed the usefulness of thermal analysis for practical characterization of polymeric materials, and reproducibility and causes of errors in the measurements were elucidated. Although there remains room for further improvement, these techniques can be applied to industrial standardization. These results are encouraging for industrial standardization of thermal analysis in other fields of materials characterization.

However, to obtain comparable data, calibration, especially temperature calibration, by standard materials is essential, because temperature gradients within and around the sample are inevitable in linear-heating thermal analysis and hence the precision and accuracy of temperature measurements are limited in these techniques. For calibration purposes, the ICTA-NIST certified reference materials are very useful but need some modification. They should be used not only for mutual comparison among data but also for temperature calibration. Furthermore, it is necessary to establish similar certified reference materials for other thermoanalytical techniques. For thermomechanical analysis and thermodilatometry, pure metal plates are very good potential standard materials for temperature calibration. In relation to temperature calibration, adjustment of the thermocouple position is also very important to decrease the effect of the inevitable temperature gradient mentioned above.

Similarities and differences between heat-flux and power-compensation DSC were brought out by the round-robin test, in which various DSCs were used. For both types of DSC it was pointed out that base line stability is very important to get reproducible heats of transition for polymeric materials, because they have wide temperature ranges of melting and crystallization. Two possibilities were identified to increase accuracy and precision. As potential standard materials for measurement of heats of transition, pure metals were proposed and shown to be good. Standard materials are required for this purpose, with recommended values of the heat of melting.

Heat capacity measurement by both types of DSC was satisfactorily made with high precision. It can also be applied to the measurement of transition heat as one of the above alternatives.

Reproducibility of mass loss measurements is very good in TG, but that of decomposition temperatures determination is not so good. Their comparison with the Curie point measurement revealed that the main causes for this seem to be sample handling, atmosphere control etc. Detailed specification of these is needed to improve reproducibility.

TMA was shown to be an alternative technique for measuring softening temperature, and because it can be applied to a high temperature range, this technique is very useful for high-temperature engineering plastics. The results by TMA were satisfactorily compared with data by the conventional method, which can be replaced by TMA. TMA instruments are also applicable to thermodilatometry with low loads, and satisfactory results were obtained by using the potential standard material of quartz glass for base line calibration.

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Zusammenfassung — Um den Anforderungen der Industriestandards für die thermische Analyse in der japanischen Polymerindustrie zu entsprechen, wurden in letzter Zeit DSC-, TG- TMA- und TD- "Round-robin" Tests durchgeführt, deren Resultate hier im Überblick dargestellt werden.

Die getesteten DSC-Anwendungen dienten nicht nur der Bestimmung der Umwandlungstemperatur, sondern auch der Messung von Umwandlungswärme und Wärmekapazität. Die Aufgabengruppe TG richtete sich nicht auf Untersuchungen der langfristigen thermischen Lebensdauer, jedoch auf relative thermische Stabilität beim Formen und bei der Bestimmung von Füllstoffgehalten, Lösungsmittelrestgehalten usw.

TMA ergab sich anstelle des temperaturbegrenzten Vicat'schen Tests als ein nützliches Hilfsmittel zur Messung der Erweichungstemperatur und der Formbeständigkeit / in der Wärme, insbesondere bei technischen Hochtemperaturplasten. Zur Temperaturkalibrierung von DSC und TG wurden ICTA-NIST zertifizierte Bezugssubstanzen zusammen mit anderen potentiellen Temperaturstan-

dards verwendet; einige anorganische Substanzen und Legierungen sollten reinen Metallen nicht vorgezogen werden. Für TMA und TD erwiesen sich Metallplatten für die Temperaturkalibrierung als sehr nutzbringend. Die Analyse der "Round-robin" Testresultate erklärte auch den Stellenwert der praktischen Anwendungen der Thermoanalyse, wie z.B. der Reproduzierbarkeit oder der Fehlerursachen.