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A ROUND-ROBIN TEST OF THE SOFTENING TEMPERATURE OF PLASTICS BY THERMOMECHANICAL ANALYSIS

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ABSTRACT

The accuracy of the determination of the softening temperatures of thermoplastics by the penetration method of thermomechanical analysis was examined by a round-robin test, in which 15 laboratories participated. Film samples of polyoxymethylene, polycarbonate, polyarylate, poly(ether ether ketone), poly(ethylene terephthalate) and poly(phenylene sulphide) were used for the test. The correction of measured temperatures using the melting points and the measured softening temperatures of pure metals was effective in decreasing the very large scatter observed between the reported values from the laboratories. The scatter in the corrected temperatures under a load of 50 gf was in the range 1.32–6.52°C (standard deviation) and 0.52–3.02% (coefficient of variance). This method could be standardized as a new testing method; it can be correlated with conventional methods and can be used for measurements at higher temperature.

INTRODUCTION

A number of practical test methods have been widely used for the determination of the softening temperatures of plastics in order to evaluate their thermal stabilities, e.g. Vicat indentation test, heat distortion test, etc. However, in recent years, evaluation using conventional methods has often proved to be difficult when testing newly developed plastics with high heat stabilities. The softening temperatures of these new plastics are higher than the temperature limit for heating silicone oils which are used as the liquid heat-transfer medium in the testing apparatus. Thermomechanical analysis (TMA) can be used as a new testing method to solve this problem.

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This paper is concerned with an interlaboratory test (round-robin test, RRT) which was conducted to confirm the accuracy of the determination of the softening temperatures of film or sheet samples of thermoplastics by TMA.

Before this RRT, three preliminary RRTs were carried out. The following findings were obtained from the preliminary RRTs: (i) the penetration method, which is one of several methods of TMA, can be applied to the measurement of the softening temperature of plastics; (ii) the thickness of the testing sample should not be larger than the TMA range, which is a measure of the sensitivity of the apparatus for detecting penetration; (iii) appropriate pure metals in plate form can be used as potential standard materials for correcting the measured temperatures. The procedures used in this RRT were decided with reference to the preliminary RRTs.

EXPERIMENTAL

Participating laboratories

The 15 laboratories shown in Table 1 participated in the RRT; nine are public institutes, two are testing laboratories, one is a national institute and three are private enterprises (two of these are manufacturers of TMA apparatus). They were divided into two groups, A and B.

TABLE 1

Participating laboratories in the round-robin test

Laboratories	Group
Hokkaido Industrial Research Institute	A
Gunma-ken Industrial Research Laboratory	A
Industrial Technology Research Institute of Saitama	A
Industrial Research Institute of Nagano	A
Gifu Prefecture Industrial Research Technical Centre	A
Industrial Research Institute, Hiroshima Prefecture West	A
Tokushima Prefecture Industrial Research Institute	A
Industrial Research Centre of Ehime Prefecture	A
Osaka Municipal Technical Research Institute	A
Chemicals Inspection and Testing Institute, Japan	A
Japan High Polymer Centre	A B
Government Industrial Research Institute, Osaka	A B
Showa Denko Co. Ltd.	B
Shimadzu Corporation	B
Rigaku Corporation	B

TABLE 2

Plastic and metal samples allocated to the participating laboratories in the round-robin test

Group	Plastic		Metal		
	Sample	Thickness (μm)	Sample	Purity (%)	Thickness (μm)
A	POM	500	In	99.99	500
	PC	500	Sn	99.9	300
	PAR	100	Pb	99.9	300
	PEEK	200	Zn	99.99	300
B	PET	40	Sn	99.9	350
	PPS	130	Pb	99.9	500

Samples

Polyoxymethylene (POM, supplied by Polyplastics Co., Ltd.), polycarbonate (PC, supplied by Mitsubishi Gas Chemical Co. Inc.), polyarylate (PAR, supplied by Unitika Ltd.), poly(ether ether ketone) (PEEK, supplied by Sumitomo Chemical Co., Ltd.), poly(ethylene terephthalate) (PET, supplied by Toray Industries, Inc.) and poly(phenylene sulphide) (PPS, supplied by Toray Industries, Inc.) films were used as plastic samples. Indium, tin, lead and zinc were used as metal samples. They were purchased from Japan Lamp Industries Co., Ltd. The samples allocated to groups A and B and their details are shown in Table 2.

Apparatus

With the exception of one apparatus (Mettler thermomechanical analyser-40), all apparatuses used in the laboratories were thermomechanical analysers made by Japanese manufacturers, (Rigaku Corporation (7), Shimadzu Corporation (4), Seiko Instruments and Electronics Ltd. (2) and Shinku-Riko, Inc. (1)). Two appeared on the market in 1973–1974 and the others appeared during the last few years. Detection needles with diameters of 0.5, 1.0, 1.1 or 1.2 mm were used.

Procedure for TMA

In each laboratory, experiments were carried out using the following procedures.

The plastic and metal samples were conditioned at $23 \pm 2°C$ and at a relative humidity of $50\% \pm 5\%$ (or under similar conditions) for more than 24 h before measurement. The samples were cut to a suitable form and size for the sample holder of the apparatus. The sample was mounted on the centre of the sample holder and the detection needle was set on the centre of the sample according to the instruction manual of the apparatus. A load was

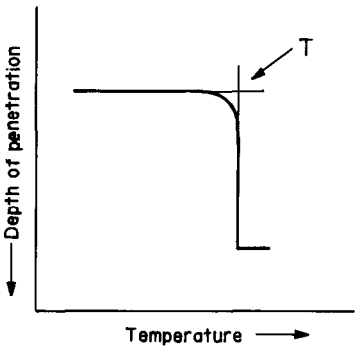

Fig. 1. Typical TMA curve of metal.

added to the needle, and the sample was heated at a rate of 5 °C min^{-1} in an atmosphere of inert gas at a flow rate of 50–100 ml min^{-1}. The loads used were 10 gf, 50 gf and 100 gf for the plastic samples and 50 gf for the metal samples. The TMA range was set close to but larger than the thickness of the sample. The TMA curve was recorded during the overall process by adjusting the position of the TMA pen. Measurements were repeated twice for every sample at a particular load.

Determination of softening temperature

The metals show a sharp change at their melting points in the TMA curve (Fig. 1). The temperature T at the intersection between the extrapolation of the baseline before penetration of the needle and extrapolation of the line showing its penetration was taken as the softening temperature. Figure 2 shows typical TMA curves of plastics. Although the baselines were often unstable, the softening temperatures were taken in the same way as for the metals (Figs. 2(a) and 2(b)). If a TMA curve changed at two steps (or more), T_1 and T_2 (and T_3, etc.) were recorded (Figs. 2(c) and 2(d)).

Correction of measured value

The measured values of the softening temperatures of the plastics were corrected (using the differences between the measured softening temperatures of the metals and their melting points (In, 156.4 °C; Sn, 231.9 °C; Pb, 327.4 °C; Zn, 419.5 °C)) by the equation

$$T_c = T_i - \Delta T_l - (T_i - T_l)\frac{\Delta T_h - \Delta T_l}{T_h - T_l}$$

$$\Delta T_h = T_h' - T_h$$

$$\Delta T_l = T_l' - T_l$$

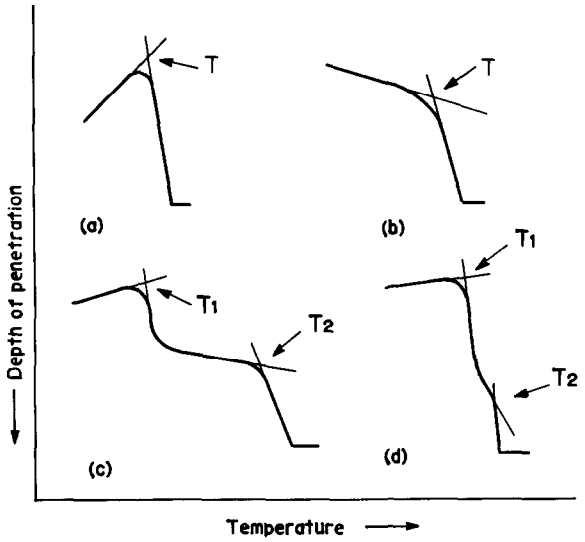

Fig. 2. Typical TMA curves of plastics.

where T_c is the corrected value, T_i is the measured value, T_h' and T_h are the measured softening temperature and the melting point respectively of the metal nearest to T_i on the higher-temperature side and T_l' and T_l are the measured softening temperature and the melting point respectively of the metal nearest to T_i on the lower-temperature side. When the T_i value was lower than the melting point of indium, it was corrected by extrapolation of the equation.

RESULTS AND DISCUSSION

In the measurements of the softening temperatures of the metal samples, differences between the repeated measured values were 4°C in one case, 3°C in four cases, 2°C in eight cases and within 1°C in the others. The reproducibility seemed to be good and was not influenced by the type of metal. However, the values varied widely between laboratories. The differences between the measured values of softening temperature and the melting points were within the following ranges: In, +0.6 – +9.6°C; Sn, −10.4–+10.6°C; Pb, −6.4–+10.1°C; Zn, −4.5–+12.5°C. These results show that a correction had to be made to the values measured by the different laboratories.

The reproducibility of the two measurements of the plastic samples was also satisfactory except in a few cases.

The measured softening temperatures of the plastic samples (average of two measurements) and the corrected values reported from the participating

TABLE 3

Softening temperature of POM

	10 gf		50 gf		100 gf	
	Measured	Corrected	Measured	Corrected	Measured	Corrected
n	12	11	12	11	10	10
X_{max} (°C)	168.0	165	168.0	162	168.5	162
X_{min} (°C)	156.5	157	154.0	157	152.0	158
$X_{max} - X_{min}$ (°C)	11.5	8	14.0	5	16.5	4
$\bar{X}$ (°C)	163.9	161.5	162.9	160.4	161.8	159.9
σ_{n-1} (°C)	3.47	2.46	4.21	1.86	4.46	1.37
CV (%)	2.12	1.53	2.58	1.16	2.76	0.86

laboratories are shown in Tables 3–8. The tables show the number n, the maximum value X_{max}, the minimum value X_{min}, the width between maximum and minimum values ($X_{max} - X_{min}$), the mean value $\bar{X}$, the standard deviation σ_{n-1} and the coefficient of variance CV of the reported values. Comparison of the amounts of scatter in the measured and corrected values, which are indicated by $X_{max} - X_{min}$, σ_{n-1} and CV, shows that the correction is effective, with the exception of T_1 of PC and T_2 of PEEK under a load of 100 gf. For example, in the measurement of POM under a load of 50 gf, $X_{max} - X_{min}$ (14.0 °C), σ_{n-1} (4.21 °C) and CV (2.58%) of the measured value are decreased to 5 °C, 1.86 °C and 1.16% respectively by the correction (Table 3). On the whole, with the exception of the two cases above, $X_{max} - X_{min}$ (ranging from 10.9 to 32.0 °C), σ_{n-1} (ranging from 3.47 to 10.10 °C) and CV (ranging from 1.76% to 4.59%) are reduced to the ranges 3.2–22 °C, 1.32–7.88 °C and 0.48–3.51% respectively by the correction.

In the RRT, three loads (10, 50 and 100 gf) were added to the detection needle of the apparatus. Effects of load on the corrected $\bar{X}$ and σ_{n-1} values are shown in Fig. 3. In the majority of cases, there is a tendency for an increasing load to lower the softening temperature. With regard to scatter, an increasing load leads to a decrease in σ_{n-1} in the measurement of POM, PC (T_2), PAR (T_2) and PEEK (T_1 and T_3) and to an increase in σ_{n-1} in PC (T_1), PAR (T_1) and PPS. In the measurement of PEEK (T_2) and PET, a load of 50 gf gives the smallest σ_{n-1} values. However, in general, the differences in the values of X and σ_{n-1} between loads of 50 gf and 100 gf are smaller than those between 10 gf and 50 gf. From these results, 50 gf is considered to be the most appropriate load for testing the softening temperature.

The diameters of the needles used in the study were in the range 0.5–1.2 mm. Diameter has no influence on the results of measurement.

The softening temperatures of thermoplastics determined by TMA are related to their melting temperatures or glass transition temperatures. For the samples used in this RRT, the softening temperatures of POM, PET, PPS and PEEK (T_3) are related to the former and those of PC (T_1 and T_2),

TABLE 4

Softening temperature of PC

	10 gf				50 gf				100 gf			
	Measured		Corrected		Measured		Corrected		Measured		Corrected	
	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2
n	7	12	7	11	9	12	8	11	7	10	7	10
X_{max} (°C)	152.0	191.0	149	181	154.0	184.0	148	174	152.0	180.5	153	171
X_{min} (°C)	140.0	165.0	139	165	137.0	158.0	136	162	138.0	156.5	137	161
$X_{max} - X_{min}$ (°C)	12.0	26.0	10	16	17.0	26.0	12	12	14.0	24.0	16	10
$\bar{X}$ (°C)	148.3	176.0	145.9	173.8	145.1	170.9	142.8	168.6	146.4	168.6	145.3	166.5
σ_{n-1} (°C)	4.24	7.04	3.72	4.17	5.92	6.49	4.30	3.44	5.20	6.68	5.68	3.27
CV (%)	2.86	4.00	2.55	2.40	4.08	3.80	3.01	2.04	3.55	3.96	3.91	1.97

TABLE 5

Softening temperature of PAR

	10 gf				50 gf				100 gf			
	Measured		Corrected		Measured		Corrected		Measured		Corrected	
	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2
n	9	11	9	10	9	11	8	10	9	7	9	7
X_{max} (°C)	189.0	240.0	187	233	193.5	230.5	187	230	198.0	228.5	193	218
X_{min} (°C)	172.0	208.0	180	213	174.0	202.0	177	208	178.5	202.5	177	203
$X_{max} - X_{min}$ (°C)	17.0	32.0	7	20	19.5	28.5	10	22	19.5	26.0	16	15
$\bar{X}$ (°C)	183.6	225.2	183.2	224.4	184.1	217.8	182.1	216.1	185.9	216.0	183.9	212.4
σ_{n-1} (°C)	5.14	10.10	2.44	7.88	6.21	9.00	3.23	6.52	5.54	9.91	4.81	6.27
CV (%)	2.80	4.49	1.33	3.51	3.37	4.13	1.77	3.02	2.98	4.59	2.61	2.95

TABLE 6

Softening temperature of PEEK

	10 gf						50 gf						100 gf					
	Measured			Corrected			Measured			Corrected			Measured			Corrected		
	T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3
n	11	9	11	10	8	10	11	9	11	10	8	10	9	5	9	9	5	9
X_{max} (°C)	150.0	166.5	351.0	144	164	344	152.0	163.5	348.5	145	161	342	152.5	161.0	347.0	144	159	338
X_{min} (°C)	132.0	154.0	327.0	130	154	332	134.5	151.0	328.0	134	155	332	134.5	157.0	328.0	137	153	332
$X_{max} - X_{min}$ (°C)	18.0	12.5	24.0	14	10	12	17.5	12.5	20.5	11	6	10	18.0	4.0	19.0	7	6	6
$\bar{X}$ (°C)	141.0	161.4	340.3	138.0	159.5	339.2	144.2	159.1	338.1	141.3	157.3	336.8	143.9	158.9	336.1	141.7	156.2	335.1
σ_{n-1} (°C)	6.11	4.47	7.47	4.24	3.02	3.39	5.51	4.04	6.41	3.13	1.98	2.66	5.21	1.67	6.22	2.12	2.17	1.83
CV (%)	4.33	2.77	2.20	3.07	1.90	1.00	3.82	2.54	1.90	2.21	1.26	0.79	3.62	1.05	1.85	1.50	1.39	0.55

TABLE 7

Softening temperature of PET

	10 gf		50 gf		100 gf	
	Measured	Corrected	Measured	Corrected	Measured	Corrected
n	5	5	5	5	5	5
X_{max} (°C)	257.3	256.5	256.0	253.9	253.8	252.6
X_{min} (°C)	242.3	251.6	242.8	250.7	242.9	248.5
$X_{max} - X_{min}$ (°C)	15.0	4.9	13.2	3.2	10.9	4.1
$\bar{X}$ (°C)	253.3	254.5	251.8	252.9	249.8	250.9
σ_{n-1} (°C)	6.38	2.40	5.37	1.32	4.57	1.68
CV (%)	2.52	0.94	2.13	0.52	1.83	0.67

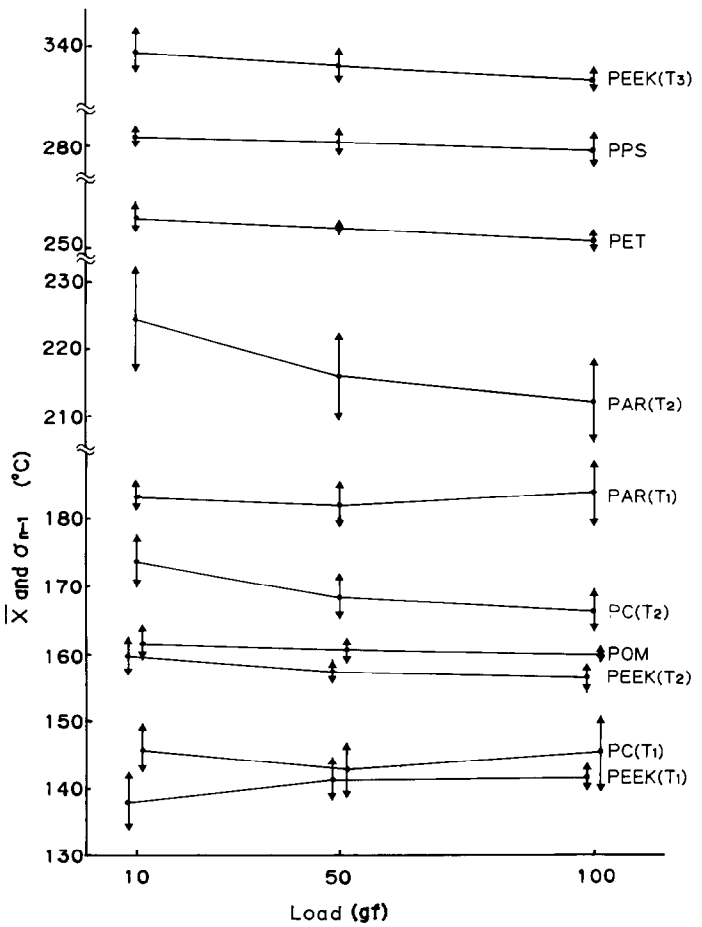

Fig. 3. Effect of load on the mean value ($\bar{X}$ corrected) and standard deviation (σ_{n-1}) corrected).

TABLE 8

Softening temperature of PPS

	10 gf		50 gf		100 gf	
	Measured	Corrected	Measured	Corrected	Measured	Corrected
n	5	5	5	5	5	5
X_{max} (°C)	285.7	284.0	284.8	283.5	283.3	283.0
X_{min} (°C)	272.7	280.6	269.7	277.8	268.9	277.1
$X_{max} - X_{min}$ (°C)	13.0	3.4	15.1	5.7	14.4	5.9
$\bar{X}$ (°C)	280.9	281.6	280.0	280.8	278.8	279.6
σ_{n-1} (°C)	4.95	1.36	6.03	2.04	5.79	2.28
CV (%)	1.76	0.48	2.15	0.73	2.07	0.81

PAR (T_1 and T_2) and PEEK (T_1 and T_2) are related to the latter. The Vicat softening temperatures of thermoplastics are also related to their melting temperatures and glass transition temperatures. In the case of PEEK, the Vicat softening temperature is only related to the melting temperature, PEEK (T_3). To examine the correlation between the softening temperature determined by TMA and the Vicat softening temperature, Vicat softening temperatures of samples of POM, PC, PAR and PEEK (which were of the

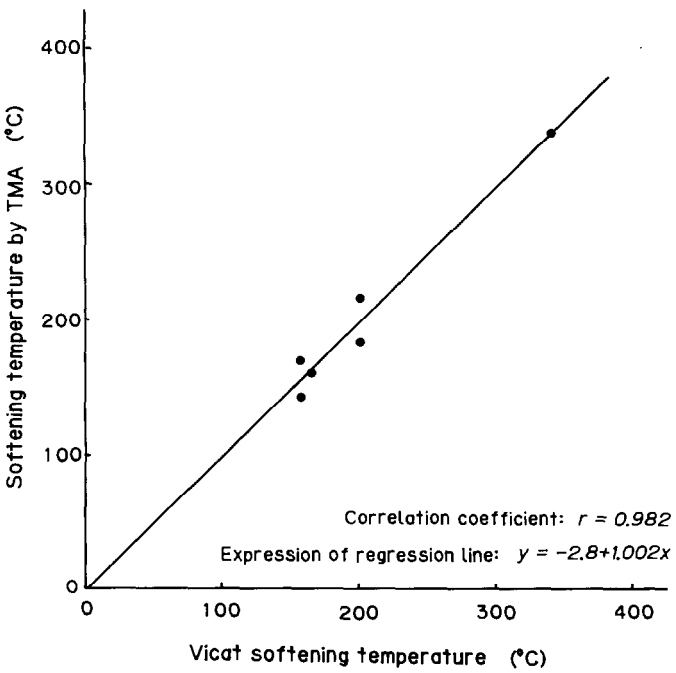

Fig. 4. Correlation between the Vicat softening temperature and the softening temperature determined by TMA.

same quality as used in the RRT but of greater thickness (sufficient to be tested)) were determined by the testing method defined by the Japanese Industrial Standard (JIS K 7206); however, the softening temperature of PEEK was determined by an improved testing method * using an air heat-transfer medium. Values of 164.9 °C, 157.3 °C, 201.3 °C and 338.9 °C were obtained for POM, PC, PAR and PEEK respectively. These values are plotted against the mean values under a load of 50 gf for POM (160.4 °C), PC (142.8 °C and 168.6 °C, T_1 and T_2), PAR (182.1 °C and 216.1 °C, T_1 and T_2) and PEEK (336.8 °C, T_3) in Fig. 4. The results suggest an adequate correlation between the Vicat softening temperature and the softening temperature determined by TMA.

CONCLUSIONS

The results can be summarized as follows: (i) the reproducibility of measurement is satisfactory; (ii) the correction using pure metals is effective in decreasing the very large scatter observed between laboratories; (iii) the most appropriate load is 50 gf; (iv) the scatter in the measurements under a load of 50 gf is in the range 1.32–6.52 °C (σ_{n-1}) and 0.52–3.02% (CV); (v) an adequate correlation with the Vicat softening temperature is suggested. The most important finding is that pure metals are useful for the correction of measured temperatures.

From the results of this RRT, it can be seen that the TMA method could be standardized as a new testing method for the determination of the softening temperatures of film or sheet samples of thermoplastics. This method can be used in the field where conventional methods cannot be employed, because it can be applied to thin and small samples and measurements at higher temperatures can be carried out easily.

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* This method is now being added to JIS K 7206 by the Japan High Polymer Centre.

Kagoshima Prefectural Institute of Industrial Technology, Industrial Products Research Institute and Ube Industries Ltd.

The preliminary and present RRTs were conducted under two systems: cooperative researcher among public institutes organized by the Government Industrial Research Institute, Osaka, and requests of the Japan High Polymer Centre to its supporting members.