International Standard 3146

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Plastics — Determination of melting behaviour (melting temperature or melting range) of semi-crystalline polymers

Plastiques — Détermination du comportement à la fusion (température de fusion ou plage de température de fusion) des polymères semi-cristallins

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 3146 was prepared by Technical Committee ISO/TC 61, *Plastics*.

This second edition cancels and replaces the first edition (ISO 3146-1974), of which it constitutes a minor revision.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Plastics — Determination of melting behaviour (melting temperature or melting range) of semi-crystalline polymers

0 Introduction

The melting behaviour of a crystalline or partly crystalline polymer is a structure-sensitive property.

In polymers a sharp melting point, such as is observed for low molecular mass substances, usually does not occur; instead a melting temperature range is observed on heating, from the first change of shape of the solid particles to the transformation into a highly viscous or viscoelastic liquid, with accompanying disappearance of the crystalline phase, if present. The melting range depends upon a number of parameters, such as molecular mass, molecular mass distribution, per cent crystallinity, and thermodynamic properties.

It may also depend on the previous thermal history of the specimens. The lower or upper limit of the melting range, or its average value, is sometimes conventionally referred to as the "melting temperature".

1 Scope and field of application

This International Standard specifies three methods for evaluating the melting behaviour of semi-crystalline polymers.

Section one specifies a capillary tube method (method A), which is based on the changes in shape of the polymer. This method is applicable to all polymers and their compounds, even if there is no crystalline phase.

Section two specifies a polarizing microscope method (method B), which is based on changes in the optical properties of the polymer. This method is applicable to polymers containing a birefringent crystalline phase; it may not be suitable for plastics compounds containing pigments and/or other additives which could interfere with the birefringence of the polymeric crystalline zone.

Section three specifies a thermal analytical method (method C), having two variants :

- method C1, which uses Differential Thermal Analysis (DTA);
- method C2, which uses Differential Scanning Calorimetry (DSC).

Both are applicable to all polymers containing a crystalline phase and their compounds.

The melting temperatures determined by the different methods usually differ by several kelvins for the reasons explained in the Introduction.

Of the methods given above, experiments have indicated DSC (Differential Scanning Calorimetry) to be the method of choice as having the best reproducibility of results.

2 Definitions

2.1 semi-crystalline polymers : Polymers containing a crystalline phase surrounded by amorphous materials.

2.2 melting range : The temperature range over which crystalline polymers lose their crystallinity when heated.

NOTE — The conventional "melting temperatures" determined by methods A and B are defined in clauses 3 and 8.

Section one : Method A — Capillary tube

3 Principle

Heating of a specimen, at a controlled rate, and observation for change in shape.

Reporting of the temperature of the specimen at the first visible deformation as the melting temperature.

NOTE — This method may also be used for non-crystalline materials according to the relevant specifications or by agreement between the interested parties.

4 Apparatus (see figure 1)

4.1 Melting apparatus, consisting of the following items :

a) cylindrical metal block, the upper part of which is hollow and forms a chamber;

b) metal plug, with two or more holes, allowing a thermometer and one or more capillary tubes to be mounted into the metal block a);

c) heating system for the metal block a) provided, for example, by an electrical resistance enclosed in the block;

d) rheostat for regulation of the power input, if electrical heating is used;

e) four windows of heat-resistant glass on the lateral walls of the chamber, diametrically disposed at right angles to each other. In front of one of these windows is mounted an eyepiece for observing the capillary tube. The other three windows are used for illuminating the inside of the enclosure by means of lamps.

NOTE — Other suitable melting apparatuses may be used, provided that they give the same results.

4.2 Capillary tube, of heat-resistant glass, closed at one end.

NOTE — The maximum external diameter should preferably be 1,5 mm.

4.3 Calibrated thermometer, graduated in divisions of 1 K. The thermometer probe shall be positioned in such a way that heat dispersion in the apparatus is not impeded.

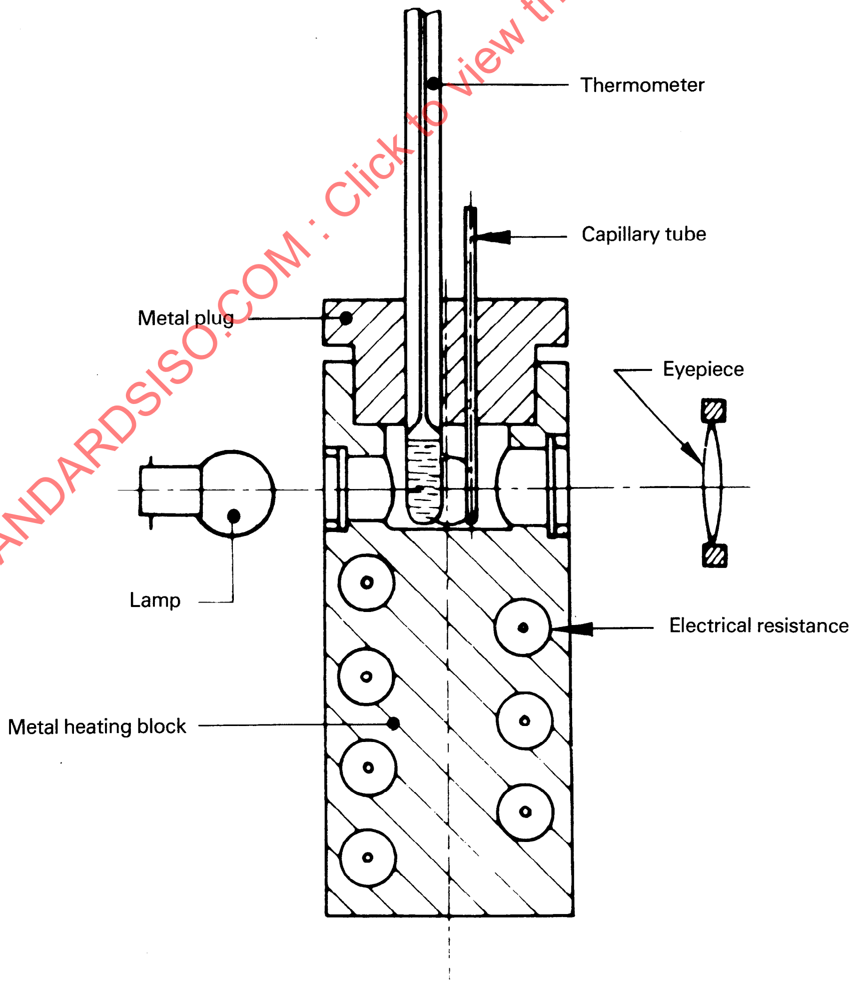

Figure 1 — Apparatus for method A

NOTE — Other suitable temperature-measuring devices may be used.

5 Test specimens

The specimens used shall be representative of the sample of material to be tested.

5.1 Characteristics

Powder of particle size up to 100 µm or cut pieces of films of thickness 10 to 20 µm should preferably be used. Comparison tests shall be carried out on specimens of the same or similar particle size, or similar thickness in the case of layers or films.

5.2 Conditioning

If not otherwise specified or agreed to by the interested parties, the sample shall be conditioned at 23 ± 2 °C and relative humidity of 50 ± 5 % for 3 h prior to the measurement.

6 Procedure

6.1 Calibration

Calibrate the temperature-measuring system periodically over the temperature range used for the test, with reagent grade or certified chemicals.

Chemicals recommended for calibration are listed in table 1.

6.2 Determination

6.2.1 Insert the thermometer (4.3) and the capillary tube (4.2) containing the specimen into the heating chamber [4.1a)] and start the heating. When the temperature of the specimen is about 20 K below the expected melting temperature, regulate the rate of temperature increase to 2 ± 0,5 K/min. Record the temperature at which the specimen begins to change shape.

6.2.2 Repeat the operations specified in 6.2.1 with a second specimen. If the two results obtained by the same operator on the same sample differ by more than 3 K, repeat the procedure on two new specimens.

Insufficient data are available for establishing reproducibility.

Table 1 — Calibration standards

Chemical	Melting temperature[1] (°C)
L-Menthol-1	42,5
Azobenzene	69,0
8-Hydroxyquinoline	75,5
Naphthalene	80,2
Benzyl	96,0
Acetanilide	113,5
Benzoic acid	121,7
Phenacetin [*N* (4-ethoxyphenyl) acetamide]	136,0
Adipic acid	151,5
Indium	156,4
Sulfanilamide	165,7
Hydroquinone	170,3
Succinic acid	189,5
2-Chloroanthraquinone	208,0
Anthracene	217,0
Saccharin	229,4
Tin	231,9
Tin(II) chloride	247,0
Phenolphthalein	261,5

[1] The temperatures indicated refer to theoretically pure chemicals; the values of the actual melting point for the standard materials used should be certified by the supplier.

7 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) reference of the method used (method A);

c) complete identification and description of the material tested;

d) shape and size (or mass) of the specimens;

e) previous thermal history of the specimens;

f) conditioning;

g) heating rate;

h) temperatures, in degrees Celsius or in kelvins, of two successive individual measurements, and their arithmetic mean;

i) any operational details not specified in this International Standard or regarded as optional, as well as any incidents liable to have affected the results.

Section two : Method B — Polarizing microscope

8 Principle

Heating of a specimen, positioned between the polarizer and analyser of a microscope, at a controlled rate.

Measurement of the temperature at which the crystalline polymer loses its optical anisotropy, as detected by the disappearance of birefringence, as the melting temperature.

9 Apparatus

Ordinary laboratory apparatus and

9.1 Microscope, with a disk polarizer and a cap analyser, or a polarizing microscope with built-in analyser, with magnification from X 50 to X 100.

9.2 Micro hot-stage, consisting of an insulated metal block that can be mounted slightly above the microscope stage. This block shall be

a) provided with a hole for light passage;

b) electrically heated, with adequate controls for adjustment of heating and cooling rates;

c) constructed to provide a chamber with a heat baffle and a glass cover, for carrying out measurements in an inert atmosphere;

d) provided with a hole for insertion of a temperature-measuring device near the light hole.

9.3 Thermometers, calibrated, or equivalent **temperature-measuring devices**, for the test temperature ranges.

10 Test specimens

10.1 Powdered materials

Place a 2 to 3 mg portion of the powder (particle size not more than 100 µm) on a clean slide and cover with a cover glass.

Heat the specimen, the slide and the cover on a hot-plate slightly above the melting temperature of the polymer. By a slight pressure on the cover glass, form a thin film of thickness 0,01 to 0,04 mm and allow it to cool slowly by switching off the hot-plate.

10.2 Moulded or pelleted materials

Cut from the sample, with a microtome, a film of thickness approximately 0,02 mm, place it on a clean slide and cover with a cover glass. Heat and melt it as specified in 10.1.

10.3 Film or sheet materials

Cut a 2 to 3 mg portion of the film or sheet, place it on a clean slide, cover with a cover glass and proceed as specified in 10.1.

NOTE — The preliminary melting of the specimens between slide and cover presents the advantage of destroying any birefringence due to orientation or internal stresses, and also of reducing the danger of oxidation during the test. The need for an inert gas stream — as described in 11.2 — is thus limited to very special cases. The reproducibility of the measurements is also increased. However, by agreement between the interested parties, the determination may be carried out directly on the powder or cut film piece without preliminary melting. This deviation should be stated in the test report.

10.4 Conditioning

See 5.2.

11 Procedure

11.1 Calibration

See 6.1.

11.2 Determination

Place the glass microscope slide with the specimen on the micro hot-stage (9.2). Adjust the light source to maximum light intensity and focus the microscope (9.1).

For specimens that are degradable by air, adjust the gas inlet to the stage so that a slight stream of inert gas blankets the stage, keeping it under slight positive pressure to prevent ingress of air. Rotate the analyser to obtain a dark field; the crystalline material will appear bright on a dark field. Adjust the controller to heat the stage gradually (at a rate not higher than 10 K/min) to a temperature that is lower than the melting temperature, θ_m, as determined approximately by previous test, by the following amounts :

10 K for $\theta_m \leqslant 150$ °C

15 K for 150 °C $< \theta_m \leqslant 200$ °C

20 K for $\theta_m > 200$ °C

Then adjust the controller so that the temperature rises at a rate of 1 to 2 K/min.

Observe the temperature at which birefringence disappears, leaving a totally dark field. Record this temperature as the melting temperature of the sample.

Turn off the heating and remove the glass cover, heat baffle and specimen slide.

Repeat the procedure with another specimen. If the two results obtained by the same operator on the same sample differ by more than 1 K, repeat the procedure on two new specimens.

According to the results of round robins, the repeatability was 2 K. Insufficient data are available for establishing reproducibility.

12 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) reference of the method used (method B);

c) complete identification and description of the material tested;

d) shape and size (or mass) of the specimens;

e) previous thermal history of the specimens;

f) conditioning;

g) description of preliminary heating on the slide, if applicable;

h) presence and type of inert gas, if applicable;

i) heating rate;

j) temperatures, in degrees Celsius or kelvins, of two successive individual measurements and their arithmetic mean;

k) any operational details not specified in this International Standard or regarded as optional, as well as any incidents liable to have affected the results.

Section three : Method C — Thermal analysis (DTA or DSC)

13 Additional definitions

13.1 Differential Thermal Analysis; DTA :[1] A technique in which the temperature difference between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature programme.

NOTE — The record is the differential thermal or DTA curve; the temperature difference, ΔT, should be plotted on the ordinate with endothermic reactions downwards and temperature, T, or time, t, on the abscissa, increasing from left to right.

13.2 Differential Scanning Calorimetry; DSC :[1] A technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature programme.

NOTE — Two modes, power-compensation differential scanning calorimetry and heat-flux differential scanning calorimetry, can be distinguished, depending on the method of measurement used.

13.3 baseline :[2] The portion or portions of the DTA or DSC curve for which ΔT or the heat flux is approximately constant (approximately zero in DTA).

For example, see AB and DE in figure 2.

13.4 peak :[2] That portion of a DTA or DSC curve which departs from, and subsequently returns to, the baseline.

For example, see BCD in figure 2.

NOTE — A peak is attributable to the occurrence of some single process. It is normally characterized by a deviation from the established baseline, a maximum deflection, and a re-establishment of a baseline, not necessarily identical to that before the peak.

13.5 endothermic peak; endotherm :[2]

(1) In DTA, a peak where the temperature of the sample falls below that of the reference material; that is ΔT is negative. (The melting phenomenon is an endothermic change.)

(2) In DSC, a peak where the energy input to the sample is larger than that to the reference material.

13.6 peak height :[2] The distance, vertical to the temperature axis, between the interpolated baseline and the peak tip.

For example, see CF in figure 2.

NOTE — There are several ways of interpolating the baseline; that shown in figure 2 is only an example. Locations of points B and D depend on the method of interpolation of the baseline. Other examples of interpolation of the baseline are shown in figure 3.

13.7 peak area :[2] The area enclosed between the peak and the interpolated baseline(s). (See the note to 13.6.)

For example, see BCDB in figure 2.

13.8 extrapolated onset temperature :[2] The temperature determined by the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak (for example, tangent t in figure 2) with the extrapolated baseline (for example BG in figure 2).

For example, see G in figure 2, and figure 3.

NOTE — For polymers having a wide melting range, the extrapoled onset temperature indicates the initial point of the rapid rise of the melting curve, but not necessarily the initial melting.

13.9 peak temperature :[2] The temperature at the time at which the differential temperature or heat flux during that peak has the maximum value.

For example, see C in figure 2.

13.10 sample :[2] The actual material to be tested, whether diluted with an inert material or undiluted.

13.11 specimens :[2] Portions of the sample to be tested and the reference material.

13.12 reference material :[2] A substance known to be thermally inactive over the temperature range of interest, for example α-aluminium oxide (α-Al_2O_3).

13.13 sample holder :[2] The container or support for the test portion of the sample.

13.14 reference holder :[2] The container or support for the reference material.

13.15 specimen holder :[2] The complete assembly in which the specimens are housed. When the heating or cooling source is incorporated in one unit with the containers or supports for the sample and reference material, this is regarded as part of the specimen-holder assembly.

13.16 block :[2] A type of specimen-holder assembly in which a relatively large mass of materials is in intimate contact with the specimens or specimen holders.

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[1] Definition taken from : Nomenclature Committee of the International Confederation for Thermal Analysis. Nomenclature in thermal analysis : Part IV. *J. Thermal Anal.* **13** 1978 : 387-392.

[2] Definition taken from : Nomenclature Committee of the International Confederation for Thermal Analysis. Nomenclature in thermal analysis : Part II. *Talanta* **19** 1972 : 1079-1081.

13.17 differential thermocouple; ΔT thermocouple :[1] The thermocouple system used to measure temperature or heat-flux differences.

14 Principle

Heating of a sample and an appropriate reference material at a controlled rate in a suitable DTA (method C1) or DSC (method C2) apparatus.

Recording of a DTA or DSC curve from which one or several characteristic points, related to the melting behaviour, are determined.

15 Apparatus

15.1 Differential thermal analyser or differential scanning calorimeter.

Most commercially available and custom-built instruments may be used.

The principal design characteristics of such instruments are

a) a heated block with two holders for the specimens identically positioned and guaranteeing the same heat transfer conditions for both;

b) a temperature-recording system;

c) an electrical heater in the block or a furnace with adequate controls for adjustment of heating rate to linear conditions within ± 0,5 K/min.

Synchronous recordings of the DTA curve and the temperature difference ΔT shall permit temperature recording with a sensitivity not less than 2 K per millimetre on the recorder scale.

The DSC apparatus is constructed similarly to the DTA apparatus but with separate compensating devices for the two specimen holders and with electronic equipment maintaining the temperatures of the specimens of the sample and reference material at the same level by variation of the required power input.

The peak area shall be not less than 2 cm^2; the peak height shall be at least 10 times the height of the noise level.

15.2 Thermocouples, rigidly fixed in the specimen compartments, possessing identical characteristics within the graduation precision limits.

15.3 Equipment for filling the specimen containers with inert gas, or for passage of a constant measured flow of inert gas through the containers.

16 Test specimens

16.1 Characteristics

Recommended specimens are given in table 2.

Since milligram quantities of material are used, it is essential to ensure that the specimens are homogeneous and representative.

Table 2 — Characteristics of test specimens

Sample form	Particle size	Mass of test portion
Powder	diameter : up to 0,5 mm	up to 50 mg
Cut film	thickness : 0,05 to 0,50 mm area : 0,25 to 4,00 mm^2	
Fibre	diameter : up to 0,50 mm length : up to 2,00 mm	

NOTE — Since the results are affected by the mass of the specimen and by the particle size and shape, the specimens to be compared should have approximately the same particle size and shape and the same mass.

16.2 Conditioning

See 5.2.

17 Procedure

17.1 Calibration

Calibrate the temperature measuring system periodically over the temperature range used for the test.

Certified reference materials are available and are listed in table 3.

Table 3 — DTA reference materials for transition temperatures in the range 125 to 435 °C

Reference material[1]	DTA mean values, (°C)	
	Extrapolated onset temperature, T_o	Peak temperature, T_p
Potassium nitrate	128	135
Indium metal	154	159
Tin metal	230	237
Silver sulfate	424	433

1) ICTA-NBS Certified Reference Materials for Differential Thermal Analysis, available from the US National Bureau of Standards, Washington, DC 20234, USA. The indicated values refer only to a specific certified batch.

NOTE — The characteristic points (T_o and T_p) are not to be confused with the true melting temperatures as reported in the literature.

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[1] Definition taken from : Nomenclature Committee of the International Confederation for Thermal Analysis. Nomenclature in thermal analysis : Part II. *Talanta* **19** 1972 : 1079-1081.