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Plastics — Determination of melting behaviour (melting temperature or melting range) of semi-crystalline polymers by capillary tube and polarizing-microscope methods

Plastiques — Détermination du comportement à la fusion (température de fusion ou plage de températures de fusion) des polymères semi-cristallins par méthodes du tube capillaire et du microscope polarisant

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 249, *Plastics,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This fourth edition cancels and replaces the third edition (ISO 3146:2000), which has been technically revised. It also incorporates the Technical Corrigendum ISO 3146:2000/Cor 1:2002.

The main changes compared to the previous edition are as follows:

- the specifications of the apparatus and measurement procedure have been revised;
- the table of calibration standards has been revised by adding further entries, synonyms and CAS numbers of organic chemicals, correcting errors and modifying melting temperatures according to added references.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The melting behaviour of a crystalline or semi-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. The melting range depends upon a number of parameters, such as molecular mass, molecular mass distribution, per cent crystallinity, and thermodynamic properties.

The melting range can also depend on experimental parameters such as previous thermal history of the specimen, heating or cooling rate, etc. The lower or upper limit of the melting range, or its average value, is sometimes conventionally referred to as the “melting temperature”.

The melting temperatures determined by different methods can differ by several kelvins for above reasons.

Plastics — Determination of melting behaviour (melting temperature or melting range) of semi-crystalline polymers by capillary tube and polarizing-microscope methods

1 Scope

This document specifies two methods for evaluating the melting behaviour of semi-crystalline polymers.

a) Method A: Capillary tube

This method is based on the changes in shape of the polymer. It is applicable to all semi-crystalline polymers and their compounds.

NOTE 1 Method A can also be useful for the evaluation of the softening of non-crystalline solids.

b) Method B: Polarizing microscope

This method is based on changes in the optical properties of the polymer. It is applicable to polymers containing a birefringent crystalline phase. It might not be suitable for plastics compounds containing pigments and/or other additives which can interfere with the birefringence of the polymeric crystalline zone.

NOTE 2 Another method applicable to semi-crystalline polymers is described in ISO 11357-3.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 291, *Plastics — Standard atmospheres for conditioning and testing*

ISO 472, *Plastics — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
melting range
temperature range over which crystalline or semi-crystalline polymers lose their crystalline characteristics or particulate shape when heated

Note 1 to entry: The “melting temperatures” determined by methods A and B are specified in 4.1 and 5.1.

4 Method A — Capillary tube

4.1 Principle

A test sample is heated at a controlled rate, and the temperature of the sample measured at the first visible change in shape and again at the disappearance of the last remnants of the crystalline phase.

The first temperature is taken as the melting temperature of the sample, while the range between the two temperatures describes its melting range.

NOTE This method can be used for non-crystalline materials where required by the relevant specifications or by agreement between the interested parties.

4.2 Apparatus (see Figure 1)

4.2.1 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 in the metal block;

c) heating system for the metal block equipped with a suitable temperature control device;

d) 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 an eyepiece is mounted 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 types of melting apparatus can be used, provided that they give the same results.

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

The maximum external diameter should preferably be 1,8 mm.

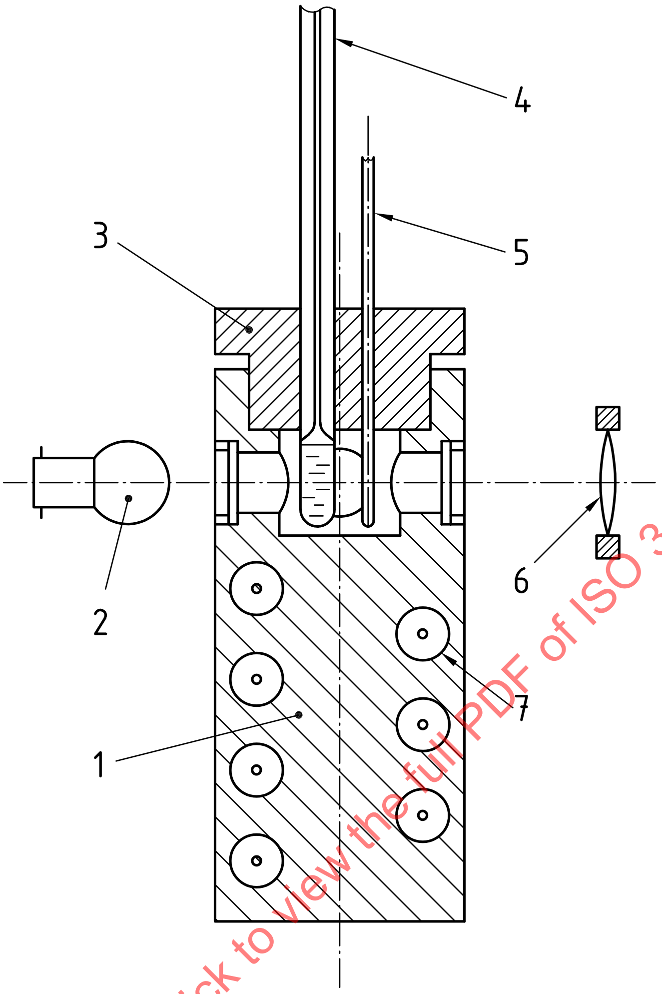
4.2.3 Calibrated thermometer, graduated in divisions of 0,1 °C. The thermometer bulb shall be positioned in such a way that heat dispersion in the apparatus is not impeded.

NOTE Other suitable temperature-measuring devices can be used.

4.3 Test samples

4.3.1 General

The test samples used shall be representative of the material to be tested.



Key

1	metal heating block
2	lamp
3	metal plug
4	thermometer
5	capillary
6	eyepiece
7	electrical resistance

Figure 1 — Apparatus for method A

4.3.2 Characteristics

Powder of particle size up to 100 µm or cut pieces of film of thickness 10 µm to 20 µm should preferably be used.

Comparison tests shall be carried out on test samples of the same or similar particle size, or of similar thickness in the case of layers or films.

4.3.3 Conditioning

If not otherwise specified or agreed between the interested parties, the test sample shall be conditioned at (23 ± 2) °C and a relative humidity of (50 ± 5) % for 3 h in accordance with ISO 291 prior to the measurement.

4.4 Procedure

4.4.1 Calibration

Periodically calibrate the thermometer with reagent grade or certified chemicals over the temperature range used for the test.

Chemicals recommended for calibration purposes are listed in Table 1.

Table 1 — Calibration standards

Chemical		**CAS Number**	**Melting temperature**[a] **°C**
IUPAC Name	**Synonym**		
Gallium		7440-55-3	29,76[2]
Phenyl 2-hydroxybenzoate	Phenyl salicylate	118-55-8	41,79[2]
5-Methyl-2-(propan-2-yl) cyclohexan-1-ol	L-Menthol (-)-Menthol 5-Methyl-2-isopropylcyclohexanol, [1R-(1α,2β,5α)]-	2216-51-5	43[3]
1-Methyl-4-nitrobenzene	4-Nitrotoluene	99-99-0	51,61[2]
(*E*)-Diphenyldiazene	trans-Azobenzene	17082-12-1	67,88[3]
1,1'-Biphenyl	Biphenyl Phenyl benzene	92-52-4	68,93[2]
Quinolin-8-ol 8-Quinolinol	8-Hydroxyquinoline Hydroxybenzopyridine	148-24-3	75,5[3]
Naphthalene Bicyclo[4.4.0]deca-1,3,5,7,9-pentaene		91-20-3	80,23[2]
Diphenylethanedione 1,2-Diphenylethane-1,2-dione	Benzil Dibenzoyl Diphenylglyoxal	134-81-6	94,85[2]
N-Phenylethanamide	Acetanilide (N-Phenylacetamid)	103-84-4	114,34[2]
Benzoic acid Benzenecarboxylic acid	Carboxybenzene Phenylmethanoic acid	65-85-0	122,35[2]
N-(4-Ethoxyphenyl)acetamid	Phenacetin *p*-Acetophenetidin	62-44-2	137,5[3]
2,2-Diphenylacetic acid	Diphenylacetic acid 2,2-diphenylethanoic acid	117-34-0	147,19[2]
1,6-Hexanedioic acid	Adipic acid Butane-1,4-dicarboxylic acid	124-04-9	152,5[3]
Indium		7440-74-6	156,60[2]
4-Amino benzene sulfonamide	Sulfanilamide	63-74-1	165,5[3]
1,4-Benzene-1,4-diol	Hydroquinone Quinol 1,4-Dihydroxy benzene	123-31-9	172,5[3]
4-Methoxybenzoic acid	p-Anisic acid	100-09-4	183,28[2]

[a] The temperatures indicated refer to the normal melting point of pure chemicals; preferably, the value of the actual melting point for the standard materials used should be certified by the supplier.

Table 1 *(continued)*

Chemical		CAS Number	Melting temperature[a] °C
IUPAC Name	**Synonym**		
1,4-Butanedioic acid	Succinic acid	110-15-6	187,9[3]
2-Chloroanthracene-9,10-dione	2-Chloroanthraquinone	131-09-9	209,83[2]
Anthracene Tricyclo[8.4.0.03,8]tetradeca-1,3,5,7,9,11,13-heptaene	Paranaphtalene	120-12-7	215,76[3]
1,1-dioxo-1,2-benzothiazol-3-on	Saccharin Benzoic sulfimide	81-07-2	228[2]
Tin		7440-31-5	231,93[2]
9H-Carbazole	Carbazole Dibenzopyrrole	86-74-8	245,80[2]
Tin(II) chloride Tin dichloride		7772-99-8	247,1[4]
(3,3-Bis(4-hydroxyphenyl)-2-benzofuran-1(3H)-one)	Phenolphthalein	77-09-8	262,5[3]
Anthraquinone	9,10-Anthracenedione	84-65-1	284,52[2]

[a] The temperatures indicated refer to the normal melting point of pure chemicals; preferably, the value of the actual melting point for the standard materials used should be certified by the supplier.

4.4.2 Determination

4.4.2.1 Insert the thermometer (4.2.3) and the capillary tube (4.2.2) containing the test sample into the metal block [4.2.1 a)] and begin heating. Adjust the controller [4.2.1 d)] to heat the specimen gradually (at a rate not higher than 10 K/min) to a temperature that is about 20 K lower than the expected melting temperature. When the temperature of the test sample is about 20 K below the expected melting temperature, adjust the rate of temperature increase to (2 ± 0,5) K/min. Record the temperature at which the test sample begins to change shape.

Continue heating at the same rate. Record the temperature at which the last remnants of the crystalline phase disappear.

4.4.2.2 Repeat the operations specified in 4.4.2.1 with a second test sample. 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 test samples.

4.5 Test report

The test report shall include the following information:

a) a reference to this document, including its year of publication;

b) the method used (method A);

c) all details necessary for complete identification of the material tested;

d) the shape and size (or mass) of the test samples;

e) the previous thermal history of the test samples;

f) the conditioning procedure used;

g) the exact heating rate used;

h) the temperatures, in degrees Celsius, of two successive determinations, and their arithmetic mean for the temperature at which the specimen begins to change shape and for the temperature at which the last remnants of crystalline phase disappear;

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

j) the date of test.

5 Method B — Polarizing microscope

5.1 Principle

A test sample positioned between the disc polarizer and the cap analyser of a microscope is heated at a controlled rate.

The temperature at which the crystalline phase of the polymer loses its optical anisotropy is measured as detected by the disappearance of birefringence and reported as the melting temperature.

5.2 Apparatus

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

5.2.2 Microscope 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 the passage of light;

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

c) optionally, the hot stage may be 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 the insertion of a temperature-measuring device near the light hole a).

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

5.3 Test samples

5.3.1 Powdered materials

Place a sufficient amount of the powder sample (particle size <100 μm) to fully cover the cross-section of the microscope light beam on a clean glass slide and cover with a cover glass.

NOTE 1 Depending on the microscope used samples of <1 mg can be sufficient.

NOTE 2 Depending on the effective heating rate, the temperature and time at which the test sample is held in the molten state and the effective cooling rate, the results of subsequent melting can differ.

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