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Plastics — Epoxy resins — Determination of degree of crosslinking of crosslinked epoxy resins by differential scanning calorimetry (DSC)

Plastiques — Résines époxydes — Détermination du degré de réticulation des résines époxydes réticulées par analyse calorimétrique différentielle (DSC)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 14322:2012), of which it constitutes a minor revision.

The changes compared to the previous edition are as follows:

— the title has been updated (DSC has been added at the end);

— Clause 2 has been updated;

— the subclauses under 7.2 have been renumbered;

— editorial changes have been applied.

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

It is possible to determine the degree of crosslinking of a crosslinked epoxy resin by observing changes in its mechanical, electrical or thermal properties.

However, such an approach is inadequate in cases in which the test sample is to be evaluated as is or is to be examined under various crosslinking conditions. This document provides a method whereby the degree of crosslinking is determined without the need for complicated procedures for preparing, conditioning or configuring the test sample. The degree of crosslinking is determined by comparing the heat of the crosslinking reaction for the test sample with that of a reference sample, using a differential scanning calorimeter.

The advantages of this method are that sample preparation is simple and measurements can be made with very small amounts of sample. For these reasons, this document is useful for investigations of, and in establishing conditions for, crosslinking reactions. It can also be used for production and quality control.

Finally, since epoxy resin systems are highly diverse, the applicability of this document to each resin system needs be established. A technique to test the applicability to an epoxy resin system is included in this document.

Plastics — Epoxy resins — Determination of degree of crosslinking of crosslinked epoxy resins by differential scanning calorimetry (DSC)

SAFETY STATEMENT — Persons using this document should be familiar with normal laboratory practice, if applicable. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

1 Scope

This document specifies a method whereby the heat of reaction generated during epoxy resin crosslinking is measured by differential scanning calorimetry (DSC). The degree of crosslinking is determined based on this result.

This method is applicable to epoxy resin systems with a moderate or slow crosslinking-reaction speed. It might not be applicable to systems with a fast crosslinking-reaction speed at ambient temperature.

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 documents. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11357-1, *Plastics — Differential scanning calorimetry (DSC) — Part 1: General principles*

ISO 11409, *Plastics — Phenolic resins — Determination of heats and temperatures of reaction by differential scanning calorimetry*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11357-1 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 http://www.electropedia.org/

3.1
degree of crosslinking
value which indicates the extent of the crosslinking reaction of an epoxy resin system

Note 1 to entry: The degree of crosslinking is expressed as a percentage and calculated in accordance with Formula (2).

3.2
uncrosslinked epoxy resin system
epoxy resin system immediately after mixing the system components, before any crosslinking has taken place

3.3
total heat of reaction
gross amount of reaction heat produced by an *uncrosslinked epoxy resin system* (3.2) during complete crosslinking, as determined by DSC

Note 1 to entry: It is expressed in joules per gram ($J \cdot g^{-1}$).

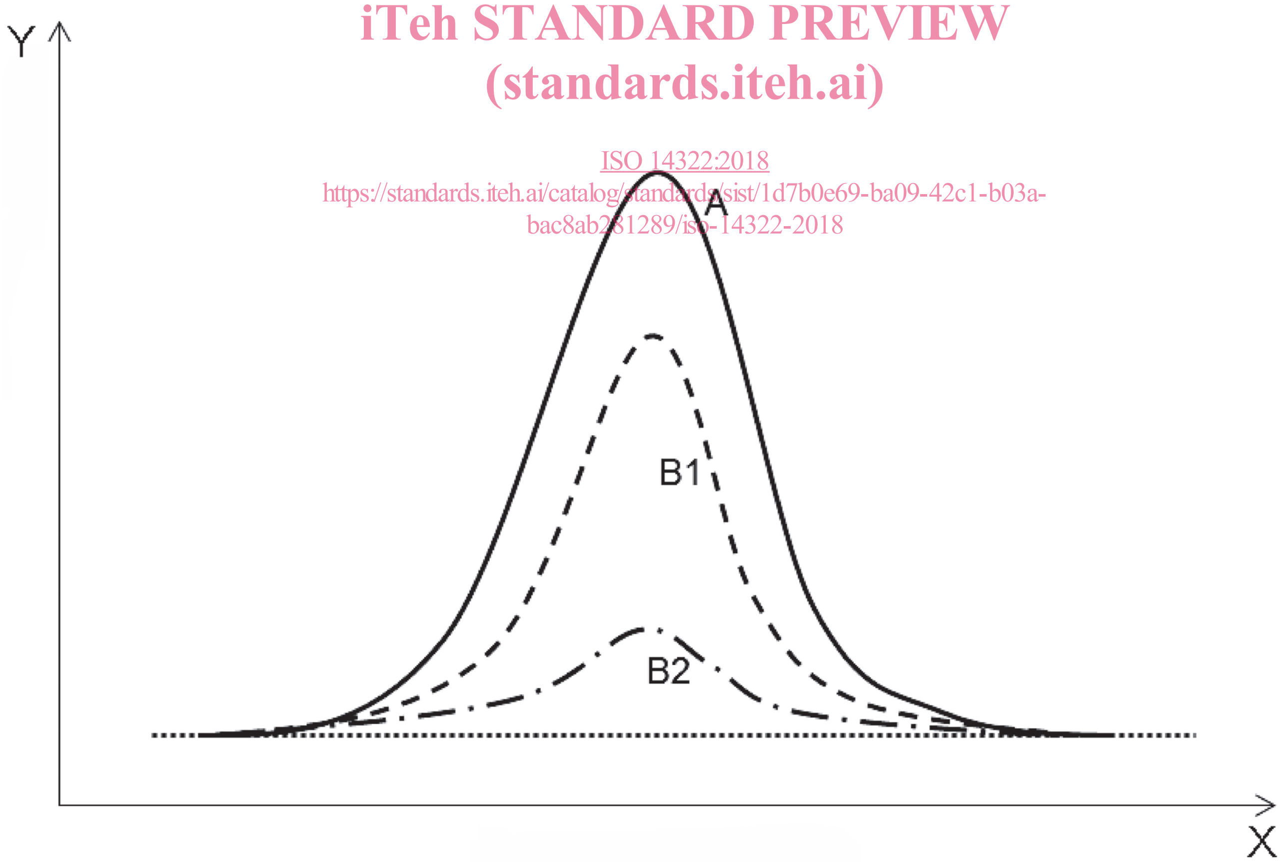
4 Principle

The total heat of reaction is first measured by DSC, using a test sample taken from the uncrosslinked epoxy resin system. Curve A in Figure 1 is an example of such a DSC curve.

The heat of reaction of a test sample of the (partly) crosslinked resin system under investigation is then measured, using the same DSC apparatus and under the same conditions as those used to measure the total heat of reaction, in order to determine the heat of reaction due to the remaining reactive groups as the reaction goes to completion. Curves B1 and B2 in Figure 1 are examples of DSC curves obtained with such test samples.

Curve B1 shows a case where crosslinking did not progress to a large extent before the DSC measurement and curve B2 shows a case where crosslinking progressed considerably before the DSC measurement.

The degree of crosslinking of the (partly) crosslinked resin system is determined from the heat of reaction of this crosslinked resin system and the total heat of reaction of the uncrosslinked resin system [see Formula (2)].



Key

X temperature or time

Y heat flow rate (exothermic)

Figure 1 — DSC curve (schematic)

Crosslinking epoxy resin systems are highly diverse, and the systems to which this document can be applied are limited due to measurement-related constraints of the method used. For example, the method cannot be applied to a crosslinking epoxy resin system for which the reaction progresses too far before the system components can be thoroughly mixed and subjected to DSC measurement. In such a system, it is not feasible to determine the total heat of reaction accurately.

For this reason, a preliminary test (see 7.2) is used in order to determine if this document is applicable to the epoxy resin system of interest.

5 Materials

5.1 Calibration material, selected in accordance with ISO 11357-1.

NOTE Indium is typically used.

5.2 Epoxy resin system, including the following:

5.2.1 Epoxy resin, as specified in the test resin system formulation.

5.2.2 Hardener, as specified in the test resin system formulation.

5.2.3 Catalyst, as specified in the test resin system formulation.

6 Apparatus

6.1 DSC apparatus, having the following characteristics:

a) a heating rate of up to 10 °C per minute;

b) automatic recording of the differential heat flow between the test sample and the reference material;

c) the ability to measure heat flux or energy difference with a minimum precision of ± 1 %;

d) the ability to measure the test sample temperature to within ± 0,1 °C;

e) an operating range extending at least from 20 °C to 300 °C.

6.2 Gas flow device, constructed such that the gas flows around the test sample, and including a gas flow meter capable of measuring the gas flow rate in a range from 10 ml to 50 ml per minute.

6.3 Sample holder (pan), made from a material with a high thermal conductivity, which is not eroded by the test sample.

6.4 Recorder, capable of recording DSC curves automatically.

6.5 Analytical balance, capable of weighing to 0,01 mg.

7 Procedure

7.1 Calibration

Calibration shall be in accordance with ISO 11357-1.