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

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The UK participation in its preparation was entrusted to Technical Committee PRI/42, Fibre reinforced thermosetting plastics and prepregs.

A list of organizations represented on this committee can be obtained on request to its secretary.

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

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

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Foreword

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ISO 14322 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

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 International Standard 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 International Standard 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 International Standard to each resin system needs be established. A technique to test the applicability to an epoxy resin system is included in the standard.

INTERNATIONAL STANDARD ISO 14322:2012(E)

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

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1 Scope

This International Standard 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 referenced documents are indispensable for the application 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 11357-1:2009, *Plastics — Differencial scanning calorimetry (DSC) — Part 1: General principles*

ISO 11409:1993, *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.

3.1
degree of crosslinking
value, calculated in accordance with Equation (2) in Clause 8, which indicates the extent of the crosslinking reaction of an epoxy resin system, expressed as a percentage

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 (see 3.2) during complete crosslinking, as determined by DSC, expressed in joules/gram

4 Principle

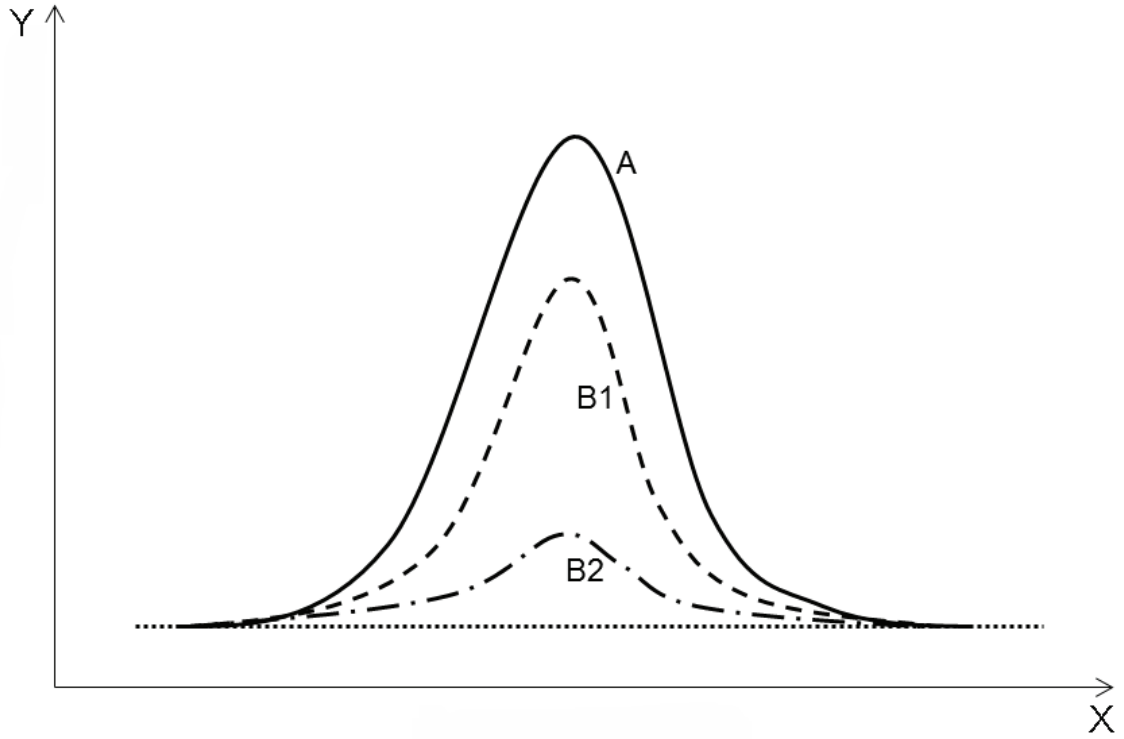
The total heat of reaction is first measured by DSC, using a test sample taken from the uncrosslinked epoxy resin system. Curve A in Figure 1 is an example of such a DSC curve.

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 Equation (2) in Clause 8].



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 International Standard 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 International Standard is applicable to the epoxy resin system of interest.

5 Materials

5.1 Calibration material, selected in accordance with ISO 11357-1:2009, 8.2.

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 11357-1:2009, Clause 8.

7.2 Preliminary test

7.2.1 This International Standard is applicable to crosslinking epoxy resin systems for which acceptable agreement is obtained between the total heat of reaction for two test samples which are taken at the same time from the same uncrosslinked epoxy resin system and are measured consecutively under the same conditions using the same DSC apparatus.

7.2.2 Mix well the epoxy resin system components (epoxy resin and other ingredients) to produce a mixture of the uncrosslinked epoxy resin system under test.

7.2.3 Using an analytical balance, immediately weigh out, to the nearest 0,01 mg, a 10 mg to 20 mg test sample from this mixture and put it into the pan of the DSC apparatus.

7.2.4 Carry out the DSC measurement in accordance with a previously developed time-temperature programme. The programme defines the starting temperature, the heating rate, the final temperature and the cooling time. Calculate the total heat of reaction (H_{T1}) as specified in ISO 11409:1993, 4.5.3.1.

NOTE A starting temperature which is at least 30 °C below the temperature at which the crosslinking reaction begins, a heating rate of 10 °C/min and final temperature of 250 °C have been used successfully.

7.2.5 Immediately after the first measurement, cool down the apparatus at cooling rate about 30 °C/min.

7.2.6 From the mixture prepared in 7.2.2, weigh out a second test sample in the same way as described in 7.2.3 and carry out a second DSC measurement under the same conditions as were used for the first test sample. Calculate the total heat of reaction (H_{T2}) for this second test sample as specified in ISO 11409:1993, 4.5.3.1.

7.2.7 If H_{T1} and H_{T2} satisfy the following inequality, this International Standard is applicable to the epoxy resin system concerned. In this case, proceed to 7.3 for the measurement of the DSC curve given by the (partly) crosslinked resin.

$$\frac{\left|H_{T_1} - H_{T_2}\right|}{\left(H_{T_1} + H_{T_2}\right)/2} \times 100 \leq 10\ \% \qquad (1)$$

NOTE An example of a preliminary test is given in Annex A.

7.3 DSC measurement on the crosslinked resin under investigation

7.3.1 Using an analytical balance, weigh, to the nearest 0,01 mg, 10 mg to 20 mg of the (partly) crosslinked resin and put it into the pan of the DSC apparatus.

7.3.2 Carry out the DSC measurement under the same conditions as in the preliminary test (see 7.2) and calculate the heat of reaction as specified in of ISO 11409:1993, 4.5.3.1.

7.3.3 Repeat the measurement with a second test sample of the (partly) crosslinked resin and determine the average of the heats of reaction obtained in the two measurements. This average is used as the heat of reaction of the crosslinked sample (H_S) in the calculation in Clause 8.

8 Expression of results

Calculate the degree of crosslinking as follows:

$$\text{Degree of crosslinking (\%)} = \left(1 - \frac{H_S}{H_T}\right) \times 100 \qquad (2)$$

where

H_T is the total heat of reaction obtained from the preliminary test described in 7.2 (the average of the two measured values H_{T1} and H_{T2}) (J/g);

H_S is the heat of reaction of the (partly) crosslinked resin (the average of the two measured values as determined in 7.3) (J/g).

9 Precision

9.1 General

Precision data were determined from a round-robin experiment organized in 2007 involving six laboratories in Japan.

9.2 Materials and crosslinking conditions

— Epoxy resin: Bisphenol-A-type epoxy resin; hardener: acid anhydride.

— Three different samples were tested, obtained by different crosslinking conditions: 100 °C for 60 min, 100 °C for 90 min and 150 °C for 120 min.

9.3 Precision of the method

The resulting data, which were analysed in accordance with ISO 5725-2, are given in Table 1.

Table 1 — Precision data

Samples (crosslinking conditions)	Degree of crosslinking, % (averaged)	Repeatability s_r	Reproducibility s_R
Sample A (100 °C for 60 min)	69,3	1,24	3,14
Sample B (100 °C for 90 min)	84,6	0,95	5,23
Sample C (150 °C for 120 min)	98,1	0,69	1,94

10 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for the identification of the epoxy resin system investigated, e.g. epoxy resin, hardener, catalyst;

c) a description of the DSC apparatus used;

d) the heating rate used;

e) the results of the preliminary test (see 7.2);

f) the method used to integrate the area under each curve;

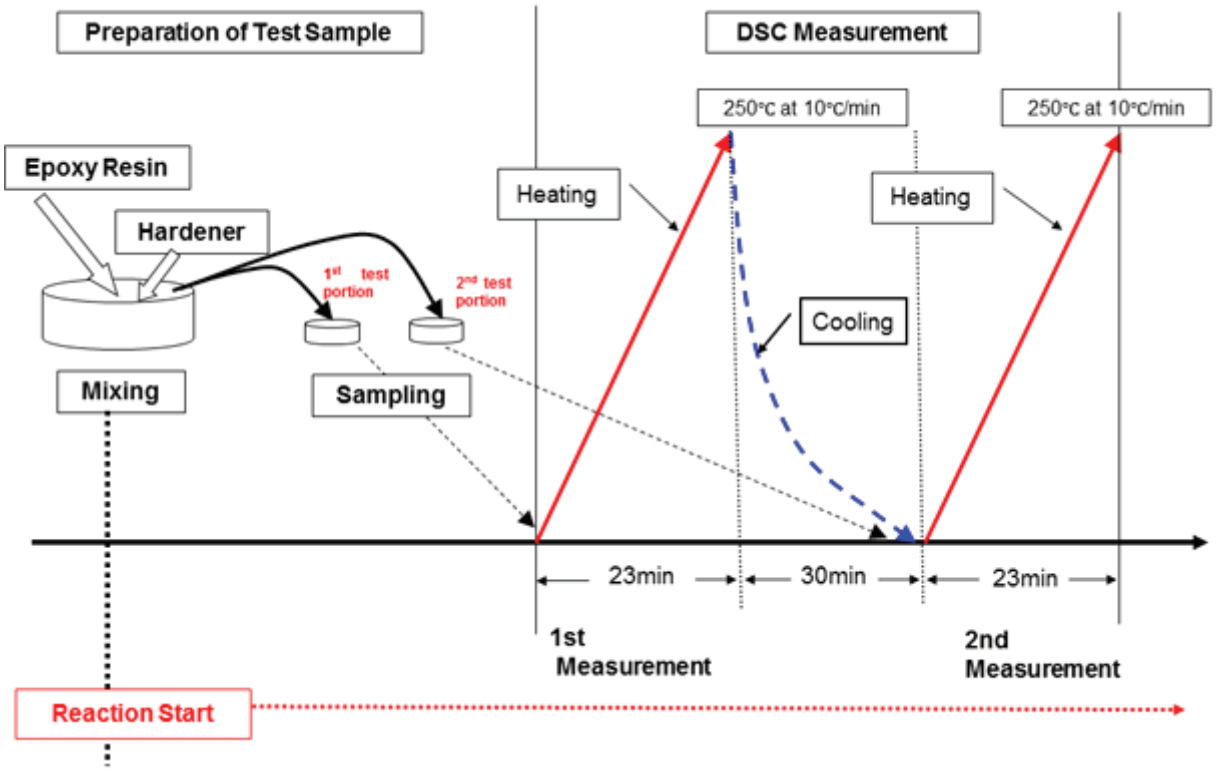
g) the degree of crosslinking of the epoxy resin system investigated, calculated as specified in Clause 8;

h) copies of the DSC curves obtained;

i) the date of the test.

Annex A
(informative)

Example of a procedure used for the preliminary test, with typical operating conditions



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