INTERNATIONAL STANDARD

ISO 20368

First edition
2017-11

Plastics — Epoxy resins — Determination of degree of crosslinking of crosslinked epoxy resins by Fourier Transform Infrared (FTIR) Spectroscopy

Plastiques — Résines époxy — Détermination du degré de réticulation des résines époxy réticulées par spectroscopie infrarouge à transformée de Fourier (FTIR)

Reference number
ISO 20368:2017(E)

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Foreword

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This document 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 approaches are inadequate in cases where the test sample 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 measuring the disappearance of the epoxy group during the resin crosslinking, using Fourier Transform Infrared spectroscopy.

The advantages of this method are that sample preparation is simple, measurements can be made with very small amounts of resin and it is possible to measure the reaction rate of the epoxy group for an epoxy compound containing another active functional group. For these reasons, this document is useful for investigations and for establishing conditions for crosslinking reactions. It can also be used for production and quality control.

Since epoxy resin systems are highly diverse, the applicability of this document to each resin system is intended to be established prior determination. A technique to test the applicability to any epoxy resin system is included in this document.

Plastics — Epoxy resins — Determination of degree of crosslinking of crosslinked epoxy resins by Fourier Transform Infrared (FTIR) Spectroscopy

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 for determining the degree of crosslinking of crosslinked epoxy resins by the disappearance of the epoxy group during epoxy resin crosslinking measured by Fourier Transform Infrared (FTIR) (with a transmittance mode) spectroscopy.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

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

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

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

Note 1 to entry: See Formula (4) in Clause 8.

Note 2 to entry: It is expressed as a percentage.

3.2
height of absorption peak
greatest distance in the ordinate direction between the virtual baseline and the FTIR absorption curve during a peak

Note 1 to entry: The virtual baseline is drawn simply by connecting the peak onset and peak end by a straight line.

Note 2 to entry: When the separation of the specified peak and other peaks is incomplete, the virtual baseline can be drawn by connecting a peak onset and a peak end which are selected optionally in serial peaks including the specified peak by a straight line.

3.3
peak height ratio
value calculated by dividing the peak height of the epoxy group absorption (wave number 900~915 cm^{-1}) by the peak height of the internal standard group absorption which is not changed by a crosslinking reaction

Note 1 to entry: The methylene group absorption band (near 2 930 cm^{-1}) is recommended for use as the internal standard group absorption.

4 Principle

The degree of crosslinking of the epoxy resin is determined by the peak height ratio of the crosslinked state and the uncrosslinked state of the epoxy resin as measured through FTIR (with a transmittance mode).

Firstly, the height of the epoxy group absorption peak (Pa1) and the height of the internal standard group absorption peak (Pa2) are measured by FTIR using a sample taken from the epoxy resin in an uncrosslinked state (see Figure 1).

The peak height ratio of the uncrosslinked state (X) is obtained using Formula (1):

$$X=Pa1/Pa2 \quad (1)$$

Secondly, the height of the epoxy group absorption peak (Pb1) and the height of the internal standard group absorption peak (Pb2) are measured by FTIR using a sample taken from the epoxy compound in a crosslinked state (see Figure 2).

The peak height ratio of the crosslinked state (Y) is obtained using Formula (2):

$$Y=Pb1/Pb2 \quad (2)$$

The degree of crosslinking is determined by Formula (4) in Clause 8.

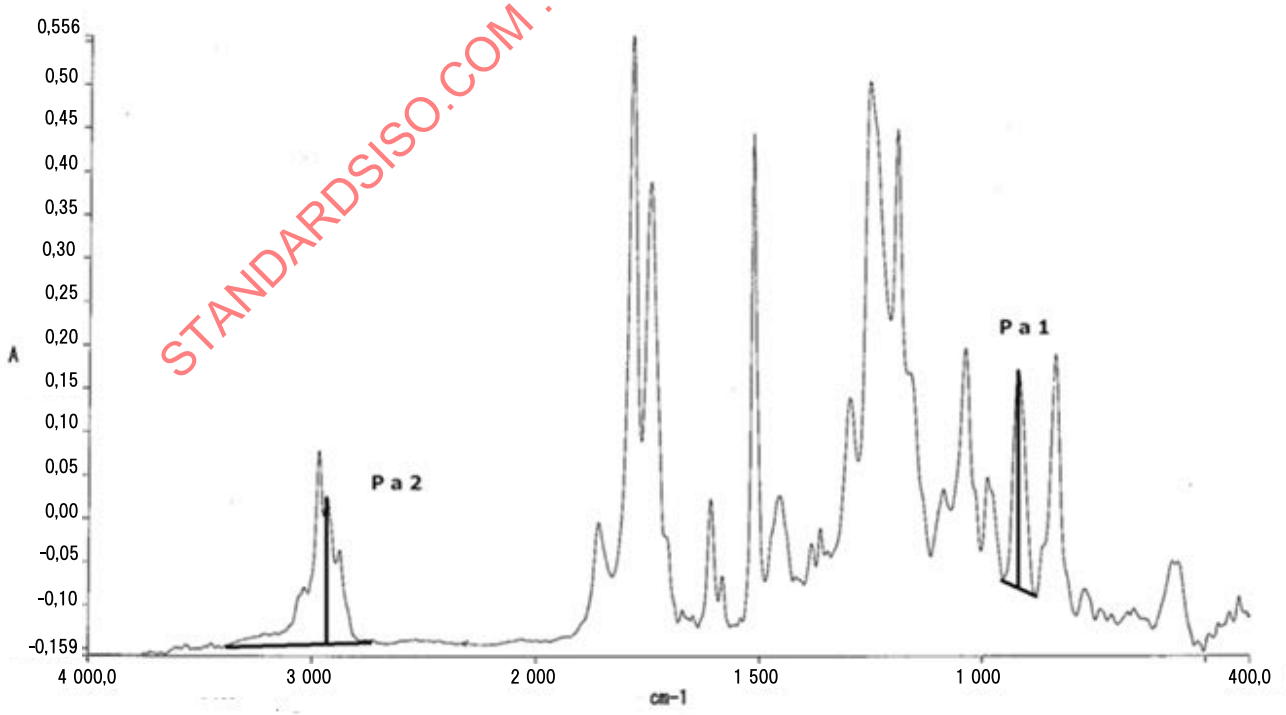

Figure 1 — Spectrum of uncrosslinked epoxy resins

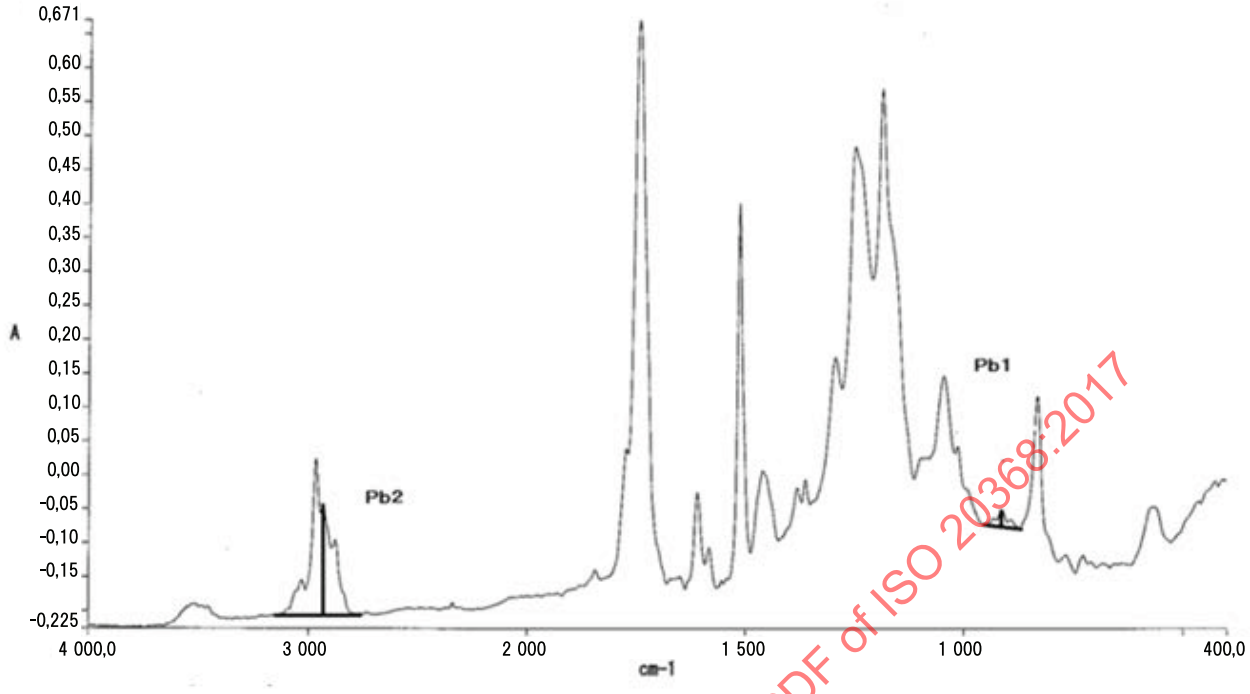

Figure 2 — Spectrum of crosslinked epoxy resins

5 Materials

5.1 **Epoxy resin**, as specified in the test resin system formulation.

5.2 **Hardener**, as specified in the test resin system formulation.

5.3 **Catalyst**, as specified in the test resin system formulation.

6 Apparatus

6.1 **FTIR Spectrophotometer**, having the following characteristics:

a) an operating range of the wave number from 4 000 cm^{-1} to 650 cm^{-1};

b) the capable cumulative number shall be more than 16.

6.2 **Micropipette**, with capacity 1 µl to 10 µl.

6.3 **Silicon wafer**, having the following characteristics:

a) single-side polished monocrystalline silicon wafer;

b) thickness of 625 µm ± 15 µm;

c) total thickness variation (TTV)of 10 µm;

d) total dimensions of the wafer (150 mm; 6 inch wafer).

6.4 **Analytical balance**, accurate to 0,1 mg.

7 Procedure

7.1 Preparation of measuring

For the accurate and effective use of the FTIR spectrophotometer, follow the instruction manual or others. Prior to the measurements, check the apparatus according to the specified procedures, and confirm that the instrument works correctly. Turn on the power source and allow it to warm up and stabilize. If necessary, carry out measurement using a standard substance, and confirm that the measured spectrum peaks, their repeatability and other values stand within the specified range.

7.2 Preliminary test

7.2.1 General

This document is applicable to crosslinking epoxy resin systems for which acceptable agreement is obtained between the peak height ratio for two uncrosslinked test samples which are taken at the same time and are measured under the same conditions using the same FTIR spectrophotometer.

7.2.2 Procedure for preliminary test

7.2.2.1 Mix the epoxy resin system components (epoxy resin and other ingredients) well to produce a mixture of the uncrosslinked epoxy resin system to be tested.

7.2.2.2 Using a micropipette, immediately measure a 5 µl to 10 µl test sample from this mixture and put it on the polished surface of a silicon wafer which is 15 mm ± 2 mm square. When a micropipette cannot be used, use an analytical balance to weigh a 5 mg to 10 mg test sample from the mixture immediately and put it on the polished surface of the silicon wafer.

Place and push a second silicon wafer (15 mm ± 2 mm square) on top of the first one putting the polished surfaces, facing each other on the inside. Wipe off any excess sample.

This sample is used as a test sample.

7.2.2.3 Determine the background FTIR spectrum of two silicon wafers which are 15 mm ± 2 mm squares and are stacked with the polished surfaces facing each other.

NOTE Those two silicon wafers can be different from that used for producing the test sample in 7.2.2.2.

7.2.2.4 Measure the FTIR spectrum of the test sample. From the spectrum, determine the peak height ratio as described in Clause 4. This ratio is designated as X1.

7.2.2.5 From the mixture prepared in 7.2.2.1, prepare a second test sample in the same way as described in 7.2.2.2 and carry out a second FTIR measurement under the same conditions as were used for the first test sample. Determine the peak height ratio as described in Clause 4. This ratio is designated as X2.

It is required that the second FTIR measurement occur within 5 min of the first.

7.2.2.6 If X1 and X2 satisfy the following inequality, this document is applicable to the epoxy resin system evaluated. In this case, proceed to 7.3 for the measurement of the FTIR spectrum given by the (partly) crosslinked resin.

$$\frac{2|X1-X2|}{(X1+X2)} \leq 0,1 \qquad (3)$$

7.2.2.7 If the epoxy resin system meets the requirement in 7.2.2.6, determine the average peak height ratio from the two measurements. This average is used as the peak height ratio of the uncrosslinked sample (X) in the calculation in Clause 8.

7.3 FTIR measurement on the crosslinked sample under investigation

7.3.1 Prepare the crosslinked sample with the heating conditions previously specified. See 9.2 for examples of suitable heating conditions.

7.3.2 Measure the FTIR spectrum of the crosslinked sample (see 7.3.1) in the same way as described in 7.2.2.3 and 7.2.2.4 and determine the peak height ratio as described in Clause 4. This ratio is designated as Y1.

7.3.3 Repeat the measurement with a second test sample of the (partly) crosslinked sample and determine the peak height ratio as described in Clause 4. This ratio is designated Y2. Determine the average peak height ratio from the two measurements. This average is used as the peak height ratio of the crosslinked sample (Y) in the calculation in Clause 8.

8 Expression of results

Calculate the degree of crosslinking using Formula (4):

$$Cr = (1 - Y/X) \times 100 \quad (4)$$

where

Cr is the degree of crosslinking (%);

X is the peak height ratio obtained from the preliminary tests (the average of the two measured values);

Y is the peak height ratio of the (partly) crosslinked resin (the average of the two measured values).

See Formulae (1) and (2) in Clause 4.

9 Precision

9.1 General

Precision data were obtained from an interlaboratory test organized in 2015 in Japan, with eight laboratories participating.

9.2 Materials and crosslinking conditions

a) The materials used were as follows:

1) epoxy resin: bisphenol A type epoxy resin,

2) hardener: methyltetrahydrophthalic anhydride,

3) catalyst: 2,4,6-tris(dimethylaminomethyl)phenol.

b) Three different samples were tested, obtained by different crosslinking conditions:

1) at 100 °C for 60 min,

2) at 100 °C for 90 min,