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Thermosetting resin and UV curable resin — Determination of shrinkage by continuous measurement method

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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*.

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 use of resin first requires curing it under specific conditions that vary depending on the product specification. During this curing process, chemical reactions occur and volatiles evaporate, and so the resin shrinks. This can cause defects, strength reduction, and the deformation of the finished parts or products, especially in high precision required applications.

The conventional method which measures the shrinkage of resin based on specific gravity requires long measurement time and an amount of resin about a few cubic centimetres. This sample size is larger than what is actually used in many applications such as the epoxy encapsulation compounds for integrated circuits, resin coating or adhesive for electronic devices. In order to improve the quality control and further promote the technical advancement of high precision production, a convenient and high accuracy method for determining the shrinkage of resin is essential.

A totally new measurement method has been developed to meet this demand, allowing to measure curing shrinkage continuously with just a trace amount of resin. Moreover, since measurements are taken continuously, the curing behaviour of resin such as thermal expansion and thermal contraction are also observed. This measurement method is described in this document.

Thermosetting resin and UV curable resin — Determination of shrinkage by continuous measurement method

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.

1 Scope

This document specifies the continuous measurement method of shrinkage for thermosetting resin and/or UV curable resin.

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 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 http://www.electropedia.org/

3.1
UV curable resin
resin which is cured by receiving energy from UV rays

3.2
thermosetting resin
resin which is cured by receiving energy from heat

3.3
curing condition
UV irradiation and/or heating condition for curing resin

3.4
curing shrinkage
ratio of the change in resin volume due to curing process to the resin volume before curing

Note 1 to entry: Percentage of shrinkage due to curing of resin.

4 Principle

Cure the resin inside a sample container and continuously measure the changes of sample thickness. Since the horizontal cross-sectional area of resin sample remains constant due to the sidewalls of the sample container, the changes in sample volume are proportional to the changes in the sample

thickness. Therefore, shrinkage of resin is calculated from the changes in sample thickness, as shown in Formula (1).

$$A = (T_1 - T_2) / T_1 \times 100 \quad (1)$$

Where

A is the shrinkage, in %;

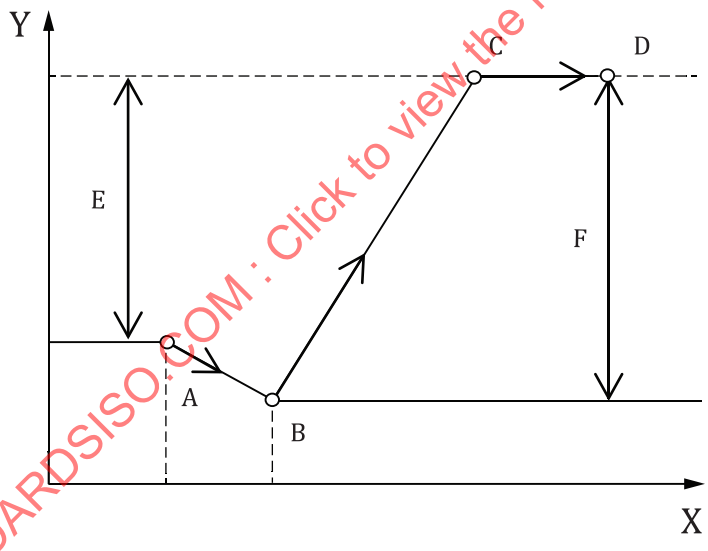
T_1 is the initial sample thickness;

T_2 is the sample thickness at an arbitrary time.

In addition to the determination of the curing shrinkage, this continuous measurement technique also allows to see the volumetric changing behaviour of a resin at the time it is being irradiated by UV, heated, or cooled during the curing process.

NOTE 1 Typically, upon irradiation by UV rays, UV curable resins expand immediately then contract as curing proceeds (see Figure 1). However, some types of UV curable resin exhibit fast reactions wherein shrinkage starts immediately right after irradiation (see Figure B.1).

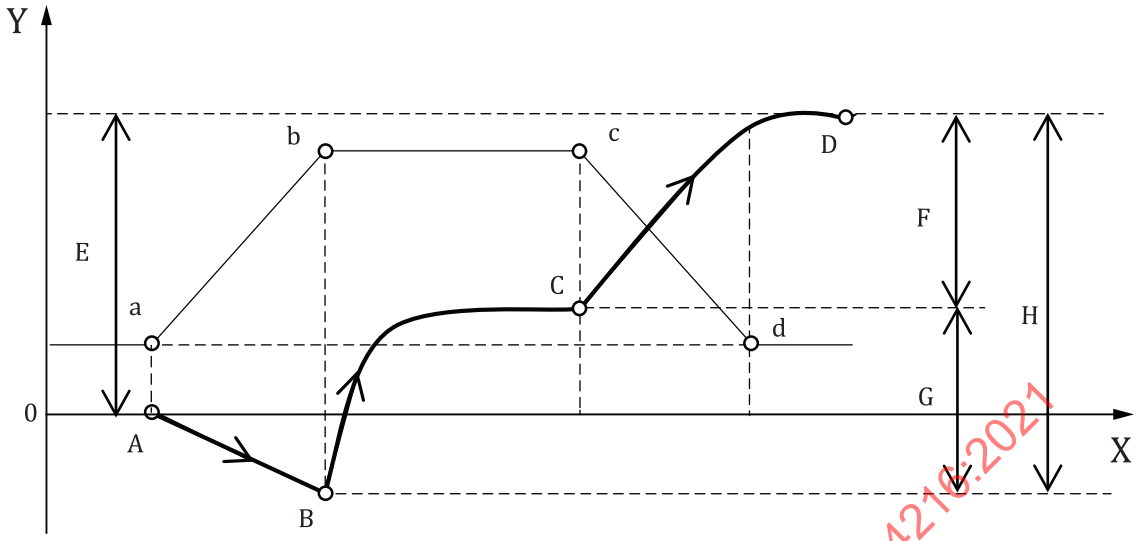
NOTE 2 When a thermosetting resin undergoes heating, thermal expansion occurs due to the increase in the resin temperature. This expansion continues as the temperature rises. When the curing temperature is reached, the curing begins and the resin starts to contract. This shrinkage continues until the resin is fully cured and returned to room temperature (see Figure 2).



Key

X time (s)
Y volumetric shrinkage (%)
A irradiation start point = curing start point
B shrinkage start point
C curing finish point
D shrinkage finish point
E curing shrinkage
F maximum shrinkage

Figure 1 — Curing behaviour of UV curable resin



Key

X	time (min)	a, d	room temperature
Y	volumetric shrinkage (%) temperature(°C)	b, c	curing temperature
A	start heating point		
B	start curing point		
C	curing finish point		
D	shrinkage finish point		
E	curing shrinkage		
F	shrinkage by cooling		
G	shrinkage by reaction		
H	maximum shrinkage		

Figure 2 — Curing behaviour of thermosetting resin

5 Test methods and test conditions

5.1 Test methods

The test methods are classified according to the curing conditions applied to the resin. There are three different types of curing condition: UV curing, thermal curing, and a combination of UV and thermal curing.

5.2 Test conditions

Conduct measurements in the standard laboratory atmosphere of 23 °C ± 2 °C (73,4 °F ± 3,6 °F) and 50 % ± 5 % relative humidity, unless otherwise specified in the experiment conditions.

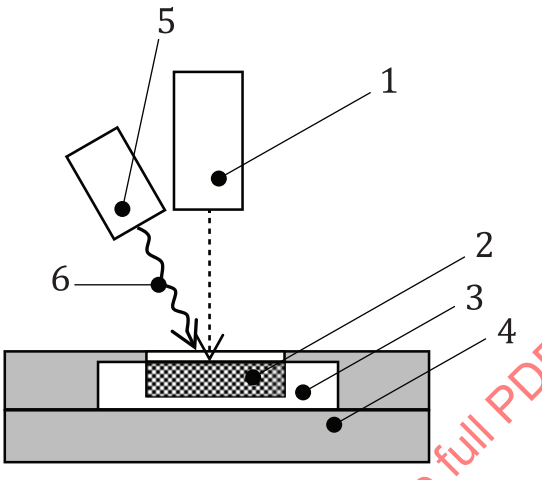
6 Number of measurements

Three or more samples shall be tested for each curing condition.

7 Apparatus

7.1 Apparatus configuration

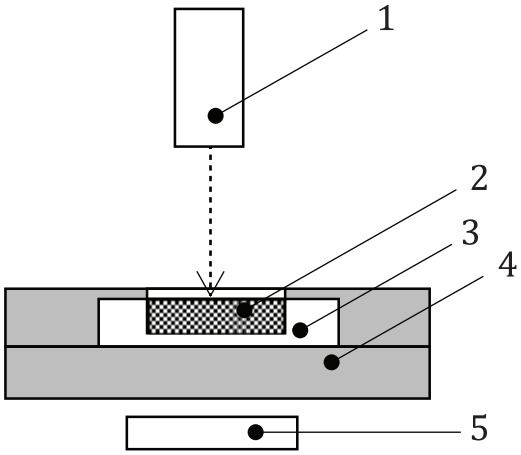
An apparatus for measuring the curing shrinkage of resin by this method is a system that consists of different units. Primarily, it includes a sample container, displacement gauge, UV irradiation device, heating/cooling device, etc. Figure 3 shows an example of an apparatus configuration compatible with a UV curable resin, and Figure 4 shows an example of an apparatus configuration corresponding to a thermosetting resin.



Key

1 displacement gauge
2 sample
3 sample container
4 measuring stage
5 UV irradiation device
6 UV beams

Figure 3 — Example of an apparatus applied for UV curable resin



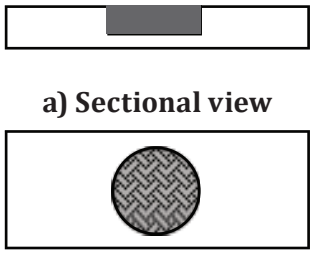
Key

1 displacement gauge
2 sample
3 sample container
4 measuring stage
5 heating/cooling device

Figure 4 — Example of an apparatus applied for thermosetting resin

7.2 Sample container

A sample container of accurately known volume and dimensions shall be used. To ensure an accurate measurement, container material should be used which does not cause either the detachment of resin from the bottom after curing or absorb the sample via the wall surfaces. Moreover, in order to calculate easily the container capacity/volume, the sample container should have a smooth bottom surface and cylindrical shape.



a) Sectional view

b) Top view

Figure 5 — Sample container

(Typical dimensions)

Depth: 0,5 mm to 3 mm

Inner diameter: 10 mm to 15 mm

7.3 Displacement gauge (thickness meter)

The displacement gauge shall be a non-contact type that does not affect the sample and can capture displacement data over time. Moreover, its resolution shall be lower than $1/10^{th}$ the change in sample thickness.

NOTE Non-contact displacement gauge can be a laser displacement gauge, a spectral interference laser displacement gauge, etc.

7.4 UV irradiation device

A UV irradiation device used in shrinkage measurement of a UV curable resin consists of a light source unit and a wavelength selection unit. It shall be capable of irradiating the sample uniformly and with sufficient illuminance to cure the resin.

7.5 Heating/cooling device

A heating/cooling device that can control the temperature of measuring stage, maintain it within ±3 °C of the setting value (room temperature to curing temperature), and provide enough heating and cooling capacity shall be used.

For example, when the sample is an epoxy resin, a device which has heating capacity of at least 150 °C shall be used to obtain a sufficient curing state.

7.6 Data processing unit

The measurement data is calculated according to Clause 10 and shall be sequentially recorded as a volume reduction rate over time. The capture interval and processing speed of the data processing unit shall be compatible with the curing rate of the sample.

8 Curing method

8.1 UV curable resin curing method

UV curable resins are cured by uniform and controlled exposure to UV radiation for a suitable time under appropriate material-dependent conditions. Parameters such as the irradiation intensity necessary for curing, type of light source, and ambient atmosphere conditions shall be prepared for this.

8.2 Thermosetting resin curing method

For curing a thermosetting resin, a device (see Figure 4) shall be used which can control the temperature for heating and cooling. The resin is cured by running a suitable temperature program. Parameters such as the temperatures necessary for curing, retention time, heating and cooling speed shall be prepared for this.

9 Measurement procedure

a) Prior to the measurement, prepare the experiment parameters and devices according to the sample specifications and curing conditions described in Clause 5.

b) Fill the resin into the sample container to form a smooth surface. In the case of high viscosity resins, the sample should be allowed to stand until the material distributes and the surface smoothens. Additionally, in the case of thixotropic resins which do not become flat after standing, use a spatula to smoothen the surface.

   If there are fine air bubbles in the resin, they shall be removed by a defoaming process suitable for the sample. This can be done before or after fill the resin into the sample container.

c) Set the sample container on the measurement stage.

d) Check the thickness measured at the centre of the sample via the displacement gauge to determine the sample volume before curing. This step is automatically done by the apparatus, given that this is a continuous measurement method.

e) Cure the sample according to the prepared conditions of step (a). In this process, the change of sample thickness is measured continuously by the displacement gauge and the volume reduction rate is plotted by the data processing device. Depending on material, the data acquisition interval of the displacement gauge is determined.

f) After curing and returning to the initial temperature at the start of measurement, the shrinkage end point shall be determined as the point at which the shrinkage of the sample in the last 5 min is below 0,2 % of the initial sample volume.

NOTE 1 An example of influencing factors in measurement is shown in Annex A.

NOTE 2 A measurement example is shown in Annex B and a measurement report example is given in Annex C.

10 Expression of results

10.1 Volumetric shrinkage

Volumetric shrinkage, $A(t)$, from the start of the curing to an arbitrary time is defined by Formula (2).

Since the resin is cured in the container, the horizontal cross-sectional area of the sample is limited by the sample container. Hence, the horizontal cross-sectional area does not change during the measurement process. Therefore, only the sample thickness changes affect the volumetric shrinkage.

$$A(t)=\frac{V_o-V_t}{V_o}\times 100=\frac{T_o-T_t}{T_o}\times 100 \tag{2}$$

where

A is the volumetric shrinkage at an elapsed time due to the applied curing condition;

t is the elapsed time after starting the measurement;

V_o is the initial volume (mm^3) at $t = 0$, $V_o = T_o \times S$;

$V(t)$ is the sample volume (mm^3) at time t, $V_t = T_t \times S$;

S is the sample horizontal cross-sectional area (mm^2), (Figure 6);

T_o is the sample thickness (mm) at time t = 0, [Figure 6 a)];

$T(t)$ is the sample thickness (mm) at an elapsed time t by an arbitrary curing condition, [Figure 6 b)].

10.2 Curing shrinkage

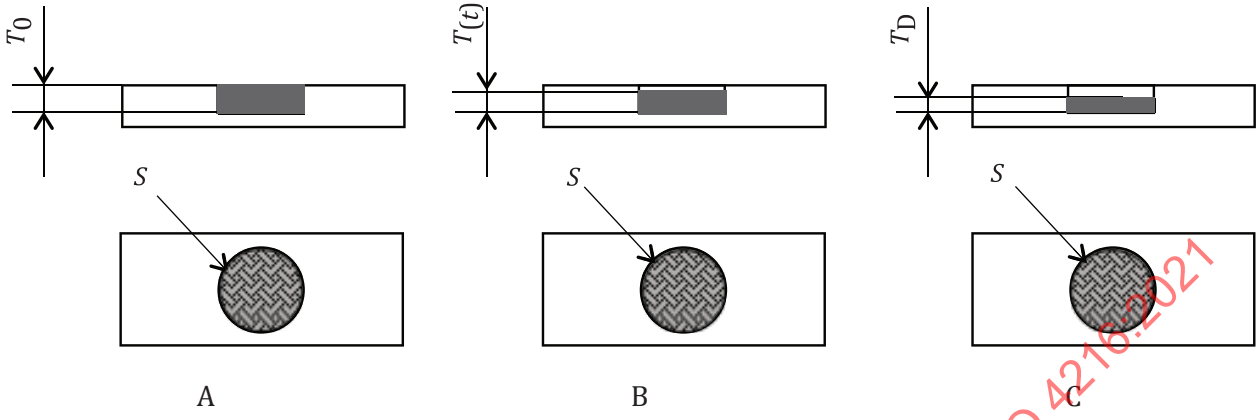
The curing shrinkage of a resin from start to the end of measurement (A_D) is defined by the Formula (3).

$$A_D=\frac{V_o-V_D}{V_o}\times 100=\frac{T_o-T_D}{T_o}\times 100 \tag{3}$$

where

V_D is the sample volume (mm^3) at the end of curing process [D – Figure 1 or Figure 2)];

T_D is the sample thickness (mm) at the end of curing process [Figure 6 c)].



a) Start of measurement **b) During measurement** **c) End of measurement**

Key

A initial

B after an elapsed time

C end of shrinkage

Figure 6 — Sample thickness and horizontal cross-sectional area

11 Test report

For each test method, the test report shall specify the following:

a) a reference of this document, i.e. ISO 4216:2021;

b) measurement date;

c) name of the measurement device used;

d) all the details necessary to identify the sample;

e) temperature at the start of measurement;

f) resin curing method (i.e. thermal curing or UV curing);

g) curing condition:

- UV curing: irradiation wavelength, irradiation intensity on the sample surface, irradiation time;
- thermal curing: all details of temperature program, including temperature, heating/cooling speed, retention time for each step;

h) volume and depth of sample container;

i) the measurement results obtained (i.e. shrinkage);

j) notices of any operating details not specified in this document, or regarded as optional, or any unusual features observed during the test.

Annex A
(informative)

Influencing factors on measurement

The measurement should be made in consideration of the following factors.

a) Influence of temperature on the measurement device

Depending on the measurement temperature, thermal expansion affects the measurement stage and sample container.

b) Displacement gauge accuracy

Mechanical error occurs in the measured value depending on the accuracy of the displacement gauge. For example, when the accuracy of a displacement gauge is 1 µm, a mechanical error of 0,1 % occurs in the measured value of the sample which its thickness before measurement (T_o) is 1 mm.

c) Influence of sample absorption on inner wall of the sample container

When the sample is adsorbed toward the inner wall of the sample container prior to and during the curing, a meniscus is formed. This means that a smaller than actual volume of the cured sample is used for calculating shrinkage. Therefore, the obtained shrinkage is an upper limit to the actual value.

For example, a measurement is carried out in a Ø10 mm, 1 mm thickness sample container (volume 78,5 mm^3). When the absorption (meniscus) occurs at an angle of 45° on a sample with a film thickness displacement of 0,1 mm (volume shrinkage 10 %, volume 70,65 mm^3), the volume of the meniscus formation (0,16 mm^3) is approximately 0,2 % of the initial volume, and the volume shrinkage is calculated 0,2 % bigger than the actual value.

d) Change in horizontal cross-sectional area in shrinkage

When a separation occurs between the container wall and the resin after curing, this means that the horizontal cross-sectional area of the sample also shrunk. Here, the cross-section shrinkage is usually greatest at the top of the sample and lowest at the bottom, resulting in a flat cone-shaped cured sample. With this, a bigger than actual volume of cured sample is used for calculating curing shrinkage.

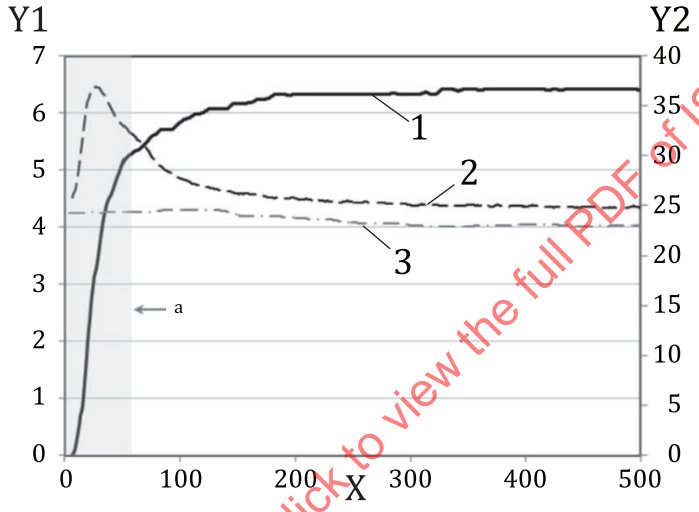
For example, a measurement is carried out in a Ø10 mm, 1 mm thickness sample container (volume 78,5 mm^3), in which a cured sample has a measured thickness displacement of 0,1 mm (volume shrinkage 10 %, volume 70,65 mm^3). If the gap from the container wall to the top side of the sample surface is 0,5 mm and there is no separation at the bottom (0 mm gap at the bottom), the volume of this gap space (6,7 mm^3) is approximately 8,5 % of the initial volume. Therefore, the curing shrinkage is calculated 8,5 % smaller than the actual value, resulting in a big error.

Annex B
(informative)

Examples of measurement result

B.1 Example of volumetric shrinkage of UV curable resin

When a UV curable resin is irradiated by a UV light source, the shrinkage starts immediately and continues to contract further after the irradiation time. Figure B.1 shows an example of a volumetric shrinkage measurement result of a UV curable resin irradiated by UV light for 60 s.



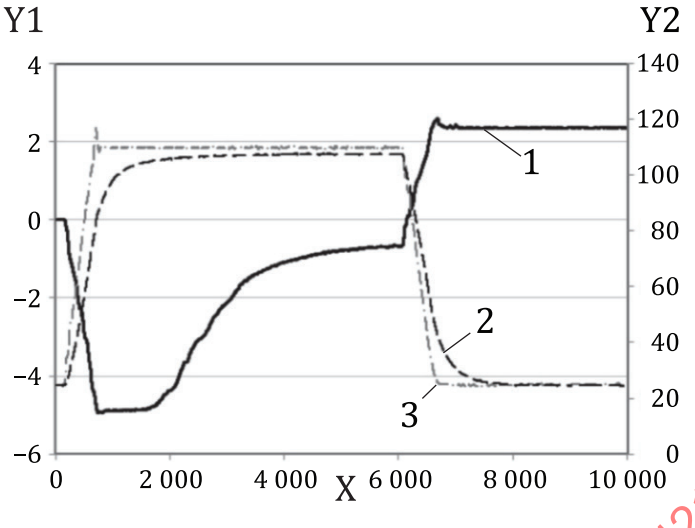
Key

Y1 volume shrinkage, in per cent (%)
Y2 temperature, in degree Celsius (°C)
X time, in seconds (s)
1 shrinkage
2 stage temperature
3 sample surface temperature
a Irradiation time (60 s).

Figure B.1 — Measurement example of curing shrinkage — UV curable resin

B.2 Volumetric shrinkage of thermosetting resin

A thermosetting resin expands during heating, starts to shrink when the curing temperature is reached, and continues to shrink further upon cooling to room temperature. Figure B.2 shows an example of volumetric shrinkage during curing when a thermosetting resin is heated and maintained at 110 °C then cooled to room temperature.



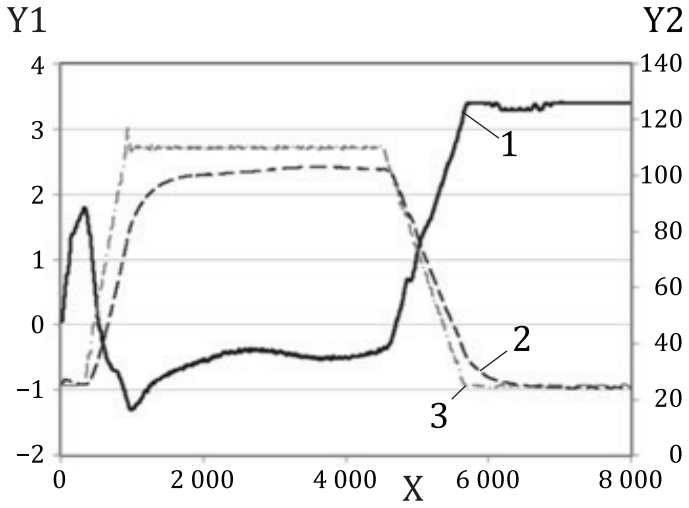
Key

Y1 volume shrinkage, in per cent (%)
Y2 temperature, in degree Celsius (°C)
X time, in seconds (s)
1 shrinkage
2 stage temperature
3 sample surface temperature

Figure B.2 — Measurement example of curing shrinkage — Thermosetting resin

B.3 Example of volumetric shrinkage measurement of a resin that requires thermosetting in addition to UV curing

In the case of a resin that requires heat curing after a UV curing step, the resin starts to shrink immediately after the UV irradiation and expands when heating starts. After that, when the curing temperature is reached, the shrinkage starts again, and when the temperature is lowered to room temperature, the shrinkage further progresses. Figure B.3 shows an example of the measurement result of the volumetric shrinkage when the resin is irradiated first by UV light then heated, maintained, and lowered to room temperature.



Key

Y1 volume shrinkage, in per cent (%)
Y2 temperature, in degree Celsius (°C)
X time, in seconds (s)
1 shrinkage
2 stage temperature
3 sample surface temperature

Figure B.3 — Measurement example of curing shrinkage — (UV + thermal curing resin)

Annex C
(informative)

Example of measurement report

C.1 Listed items example

The following is an example of the items described in the test report.

C.2 Test report (Thermosetting resin example)

1) Measurement method

Continuous measurement of shrinkage of thermosetting resin was performed according to ISO 4216:2021

(UV curable resin and thermosetting resin – continuous measurement method of shrinkage).

Material: Epoxy resin (name) manufactured by (lot number xxxxxxxx)

Sample quantity: 3

Measurement date: YYYY/MM/DD

Measurement device name: (device) name manufactured by (company name)

Measurement condition: the curing condition and details are as follows:

a) Sample container dimension: diameter 10 mm (cross section area 78,5 mm^2), depth 1 mm.

b) Material curing method: Thermosetting

c) Specific curing condition (thermosetting setting condition):

The heating conditions of the measurement stage (hot plate) are as follows:

i) Initial temperature and retention time (25 °C, 2 min)

ii) Heating temperature and heating time (150 °C, 12 min), heating retention time (30 min)

iii) Initial temperature and cooling time (25 °C, 12 min), retention time (30 min)

2) Measurement result

The obtained volumetric shrinkage, measurement stage temperature, and sample surface temperature are plotted below.