INTERNATIONAL
STANDARD

ISO
17304

First edition
2013-12-01

Dentistry — Polymerization shrinkage: Method for determination of polymerization shrinkage of polymer-based restorative materials

Médecine bucco-dentaire — Rétraction à la polymérisation: Méthode de détermination de la rétraction à la polymérisation des matériaux de restauration à base de polymères

Reference number
ISO 17304:2013(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

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. 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. 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.

The committee responsible for this document is ISO/TC 106, *Dentistry*, Subcommittee SC 1, *Filling and restorative materials*.

Introduction

This International Standard specifies a test method for the determination of the polymerization shrinkage of external energy-activated polymer-based restorative materials of Class 2, Group 1 (see ISO 4049) and similar core materials.

Many test methods have been used over many years to determine this property but no International Standard test has so far been adopted. The method specified herein is a simple method that provides reproducible results that will aid users in the comparison of test data. It was developed and verified by a comprehensive interlaboratory test programme comparing it with other methods.

Dentistry — Polymerization shrinkage: Method for determination of polymerization shrinkage of polymer-based restorative materials

1 Scope

This International Standard specifies a test method for the measurement of the polymerization shrinkage of external energy-activated polymer-based restorative materials such as composites and core materials.

The method is not suitable for Class 1 (self-curing, see ISO 4049) polymer-based restorative materials.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1183-1, *Plastics — Methods for determining the density of non-cellular plastics — Part 1: Immersion method, liquid pyknometer method and titration method*

ISO 1942, *Dentistry — Vocabulary*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 4049, *Dentistry — Polymer-based restorative materials*

ISO 10650 (all parts), *Dentistry — Powered polymerization activators*

3 Terms and definitions

For the purposes of this document, the terms and definitions in ISO 1183-1, ISO 1942, ISO 4049, and the following apply.

3.1
high-viscosity materials
polymer-based restorative materials having little flow so that they hold their shape on moulding

3.2
flowable materials
polymer-based restorative materials having low viscosity so that they do not hold their shape on moulding

4 Test method

4.1 Principle

The polymerization shrinkage of external energy-activated polymer-based restorative materials is determined using density determinations in accordance with the buoyancy method (Archimedes' principle). This test method accords with method A (immersion method), described in general terms in ISO 1183-1.

Ensure that test conditions such as temperature, duration of exposure, and distance between light guide and the test specimen are controlled and reproducible. Pre-test storage conditions of the polymer prior to its measurement are also specified to ensure the maximum achievable polymerization in the test conditions so that the most complete possible shrinkage of the materials will be achieved. This way, differences in the rate of polymerization will, to a large extent, be balanced out.

4.2 General

Perform all measurements at a room temperature of (23 ± 2) °C.

Store all specimens at a temperature of (23 ± 2) °C for at least 30 min before the start of measurement.

Perform all measurements of the unpolymerized specimens under yellow light.

NOTE 1 Yellow light may be created by filtering ambient lighting with a suitable filter1).

When handling test materials, wear appropriate rubber gloves, e.g. latex or nitrile.

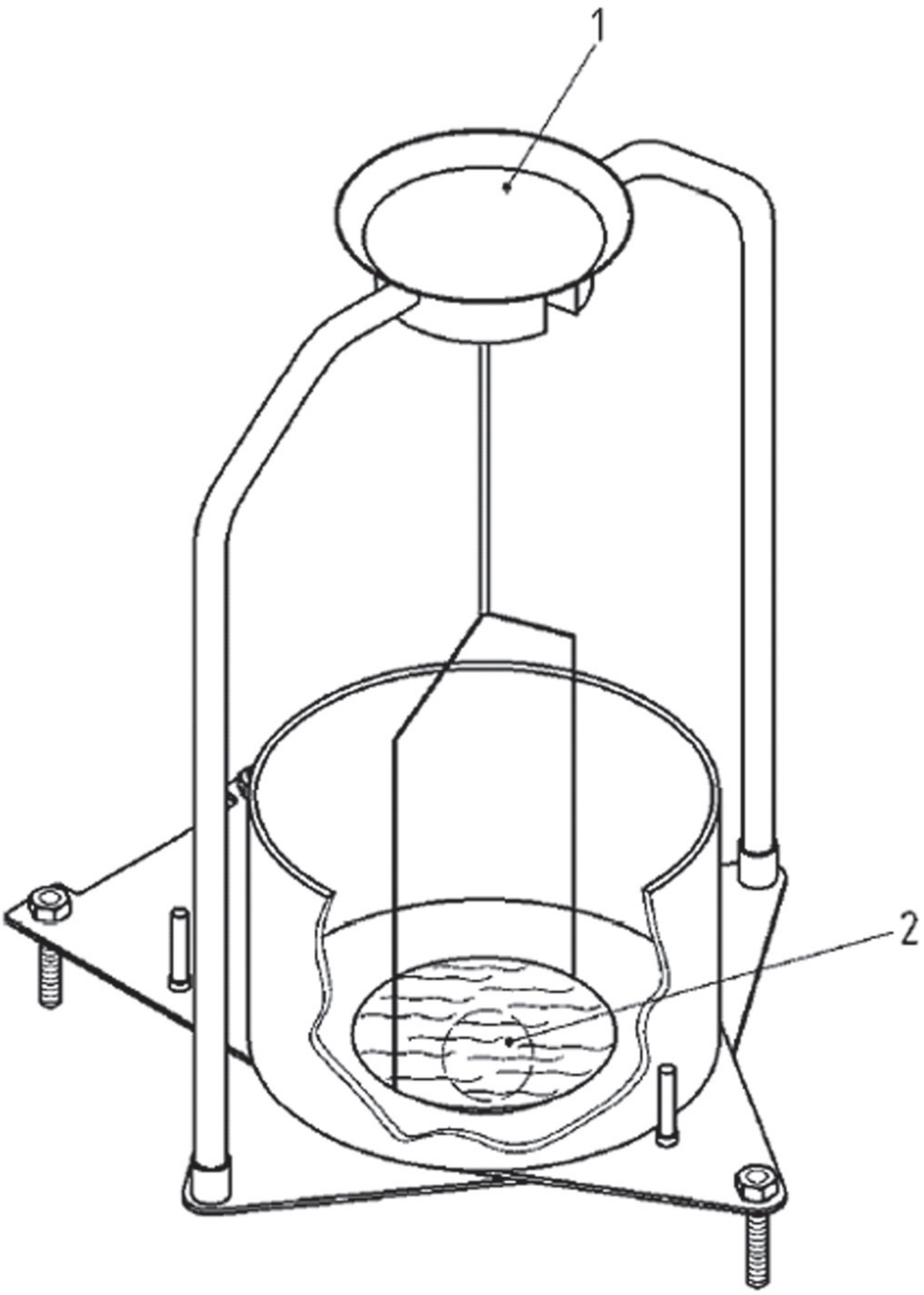
The temperature fluctuation during the measurement of the unpolymerized specimens and the polymerized specimens shall be less than 1,0 °C.

NOTE 2 Measurements can be performed at temperatures between 21 °C and 25 °C. Temperature variations during measurement below 1,0 °C do not significantly influence the results.

Perform the corresponding density measurements for the unpolymerized and the polymerized specimens on the same day.

---

1) Details of suitable products are available from the secretariat of ISO/TC 106.



Key

1 position 1: for the specimen in air (dry)

2 position 2: for the specimen in the buoyancy medium

Figure 1 — Example of a density determination apparatus

4.3 Materials and reagents

4.3.1 General reagent — water, use water prepared in accordance with ISO 3696 Grade 3.

4.3.2 Sodium lauryl sulphate, with at least 99,0 % (mass concentration) purity.

NOTE The CAS number of sodium lauryl sulphate is 151–21–3.

4.3.3 Test material — External-energy activated polymer-based restorative material or polymeric core material.

4.4 Apparatus

4.4.1 Analytical balance, accurate to 0,000 1 g**.**

4.4.2 Density determination apparatus, consisting essentially of a platform, beaker, pan hanger assembly, and thermometer (see Figure 1).

NOTE This equipment may be obtained from scale manufacturers as a special accessory (density determination kit).

4.4.3 Thermometer, accurate in the range 20 °C to 30 °C, graduated in steps of 0,1 °C.

4.4.4 External energy source, with a radiant exitance of at least 500 mW/cm^2 in the range of 400 nm to 515 nm [determined in accordance with ISO 10650 (all parts)] and recommended by the manufacturer of the test material for use with that material.

4.4.5 Vacuum pump, with pressure gauge (manometer), accurate to 10 mbar.

4.4.6 Desiccator, with a valve and capable of being connected to the vacuum pump (4.4.5)

4.4.7 Oven, capable of being maintained at (37 ± 2) °C.

4.4.8 Spatula.

4.4.9 Transfer medium, suitable for the unpolymerized paste, e.g. microscope slide.

4.4.10 Volumetric flask, of size 500 ml, with stopper.

4.4.11 Smooth, non-absorbent, stable base, e.g. mixing (conditioner) block.

4.4.12 Glass dish, for use with flowable materials, fitting to the measurement pans of the determination apparatus (4.4.2), e.g. diameter of about 20 mm and a height of about 10 mm.

4.5 Buoyancy medium

4.5.1 Determination of immersion depth

The immersion depth of the lower weighing pan of the density determination apparatus (4.4.2) shall be at least 20 mm to ensure complete immersion. Immersion depth is measured from the upper edge of the weighing pan to the meniscus of the buoyancy medium.

For flowable materials, the specimen and the dish shall be completely immersed.

NOTE The density determination apparatus supplied by various manufacturers differ with regard to the height and diameter of their water bowls. It is necessary to establish a standard immersion depth for the lower weighing pan in the buoyancy medium to ensure complete immersion.

4.5.2 Preparation of the buoyancy medium

Weigh (5,000 ± 0,001) g of sodium lauryl sulphate (4.3.2), place it into the volumetric flask (4.4.10), and then add water (4.3.1) until a final weight of (500 ± 0,001) g is reached. Seal the flask and shake it until a homogeneous solution is achieved, as determined by visual inspection without magnification. Prepare the buoyancy medium at least 24 h prior to testing.

NOTE 1 This solution can be stored for four weeks at room temperature.

On the day of the test, pour the necessary amount of buoyancy medium into the water bowl of the determination apparatus in accordance with the distance specifications in 4.5.1 and place it in the desiccator (4.4.6).

Degas the buoyancy medium by evacuating the desiccator at a temperature of (23 ± 2) °C using the vacuum pump (4.4.5). Immediately after a vacuum pressure of (50 ± 10) mbar is attained, close the desiccator vacuum port. After (20 ± 5) min, carefully ventilate the dessicator.

NOTE 2 This pressure was chosen so that the water does not boil.

Afterwards, the buoyancy medium shall be kept at a temperature of (23 ± 2) °C for at least 2 h.

Read the density of the buoyancy medium for the current measuring temperature from Table 1.

NOTE 3 The density of water is applied instead of the precise density of the buoyancy medium. The dependence on temperature will thereby be taken into account. The accuracy of the measured polymerization shrinkage will thereby not be impaired because the differences in the respective densities balance each other out.

4.5.3 Number of specimens

For the testing of unpolymerized pastes, prepare 6 specimens of 1,0 g each.

For the testing of polymerized pastes, prepare 12 specimens of 0,5 g each.

4.6 Preparatory treatment of the test material

4.6.1 General

The dispensing, movement, and storage of the unpolymerized material shall take place under yellow light. See 4.2.

The first 3 mm of the expressed material shall not be used.

4.6.2 Test material pastes in syringes

Deploy test material pastes in syringes directly without further preparatory treatment prior to the determination of the polymerization shrinkage.

4.6.3 Test material pastes in single-dosage containers

Pre-treat test material pastes in single-dosage containers (e.g. compules, carpules) before use in the following way.

Squeeze the material out slowly and without bubbles onto the smooth, non-absorbent, stable base (4.4.11). Store this block and material for two days at (37 ± 2) °C in the oven (4.4.7) with light excluded.

Condition the material at a temperature of (23 ± 2) °C for 1 h before measurement.

NOTE This period of storage serves to remove any entrapped air bubbles from the material that may have been introduced during the expression or movement of the material.

Table 1 — Density of water at different measuring temperatures [Reproduced from Handbook of Chemistry and Physics, 91st edition, (2010-2011), Section 6, CRC Press]

Temperature °C	**Density** ρ_0 g/ml	**Temperature** °C	**Density** ρ_0 g/ml
21,0	**0,99800**	**23,0**	**0,99754**
21,1	0,99797	23,1	0,99752
21,2	0,99795	23,2	0,99749
21,3	0,99793	23,3	0,99747
21,4	0,99791	23,4	0,99745
21,5	0,99789	23,5	0,99742
21,6	0,99786	23,6	0,99740
21,7	0,99784	23,7	0,99737
21,8	0,99782	23,8	0,99735
21,9	0,99780	23,9	0,99732
22,0	**0,99777**	**24,0**	**0,99730**
22,1	0.99775	24,1	0,99728
22,2	0,99773	24,2	0,99725
22,3	0,99771	24,3	0.99723
22,4	0,99768	24,4	0,99720
22,5	0,99766	24,5	0,99718
22,6	0,99764	24,6	0,99715
22,7	0,99762	24,7	0,99712
22,8	0,99759	24,8	0,99710
22,9	0,99757	24,9	0,99710
		25,0	**0,99705**

4.7 Determination of polymerization shrinkage

4.7.1 Determination of the density of the unpolymerized specimens of high-viscosity materials

4.7.1.1 Procedure

Carry out the procedure six times. Use one test specimen at each determination.

Mould the test material paste, pre-treated in accordance with 4.6, into six ball-shaped specimens of mass (1,00 ± 0,10) g each using gloved fingers, avoiding the formation of air inclusions.

Appropriate protective gloves should be used.

The following two test positions are specified:

a) position 1 of the measuring apparatus: position of the specimen in air;

b) position 2 of the measuring apparatus: position of the specimen in the buoyancy medium.

Tare the balance (4.4.1) with the density determination apparatus (4.4.2) in place. Place one of the specimen balls in position 1 of the measuring apparatus. Measure the mass and record this measurement as $m_{u,1}$. Remove the specimen from the balance.

Measure the temperature of the buoyancy medium using the thermometer (4.4.3) and record this measurement. Tare the balance again. Place the specimen in position 2 of the measuring apparatus. Measure the mass of the specimen in the buoyancy medium and record this measurement as $m_{\mathrm{u},2}$. While doing this, carefully remove any adhering air bubbles.

Discard the test specimens after the tests.

4.7.1.2 Individual densities of the unpolymerized specimens of high-viscosity material

Calculate the density, ρ_u, for each unpolymerized specimen using Formula (1):

$$\rho_\mathrm{u} = \frac{m_{\mathrm{u},1} \times \rho_0}{m_{\mathrm{u},1} - m_{\mathrm{u},2}} \tag{1}$$

where

ρ_u is the individual density of the unpolymerized specimen, in g/ml;

$m_{\mathrm{u},1}$ is the mass of the unpolymerized specimen in position 1 in air, in g;

$m_{\mathrm{u},2}$ is the mass of the unpolymerized specimen in position 2 in the buoyancy medium, in g;

ρ_0 is the density of the buoyancy medium, in g/ml, at its temperature at the respective time of measurement.

4.7.1.3 Mean of the density of the unpolymerized specimens of high-viscosity materials

Calculate the mean of the individual density of the six unpolymerized specimens. Express the mean for the density of the unpolymerized specimens as $\overline{\rho_\mathrm{u}}$ and round to four decimal places. Discard one obvious outlier. If there is more than one outlier, repeat this series of measurements.

NOTE A coefficient of variance of more than 0,5 % indicates the existence of one or more outliers. An outlier test, e.g. Grubbs, may also be used.

4.7.1.4 Standard deviation for the mean of the unpolymerized specimens of high-viscosity material

Calculate the standard deviation for the mean of the unpolymerized specimens, σ_u, using Formula (2):

$$\sigma_\mathrm{u} = \sqrt{\frac{\sum_{i=1}^{n} \left(\rho_1 - \overline{\rho_\mathrm{u}}\right)^2}{n-1}} \tag{2}$$

where

σ_u is the standard deviation of the density of the unpolymerized specimen, in g/ml;

ρ_i is the individual density of the respective unpolymerized specimen, in g/ml;

$\overline{\rho_\mathrm{u}}$ is the mean of the density of the unpolymerized specimen, in g/ml;

n is the number of measured specimens.

Express the standard deviation of the mean of the unpolymerized specimen to four decimal places.

4.7.2 Determination of the density of the unpolymerized specimens of flowable materials

4.7.2.1 Density of the glass dish (4.4.12)

Determine the density of the glass dish according to the procedure described in 4.7.1.1 using the glass dish instead of the unpolymerized specimen. Perform the measurement three times.

Calculate the density of the glass dish, ρ_d, using Formula (3):

$$\rho_\mathrm{d} = \frac{m_{\mathrm{d},1} \times \rho_0}{m_{\mathrm{d},1} - m_{\mathrm{d},2}} \tag{3}$$

where

ρ_d is the individual density of the glass dish, in g/ml;

$m_{\mathrm{d},1}$ is the mass of the glass dish in position 1 in air, in g;

$m_{\mathrm{d},2}$ is the mass of the glass dish in position 2 in the buoyancy medium, in g;

ρ_0 is the density of the buoyancy medium, in g/ml, at the temperature at the respective time of measurement.

Calculate the mean of the three individual values of the density of the glass dish and record this value as $\rho_{\mathrm{d,m}}$.

4.7.2.2 Procedure

Dispense a mass of (1,00 ± 0,10) g of the flowable test material, pre-treated in accordance with 4.6, into the dish. Avoid the formation of air inclusions while doing this.

The following two test positions are specified:

a) position 1 of the density determination apparatus: position of the specimen and dish in air;

b) position 2 of the density determination apparatus: position of the specimen and dish in the buoyancy medium.

Tare the balance (4.4.1) with the density determination apparatus (4.4.2) in place. Place the specimen and dish in position 1 of the measuring apparatus. Measure the mass of the specimen and dish and record this value as $m_{\mathrm{ud},1}$. Remove the specimen and dish from the balance.

Measure the temperature of the buoyancy medium using the thermometer (4.4.3) and record this measurement. Tare the balance again. Place the specimen and dish in position 2 of the density determination apparatus. Measure the mass of the specimen and dish in the buoyancy medium and record this value as $m_{\mathrm{ud},2}$. During this procedure, carefully remove any air bubbles adhering to the specimen.

After the test, clean the dish carefully, disposing of the test specimen. Repeat the test on five more specimens. Discard the test specimens after the tests.

4.7.2.3 Individual densities of the unpolymerized specimens of flowable materials

For each unpolymerized specimen, calculate the individual density, ρ_{u}, using Formula (4)

$$\rho_{\mathrm{u}} = \frac{m_{\mathrm{ud},1} - m_{\mathrm{d},1} \times \rho_0}{m_{\mathrm{ud},1} - \left(\dfrac{m_{d,1} \times \rho_0}{\rho_{\mathrm{d,m}}} \right) - m_{\mathrm{ud},2}} \tag{4}$$

where

ρ_{u} is the individual density of each unpolymerized specimen, in g/ml;

$m_{\mathrm{d},1}$ is the mass of the glass dish in position 1 in air, in g;

$m_{\mathrm{ud},1}$ is the mass of the unpolymerized specimen and the glass dish measured together in position 1 in air, in g;

$m_{\mathrm{ud},2}$ is the mass of the unpolymerized specimen and the glass dish measured together in position 2 in the buoyancy medium, in g;

$\rho_{\mathrm{d.m}}$ is the mean density of the glass dish, in g/ml, determined in accordance with 4.7.2.1;

ρ_0 is the density of the buoyancy medium, in g/ml, at its temperature at the respective time of measurement.

4.7.2.4 Mean of the density of the unpolymerized specimens of flowable materials

Calculate the mean from the density of each unpolymerized specimen. Express this mean for the density of the unpolymerized specimen as $\overline{\rho_{\mathrm{u}}}$ and round to four decimal places. Discard any single obvious outlier. If more than one obvious outlier appears, repeat the series of measurements.

See NOTE in 4.7.1.3.

4.7.2.5 Standard deviation for the mean of the unpolymerized specimens of flowable materials

Calculate the standard deviation for the mean of the unpolymerized specimens according to 4.7.1.4.

4.7.3 Determination of the density of the polymerized material

4.7.3.1 Preparation of the test specimens

Mould 12 specimens of high-viscosity test material paste, pre-treated in accordance with 4.6, into balls of mass (0,50 ± 0,05) g each using gloved fingers (see NOTE in 4.7.1.1). Avoid air inclusions while doing this.

NOTE 1 The specimens are small to allow complete polymerization of each. Two polymerized specimens are used in each test (4.7.3.2).

Prepare flowable materials in the glass dish (4.4.12).

NOTE 2 A Dappen dish can be used for easy handling and curing of the materials.

Place each specimen on the stable base (4.4.11) and irradiate using the external energy source (4.4.4) for at least 40 s. The distance between the (fibre-optic) light guide of the energy source and the test specimen shall be less than 3 mm. Do not touch the specimen during this process.

After the first exposure, turn the specimen over by an angle of 180° onto the side that faces the external energy source and irradiate for a second time for at least 40 s. Afterwards, store the test specimen dry at a temperature of (37 ± 2) °C in the oven (4.4.5) for (24 ± 2) h. Then remove the test specimen from the oven and store at (23 ± 2) °C for 1 h.

4.7.3.2 Procedure

Tare the balance (4.4.1) with the density determination apparatus (4.4.2) in place. Place two of the test specimens in position 1 of the measuring apparatus and measure their total mass and record this measurement as $m_{c,1}$. Remove the test specimens from the balance.

Measure the temperature of the buoyancy medium and record this value.

Tare the balance again. Place the same two test specimens in position 2 of the measuring apparatus and measure their total mass in the buoyancy medium; record this value as $m_{c,2}$. Carefully remove any adhering air bubbles during this procedure.

Repeat the test five times with further pairs of test specimen for each test. Discard the specimens after the tests.

4.7.3.3 Individual density of each polymerized specimen

Calculate the density, ρ_c, of each pair of polymerized specimens using Formula (5):

$$\rho_c = \frac{m_{c,1} \times \rho_0}{m_{c,1} - m_{c,2}} \qquad (5)$$

where

ρ_c is the individual density of the respective polymerized specimen, in g/ml;

$m_{c,1}$ is the mass of the respective polymerized specimen in position 1 in air, in g;

$m_{c,2}$ is the mass of the respective polymerized specimen in position 2 in the buoyancy medium, in g;

ρ_0 is the density of the buoyancy medium, in g/ml, at the respective measuring temperature.

4.7.3.4 Mean of the density of the pairs of polymerized specimens

Calculate the mean of the individual densities of the pairs of polymerized specimens. Express this mean for the density of the polymerized specimen as $\overline{\rho_c}$ and round to four decimal places. Discard a single obvious outlier. If more than one obvious outlier appears repeat the series of measurements.

See NOTE in 4.7.1.3.

4.7.3.5 Standard deviation of the density of the pairs of polymerized specimens

Calculate the standard deviation of the mean of the polymerized specimens, σ_c, using Formula (6):

$$\sigma_c = \sqrt{\frac{\sum_{i=1}^{n} (\rho_i - \overline{\rho_c})^2}{n-1}} \tag{6}$$

where

σ_c is the standard deviation of the density of the polymerized specimen, in g/ml;

ρ_i is the individual density of the respective polymerized specimen, in g/ml;

$\overline{\rho_c}$ is the mean of the density of the polymerized specimen, in g/ml;

n is the number of measured specimens.

Express the standard deviation of the density of the pairs of polymerized specimens to four decimal places.

4.7.4 Polymerization shrinkage

Calculate the polymerization shrinkage, S in percentage using the calculated average densities of the polymerized and unpolymerized specimens using Formula (7):

$$S = \left(\frac{\overline{\rho_c} - \overline{\rho_u}}{\overline{\rho_c}} \right) \times 100 \tag{7}$$

where

S is the polymerization shrinkage, in percentage terms;

$\overline{\rho_u}$ is the mean of the density of the unpolymerized specimen, in g/ml;

$\overline{\rho_c}$ is the mean of the density of the polymerized specimen, in g/ml.

Express the polymerization shrinkages as a percentage and round to one decimal place.

4.7.5 Standard deviation for polymerization shrinkage

Calculate the standard deviation for polymerization shrinkage, σ_S, in percentage from the densities for the polymerized and unpolymerized specimens and their respective standard deviations using Formula (8):

$$\sigma_s = \frac{100}{\overline{\rho_c}^2} \times \sqrt{\overline{\rho_u}^2 \times \sigma_c^2 + \overline{\rho_c}^2 \times \sigma_u^2} \qquad (8)$$

where

σ_S is the standard deviation for polymerization shrinkage, in percentage terms;

$\overline{\rho_u}$ is the mean of the density of the unpolymerized specimen, in g/ml;

$\overline{\rho_c}$ is the mean of the density of the polymerized specimen, in g/ml;

σ_u is the standard deviation of the density of the unpolymerized specimen, in g/ml;

σ_C is the standard deviation of the density of the polymerized specimen, in g/ml.

Express the standard deviation for polymerization shrinkage as a percentage and round to one decimal place.

4.8 Test report

The test report for the measurement of the polymerization shrinkage shall contain at least the following details:

a) trade name and type of the material tested (e.g. high viscosity, flowable);

b) lot number (batch description) of the material tested;

c) form of the direct packaging of the material (e.g. syringe, single dose);

d) shade of the material tested (if appropriate);

e) external energy source used and the applied radiant exitance [determined in accordance with ISO 10650 (all parts)];

f) mean value of the measured polymerization shrinkage with its standard deviation;

g) reference to this International Standard (i.e. ISO 17304);

h) date of performance of the test.

ICS 11.060.10

Price based on 12 pages