INTERNATIONAL STANDARD

ISO 11667

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Fibre-reinforced plastics — Moulding compounds and prepregs — Determination of resin, reinforced-fibre and mineral-filler content — Dissolution methods

Plastiques renforcés de fibre — Préimprégnés et compositions de moulage — Détermination des taux de résine, de fibre de renfort et de charge minérale — Méthodes par dissolution

Reference number
ISO 11667:1997(E)

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11667 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 13, *Composites and reinforcement fibres*.

Annex A of this International Standard is for information only.

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Fibre-reinforced plastics — Moulding compounds and prepregs — Determination of resin, reinforced-fibre and mineral-filler content — Dissolution methods

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies two dissolution methods for the determination of the resin, reinforcement-fibre and mineral-filler contents of moulding compounds and prepregs.

Method A: Extraction by Soxhlet. In cases of dispute, this method is the reference method.

Method B: Extraction by immersion in solvent in a beaker. This method uses simpler equipment, making it suitable for quality assurance testing.

This International Standard is applicable to the following types of material:

— prepregs made from yarns, rovings, tapes and fabrics;

— SMC, BMC and DMC moulding compounds.

Typically, reinforcement fibres are coated with sizing or finishes. These normally dissolve with the resin and are, therefore, included in the resin content.

This International Standard is not applicable to the following types of reinforced plastic:

— those containing reinforcements which are soluble (or partly soluble) in the solvents used to dissolve the resin;

— those in which the resin is partly or fully cured and so not fully soluble in organic solvents.

NOTE — ISO 1172:1996, *Textile-glass-reinforced plastics — Prepregs, moulding compounds and laminates — Determination of the textile-glass and mineral-filler content — Calcination methods*, may be used where the resin is cured.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 291:1997, *Plastics — Standard atmospheres for conditioning and testing.*

ISO 472:1988, *Plastics — Vocabulary.*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

3 Definitions

For the purposes of this International Standard, the relevant definitions given in ISO 472 apply, with the following addition:

3.1 elementary unit

Smallest normally commercially available entity of a given product.

4 Principle

The non-soluble material content (reinforcement fibre + filler) is obtained by the measurement of the difference in the mass of a test specimen before and after extraction by solvent under defined conditions.

The soluble part (resin) is extracted either in a Soxhlet apparatus (method A) or by immersion in a beaker (method B).

When the material under test contains fillers, the separation between fibres and fillers is obtained either by reacting the mineral filler with hydrochloric acid (method A) or by successive filtration without the use of acid (method B).

The masses before dissolution, after dissolution and after reaction with acid or filtration enable the reinforcement, resin and filler contents to be calculated.

5 Sampling

5.1 The test shall be carried out on two specimens which are as identical as possible. On prepreg fabrics, the specimens shall be taken at least 50 mm from the edge.

Two test specimens are sufficient providing that the difference between the values obtained is 5 % or less. If this is not the case, a third specimen shall be tested which is as identical to the other two as possible.

5.2 In order to obtain an evaluation result that is as representative as possible of the resin, reinforcement-fibre and mineral-filler content of the elementary unit examined, this test procedure may need to be repeated a certain number of times, at specific places in the elementary unit. The number and location of the tests required should be defined either in the product specification or by the person requesting the analysis. Alternatively, the number and location may be decided by prior experience.

5.3 For all tests which are not carried out on elementary units, take test specimens that are as representative of the material under test as circumstances allow.

6 Preparation of test specimens

Unless otherwise specified, it is recommended that the test specimens be cut in a shape which allows them to fit into the thimble of the Soxhlet apparatus or the beaker used for the extraction.

The mass should preferably be in the range 2 g to 20 g.

NOTE — For SMC, BMC and DMC tested by method B, a larger test specimen may be used if this is more representative of the material.

In the case of prepregs and moulding compounds which contain solvents or free monomer, care shall be taken to avoid loss of volatile matter. It is recommended that materials containing free monomer should not be left unprotected for more than 5 min before commencing the test procedure. For SMC, the protective release film shall not be remove from the laboratory sample or test specimen until just before commencing the test procedure. All prepreg and moulding-compound laboratory samples, including SMC, shall be sealed in a vapour-proof plastic bag immediately after the laboratory sample is taken.

7 Test methods — General

The method used to dissolve the resin depends on the accuracy of the result required by the person ordering the test. The procedures for separating the reinforcement fibre from the mineral filler are different in the two methods.

The method requires the masses of all specimens to be brought to a constant value by repetition of the drying and dissolution stages and by reweighing until the difference between two consecutive weighings is less than 1 mg. In those cases where known materials are being tested regularly, however, it is permitted to define, by experimentation, minimum times for dissolution and drying, to be certain that constant mass has been reached.

8 Method A: Extraction by Soxhlet

8.1 Reagents

The solvent used shall be capable of completely extracting all the resin from the test specimen.

Solvents suitable for the more common resins include:

dichloromethane;

acetone;

methyl ethyl ketone (butan-2-one);

denatured ethanol.

Other solvents may be used as necessary to achieve complete extraction.

8.2 Apparatus

Normal laboratory equipment, plus the following:

8.2.1 Balance, accurate to 0,5 mg and graduated to 0,1 mg.

8.2.2 Soxhlet extraction apparatus with a **thimble** large enough to contain the whole of the test specimen.

8.2.3 Cutting tool.

8.2.4 Desiccator, containing a suitable drying agent (e.g. silica gel).

8.2.5 Ventilated drying oven, set at 105 °C ± 3 °C.

8.3 Procedure

For each test specimen, proceed as follows:

8.3.1 Preparation of extraction thimble

Dry the extraction thimble in the oven (8.2.5) at 105 °C ± 3 °C for 1 h.

Cool to room temperature in the desiccator (8.2.4).

Weigh on the balance (8.2.1) to 1 mg. Continue to constant mass (see clause 7) and record the mass, in grams, as m_1.

8.3.2 Weighing the test specimen and solvent extraction of the resin

Using the cutting tool (8.2.3), cut the test specimen into pieces of a convenient size and place in the thimble (see 8.2.2), being careful that no fragments are lost. Weigh the whole to the nearest 1 mg. Record the mass, in grams, as m_2.

Place the thimble and its contents in the siphon of the extraction apparatus (8.2.2). Fit the condenser, siphon tube and flask together and add a suitable quantity of methyl ethyl ketone or other suitable solvent (see 8.1), or that specified in the material specification.

Regulate the heating rate of the mantel so that the siphoning rate is sufficient to achieve complete extraction of the resin in 1 h.

Carry out the test for this period or as given in the specification for the particular material.

Remove the thimble and contents. Dry in the oven and allow to cool in the desiccator. Weigh to the nearest 1 mg. Continue to constant mass (see clause 7) and record the mass, in grams, as m_3.

For materials containing no mineral fillers, the mass m_3 may be used to determine the reinforcement-fibre content.

For materials which contain mineral fillers, the reinforcement fibre and the mineral filler must first be separated, using the procedure given in 8.4.

8.4 Separation of reinforcement fibre from mineral filler

8.4.1 Reagents

8.4.1.1 Hydrochloric acid, concentration 35 % (V/V), commercial grade.

8.4.1.2 Denatured ethanol.

8.4.1.3 Chromic acid mixture, for cleaning. Recommended composition: 7 g of sodium dichromate in 100 ml of concentrated sulfuric acid.

8.4.2 Apparatus

The apparatus specified in 8.2, plus the following:

8.4.2.1 Glass rod.

8.4.2.2 Sintered-glass filter, diameter 40 mm, porosity P 160 (100 µm to 160 µm — see ISO 4793).

8.4.2.3 250 ml beaker.

8.4.2.4 Filter suction flask.

8.4.2.5 Tweezers.

8.4.3 Procedure

For each test specimen, proceed as follows:

8.4.3.1 Preparation of sintered-glass filter

Before the test, clean each filter (8.4.2.2) by soaking in chromic acid mixture (8.4.1.3). Then rinse with warm water followed by denatured alcohol (8.4.1.2). Place the filter on the filter suction flask (8.4.2.4) and apply suction. Place the filter in the oven at 105 °C ± 3 °C until constant mass is reached (see clause 7). Record the mass, in grams, as m_8.

8.4.3.2 Separation of the reinforcement fibre from the mineral filler when the mineral filler completely dissolves in hydrochloric acid

Place in the 250 ml beaker (8.4.2.3) 5 ml of hydrochloric acid per gram of residue remaining after dissolution of the resin.

Using the glass rod (8.4.2.1), slowly add the residue to the acid in the beaker. Stir carefully to ensure that all the residue has reacted with the acid, assuring that the bubbling caused by the acid reacting with the carbonate fillers does not cause splashing.

When the bubbling has finished, rinse the thimble with water, pouring the washings into the 250 ml beaker. Repeat, if necessary, until all the residue has been transferred to the beaker.

Add an additional 50 ml of water to the beaker.

Place the filter, which has been previously dried and weighed (mass m_8), on the suction flask and apply suction.

Slowly pour the supernatant acid in the beaker on to the filter.

Rinse the reinforcement fibre left in the beaker with water, pouring the washings on to the filter, then rinse with denatured ethanol while agitating with the glass rod. Pour this ethanol on to the filter. Repeat this operation four or five times until the fibre is thoroughly clean.

Transfer the fibre on to the filter using the glass rod and a jet of denatured ethanol.

Rinse twice with denatured ethanol.

Dry the filter to constant mass in the oven.

Cool in the desiccator and weigh. Record the mass, in grams, as m_9.

Alternatively, the procedure described in informative annex A may be used where the fibre length is $\geqslant$ 12 mm. The alternative procedure may also be used where a quick method is required. The procedure given in 8.4.3.2 shall, however, always be used as the reference method.

8.4.3.3 Separation of the reinforcement fibre from the mineral filler when the mineral filler does not completely dissolve in hydrochloric acid

When fillers insoluble in hydrochloric acid remain on the filter after the filtration carried out to determine the mass m_9, continue as follows:

Using tweezers (8.4.2.5), pick out all the fibres on the filter.

Reweigh the filter with the insoluble fillers on it.

Record this mass, in grams, as m_{10}.

NOTE — If the reinforcement-fibre filaments are very short, it may not be possible to separate them from the filler manually. In which case, the method given here will not give an accurate measure of the reinforcement-fibre and mineral-filler contents separately, although the combined filler and fibre content can be determined.

8.5 Method of calculation and expression of results

8.5.1 Calculation of the resin content

Calculate, for each test specimen, the resin content MR, expressed as a percentage of the original mass, from the equation:

$$\mathrm{MR} = \frac{m_2 - m_3}{m_2 - m_1} \times 100 \qquad \ldots (1)$$

where

m_1 is the initial mass, in grams, of the thimble;

m_2 is the initial mass, in grams, of the thimble plus test specimen;

m_3 is the final mass, in grams, after solvent extraction, of the thimble and residue.

NOTE — In equation (1), the volatile-matter content and all of the size coating on the reinforcement fibre is included in the resin content.

If the results of the two determinations differ by more than 5 %, carry out a supplementary determination on a third specimen from the same location in the elementary unit or laboratory sample (see clause 5).

8.5.2 Calculation of the reinforcement-fibre and mineral-filler contents

In the case when no mineral filler is present, calculate the reinforcement-fibre content MFT, expressed as a percentage of the original mass, from the equation:

$$\mathrm{MFT} = 100 - \frac{m_2 - m_3}{m_2 - m_1} \times 100 \qquad \ldots (2)$$

where

m_1, m_2 and m_3 are as defined in 8.5.1.

NOTE — If mineral filler is present but has not been separated from the fibre, then the total fibre and filler content is given by MFT.

When all the mineral filler has dissolved in the acid, calculate the reinforcement-fibre content MFR, expressed as a percentage of the original mass, from the equation:

$$\mathrm{MFR} = \frac{m_9 - m_8}{m_2 - m_1} \times 100 \qquad \ldots (3)$$

where

m_8 is the mass, in grams, of the dry filter;

m_9 is the mass, in grams, of the dry filter plus contents after reaction of the extraction residue with acid.

Calculate the mineral-filler content MFM, expressed as a percentage of the original mass, from the equation:

$$\mathrm{MFM} = \frac{m_3 - m_1}{m_2 - m_1} \times 100 - \frac{m_9 - m_8}{m_2 - m_1} \times 100 \qquad \ldots (4)$$

In the case when fillers insoluble in hydrochloric acid remain on the filter after the filtration, replace m_8 in equations (3) and (4) by m_{10}, where m_{10} is the mass, in grams, of the dry filter plus undissolved mineral filler.

If the results of the two determinations differ by more than 5 %, carry out a supplementary determination on a third specimen from the same location in the elementary unit or laboratory sample (see clause 5).

Express the result of the test as the average of the two (or more) individual determinations.

9 Method B: Extraction by immersion in solvent in a beaker

9.1 Reagents

The solvent used shall be capable of completely extracting all the resin from the test specimen.

Solvents suitable for the more common resins include:

dichloromethane;

acetone;

methyl ethyl ketone (butan-2-one);

denatured ethanol.

Other solvents may be used as necessary to achieve complete extraction.

9.2 Apparatus

Normal laboratory equipment, plus the following:

9.2.1 Balance, accurate to 0,5 mg and graduated to 0,1 mg.

9.2.2 Cutting tool.

9.2.3 Desiccator, containing a suitable drying agent (e.g. silica gel).

9.2.4 Ventilated drying oven, set at 105 °C ± 3 °C.

9.2.5 250 ml beaker.

9.2.6 500 ml beaker.

9.2.7 1000 ml filter suction flask.

9.2.8 Watchglass.

9.2.9 Glass rod.

9.2.10 Wire gauze, mesh size 80 µm to 100 µm.

9.2.11 Evaporating dish, diameter 80 mm.

9.2.12 2 litre beaker.

9.2.13 Sintered-glass filter, diameter 40 mm, porosity 4 (mesh size 5 µm to 15 µm).

9.2.14 Vacuum pump, fitted with a trap.

9.3 Procedure

For each test specimen, proceed as follows:

9.3.1 Weighing the test specimen and solvent extraction of the resin

Dry the 250 ml beaker (9.2.5) for 10 min in the oven (9.2.4) at 105 °C ± 3 °C.

Allow to cool to ambient temperature in the desiccator (9.2.3).

Weigh the 250 ml beaker on the balance (9.2.1) to the nearest 1 mg. Record the mass, in grams, as m_4.

Using the cutting tool (9.2.2), cut the test specimen into pieces of a convenient size and place in the 250 ml beaker, being careful that no fragments are lost. Weigh the whole to the nearest 1 mg. Record the mass, in grams, as m_5.

Transfer the specimen from the 250 ml beaker to the 500 ml beaker (9.2.6).

Rinse the 250 ml beaker with a small quantity of solvent to remove any traces of resin left by the specimen and pour the washings into the 500 ml beaker.

Pour enough solvent into the 500 ml beaker to cover the specimen completely. Cover the beaker with watchglass (9.2.8).

Leave the solvent in contact with the specimen at ambient temperature until dissolution of the resin is complete, stirring the mixture from time to time to help dissolution of the resin and fibre separation.

An ultrasonic bath may be used to improve resin dissolution and fibre separation.

9.3.2 Separation of reinforcement fibre from mineral filler

Separate the reinforcement fibre from the mineral filler as follows:

Place the wire gauze (9.2.10) over the 2 litre beaker (9.2.12). Pour the solvent into the beaker, allowing the reinforcement fibre to collect on the wire gauze.

Rinse the fibre several times with solvent (four times at least), being careful to avoid washing fibre through the wire gauze.

When the fibre is clean (when the solvent is clear), use a minimum of solvent to wash the fibre into the evaporation dish (9.2.11), which has been previously dried and weighed (mass m_6). Holding the wire gauze upside down over the evaporating dish, transfer any remaining fibre into the dish using a brush.

9.3.3 Determination of mass of fibre

Dry the evaporating dish and contents for 1 h in the oven at 105 °C ± 3 °C.

Allow to cool in the desiccator.

Weigh the evaporating dish and contents together to the nearest 1 mg. Continue to constant mass (see clause 7) and record the mass, in grams, as m_7.

9.3.4 Determination of mass of mineral filler

9.3.4.1 Preparation of sintered-glass filter

Before the test, clean each filter (9.2.13) by soaking in chromic acid mixture (8.4.1.3). Then rinse with warm water followed by denatured ethanol (8.4.1.2). Place the filter in the oven (9.2.7) and apply suction. Place the filter on a filter suction flask (9.2.7) and apply suction. Place the filter on a filter suction flask (9.2.7) and apply suction. Place the filter in the oven at 105 °C ± 3 °C until constant mass is reached (see clause 7). Record the mass, in grams, as m_8.

9.3.4.2 Separation of the mineral filler from the solvent

The 2 litre beaker contains the dissolved resin and the mineral filler (see 9.3.2).

Let this mixture settle until the solvent is clear.

Remove as much of the solvent as possible using the vacuum pump fitted with a trap (9.2.14). Care is needed to avoid losing any of the mineral filler.

Place the previously dried and weighed sintered-glass filter on to a suction filter flask.

Transfer the remaining contents of the 2 litre beaker on to the filter. Rinse the beaker several times with solvent to ensure that no mineral filler remains in the beaker, pouring the washings on to the filter.

Dry the filter and mineral filler in the oven for 1 h at 105 °C ± 3 °C.

Cool in the desiccator and weigh. Continue to constant mass (see clause 7) and record the mass, in grams, as m_9.

9.4 Method of calculation and expression of results

9.4.1 Calculation of the reinforcement-fibre content

Calculate, for each test specimen, the reinforcement-fibre content MFR, expressed as a percentage of the original mass, from the equation:

$$\mathrm{MFR} = \frac{m_7 - m_6}{m_5 - m_4} \times 100 \qquad \text{. . . (5)}$$

where

m_4 is the mass, in grams, of the dried 250 ml breaker;

m_5 is the mass, in grams, of the dried 250 ml breaker plus test specimen;

m_6 is the mass, in grams, of the dried evaporating dish;

m_7 is the mass, in grams, of the dried evaporating dish and contents.

If the results of the two determinations differ by more than 5 %, carry out a supplementary determination on a third specimen from the same location in the elementary unit or laboratory sample (see clause 5).

Express the result of the test as the average of the two (or more) individual determinations.

9.4.2 Calculation of the mineral-filler content

Calculate, for each test specimen, the mineral-filler content MFM, expressed as a percentage of the original mass, from the equation:

$$\text{MFM} = \frac{m_9 - m_8}{m_5 - m_4} \times 100 \qquad \text{. . . (6)}$$

where

m_8 is the mass, in grams, of the dry filter;

m_9 is the mass, in grams, of the dry filter and contents.

If the results of the two determinations differ by more than 5 %, carry out a supplementary determination on a third specimen from the same location in the elementary unit or laboratory sample (see clause 5).

Express the result of the test as the average of the two (or more) individual determinations.

9.4.3 Calculation of the resin content

Calculate, for each test specimen, the resin content MR, expressed as a percentage of the original mass, from the equation:

$$\text{MR} = 100 - (\text{MFR} + \text{MFM}) \qquad \text{. . . (7)}$$

where MFR and MFM are as defined in 9.4.1 and 9.4.2.

If the results of the two determinations differ by more than 5 %, carry out a supplementary determination on a third specimen from the same location in the elementary unit or laboratory sample (see clause 5).

Express the result of the test as the average of the two (or more) individual determinations.

10 Precision

The precision of this test method is not known because inter-laboratory data are not available. When data have been obtained from inter-laboratory trials, a precision statement will be added at the following revision.

11 Test report

The test report shall include the following information:

a) a reference to this International Standard and the method used (A or B);

b) all details necessary for complete identification of the material tested;

c) the sampling method used;

d) the number of specimens tested;