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Plastics — Polyamides — Determination of viscosity number

Plastiques — Polyamides — Détermination de l'indice de viscosité

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

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.

ISO 307 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*.

This fifth edition cancels and replaces the fourth edition (ISO 307:2003), which has been technically revised.

Introduction

This International Standard specifies a method for the determination of the viscosity number of dilute solutions of polyamides in certain specified solvents. The determination of the viscosity number of a polyamide provides a value that depends on the molecular mass of the polymer, but does not strictly correlate with the molecular mass.

Additives such as flame-retardants and modifiers often interfere with the viscosity measurement and may have an increasing effect on the viscosity number in one solvent and a decreasing effect in another solvent. The extent of the effect depends among others on the additive, the quantity of the additive, the presence of other additives and reactions.

The viscosity number of a polyamide sample containing additives that interfere with the viscosity measurement, measured in a specific solvent, represents a specific viscosity number for the polyamide under investigation and the actual measurement conditions. The measured viscosity number cannot, in principle, be converted from one solvent to another and is only suitable for intra-product comparison.

The viscosity number of pure polyamides or polyamides containing additives that do not interfere with the viscosity measurement can be converted from one solvent to another by a general relationship for that type of polyamide.

Polyamide test samples for the determination of the viscosity number must be completely soluble in the solvents mentioned. Additives contained in them, like glass and carbon fibres, must be separated from the solution.

As it is not possible to distinguish between extractables such as caprolactam, its oligomers and other extractable additives, these are considered as an essential part of the sample and therefore included in the sample mass.

The test method is applicable for production control and intra-product comparison even if the polyamide contains additives that do interfere with the viscosity measurement. However, it should be realised that deviations of the viscosity number can be caused by either the polyamide itself, effects caused by the additives present, or a combination of these.

The interference of additives with the viscosity determination can be checked by comparing the viscosity results of dry blend mixtures and regular production samples at several concentrations of the additive under investigation and in the solvents concerned. It should be noted that the other additives present also could influence the viscosity result.

The repeatability and reproducibility of the test method are strongly influenced by the correctness of the solvent concentration, the use of the Hagenbach correction if applicable and the temperature of the solvent on diluting the sample solution.

In this International Standard two specific viscometers are recommended. Furthermore, other types of viscometers listed in ISO 3105 may also be used, provided that the results are demonstrated to be equivalent to those measured with the recommended viscometers. It is to be expected that in the next revision the use of the other types of viscometers will be excluded.

Plastics — Polyamides — Determination of viscosity number

1 Scope

This International Standard specifies a method for the determination of the viscosity number of dilute solutions of polyamides in certain specified solvents.

Polyamide samples must be completely soluble in the solvents mentioned. Additives such as flame-retardants and modifiers often interfere with the viscosity measurement, having an increasing effect on the viscosity number in formic acid and a decreasing effect on the viscosity number in sulfuric acid. The extent of the effect for polyamide compounds depends on the additive, the quantity of the additive, the presence of other additives and the compounding conditions.

For pure polyamides or polyamides containing additives that do not interfere with the viscosity measurement, the determination of the viscosity number of a polyamide provides a measure of the molecular mass of the polymer. The viscosity number of pure polyamides or polyamides which contain additives that do not interfere with the viscosity measurement can be converted from one solvent to another.

The viscosity number of polyamides containing additives that do interfere with the viscosity measurement is specific to the solvent used and the material composition. In this case, the measured viscosity number cannot be converted from one solvent to another.

The method is applicable to the polyamides designated PA 46, PA 6, PA 66, PA 69, PA 610, PA 612, PA 11, PA 12, PA 6T/66, PA 6I/6T, PA 6T/6I/66, PA 6T/6I, PA 6I/6T/66 and PA MXD6 as defined in ISO 1874-1, as well as to copolyamides, compounds of polyamides and other polyamides that are soluble in one of the specified solvents under the specified conditions.

The method is not applicable to polyamides produced by anionic polymerization of lactams or produced with cross-linking agents; such polyamides are normally insoluble in the specified solvents.

The viscosity number is determined by the general procedure specified in ISO 1628-1, observing the particular conditions specified in this International Standard.

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 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 1628-1, *Plastics — Determination of the viscosity of polymers in dilute solution using capillary viscometers — Part 1: General principles*

ISO 1874-1, *Plastics — Polyamide (PA) moulding and extrusion materials — Part 1: Designation*

ISO 3105, *Glass capillary kinematic viscometers — Specifications and operating instructions*

ISO 3451-4, *Plastics — Determination of ash — Part 4: Polyamides*

ISO 15512, *Plastics — Determination of water content*

ASTM D789, *Standard test methods for determination of relative viscosity of polyamide (PA)*

JIS K 6920-2:2000, *Plastics — Polyamide (PA) moulding and extrusion materials — Part 2: Preparation of test specimens and determination of properties*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1628-1 and the following apply.

3.1
viscosity number of a polymer
number calculated by the following formula for the viscometers mentioned in this International Standard and flow times long enough so that no kinetic energy correction need be applied:

$$\mathrm{VN} = \left(\frac{\eta}{\eta_0} - 1 \right) \times \frac{1}{c} \tag{1}$$

where

η is the viscosity of a solution of the polymer in a specified solvent, in Pascal seconds or $N/m^2 \cdot s$;

η_0 is the viscosity of the solvent, expressed in the same units as η;

$\frac{\eta}{\eta_0}$ is the relative viscosity of a solution of the polymer in a specified solvent;

c is the concentration, in grams per millilitre, of the polymer in the solution;

VN is the viscosity number, expressed in millilitres per gram.

NOTE 1 For a particular viscometer used and with substantially equal densities of the solvent and solution, the viscosity ratio is given by the flow time ratio for the solution concentration:

$$\frac{\eta}{\eta_0} \tag{2}$$

where

$\frac{\eta}{\eta_0}$ is the relative viscosity of a solution of the polymer in a specified solvent.

NOTE 2 As mentioned in ISO 3105, in case of flow times below 200 s and 60 s, for type 1 and type 2 Ubbelohde viscometers respectively, a correction for kinetic correction has to be applied: the so-called Hagenbach correction. For other types of viscometers, the kinetic energy correction has to be applied if the correction is $\geqslant$ 0,15 %.

NOTE 3 The flow time of a liquid is related to its viscosity by the formula

$$v = \frac{\eta}{\rho} = C \times t - \left(\frac{A}{t^2} \right) \tag{3}$$

where

v is the viscosity/density ratio, in metres squared per second;

ρ is the density of the liquid, in kilograms per cubic metre;

C is the constant of the viscometer, in metres squared per second squared;

t is the flow time, in seconds;

A is the parameter of the kinetic correction in metres squared seconds.

NOTE 3 For a particular viscometer used, with substantially equal densities of the solvent and solution and a given kinetic factor, the viscosity ratio

$$\frac{\eta}{\eta_0} \tag{4}$$

is given by the flow time ratio for the solution concentration in this International Standard, each flow time reduced with the so-called Hagenbach correction (in seconds) given by the manufacturer for the viscometer as a function of the flow time.

4 Principle

The times of flow of a solvent and a solution of the polyamide at a concentration of 0,005 g/ml in the solvent are measured at 25 °C, the same viscometer being used for both measurements. The viscosity number is calculated from these measurements and from the known concentration of the solution.

5 Reagents and materials

5.1 Solvents and reagents

Only reagents of recognised analytical grade and only distilled water or water of equivalent purity shall be used.

WARNING — Some chemicals, for example 1,1,2,2-tetrachloroethane, are prohibited in some countries. The user shall check on the national regulations before applying the chemicals mentioned in this standard.

Avoid contact with the skin and inhalation of any vapours of the solvents and cleaning liquids.

5.1.1 Sulfuric acid, 96,00 % ± 0,20 % (by mass) solution.

For the determination of the concentration of commercial sulfuric acid (95 % to 98 %) and adjustment to 96,00 %, see Annexes A and B.

5.1.2 Formic acid, 90,00 % ± 0,15 % (by mass) solution.

The solvent shall be stored in a brown glass bottle. Its concentration shall be checked at least every 2 weeks. It shall not contain more than 0,2 % acetic acid or methyl formate.

For the determination of the concentration of commercial formic acid (90 %) and adjustment to 90,00 % ± 0,15 %, see Annexes C and D.

5.1.3 *m*-Cresol, meeting the following specifications:

— appearance: clear and colourless

— *m*-cresol content: 99 % (by mass) min.

— *o*-cresol content: 0,3 % (by mass) max.

— water content: 0,13 % (by mass) max.

m-Cresol of the required purity can be obtained by distillation of chemically pure *m*-cresol, preferably in vacuum.

To avoid oxidation, nitrogen shall be used for pressure compensation. Its purity may be checked by gas chromatography. The solvent shall be stored in a brown glass bottle.

5.1.4 Phenol, 99 % (by mass) min.

5.1.5 1,1,2,2-tetrachloroethane, 99,5 % (by mass) min.

5.1.6 Phenol/1,1,2,2-tetrachloroethane.

Weigh out 6 parts by mass of phenol (5.1.4) and dissolve in 4 parts by mass of 1,1,2,2-tetrachloroethane (5.1.5). Work to an accuracy of 1 % or better in the weighings. Stir the mixture in its original container at 23 °C to prevent crystallization.

5.1.7 Orthophosphoric acid, 85 % (by mass), density 1,71 g/l.

5.1.8 *m*-Cresol/phosphoric acid.

Transfer 50 ml of *m*-Cresol (5.1.3) into a weighing flask (6.4) and add with a glass pipette (6.5) 0,14 ml of orthophosphoric acid (5.1.7). Close the flask and stir with a magnetic stirrer for 30 min at 100 °C. Add the solution to approximately 800 ml of *m*-cresol in a volumetric flask while continuously stirring. Rinse the weighing flask several times with *m*-cresol and add this to the *m*-cresol solution. Remove the magnetic stirrer and dilute to the mark. Stir the solution for 30 min.

5.2 Cleaning liquids

5.2.1 Chromic acid solution, prepared by mixing equal volumes of sulfuric acid (96 %, ρ_0 = 1,84 g/ml, industrial quality) and a saturated solution of potassium dichromate (99,5 %, industrial quality). If required, the chromic acid solution may be replaced by other equally effective cleaning liquids.

5.2.2 Acetone (99,5 %, industrial quality), or any water-soluble low-boiling-point solvent (industrial quality).

6 Apparatus

6.1 Vacuum drying cabinet, with pressure less than 100 kPa.

6.2 Balance, accurate to 0,1 mg.

6.3 Volumetric flask, of capacity 50 ml or 100 ml, complying with the requirements of ISO 1042, fitted with a ground-glass stopper.

6.4 Weighing flask, 100 ml, fitted with a ground-glass stopper.

6.5 Pipette, 0,2 ml, readable to 0,01 ml.

6.6 Shaking apparatus or magnetic stirrer.

6.7 Sintered-glass filter, with a pore size between 40 µm and 100 µm (grade P 100), or stainless-steel sieve, with apertures of about 0,075 mm^2.

6.8 Viscometer, of the suspended-level Ubbelohde type, complying with the requirements of ISO 3105. The essential dimensions of the viscometer are shown in Figure 1. For use with the formic acid solution (5.1.2), the inside diameter of the capillary shall be 0,58 mm ± 2 % (complying with the requirements of size No. 1 of ISO 3105). For use with the sulfuric acid solution (5.1.1) or *m*-cresol (5.1.3), the inside diameter of the capillary shall be 1,03 mm ± 2 % (complying with the requirements of size No. 2 of ISO 3105).

Other types of viscometer listed in ISO 3105 may be used, provided that the results are demonstrated to be equivalent to those of the Ubbelohde viscometers specified above. In cases of dispute, the recommended viscometer shall be used.

ISO 1628-1 shall be followed on selecting other type(s) of viscometer.

NOTE In this International Standard, the No. 1 and No. 2 Ubbelohde viscometers according to ISO 3105 are recommended. It is to be expected that at the next 5 year revision only these two viscometers will be allowed.

6.9 Thermometer, a liquid-in-glass, "total immersion" thermometer, reading to 0,05 °C in the range to be used and in a known state of calibration, is suitable. Other thermometric devices of at least equal precision may be used.

6.10 Thermostatic bath, capable of being maintained and controlled at 25,00 °C ± 0,05 °C.

6.11 Time device, for example a stop-watch, accurate to 0,1 s.

6.12 Centrifuge.

7 Preparation of test samples

7.1 General

Polyamide test samples for the determination of the viscosity number shall be soluble in the solvents mentioned, except for additives present, such as reinforcement-fillers.

NOTE The dissolution time of some samples may be too long for adequate production control. In these cases the material may be ground in order to shorten the dissolution time, provided that the results are demonstrated to be equivalent.

7.2 Samples containing less than 98 % (by mass) polyamide

For samples containing more than 2 % additives, the amount of additives shall be either determined by a specifically developed method or taken from the recipe. The method of determination will be mentioned in the report.

The water content of the sample shall be determined according to ISO 15512. The ash content shall be determined according to ISO 3451-4.

The correct amount of polyamide sample to be weighed out is calculated using the equation in Clause 8.

Some additives, e.g. antimony trioxide and zinc sulfide, are completely volatilized during the calcination according ISO 3451-4. Materials reinforced with glass fibre contain flame-retardant antimony trioxide and/or other volatilizable additives. If the total content of additives is more than 2 %, these shall be brought into account by the formulation of the sample for calculating the exact test portion.

NOTE For production quality control purposes, the laboratory response time for determination of the additives may be too long for adequate production control. In these cases the additive(s) content in the production recipe can be used for calculating the amount of sample, if the total variation of the polymer content is less than 4 % (by mass), e.g. 65 % PA would range from 63 % to 67 %.

8 Calculation of test portion

Calculate the mass m_c, in milligrams, of the test portion according to Equation (5):

$$m_c = \frac{250}{1 - \frac{w_1 + w_2 + w_3}{100}} \quad (5)$$

where

w_1 is the water content of the sample, expressed as a percentage by mass, determined in accordance with ISO 15512;

w_2 is the content of inorganic materials (for example fillers or glass fibres) in the sample, expressed as a percentage by mass, determined in accordance with ISO 3451-4;

w_3 is the content of other materials (for example other polymers, such as polyolefins, or additives, such as flame-retardants), expressed as a percentage by mass, determined by appropriate methods.

For the content of the additive(s) which cannot be determined, the content according to the product recipe shall be used.

9 Selection of solvent

The value of the viscosity number of a polyamide depends on the solvent used.

The solvent or solvents to be used for a particular polyamide are specified below.

a) For PA 6, PA 46, PA 66, PA 69, PA 610, PA MXD6 and corresponding copolyamides, formic acid solution or sulfuric acid shall be used as solvent. For polyamides containing additives that liberate gases in acidic solvents, *m*-cresol shall be used as the solvent. In cases of dispute, formic acid shall be used as a solvent.

b) For PA 612, the sulfuric acid solution or *m*-cresol shall be used as solvent. In cases of dispute, *m*-cresol shall be used.

c) For PA 11, PA 12, PA 11/12 copolymers, *m*-cresol shall be used as a solvent. In cases of dispute about ammonium carboxylate influencing viscosity through the formation of end-group associations, additional measurements shall be made using *m*-cresol/phosphoric acid solution as a solvent (5.1.8).

d) For PA 6T/66, PA 6I/66, PA 6I/6T, PA 6T/6I/66, PA 6T/6I, PA 6I/6T/66, *m*-cresol or phenol/1,1,2,2-tetrachloroethane shall be used as solvent. In cases of dispute, *m*-cresol shall be used.

e) For other polyamides, any of the mentioned solvents may be used.

NOTE 1 In the future revision of this International Standard, it is the intention that for a given PA only one solvent will be allowed.

NOTE 2 Viscosity numbers of polyamides not containing additives that interfere with the viscosity measurement can be converted from one solvent to another by a general interconversion formula. Graphs for interconversion are mentioned in Clause 13 and presented in Annex E. The reliability of the conversions is discussed in Annex E.

10 Procedure

10.1 Cleaning of the viscometer

Clean the viscometer (6.8) prior to the first use, again after discordant readings (for example, when two successive determinations of the efflux time of the solvent differ by more than 0,4 s) and, further, at intervals during regular use. For this purpose allow it to stand for at least 12 h filled with a cleaning agent (5.2), for example chromic acid solution (5.2.1). Remove the cleaning agent, rinse the viscometer with water then with acetone (5.2.2) and dry, for example by a slow stream of filtered air or in the vacuum drying cabinet (6.1).

After each determination, drain the viscometer, rinse with the solvent, then with water, followed by, for example, acetone (5.2.2) and dry as described above.

However, if the next solution to be measured is of a polyamide of the same type and of a similar viscosity, it is permissible to drain the viscometer, wash it with the solution to be measured, and then fill it with this solution.

NOTE In the case of, for example, production control and automated flow time measurement the viscometer may be filled with the solvent in anticipation of the next sample.

10.2 Preparation of test solution

10.2.1 General

Three different methods for preparing the test solution are described in this International Standard. The first volumetric method (10.2.2), without correction for the volume of insoluble additives in the test portion, is equal to the method described in the previous version (ISO 307:2003). For practical reasons, test portion masses of ($m_c \pm 5$) mg are allowed. For pure polyamide, this results in a concentration range of 0,004 9 g/ml to 0,005 1 g/ml. The actual polymer concentration is taken into account in the calculation of the viscosity number. For samples containing insoluble additives, a test portion of exactly the calculated mass will give a solution that is almost equal to 0,005 g/ml.

The second volumetric method (10.2.3) and the gravimetric method (10.2.4) take into account the insoluble additives and the polyamide volume. The latter two methods are often used in combination with (semi-)automatic viscosity measurement equipment.

NOTE For polyamide samples containing only insoluble additives, the concentration of the solution prepared according to the volumetric or gravimetric method will be exactly 5 mg/ml.

10.2.2 Volumetric method

Weigh, to the nearest 0,2 mg, a test portion of ($m_c \pm 5$) mg, where m_c is the mass calculated in accordance with Clause 8, working rapidly to minimize moisture pick-up by the polymer. If the weighing takes more than 2 min, reject the material and begin another weighing.

Transfer the test portion to the 50 ml volumetric flask (6.3) and add about 40 ml of the solvent (see Clause 9). Close the flask and shake the contents, or stir with the magnetic stirrer (6.6), until the polymer has dissolved. This may take from approximately half an hour to several hours, depending on the type of polyamide and the particle size of the test portion. When sulfuric acid or formic acid solution is used as the solvent, the temperature shall not exceed 30 °C. When *m*-cresol or phenol/1,1,2,2-tetrachloroethane is used as the solvent, the temperature may be raised to 95 °C to 100 °C. If, in the latter case, dissolution takes more than 2 h, this shall be reported. For PA 6T/66, suitable conditions have been found to be 2 h at 90 °C.

When dissolution is complete, cool the solution to 25 °C ± 2 °C, dilute to the mark with the solvent and mix well. If the magnetic stirrer (6.6) is used, remove it from the solution before dilution and rinse it with the solvent, adding the rinsings to the flask before further dilution