INTERNATIONAL STANDARD

ISO
24076

Plastics — Polypropylene (PP) — Determination of isotactic index by low-resolution nuclear magnetic resonance spectrometry

Plastiques — Polypropylène (PP) — Détermination de l'indice isotactique par spectrométrie de résonance magnétique nucléaire à basse résolution

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 24076:2021
https://standards.iteh.ai/catalog/standards/sist/1af3c2e8-b5ba-40f8-8358-
8f0bceb22689/iso-24076-2021

COPYRIGHT PROTECTED DOCUMENT

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 (see 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 (see 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.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic 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 LR-NMR method in this document is a relative method established with ISO 9113 as the absolute method. The method and concept of isotactic index of polypropylene are specified in ISO 9113, that is, the polypropylene sample is separated into the extractable and the unextractable matter by n-heptane extraction, and the percentage of unextractable matter in the sample is calculated as isotactic index.

Isotactic index in ISO 9113 sounds similar to tacticity (isotacticity or stereotacticity) of polymer chain, but the concept and result are different. The result is related to but not equal to the tacticity (isotacticity or stereotacticity) of molecular chain, which can be determined by high resolution carbon-13 nuclear magnetic resonance and infrared method. The result of ISO 9113 is also related to crystallization, molecular weight, chain entanglement of the sample, solvent solubility and other effects.

For solid polymers, extraction always takes a long time for the diffusion of long molecular chain from polymer to solvent. To improve test efficiency, relative methods are developed. This document provides a relative non-destructive method for the determination of isotactic index by low-resolution nuclear magnetic resonance spectrometry through a calibration curve establishing with magnetic signal and isotactic index determined by ISO 9113. No solvent is used, and the determination efficiency is improved during samples measurement procedure except for the calibration part.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Plastics — Polypropylene (PP) — Determination of isotactic index by low-resolution nuclear magnetic resonance spectrometry

1 Scope

This document specifies a relative method for the determination of polypropylene (PP) isotactic index by low-resolution pulsed nuclear magnetic resonance spectroscopy (LR-NMR).

This method enables the identification and coding of types H propylene (PP-H) plastics according to ISO 19069-1.

This method is suitable for base polymers and is not applicable for mixtures.

NOTE   The direct method for the determination of polypropylene isotactic index is specified in ISO 9113.

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 9113, *Plastics — Polypropylene (PP) and propylene-copolymer thermoplastics — Determination of isotactic index*

3 Terms and definitions

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

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

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

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

3.1
isotactic index
II
percentage mass fraction of unextractable matter content in polypropylene, which cannot be extracted from polypropylene by boiling n-heptane

4 Principle

The sample is placed in LR-NMR. After electromagnetic equilibration in the static magnetic field of the NMR spectrometer and application of a 90° radio frequency pulse, the magnetization decay signal curve from the protons of the sample is recorded. The signal of the un-extractable matter in the sample drops much faster than that of extractable matter. In the signal curve, initial signal corresponds to the whole sample including the un-extractable and the extractable matter, and later slower dropping signal corresponds to the extractable matter in the sample. So, the magnetization decay signal and the isotactic index of the sample are related.

The isotactic index is either calculated from the ratio between the magnetization decay signal of the un-extractable part and the entire sample detected by a ratio probe (method A ratio method), or from

the ratio between the magnetization decay signal of the extractable part and the mass of the sample-detected by an absolute probe (method B absolute method), using an appropriate calibration. The calibration curve is constructed using the magnetization decay signal and isotactic index determined by n-Heptane extraction method specified in ISO 9113.

5 Apparatus

Usual laboratory apparatus and glassware and, in particular, the following.

5.1   LR-NMR, of frequency 18 MHz to 25 MHz, typical of 20 MHz and 23 MHz; a probe of 10 mm diameter for method A, or a probe of 26 mm diameter for method B; temperature of probe and magnet field being 40 °C ± 0,1 °C.

NOTE   The probe of other diameter can also be used according to instrument parameters.

5.2   Sample tube, of glass with outer diameter 10 mm ± 0,25 mm, wall thickness 0,9 mm ± 0,25 mm, and length at least 150 mm, for method A; of glass with outer diameter 26 mm ± 0,25 mm, wall thickness 1,3 mm ± 0,25 mm, and length at least 200 mm, for method B.

NOTE   The sample tube of other size can also be used according to probe parameters.

5.3   Oven, shall be capable of being maintained at the temperature of 140 °C ± 2 °C, provided with vacuum lines of 25 kPa or less.

5.4   Thermostatic apparatus, shall be capable of being maintained at the temperature of 40 °C ± 0,1 °C.

5.5   Balance, shall be accurate to the nearest 0,000 1 g, only for method B.

6 Preparation of sample

6.1 General

The test sample and the reference sample can be in the form of powder or pellets. Place at least 10 g of the sample in a glass container, and put it in the oven (5.3) for 2 h at 140 °C ± 2 °C under 25 kPa nitrogen vacuum or less for complete drying and annealing, then cool in a desiccator to room temperature.

6.2 Reference samples

At least five reference samples with different isotactic index shall be used. The isotactic index of reference samples shall cover the general range, and its distribution shall be homogeneous as far as possible.

NOTE   The isotactic index of reference samples can be 94 % to 99 %. The reference samples can be collected by the user or offered by spectrometer manufacturer.

7 Method A — Ratio method

7.1 Procedure

7.1.1 Measurement of reference samples by n-heptane extraction

The isotactic index of reference samples shall be measured by extraction method specified in ISO 9113.

7.1.2 LR-NMR measurement procedure of reference samples

7.1.2.1 Put the reference sample into a sample tube (5.2), with a depth of between 30 mm and 50 mm.

NOTE The sample amount can be specified by the spectrometer manufacturer which matches to the probe height.

7.1.2.2 Put the tube in thermostatic apparatus (5.4) for a minimum of 30 min to achieve temperature equilibration.

7.1.2.3 Transfer the tube to LR-NMR probe (5.1) within 15 s. Hold for 15 min to achieve temperature equilibration.

NOTE Experience shows that it is easy to transfer a tube from thermostatic apparatus to LR-NMR probe within 15 s.

7.1.2.4 Measure the magnetization decay signal. The typical signal range corresponding to the sample is 7 μs to 9 μs, and that of extractable matter is 50 μs to 90 μs.

NOTE For exact magnetization decay signal time, refer to the spectrometer manufacturer's instructions.

7.1.3 LR-NMR measurement procedure of test samples

Shall be the same as that of reference samples (see 7.1.2) except that the reference sample is replaced by the test sample.

7.2 Calculation

7.2.1 Calibration curve

Prepare calibration curve by plotting II' obtained from extraction method against LR-NMR signal. An example of a calibration curve for method A is shown in Annex A.

The Formula (1) is obtained by linear regression method according to the calibration curve.

$$II' = a \times \frac{N'_{1a} - N'_{2a}}{N'_{1a}} + b \tag{1}$$

where

II' is the isotactic index of the reference sample determined by n-heptane extraction specified in ISO 9113, expressed in percent (%);

N'_{1a} is the average magnetization decay signal of the reference sample measured by method A;

N'_{2a} is the average magnetization decay signal of the extractable matter in the reference sample measured by method A;

a is the slope of the calibration curve;

b   is the intercept of the calibration curve.

7.2.2 Calculation of isotactic index II_{na}

Isotactic index II_{na} is given by the Formula (2).

$$II_{na} = a \times \frac{N_{1a} - N_{2a}}{N_{1a}} + b \qquad (2)$$

where

II_{na} is the isotactic index of the test sample determined by method A, expressed in percent (%);

N_{1a} is the average magnetization decay signal of the test sample;

N_{2a} is the average magnetization decay signal of the extractable matter in the test sample;

a is the slope of the calibration curve;

b is the intercept of the calibration curve.

8 Method B — Absolute method

8.1 Procedure

8.1.1 Measurement of reference samples by n-heptane extraction

See 7.1.1.

8.1.2 LR-NMR measurement procedure of reference samples

8.1.2.1 Weigh approximately 5 g of the reference sample, to the nearest 1 mg, put them into a sample tube (5.2) within the height of LR-NMR probe.

NOTE   The sample amount can be specified by the spectrometer manufacturer which matches to the probe height.

8.1.2.2 See 7.1.2.2.

8.1.2.3 See 7.1.2.3.

8.1.2.4 Measure the magnetization decay signal. The typical signal range corresponding to extractable matter is 100 μs to 120 μs

NOTE   For exact magnetization decay signal time, refer to spectrometer manufacturer's instructions.

8.1.3 LR-NMR measurement procedure of test samples

Shall be the same as that of reference samples (see 8.1.2) except that the reference sample is replaced by the test sample.

8.2 Calculation

8.2.1 Calibration curve

Prepare calibration curve by plotting II' obtained from extraction method against LR-NMR signal. An example of a calibration curve for method B is shown in Annex B.