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Standard Guide for
Measurement of Polyolefin Properties Using TD-NMR Relaxometry[1]

This standard is issued under the fixed designation D8539; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide is intended to provide suggested approaches and criteria for the determination of polyolefin properties via time-domain Nuclear Magnetic Resonance (TD-NMR) Relaxometry. Though any crystallinity or morphology related property can be determined using this method (**1**), (**2**)[2], the focus of this guide is on the prediction of Xylene Solubles content for polypropylene and density (**3**) for polyethylene as these are the most commonly specified properties for polyolefin manufacturers. Please note that other properties such as flexural modulus, Izod, Charpy, intrinsic viscosity, decalin/hexane solubles and others can be determined as well.

1.2 *High-Level Purpose*—The purpose of this guide includes:

(1) educating new users on the use of TD-NMR Relaxometry to determine properties of polyolefins in manufacturing plants and laboratories;

(2) providing a standard terminology that can be used by different vendors and end users;

(3) establishing minimum requirements for apparatus, data acquisition, analysis, calibration and validation;

(4) providing guidance for the specification, evaluation, cost justification, implementation, project management, training, and documentation of TD-NMR Relaxometers; and

(5) providing a functional requirements checklist for TD-NMR Relaxometers for use in polyolefin plants and laboratories that can be integrated with existing systems.

1.3 *Audience*—This guide has been created with the needs of the following stakeholders in mind:

(1) end users of TD-NMR Relaxometers for use in polyolefin plants and laboratories,

(2) implementers of TD-NMR Relaxometers for use in polyolefin plants and laboratories,

(3) quality personnel,

(4) information technology personnel,

(5) vendors of TD-NMR Relaxometers for use in polyolefin plants and laboratories,

(6) individuals who approve funding of TD-NMR Relaxometers for use in polyolefin plants and laboratories,

(7) applications support specialists for TD-NMR Relaxometers used in polyolefin plants and laboratories, and

(8) software test/validation specialists.

1.4 Information contained in this guide will benefit a broad audience of people who interact with a TD-NMR Relaxometer used in polyolefin plants and laboratories. New users can use this guide to understand the purpose and functions of TD-NMR Relaxometers for use in polyolefin plants and laboratories as well as the interactions between these tools with external systems. The guide might also help prospective users in understanding terminology, configurations, features, design, benefits, and costs of these analyzers. Individuals who are purchasing TD-NMR Relaxometers for use in polyolefin plants and laboratories may also use this guide to identify functions that are recommended for specific laboratory environments. Research and development staff of different commercial laboratory informatics system vendors may use the guide as a tool to evaluate, identify, and potentially improve the capabilities of their products. The vendors' sales staff may use the guide to represent functions of their laboratory informatics products to prospective customers in more generic and product-neutral terms.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—There is no known ISO equivalent to this standard guide.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.

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[2] The boldface numbers in parentheses refer to a list of references at the end of this standard.

2. Referenced Documents

2.1 *Xylene Soluble Content:*[3]

D5492 Test Method for Determination of Xylene Solubles in Propylene Plastics

2.2 *Density:*[3]

D792 Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement

D1505 Test Method for Density of Plastics by the Density-Gradient Technique

2.3 *Others:*[3]

D4808 Test Methods for Hydrogen Content of Light Distillates, Middle Distillates, Gas Oils, and Residua by Low-Resolution Nuclear Magnetic Resonance Spectroscopy

D5227 Test Method for Measurement of Hexane Extractable Content of Polyolefins

D7171 Test Method for Hydrogen Content of Middle Distillate Petroleum Products by Low-Resolution Pulsed Nuclear Magnetic Resonance Spectroscopy

2.4 *Xylene Solubles Content:*[4]

ISO 16152 Plastics—Determination of Xylene Soluble matter in polypropylene

ISO 6427 Plastics—Determination of Matter Extracted by Organic Solvents (Conventional Methods) Annex B Standard Method of Test for Determination of Polypropylene Solubility in Cold Xylene

2.5 *Density:*[4]

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

ISO 1183-2 Plastics—Methods for determining the density of non-cellular plastics—Part 2: Density gradient column method

2.6 *Others:*[4]

ISO 24076 Plastics—Polypropylene—Determination of isotactic index by low-resolution nuclear magnetic resonance spectrometry

3. Terminology

3.1 *Definitions:*

3.1.1 *calibration*—a series of mathematical operations which translates the raw FID response into a meaningful measurement. These processes include, but are not limited to: signal pre-processing, parameter extraction, and regression versus reference results.

3.1.2 *parameter extraction*—any operation that is used to generate x-inputs for the regression analysis. These processes include: curve fitting, integration, deconvolution, etc.

3.1.3 *pulse sequence*—a series of radio-frequency (RF) pulses (B_1) used to elicit a response from a sample in an NMR experiment. A pulse sequence is often defined in a file or a parameter set on the NMR instrument.

3.1.4 *reference result*—the measurement of a physical or chemical property by a primary technique (such as ASTM D5492 in the case of Xylene Solubles content) that is used as a reference input for the calibration generation.

3.1.5 *regression*—the application of a univariate or multivariate regression technique, which establishes a mathematical relationship between extracted parameters and the reference results. Once this relationship is established, the NMR instrument can be used to predict/measure properties of interest.

3.1.6 *signal processing*—any operation directly applied to the raw NMR signal such as: magnitude correction, Inverse Laplace transformation, amplitude normalization, etc.

4. Summary of Guide

4.1 The samples to be analyzed are typically polyolefin powders or pellets, that is, polyethylenes (HDPE, LLDPE or LDPE) or polypropylenes (homopolymers or co-polymers). They are introduced into the NMR Relaxometer with minimal sample preparation or none at all, and analyzed at an instrument-specific temperature. Sample conditioning as described in 8.3 is required and has to be always consistent, representative and repeatable.

4.2 NMR acquisition yields a signal known as Free Induction Decay (FID) which represents intensity versus time. In TD-NMR Relaxometry this time-domain signal is not Fourier transformed as the analysis is performed on the FID itself. The analysis itself is automated and yields a measure of crystallinity **(4)**, **(5)**. For the measurement of crystallinity, no calibration is needed as NMR is a primary method for analysis of this property. Since polyolefin manufacturers require properties to be measured that are relevant for process control **(6)** and quality control **(7)**, typically a calibration is needed to measure tacticity, for example, via Xylene Solubles content (polypropylene) or density (polyethylene); **(3)**. Typically, most or all steps of the measurements are automated and computer controlled.

5. Significance and Use

5.1 This guide is intended to assist users how to determine polymer properties in polyolefins related to their morphology **(2)** using TD-NMR Relaxometry, for example, Xylene Solubles (XS) content in polypropylene (PP).

5.2 The advantage of using TD-NMR Relaxometry lies in the fact that the method is rapid, non-destructive, cost effective, safe for the operator, environmentally friendly, and less dependent on operator consistency than traditional methods.

5.3 These polymer properties are measured for Quality Assurance (QA), Quality Control (QC) **(7)** and process control, for example, certificates of analysis (CoA) or optimization of the reaction process **(6)**. These properties are key indicators of performance characteristics and are therefore important in compounding and manufacturing of plastic products.

5.3.1 This guide is applicable in a laboratory environment, continuous inspection as a quality control or as a research tool.

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[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

It is also appropriate for use in commercial processes used to produce polyethylene and polypropylene.

5.4 TD-NMR Relaxometry can measure crystallinity content and relaxation rates directly (**4**), (**5**). Polyolefin properties used in industry that are correlated with crystallinity can be quantified. In these cases, a calibration is necessary.

5.5 As a secondary technique, results achieved by different TD-NMR Relaxometry systems, even from the same vendor, in different laboratories are not necessarily comparable and may result in biases. Therefore, the user is advised to perform measurement validation.

6. Apparatus

6.1 *Nuclear Magnetic Resonance Relaxometer:*

6.1.1 This guide describes the use of a low-field pulsed NMR relaxometer capable of measuring a nuclear magnetic resonance free-induction decay (FID) signal due to hydrogen atoms in the sample. The instrument consists of the following parts:

6.1.1.1 Permanent magnet to provide the necessary static magnetic field for the NMR experiments.

6.1.1.2 NMR probe (sample compartment) which is a radio frequency (RF) transceiver coil for excitation and detection of hydrogen nuclei relaxation as the FID signal.

6.1.1.3 Electronic units to control and monitor the resonance condition involving magnet temperature control, pulse sequence timing (**8**), RF generation, signal amplification, signal digitization, and optionally the field offset coils.

6.1.2 This guideline recommends that the relaxometer instrument is equipped with the ability to equilibrate samples within the probe at a constant temperature (typically 40 °C - 80 °C with a tolerance of ±0.1 °C; (**7**).

6.2 Sampling equipment suitable for offline, at-line, online (**9**) or inline use, that is, manual, semi-automatic or fully automatic. Options include:

6.2.1 Sample changer to hold and load samples into the NMR probe.

6.2.2 Sample delivery system which conveys sample from the process to the NMR system. The system can be manual or automatic.

6.3 Active sample conditioning apparatus internal to the NMR equipment or an external system in the form of a dry block, bath, or other temperature conditioning device into which the sample is inserted to control and stabilize sample temperature (typically at 40 °C - 80 °C with a tolerance of ±0.2 °C).

6.4 A test chamber which is typically a glass tube with an outside diameter of 10 - 30 mm depending on the application and product particle size. Any tube length that permits easy insertion into and removal from the NMR probe may be used. Alternatively, a tubeless capture system can be implemented which retains the sample directly within the probe for analysis.

7. Materials and Test Specimen

7.1 *Materials:*

7.1.1 Samples typically consist of polyolefin materials, primarily polypropylene or polyethylene. They may consist of homopolymer, co- or terpolymer materials, composed of ethylene, propylene, and higher alpha-olefins (**7**). Samples may either be exclusively polymer materials, or could additionally contain additives such as anti-oxidants or filler materials, such as talc, fibers, etc. There could also be impurities.

7.1.2 No reagents are required for this analysis.

7.2 *Test Specimen:*

7.2.1 Samples typically consist of powders, pellets or granules, but could also be analyzed in the form of flakes, films, fibers, cutouts from a dogbone (**10**), etc. For a given calibration model, they should always be in the same form since the physical form might affect results.

7.2.1.1 Powders sampled immediately after the reaction are ideal candidates for process optimization and reactor control in a manufacturing plant.

7.2.1.2 Pellets sampled post extrusion are typically analyzed for quality control and results can be used for certificates of analysis (CoA) and other purposes.

7.2.2 The sample volume affects results, so it is strongly suggested to use the same filling volume every time. Sample volumes for a given instrument are specific to that instrument. The maximum sample size is determined by magnet bore diameter, sample tubes and probe filling heights. A typical amount ranges from 100mg to 30g.

7.2.3 It is important to ensure representative sampling as outlined in 8.2.

7.2.4 The sample temperature also affects results, since the NMR signal will change with temperature. In order to compare results, NMR relaxometry experiments should be performed at a consistent sample temperature. The sample is therefore typically tempered prior to an experiment.

7.2.5 There are several other temperature effects that might affect results: Reactor resin (powder) samples should only be analyzed once by NMR Relaxometry, since annealing effects (**11**), (**12**) cause changes in the polyolefin morphology, so prediction results change when experiments are repeated with the same aliquot. In the case of pelletized materials, additives and processing techniques may stabilize the material. However, the user should verify sample stability over repeated heating and cooling cycles before relying on multiple measurements of the same aliquot for control chart generation. Heating any samples above their melting temperatures might cause further changes in the morphology.

7.2.6 Certain grades also become sticky when heated, so cleaning sample tubes might become difficult.

8. Procedure: TD-NMR Methodology

8.1 *Analysis Flow-Chart*—A typical sequence of events starting from collecting the sample to be measured to displaying the result is shown in Fig. 1. Certain steps might not be available or required depending on the application and the used TD-NMR system and vendor software.

8.2 *Sampling*—Sample collected to be analysed should be representative of the process it is collected from. Special care should be taken to avoid particle size segregation during the collection stage. The sample should be marked with a timestamp indicating when it was collected from the process. Additionally, process conditions such as catalysts type, feed