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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.*

[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.

[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.