STANDARD REFERENCE MATERIALS FOR THE POLYMERS INDUSTRY

Walter G. McDonough, Sara V. Orski, Charles M. Guttman, Kalman D. Migler, and Kathryn L. Beers, National Institute of Standards and Technology, Gaithersburg, MD

Abstract

The National Institute of Standards and Technology (NIST) provides science, industry, and government with a central source of well-characterized materials certified for chemical composition or for some chemical or physical property. These materials are designated Standard Reference Materials® (SRMs) and are used to calibrate measuring instruments, to evaluate methods and systems, or to produce scientific data that can be referred readily to a common base. In this paper, we discuss the history of polymer based SRMs, their current status, and challenges and opportunities to develop new standards to address industrial measurement challenges.

Introduction

The main purpose of standard reference materials is to provide a well characterized material with a measured value and its associated uncertainty for some measurand such as a chemical concentration or some physical property. The SRMs in our portfolio focus on thermoplastic resins and address properties such as melt flow rate, molecular mass, molecular mass distribution, limiting viscosity, intrinsic viscosity, and heat capacity. Our portfolio is a good representation of the research focus of the Polymers Division in the 1970s with the emphasis on fundamental polymer analysis. These standards were sufficient for several decades as much of industrial advances were focused on synthetic efficiency, performance, and optimization of existing polymers and polymer additives and blends through improved processability and control of material properties. Concurrently, emerging technologies advancing polymerization processes and tailoring molecular mass and chain architecture were being promoted from fundamental research to more promising industrial applications. Thus, over time existing reference materials were no longer adequate to calibrate measurements of these new advanced materials. The challenge moving forward is to add novel materials to the NIST standards portfolio that are relevant to the modern plastics industry. Reference materials and measurements together must rise to the sophistication of modern polymers.

To address this challenge, we are updating our SRM portfolio (see Table 1) through a two-phase approach. First, current standards are being assessed for long term stability and continued needs. This assessment includes testing to ensure current standards meet the certified values and uncertainties listed in their certificates. As available, these certified values are also measured with the most recent measurement methods and protocols to retain relevancy to current measurement technologies. Inventory evaluation is also essential to determine if enough reference materials remain to fulfill demand. As the supply for a particular standards decreases, replacement material must be tested and certified. Review of existing SRMs indicate that some standards are being utilized for measurements beyond their certified values, or "off label" use. This knowledge not only allows NIST to focus our resources on supporting appropriate material standards, but can inform us about unmet needs and help direct our development of new reference materials. This goal will be achieved through stakeholder engagement to investigate where new reference materials will improve accuracy in measurements for manufacturing and what new materials are relevant and have a long term impact for polymer measurements and calibrations.

Two examples of NIST reference material evaluation and development are introduced for measurement of melt flow rates and molecular mass averages to highlight current progress and challenges in standards evaluation and development.

Melt Flow SRMs

The following example describes in general terms how we address updating the certificates for our melt flow SRMs. For the most part, ASTM-D-1238-XX with the XX referring to the year/version of the standard is the method followed to make the measurements. Thus, some SRMs used today may have been measured using a prior standard method. As noted in the Significance and Use section of the test method, it is primarily used for quality control purposes on thermoplastics as the flow rate value is not a fundamental polymer property and allows the user to assess the uniformity of the resin tested. [1] Our SRMs are used as a means of calibrating the instrument. To date, all of our SRMs use Procedure A in which resin is preheated for a set time, then a fixed load is used to help push the molten polymer through an orifice for a set period of time with the mass of the extrudate weighed and the melt index given in units of g/10 min. In general for this method, only the preheating time has changed, increasing from 6 min to 7 min. When stability testing or recertifying is conducted, it is important to remember to follow the method used when the material was certified. Once satisfied that the property has not changed, new

values can be determined using the current standard method. For standard reference materials, not only is the mean and standard deviation calculated, but also the overall expanded uncertainty. For melt flow measurements, sources of uncertainty are due to:

- The repeatability of the experiment
- The instrument variability as estimated from precision tables in ASTM-D-1238
- Weighing
- Timing
- Temperature

The combined standard uncertainty is computed by root-sum-of-squares of the component uncertainties with the expanded uncertainty on the certificate being two times the combined standard uncertainty, which arises from a large number of degrees of freedom. [2] For the above sources of uncertainty, the dominant source comes from the instrument variability as estimated from precision tables in ASTM-D-1238. It was deemed to be reasonable to include this uncertainty as NIST uses a commercial instrument to conduct the experiments. The uncertainty due to temperature was the next largest source, with the remaining sources an order of magnitude less.

There has been interest expressed in having an SRM that can be used for Procedure B of ASTM D1238. This procedure is more automated than procedure A in that the flow rate is calculated from the machine measuring the volume of molten polymer pushed through the orifice over a set time. This value, combined with the density of the resin results in a melt flow rate value. Currently, the melt flow tables in ASTM D-1238 are being updated. Part of this effort includes testing materials using Procedure B. NIST could put forward one of the materials tested as a research or reference material while full scale testing is done to help the material eventually become a standard reference material. This includes a variety of molecular mass polymers and differing degrees of short and long chain branching.

Molecular Mass SRMs

Absolute techniques to measure number and mass average molecular masses, M_n and M_w, respectively, such as membrane osmometry and static light scattering, respectively, have been largely superseded by relative analytical methods such as size exclusion chromatography (SEC). SEC offers enhanced measurement precision even though material calibration standards are required to determine the molecular mass and molecular mass distribution. Standards development organizations have recognized this need and developed documentary standards for multi-detector SEC such as ISO 16014-(1 to 5) and ASTM D5296-11 to describe best practices for separation and analysis of polymers. ASTM has even assembled a task force to compare relative and absolute measurements to quantify bias, which is how well a test agrees with a generally accepted value. [3] NIST is adopting a similar approach to its molecular mass and molecular mass distribution SRMs, focusing on correlating the original certificate measurements and uncertainties with multi-detector SEC. NIST molecular mass SRMs consist of linear polyethylene, polystyrene, and poly(methyl methacrylate), which are no longer representative of the array of chemical and architectural control available to modern polymers.

A particular example is the evolution of polyolefins in industrial manufacturing. SRM 1475A, a broad distribution linear polyethylene (M_w = 52,000 g/mol) and standards derived from its fractions are widely used NIST standards for molecular mass and molecular mass distributions. These linear standards have been the hallmark of polyolefin calibration from NIST for the last 40 years. Advances in olefin methathesis using metallocene catalysts has vastly expanded the ability to control molecular mass and degree of long and short chain branching. Linear PE is not representative of the solution behavior of these materials and cannot alone be an adequate calibration standard for SEC. Novel infrared flow-through detection has expanded the ability to quantify average short chain branching at each point on a molecular mass distribution curve. Utilizing advanced metallocene catalysts, NIST is currently developing molecular mass and sequence controlled short chain branched polymers to be able to make reference materials that have quantified degree of alkyl branching (AB) and alkyl branching distributions (ABD). Furthermore, the majority of NIST standards certify either M_n or M_w, which represent only the first and second moments of the molecular mass distribution and are not fully descriptive of all molecular masses and associated error throughout the entire distribution curve. Analysis of these next-generation standards must address uncertainty in each slice of the distribution curve.

Challenges and Opportunities

Developing prototypes on new polymer standards is only the first step in creating new NIST standard reference materials. Production of a candidate material to a SRM can take three to five years from the laboratory to realization due to market research, scale-up, and exhaustive analysis to quantify all measurement uncertainties. NIST has recognized that for many fields, this time frame hinders emerging technology where non-equivalent standards are limiting further development and commercialization.

A proposed alternative is to expedite useful material to industry through the development of what are known as NIST Reference Materials (NIST RMs). These products would have “reference” rather than “certified” values and would not have all sources of uncertainty fully

estimated, as required for a SRM. Thus these materials are provided with a report of investigation, not a certificate. Vetting of the material would be achieved by measurements from NIST as well as industrial partners willing to share analysis results on a collective database. The measurement values and uncertainties of a reference material may be sufficient for industrial needs or may be able to bridge the gap in time until NIST completes the full analysis and production of the material as an SRM.

Conclusions

Standard Reference Materials are used to calibrate measuring instruments, to evaluate methods and systems, or to produce scientific data that can be referred readily to a common base. As NIST updates and expands its polymer based reference material portfolio, it must maintain the high accuracy measurements of its current standard materials in their next generation materials. NIST strives to make the most precise and accurate measurements based on absolute methods. NIST must also recognize the utility of quantification at various levels of rigor to address immediate industrial needs, especially as absolute measurements for a specific material property are under development. This strategy will allow for the transition from standards expertise in classic thermoplastics to advanced materials relevant to commercial market today and well into the future.

References

1. ASTM D1238-13
2. ISO/IEC Guide 98-3:2008
3. ASTM D5296-11

Table 1: List of polymer SRMs with the associated properties measured

705a	Polystyrene (Narrow Molecular Weight Distribution)	Certified Value
706a	Polystyrene	M_w, Intrinsic Viscosity
1474a	Polyethylene Resin	Melt Flow Rate
1476a	Branched Polyethylene Resin	Melt Flow Rate
1478	Polystyrene (Narrow Molecular Weight Distribution)	M_w, M_n, Intrinsic Viscosity
1479	Polystyrene (Narrow Molecular Weight Distribution)	M_w
1484a	Linear Polyethylene (Narrow Molecular Weight Distribution)	M_w, M_n, Limiting Viscosity
1487	Poly (methyl methacrylate) 6 K Narrow Molecular Weight Distribution	M_w, Limiting Viscosity
1488	Poly (methyl methacrylate) 29 K Narrow Molecular Weight Distribution	M_n, Limiting Viscosity
1489	Poly (methyl methacrylate) 115 K Narrow Molecular Weight Distribution	M_n, Limiting Viscosity
1496	Unpigmented Polyethylene Gas Pipe Resin	Melt Flow Rate, Intrinsic Viscosity
2881	Polystyrene Absolute Molecular Mass Distribution Standard	Molecular Mass Distribution
RM 8281	Single-Wall Carbon Nanotubes (Dispersed, Length Resolved)	Ultra violet visible (UV-Vis) and UV-Vis-near infrared (NIR) absorbance spectra, Raman scattering ratio, NIR fluorescence, atomic force microscopy, transmission electron microscopy
1473b	Low Density Polyethylene Resin	Melt Flow Rate
1475a	Polyethylene, Linear	Melt Flow Rate, M_n, M_w, M_z, Limiting Viscosity, Solid Density, Heat Capacity
1482a	Polyethylene, 14 K Molecular Weight	M_w, M_n, Intrinsic Viscosity
1483a	Polyethylene, Linear	M_w, M_n, Intrinsic Viscosity

2885	Polyethylene (6280 g/mol)	M_w, Intrinsic Viscosity
2886	Polyethylene (87000 g/mol)	M_w, Intrinsic Viscosity
2887	Polyethylene (196,400 g/mol)	M_w, Intrinsic Viscosity