

STANDARD REFERENCE MATERIALS: NON-NEWTONIAN FLUIDS FOR RHEOLOGICAL MEASUREMENTS

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Abstract

The National Institute of Standards and Technology (NIST) develops Standard Reference Materials® for calibration, quality assurance and for research into improved measurements. Two fluids that demonstrate shear thinning and normal stresses typical of polymeric fluids have been developed as standards for rheological measurements. SRM 2490 is a solution of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane. SRM 2491 is a poly(dimethylsiloxane) melt, with less temperature dependence than SRM 2490. NIST certifies the shear-rate dependence of the viscosity and first normal stress difference at 0 °C, 25 °C and 50 °C, and the linear viscoelastic behavior over the same temperature range.

Introduction

The National Institute of Standards and Technology (NIST) sells more than 1300 different Standard Reference Materials® (SRMs) for the purposes of research into improved measurement methods, for calibrating instruments to ensure accurate measurements, and to provide quality control. NIST has certified the rheological properties of two polymeric fluid Standard Reference Materials. Polymer melts and solutions often demonstrate non-Newtonian flow behavior [1-3]. Such fluids often have a viscosity that depends on the shear rate and display elastic effects like normal stresses that greatly affect their response to deformation. Accurate measurements of these material properties are critical for predicting the behavior of polymeric fluids in the complex flows they experience during processing and use. These two Standard Reference Materials are intended to provide a means for comparing different methods of measuring viscoelastic fluid behavior.

The new polymer solution, SRM 2490, consists of polyisobutylene (PIB) with a molar mass of approximately 10^6 g/mol dissolved in 2,6,10,14-tetramethylpentadecane (common name *pristane*). NIST has approximately 400 units (100 mL each) of SRM 2490 in stock. A second fluid, SRM 2491, consists of a poly(dimethylsiloxane) melt. Poly(dimethylsiloxane) is attractive for this purpose because of its stability, good handling qualities and excellent safety characteristics.

A round robin test of the SRM's is also planned, involving instrument manufacturers and users in industry and at universities. The round robin will assess the lab-to-

lab variability in these measurements, particularly in measuring normal stresses. The Statistical Engineering Division at NIST will assist in evaluating the results.

Goals

For these fluids, NIST certifies the shear-rate dependence of viscosity and first normal stress difference over a range of shear rates between 10^{-3} s⁻¹ and 100 s⁻¹, at temperatures of 0 °C, 25 °C and 50 °C. The linear viscoelastic response is also certified, along with the shift factors, over the same temperature range. SRM 2490 has a zero-shear-rate viscosity of approximately 100 Pa·s at 25 °C, while SRM 2491 has a zero-shear-rate viscosity that is approximately 1000 Pa·s at 25 °C. Other aspects of the fluids that must be considered are chemical stability (both in long-term storage and evaporation over the course of an experiment), ease of use, safety and cost. For the polymer solution SRM 2490, the problem of solvent evaporation might be the most critical aspect of stability in that it will limit the duration of experiments and may require imposing a shelf life on stored materials. The poly(dimethylsiloxane) used for SRM 2491 should present no problems with chemical stability or evaporation.

Description of SRM 2490

SRM 2490 replaces a previous Standard Reference Material (SRM 1490) [4], which was composed of polyisobutylene dissolved in normal hexadecane (common name *cetane*). Solutions of polyisobutylene have been studied extensively [4-9], as they have proven to be good examples of non-Newtonian fluids, demonstrating shear thinning and large normal stress differences. Polyisobutylene also has advantages in that the saturated hydrocarbon structure is chemically stable, and the material is safe and widely available commercially. SRM 1490 had one known limitation at the outset, in that the working temperature range of the fluid was constrained by the crystallization of n-hexadecane at 18 °C (64 °F). SRM 1490 was certified in 1977, and Zapas and Phillips [6] reported that samples stored in the laboratory for a two-year period had very reproducible viscosity behavior. However, SRM 1490 was discontinued in 1990 because the properties of newly packaged samples no longer met the original certification. Either the properties of the fluid changed during storage, or the newly packaged samples came from a container with a different concentration. Rheological measurements showed an increase in

viscosity, and Fourier Transform Infrared Spectroscopy indicated that newly packaged samples had higher concentrations of PIB than the originally certified material. Both of these results are consistent with solvent evaporation. The increase in viscosity is incompatible with chemical breakdown of either the PIB or the solvent, so we have assumed that the chemical stability of a saturated hydrocarbon structure is sufficient. Hence, the current research into a polymer solution centered on choosing a new solvent with a wider useful temperature range and a decreased rate of evaporation. Cost considerations also limited the choice of solvent to commercially available materials.

Several polyisobutylene solutions have been tested internationally in studies of elongational viscosity and the second normal stress difference. It was concluded that none of these fluids met our needs [10,11]. Information on these solutions can be found in two special issues of the *Journal of Non-Newtonian Fluid Mechanics*: Volume 35, 1990, and Volume 52, 1994, and in reference [8].

While a number of linear alkane solvents such as the n-hexadecane in SRM 1490 have been used to make polyisobutylene solutions, linear alkanes present problems for our purposes. Linear alkanes of molar mass higher than n-hexadecane crystallize at or above room temperature, while linear alkanes of molar mass lower than n-hexadecane have higher rates of evaporation. However, the saturated hydrocarbon structure of an alkane should be chemically stable. These considerations suggested the choice of an alkane with a branched structure to inhibit crystallization, and with a sufficiently high molar mass so that the evaporation rate would be lower than that of n-hexadecane. However, increasing the molar mass of the solvent decreases the rate of dissolution of the polyisobutylene, and also increases the viscosity of the solvent, which seems to decrease the handling qualities of the solution.

Several branched alkanes were tested and rejected as solvents [10,11]. The solvent finally chosen for SRM 2490 was 2,6,10,14-tetramethylpentadecane ($C_{19}H_{40}$, molar mass 269 g/mol), which has the common name *pristane*. The boiling point of pristane is 296 °C [12], and differential scanning calorimetry measurements indicate it does not freeze or vitrify down to -60 °C. The concentration of SRM 2490 was specified to have a mass fraction of 0.114 polyisobutylene (Aldrich Chemical 18,146-3 [13], molar mass $\approx 10^6$ g/mol) dissolved in 2,6,10,14-tetramethylpentadecane (Aldrich Chemical T2,280-2 [13]); this concentration was based on preliminary measurements and the measured concentration dependence of earlier PIB solutions [6]. Cannon Instruments [13] was awarded a contract to mix and package the material. To assure uniformity, all the material was mixed together in one large container and then bottled at the same time; periodic

monitoring of the fluid properties is planned. One unit of SRM 2490 consists of 100 mL of the solution packaged in an amber glass bottle, and NIST has approximately 400 units in stock.

Khalil *et al.* [9] indicated that a significant decrease in solution viscosity can occur with increased mechanical agitation during mixing, presumably reflecting some degradation of the polyisobutylene. We hoped to be able to dissolve the PIB at room temperature with a minimum of agitation. However, scaling up the process to a quantity of 45 L required some heat and agitation to accelerate the dissolution. The viscosity of the bottled solution is about two-thirds that of a quantity of the same concentration prepared in our laboratory; this result suggests some degradation during mixing, but could possibly be attributed to differences in the polyisobutylene used.

Testing and Modeling

The results of steady shear testing were reported previously [14]. More details of the testing, modeling and analysis of the behavior of SRM 2490 under steady and oscillatory shear can be found in the Certificate and report [15] that accompany the SRM, available from the NIST Standard Reference Materials Program (see the web site at <http://ts.nist.gov/ts/htdocs/230/232/232.htm>).

Master curves of the storage and loss moduli shifted to 25 °C are shown in Figure 1. Dynamic tests were performed in a Rheometric Scientific ARES rheometer [13] using 50 mm diameter parallel plates and a nominal gap of 1 mm. Tests were run using the Dynamic Frequency/Temperature Sweep template supplied with the ARES software. One sample was tested from each of 10 randomly chosen bottles. Measurements were taken at 10 °C increments from 0 °C to 50 °C. At each temperature, the frequency of oscillation was increased from 0.0398 rad/s to 100 rad/s, taking five points per decade. Tests were performed at an applied strain magnitude of 20 %. A correction was applied to account for the change in the gap caused by thermal expansion, measured to be 1.75 $\mu\text{m}/^\circ\text{C}$ (with a standard uncertainty of 0.1 $\mu\text{m}/^\circ\text{C}$).

The measurements of the storage modulus $G'(\Omega, T)$ and loss modulus $G''(\Omega, T)$ as functions of frequency Ω and temperature T are shifted to create master curves through time-frequency superposition using a shift factor function $a(T)$ [2], with

$$\begin{aligned} G'(\Omega, T) &= \frac{T\rho}{T_R\rho_R} G'(a(T)\Omega, T_R) \\ G''(\Omega, T) &= \frac{T\rho}{T_R\rho_R} G''(a(T)\Omega, T_R) \end{aligned} \quad (1)$$

where $T_R = 25$ °C is chosen as the reference temperature and ρ is the density, which is approximated as a linear

function of temperature, with $\rho(T) = \rho_R(1 - \alpha(T - T_R))$, where α is the volumetric coefficient of thermal expansion estimated as $\alpha = 6 \times 10^{-4} \text{ cm}^3/(\text{cm}^3 \text{ K})$ [16, 17]. A WLF functional form [2] is used for the shift factor $a(T)$, giving

$$a(T) = \exp\left(\frac{-C_1(T - T_R)}{C_2 + T - T_R}\right) \quad (2)$$

The logarithms of the storage and loss moduli have been fit to polynomial functions of the logarithm of the frequency for calculation of the shift factors [18]. The polynomial functions converge more quickly than an expansion in functions associated with the Rouse modes, and the resulting master curves appear to be satisfactory. The data were fit to functions of the form

$$\ln\left(\frac{G'(\Omega, T)}{1 \text{ Pa}}\right) = \ln\left(\frac{T\rho}{T_R\rho_R}\right) + \sum_{k=0}^4 p_k \left(\ln\left(\frac{a(T)\Omega}{1 \text{ rad/s}}\right)\right)^k \quad (3)$$

$$\ln\left(\frac{G''(\Omega, T)}{1 \text{ Pa}}\right) = \ln\left(\frac{T\rho}{T_R\rho_R}\right) + \sum_{k=0}^4 q_k \left(\ln\left(\frac{a(T)\Omega}{1 \text{ rad/s}}\right)\right)^k$$

The storage and loss modulus data were fit simultaneously to the functions in equation (3) to determine the parameters C_1 and C_2 in the temperature shift factor $a(T)$. The calculated parameters are given in Table 1.

Uncertainty Analyses

One very important aspect of providing certified data for a Standard Reference Material is to include estimates of uncertainties in the data as well as in any quantified parameters. The NIST method for evaluating and expressing uncertainties is outlined in NIST Technical Note 1297 [19], and is based on the policy developed by the International Standards Organization. Within this framework, the value of a measurement and its “standard uncertainty” are taken to be the mean and the standard deviation of the associated data. “Expanded” uncertainties are often reported, in which the standard uncertainty is inflated by a coverage factor, commonly equal to 2, so that the resulting interval contains 95 % of the distribution of possible values. For any measurement, there will be a number of possible sources of uncertainty that contribute to the uncertainty in the final result. The ways to estimate uncertainties are broadly grouped into two categories, Type A and Type B. An uncertainty evaluated by statistical analysis of the data is termed Type A, whereas Type B refers to an uncertainty evaluated by any means other than a statistical analysis of the data. Thus, Type A would refer to a standard deviation calculated from a set of independent measurements, or to an uncertainty estimate from a least-squares curve fit (as for the parameters in Table 1). Type B could refer to estimates of uncertainty based on manufacturer’s specifications, previous experience or general knowledge and scientific judgment. Once the sources of uncertainty have been identified, and

the uncertainties themselves quantified, those uncertainties are combined through the mathematical formula for the propagation of uncertainties. For a quantity y that is a function of a number of independent quantities x_i , with $y = f(x_i)$, the “combined standard uncertainty” in y (symbol $u_c(y)$) is calculated from the standard uncertainties in each x_i as

$$u_c(y) = \left[\sum_i \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) \right]^{1/2} \quad (4)$$

For input quantities that are not independent, there would also be terms involving the covariances, but it is typical in practice to assume that the input variables are independent of one another.

There are a number of possible sources of uncertainty in the measurements of the storage and loss moduli. The uncertainty associated with variability in the material was assessed through multiple measurements (one sample tested from each of ten randomly chosen bottles), and statistical analysis. This uncertainty evaluation is the only one considered to be of Type A. Since our intention is to certify the *mean* values of the storage and loss moduli as functions of temperature and frequency, the uncertainty calculated for this source is given by the standard deviation of the 10 measurements divided by $10^{1/2}$. This calculation gives the standard uncertainty of the mean. Other (Type B) sources of uncertainty are listed below.

1. Temperature, T
2. Frequency of oscillation, Ω
3. Cross-correlation procedure
 - a. Transducer reading
 - b. Oscillation magnitude
4. Geometry
 - a. Gap
 - b. Plate diameter
 - c. Tilt
 - d. Concentricity
5. Solvent evaporation
6. Inertia
7. Edge Effects

These influences are listed in roughly descending order of importance. The temperature and frequency of oscillation are the independent variables used to describe $G'(\Omega, T)$, $G''(\Omega, T)$ and $a(T)$. The standard uncertainty in the temperature is estimated to be $0.1 \text{ }^\circ\text{C}$, and the standard uncertainty in the frequency of oscillation Ω is estimated to be $10^{-4} \times \Omega$.

Type B uncertainties in G' and G'' are calculated through the propagation of uncertainties formula in equation (4). The uncertainties in G' and G'' arising from the stated uncertainties in the temperature and the frequency of oscillation can be calculated using the models in equations (3). Calculating the components of uncertainty arising from the other sources listed requires some analysis of the method by which G' and G'' are determined from the geometry, the boundary conditions imposed, and the measured transducer output. The fluid is

deformed by oscillating the bottom plate with respect to the upper plate. The strain $\gamma(t)$ in the fluid can be described as

$$\gamma(t) = \frac{r}{h} \phi_0 \sin(\Omega t + \varepsilon) \quad (5)$$

where r is the radial position, h is the gap between plates, ϕ_0 is magnitude of oscillation, Ω is the frequency of oscillation, and ε is a possible phase offset between the master driving signal at $\sin \Omega t$ and the resulting oscillation of the plate.

The moment $M(t)$ measured by the transducer is also a function of time, and is calculated by integrating over the area of the plate the product of the shear stress and the radial position.

$$\begin{aligned} M(t) &= \int_0^{2\pi} \int_0^R [G' \sin(\Omega t + \varepsilon) + G'' \cos(\Omega t + \varepsilon)] \frac{r^3}{h} \phi_0 dr d\theta \\ &= \frac{\pi \phi_0 R^4}{2h} [G' \sin(\Omega t + \varepsilon) + G'' \cos(\Omega t + \varepsilon)] \quad (6) \\ &= \frac{\pi \phi_0 R^4}{2h} |G^*| \sin(\Omega t + \delta + \varepsilon) \end{aligned}$$

where R is the outer plate radius, $|G^*|$ is the magnitude of the complex modulus and δ is the phase offset between the strain and the stress. A cross-correlation procedure is used to calculate the storage modulus G' and loss modulus G'' from the measured moment $M(t)$ and the measured oscillation [2, 15]. In this procedure, a measured signal is multiplied together with master signals of $\sin \Omega t$ and $\cos \Omega t$, and the result integrated over one or more periods of oscillation to calculate the magnitude of the measured signal with respect to the master signals. This procedure also acts as a filter to remove some unwanted harmonics and noise [2, 15]. The effects of uncertainties in the transducer response, the oscillation or the geometry can be calculated by evaluating their influence on the moment in equation (6) and on the subsequent result of the cross-correlation [15].

The relative expanded uncertainties of the storage and loss moduli are shown in Figure 2, where a coverage factor of 2 has been used to achieve a 95 % level of confidence in the data. The components of uncertainty arising from the cross-correlation procedure are proportional to the magnitude of the response and are the same for G' and G'' . These uncertainty components dominate the uncertainty in G' at low frequencies where G' is 2 orders of magnitude smaller than G'' . At higher frequencies, the relative expanded uncertainties in both moduli decrease to a level of approximately 2 %, except for the measurements at 50 °C, where the effects of solvent evaporation increase the uncertainties.

Conclusions

Deviations from the certified values by the previous standard fluid (SRM 1490) do not appear to have a chemical origin, but were most likely caused either by differences in sample lots or by solvent evaporation. The new standard fluid SRM 2490 is a solution of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane (pristane). The branched structure of this alkane solvent inhibits crystallization or vitrification at temperatures above -60 °C, and its rate of evaporation is approximately half that of the n-hexadecane used as a solvent for SRM 1490. The new solution was mixed and bottled by Cannon Instruments [13], and NIST has approximately 400 units (100 mL each) in stock. All the material was mixed and packaged at the same time, and the fluid properties will be monitored periodically.

This paper presents the results of dynamic measurements, along with a brief discussion of the components of uncertainty examined and the procedure for evaluating and expressing those uncertainties. A complete report of the certification of the fluid in both steady shear and dynamic tests can be found in reference [15].

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Table 1. Parameters for $G'(\Omega, T)$, $G''(\Omega, T)$ and $a(T)$ in the models found in equations (2) and (3).		
Parameter	Value	Standard Uncertainty
p_0	3.177	0.005
p_1	1.235	0.003
p_2	-0.134	0.001
p_3	2.36×10^{-3}	2.7×10^{-4}
p_4	5.20×10^{-4}	6.1×10^{-5}
q_0	4.196	0.005
q_1	0.720	0.003
q_2	-0.0719	0.0011
q_3	-3.18×10^{-3}	2.6×10^{-4}
q_4	7.06×10^{-4}	6.0×10^{-5}
C_1	8.85	0.30
C_2	192 °C	6 °C

Key Phrases

Non-Newtonian, reference standard, viscosity, normal stress, viscoelastic, storage modulus, loss modulus, time-temperature superposition

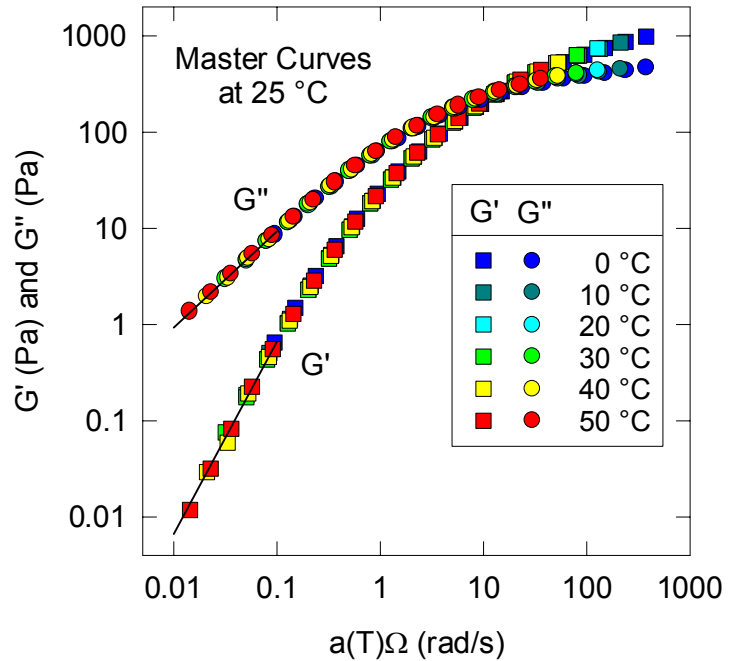


Figure 1. Master curves of the storage modulus G' and loss modulus G'' shifted to 25 °C. Lines fit through the data in the terminal region at low frequencies have slope of 1 for G'' and slope of 2 for G' .

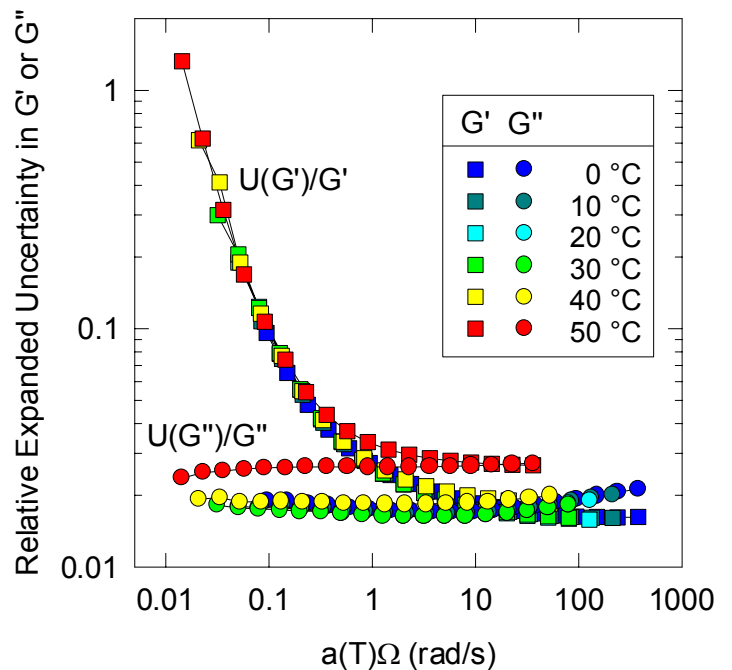


Figure 2. Relative expanded uncertainties in the storage modulus G' and loss modulus G'' , with a coverage factor of 2 to capture a 95 % level of confidence. The relative expanded uncertainty is the expanded uncertainty in the quantity divided by the quantity itself. Lines connect the points to guide the eye.