

A NONLINEAR FLUID STANDARD REFERENCE MATERIAL: PROGRESS REPORT

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Abstract

A new NIST Standard Reference Material (SRM 2490 - Nonlinear Fluid for Rheological Measurements) demonstrates shear thinning and normal stresses typical of polymeric fluids. SRM 2490 consists of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane (pristane), giving a stable fluid with a wide temperature range. NIST will certify the linear viscoelastic behavior and the shear-rate dependence of the viscosity and first normal stress difference between 0 °C and 50 °C. NIST will also use the fluid in a round robin to help the polymer community identify sources of variability in rheological measurements. Here we report progress on the project.

Introduction

The National Institute of Standards and Technology (NIST) sells over 1300 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. Polymeric fluids, such as polymer melts and solutions, often do not follow the simple, Newtonian ideal in their flow behavior [1,2]. Such fluids typically demonstrate a viscosity that depends on shear rate as well as elastic effects such as normal stresses that can 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. The new Standard Reference Material (SRM 2490) replaces a discontinued fluid (SRM 1490) to provide a means for assuring the accuracy of different types of instruments in measurements of viscoelastic fluids. This project will also include a round robin study of the new fluid to determine how much variability occurs in such measurements among a number of laboratories using different instruments.

Goals

For the new fluid, we plan to certify the shear-rate dependence of viscosity and first normal stress difference over a range of shear rates from 10^{-4} s^{-1} to 150 s^{-1} , at temperatures between 0 °C and 50 °C. The linear viscoelastic responses will also be certified along with the temperature dependence of the shift factors over the same 50 °C range.

The new fluid will be shear-thinning (this behavior being typical for polymer melts and solutions) with a zero-shear-rate viscosity of approximately 200 Pa·s (2000 poise). The viscosity and first normal stress difference will be somewhat

higher than the previous standard SRM 1490, and the new fluid will have a much wider working temperature range. Other aspects of the fluid that must be considered are stability (both in long-term storage and in the time during an experiment), ease of use, safety and cost. Assuming that the component parts of the fluid are themselves chemically stable, 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. Solvent evaporation might be one cause of the difficulties with the previous standard.

The Previous Standard

The new fluid will replace the previous Standard Reference Material (SRM 1490) [3], which was composed of a polyisobutylene (PIB) of high molar mass (approximately 10^6 g/mol) dissolved in normal hexadecane, a linear alkane with formula $\text{C}_{16}\text{H}_{34}$ and molar mass of 226 g/mol (this solvent is also called cetane because it is related to hydrocarbons originally derived from whale oil, *cetus* is Latin for whale [4]). SRM 1490 was certified in 1977, and Zapas and Phillips reported that samples stored in the laboratory for a two-year period had very reproducible viscosity behavior [5]. However, SRM 1490 was discontinued in 1990, because the properties of newly packaged samples no longer matched the original certification. Either the properties of the fluid may have changed during long-term storage, or the newly packaged samples might have been taken from a different container (records are inconclusive). Some efforts were made to determine the cause of the changes in properties. Rheological measurements showed an increase in viscosity, and Fourier Transform Infrared Spectroscopy indicated that the newly packaged samples had higher concentrations of PIB than the originally certified material. Both of these results are consistent with solvent evaporation. An increase in viscosity is incompatible with chemical breakdown of either the PIB or the solvent, and we have assumed that the chemical stability of the saturated hydrocarbon structure of these materials is sufficient. Upon deciding to create a new non-Newtonian fluid, it was concluded that SRM 1490 should not be directly duplicated because the working temperature range of the fluid was limited by the crystallization of n-hexadecane, which has a melting point of 18 °C (64 °F). Hence, the current research centers on creating a non-Newtonian fluid that has a wider useful temperature range, and on providing certification of behavior beyond the shear-rate dependence of the viscosity and first normal stress difference at a single temperature.

Other Materials Used in Round Robin Testing

Several other fluids have been tested internationally in an effort to reach a consensus regarding non-Newtonian behaviors (elongational viscosity and the second normal stress difference) that are still the subject of much research.

In general, these fluids have viscosities much lower than SRM 1490; the fluids for elongational viscosity studies are designed so that they can be extended to high strains without separation, making them difficult to load in a rheometer. In order to reduce the complexity of the problem, a fluid can be prepared to have a viscosity that is independent of shear rate, but also exhibits high normal stresses, by using a dilute solution of a high-molar-mass polymer dissolved in a relatively viscous solvent (a Boger fluid [6]). One such fluid (labeled M1) is a non-shear-thinning elastic fluid of polyisobutylene dissolved in polybutene using kerosene as an additional solvent [7,8,9]; a number of papers describing studies of this material may be found in a special issue of the *Journal of Non-Newtonian Fluid Mechanics*, Volume 35, 1990. Fluids A1 and D1 [9,10] are strongly shear-thinning fluids consisting of polyisobutylene dissolved in decahydronaphthalene (Figure 1). Fluid S1 was constructed to show shear thinning similar to fluid A1, but with a dominant relaxation time of the same order as that of fluid M1 (0.3 s as compared to 5 s for A1) [9,11,12,13]. S1 consists of polyisobutylene dissolved in decahydronaphthalene and polybutene oil, and a number of papers concerning S1 may be found in the *Journal of Non-Newtonian Fluid Mechanics*, Volume 52, 1994. Hudson and Ferguson [11] note that the properties of S1 changed during experiments and attribute the changes to evaporation of the decahydronaphthalene solvent, but they note that these changes are less apparent in fluids that contain only polyisobutylene and decahydronaphthalene. Guenet and McKenna also reported relatively rapid loss of solvent from gels of polystyrene and decahydronaphthalene [14]. Some new measurements of the rate of evaporation of several solvents (Figure 1) indicate that decahydronaphthalene has a much higher rate of evaporation than the other solvent materials examined.

Materials for the New SRM

A solution of high-molar-mass polyisobutylene is still an attractive choice for SRM 2490, because the saturated hydrocarbon structure is chemically stable, and the material is quite safe to work with (one of the uses of PIB is in chewing gum [15]). Also, PIB solutions are good examples of non-Newtonian fluids, generating large normal stress differences, and they have been investigated extensively [3,5-13,16,17]. The key to this project is thus to find a solvent for the PIB having good long-term stability, a wide working temperature range, good handling characteristics and good material safety, all at a reasonable cost.

The first attempt to overcome the difficulties with the prior Standard Reference Material focused on a high-molar-mass polyisobutylene (10^6 g/mol) dissolved in a low-molar-mass polyisobutylene oligomer (500 g/mol). This material met some of the criteria for the project, demonstrating a zero-shear-rate viscosity higher than SRM 1490 and an appropriate level of shear thinning and first normal stress difference. However, the method used to process the material was somewhat unsatisfactory, in that a third material (a small alkane solvent such as pentane or cyclohexane) was required to dissolve the high-molar-mass polymer to allow mixing with the oligomer. The most significant difficulty, however, was that the fluid was very difficult to work with, being very sticky and difficult to extract from the bottle and load in the rheometer. In essence, this fluid contained materials similar to the extensional viscosity fluid M1 discussed above, but at a higher concentration. Apparently, the high viscosity of the solvent prevents the high-molar-mass PIB from retracting quickly once it has been stretched out. The low-molar-mass polyisobutylene is itself somewhat sticky, and another commercial use of PIB is for the sticky substance in roach traps [15].

Several alternatives were considered, and it was concluded that the best choice was to use a branched alkane similar in size to the n-hexadecane as a solvent for the high-molar-mass polyisobutylene. A branched structure will inhibit crystallization, while the size of the solvent molecule represents a compromise between a desire for lower solvent viscosity and rapid dissolution (low molar mass) and a desire for lower rates of evaporation (high molar mass). The saturated hydrocarbon structure of an alkane should provide chemical stability.

Three commercially available alkanes were studied. The first solvent studied was 2,2,4,4,6,8,8-heptamethylnonane, which has the same $C_{16}H_{34}$ chemical formula and 226 g/mol molar mass as n-hexadecane, but has a branched structure more like polyisobutylene. The second solvent studied was 2,6,10,15,19,23-hexamethyltetracosane ($C_{30}H_{62}$, molar mass 423 g/mol) or squalane (*squalus* is Latin for sea fish; a related chemical, squalene, is found in shark livers [4]). The third solvent studied was 2,6,10,14-tetramethylpentadecane ($C_{19}H_{40}$, molar mass 269 g/mol) or pristane (*pristis* is Latin for shark; pristane is also found in shark livers [4]). All three of these materials dissolved the PIB completely without requiring an additional solvent. The PIB solutions made using 2,2,4,4,6,8,8-heptamethylnonane and pristane were relatively easy to work with, but the higher viscosity of the squalane led to a fluid that was sticky and difficult to load in the rheometer, so the squalane was removed from consideration. A PIB/squalane solution would probably be a good fluid for studying extensional viscosity, however. Measurements of the evaporation of the solvents from Petri dishes at room temperature in a fume hood (Figure 1) indicated that pristane was the better choice between the other two solvents. The boiling point of pristane is 296 °C

[18], and it does not freeze or vitrify down to at least -60°C . Measurements of a PIB/pristane solution in which the mass fraction of PIB is 10 % are shown in Figure 2; the zero-shear-rate viscosity of this solution is approximately 100 Pa·s. Since the target for the solution is a zero-shear-rate viscosity of 200 Pa·s, and since Zapas and Phillips [5] indicate that the viscosity of a similar PIB in n-hexadecane scales with concentration raised to the power 5.3, SRM 2490 will consist of a PIB/pristane solution in which the mass fraction of PIB is 11.4 %.

An important point is raised in the paper by Khalil, Tougui and Sigli [17] regarding the decrease in solution viscosity associated with increased mechanical agitation of the material during mixing. This decrease presumably reflects some degradation of the polyisobutylene. The mode of preparation is clearly as important a variable as the constituent materials when mixing different lots of a material intended to act as a standard.

Development of the new material will include efforts to ensure quality control during preparation as well as periodic monitoring of the properties of the fluid held in inventory. The material will be commercially prepared and bottled, acceptance tested by NIST, then statistically sampled and certified.

Round-Robin Testing

The project also includes a round robin with the new Standard Reference Material involving instrument manufacturers and users in industry and at universities. The goals of the round robin are to ensure that the chosen material is acceptable to the community, and to provide information regarding the lab-to-lab variability in the measurements, particularly with regard to normal stresses. The Statistical Engineering Division at NIST will be involved in evaluating the results of the round robin. Those who have already expressed an interest in participating in the round robin are listed below.

Instrument Manufacturers

ATS RheoSystems
Bohlin Instruments
Brookfield Engineering Laboratories
Capillary Rheometer
Goettfert
Haake
Paar Physica
Rheometric Scientific
TA Instruments
TherMold Partners
Vilastic Scientific

Industrial Users

DuPont
Fluid Dynamics
National Starch and Chemical
Phillips Petroleum
Procter and Gamble
Xerox

Academics

David Boger, University of Melbourne
Ralph Colby, Pennsylvania State University
Francis Gadala-Maria, University of South Carolina
Chris Macosko, University of Minnesota
Jaye Magda, University of Utah
Gareth McKinley, Massachusetts Institute of Technology
Skip Rochefort, Oregon State University

Conclusions

The difficulties associated with the previous fluid (SRM1490) do not appear to have any chemical origin. Instead, they are likely to have been caused either by initial differences in processing or by solvent evaporation. In the future, the preparation process and storage of the fluid will have to be monitored to eliminate these problems and to determine if some shelf life should be imposed on the fluid.

The new SRM 2490 will consist of a solution of polyisobutylene dissolved in 2,6,10,14-tetramethylpentadecane or pristane. This solvent does dissolve the high-molar-mass PIB completely (although very slowly), and the solution is very similar to SRM 1490 in that it is easy to handle and has similar viscosity and normal stress behavior (Figure 2). The boiling point of the solvent is 296°C , and the branched structure of the solvent prevents crystallization or vitrification down to temperatures at least as low as -60°C . Finally, the rate of evaporation is approximately half that of the n-hexadecane used as a solvent for SRM 1490.

We have recently contracted for the manufacture and packaging of a large quantity of the solution. SRM 2490 should be available for purchase late in 1999 from the NIST Standard Reference Materials Program [19].

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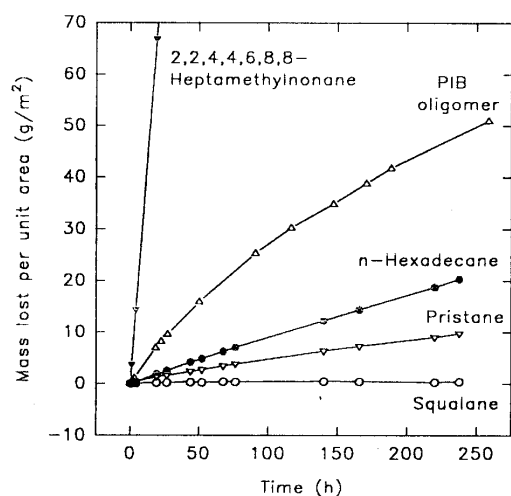
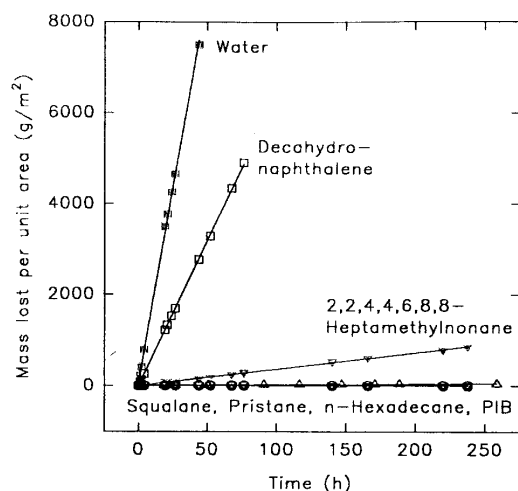


Figure 1a and 1b. Evaporation of several fluids from Petri dishes in a fume hood at room temperature. The data is the same in both plots, but the scale of the vertical axis in the lower plot is expanded. The standard uncertainty in each measurement is approximately a linear function of the mass lost per unit area given by $(0.1 \text{ g/m}^2 + (4 \times 10^{-4})(\text{mass lost per unit area}))$. Note that n-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane have the same molar mass. Also note the curvature in the evaporation of the PIB oligomer (nominally 500 g/mol) suggesting polydispersity in the fluid.

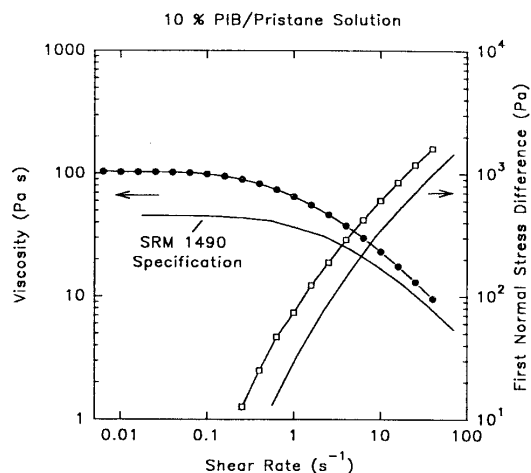


Figure 2. Viscosity and first normal stress difference as a function of shear rate for a PIB/pristane solution in which the mass fraction of PIB is 10 %. The experiments were performed at 25 °C. Each symbol represents the mean of several measurements. The standard uncertainty of the mean for the viscosity is a decreasing function of shear rate given approximately by $(0.15 \text{ Pa}\cdot\text{s})[(\text{rate}/1.0 \text{ s}^{-1})^{-0.30}]$. The standard uncertainty of the mean for the first normal stress difference is an increasing function of shear rate given approximately by $(7.5 \text{ Pa})[(\text{rate}/1.0 \text{ s}^{-1})^{0.25}]$. Also shown as solid lines are the certified values for SRM 1490 [3].