STUDIES ON THE MELT FLOW RATE OF THE SRM 1473, A LOW DENSITY POLYETHYLENE RESIN

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ABSTRACT

The melt flow rate of Standard Reference Material (SRM) 1473, a polyethylene resin, was determined to be 1.29 g/10 min at 190°C under a load of 2.16 kg using the ASTM Method D 1238-89. The average results from 42 determinations on samples with a standard deviation of a single measurement of 0.020 g/10 min. A small but measurable drift from the first timed extrudate to the third timed extrudate was observed.

1. Introduction

Melt flow rate is widely used in polymer technology as a product specification since this value, which includes a statement of the load and temperature under which it is obtained, gives an indication of the processing properties of the polymer[14]. The value of melt flow rate is expressed as the mass of polymer melt pushed from the heated cylinder of the extrusion plastometer through its precision bore orifice by its piston in a period of time, the standard units of the value being grams per ten minutes (g/10 min).

In this paper, we report the determination of melt flow rate of a polyethylene resin. This is a report on the melt index certification.

2. Experimental Procedure

2.1 Sampling and Randomization of Charge Sequence of SRM 1473

Material of the SRM 1473 came in one 50 pound bag of pellets. The material was selected by a search for a polyethylene with a melt index nearly equal to the melt index of SRM 1476. The supplier of this resin identifies it as a low density polyethylene synthesized in an autoclave environment which characteristically generates a branched product. The supplier estimates the density to be 0.918 g/cm^3. The Standard Reference Materials Program (SRMP) blended the material and divided the pellets into 369 units of 60 grams each. Fourteen of these units were chosen by stratified random selection for homogeneity and certification studies. Three charges were taken for extrusion from each of the randomly chosen bottled samples during the course of the melt flow rate experiments. In preparation for the melt flow rate determinations, the charges to be extruded were identified by ordinal numbers. Three such charge numbers were assigned to each identified sample. The sequence of numbered charges taken from the bottled samples for extrusion was randomized according to a procedure described by Natrella[5], and applying the Rand tables[6].

2.2 Instrument Calibration and Alignment

2.2.1 Temperature Indication

The temperature was indicated by a mercury column thermometer of the form described in paragraph 5.7 of the ASTM method. Calibration of the temperature indication is traceable to the Thermometry Group of the NIST Process Measurements

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Division . An iron-contantan thermocouple was calibrated by correlating its emf with the scale readings of an ASTM 68C thermometer at 10 points from 185°C to 194°C, in a constant temperature oil bath. The ASTM 68C thermometer had been calibrated at the ice point and at 190°C in the Thermometry Group of the NIST Process Measurements Division by means of a platinum resistance thermometer. The temperature indication by the scale of the cylinder thermometer in the extrusion plastometer was calibrated by correlating the thermometer scale readings with the temperature indicated by the emf from the calibrated thermocouple with its hot junction stationed in a column of polythylene melt in the bore, as described in paragraph 5.5.2 of the ASTM method. Thermal conductivity between cylinder and thermometer was enhanced by adding Wood's metal to the thermometer well in the cylinder. The uncertainty in the final temperature indication may be regarded as equal to the nominal limit of resolution on the scales of the ASTM 68C thermometer, and of the thermometer in the extrusion plastometer, 0.1 °C. The effect of a 0.1 deg error in temperature on the melt index of SRM 1473 is described in the subsequent section on error analysis.

2.2.2   Metering of Plastometer Components

The geometric dimensions of the cylinder, piston assembly, and dies were found to comply with the specifications described in the ASTM method.

The diameter of the cylinder bore was determined by a Brown and Sharpe model 599-281 Intrimik inner diameter (ID) micrometer[7]. The ID of the bore was measured at the bottom end (micrometer head resting on a die at the bottom), and at levels from 15 cm down from the top end, up to 2 cm from the top end, in 1 cm intervals. All of the resulting measurements were either 0.9543 cm, 0.9545 cm, 0.9548 cm, or 0.9550 cm, in compliance with the tolerance of this specification described in paragraph 5.2 of the ASTM method.

The apparent mass of the nominal 2.16 kg load was determined in the Mass Group of the NIST Automated Production Technology Division. The apparent mass of the nominal 2.16 kg load was found to be 2.1599 kg, well within the ±0.5% tolerance described in paragraph 5.4.4 of the ASTM method.

2.2.3   Alignment of Plastometer

The cylindrical axis of the bore was aligned with the gravity vector by the following plumb-line procedure.

First, a die was selected as the "target" die and stationed on the structural baseplate of the extrusion plastometer directly below the cylinder. Its position on the

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plane of the baseplate was adjusted to have the axis of its bore coincide with the projection from the axis of the cylinder bore onto that plane. This was accomplished by viewing the target die through the bores of two "sighting" dies, one stationed at its operational position in the bottom end of the cylinder bore and the other stationed at the top end of the cylinder bore. The position of the target die on the plane of the baseplate was adjusted until it appeared centered in the view from above the cylinder through the sighting dies in the cylinder bore.

Next a plumb-bob was suspended by a plumb-line from the axis of a die supported in the top end of the cylinder bore, with the pointer of the suspended bob extending down inside the bore of the target die. The leveling screws were adjusted until the pointer of the plumb-bob appeared to be centered inside the bore of the target die.

2.3   Melt Flow Rate of SRM 1473

The melt flow rates of SRM 1473 samples were determined by procedure A described in Section 9 of ASTM Method D 1238-89[8]. Standard test condition 190/2.16 was used. Thus the flow rate was determined at 190.0 ±0.1°C using a load of 2.16 kg. The flow rate of the melt was measured by a manually operated extrusion plastometer obtained from the Tinius Olsen Testing Machine Co.[7]

A 3.3 g charge of pellets was used for extrusions under the 2.16 kg load. With such a charge the 4 mm start section of the descending piston would partially enter the top of the guide collar at the end of the 6 min preheat interval without the necessity of any manipulative adjustment. The end of the 6 min preheat interval was marked as the beginning of timed extrusion by making the initial extrudate cut and discarding this preheat segment. Three timed extrudate segments were cut at 3 min intervals thereafter. After the third timed extrudate segment had been cut the remaining melt in the cylinder was purged and discarded. The piston, bore, and die were cleaned free of the polymer at the end of each extrusion.

3.   Data Analysis on the Melt Flow Rate of SRM 1473 Resin

Data from 42 charges were analyzed for the 2.16 kg load. The data from a single charge extrusion generally showed a very slight flow rate decrease as one went from the first timed extrudate to the third timed extrudate. Such a drift is reflected in the data shown in Table 1.

Following the ASTM Method D 1238-89, the average melt flow rate of the first timed extrudate is taken as the melt flow rate of the polymer. Thus the melt flow rate of SRM 1473 is 1.29 g/10 minutes with a standard deviation of a single measurement of

0.020 g/10 min.   The standard deviation reported above includes bottle to bottle, charge to charge, and day to day variability but does not include our estimates of systematic errors in the measurement.   Both of these kinds of errors will be discussed in the following sections.

4. Error Estimates

4.1   Repeatability and Sampling Errors

In this section we discuss the error arising from variations of the measured melt flow rate arising from sampling and bottling differences.

4.1.1   Bottle to Bottle Variability

As described in Section 2.1, 14 bottles were selected for measurement from the original bottling.   We measured three charges from each bottle.   From these we were able to estimate bottle to bottle variation.   The mean value of the melt flow rate for any bottle was found to lie within two standard deviations of the mean value of the melt flow rate for all the charges.

4.1.2   Day to Day Variability

Eight melt flow rate experiments could be done in a single day.   The plastometer was occasionally shut down for a few days before the next set of significant extrusions were conducted. With this procedure we hoped to show the effects of day to day variability on the equipment and have that reflected in our standard deviation. However in general the day to day variability was small compared to the charge to charge variability.

4.2   Systematic Errors

Obtaining a systematic error analysis of the melt flow rate is a difficult matter since the melt flow rate is not a fundamental property of the material and there is no simple relationship describing its estimation. Nonetheless we shall make an effort in this section to estimate the possible causes of error and their contribution to the overall actual error in the measurement made.

4.2.1   Instrument Variability

As noted before the estimates of our own repeatability are in Table 1. These data reflect the repeatability of our own experiments and do not reflect any instrument-to-instrument or operator-to-operator variation since we had only one of each.

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However, Table 5 in ASTM D 1238-89 provides a means of estimating the error among a large population of instruments and operators applying procedure A. Their tabulated results include the average flow rate of a polyethylene under condition 190/2.16 of 2.04 g/10 min resulting from determinations by procedure A at nine laboratories. The standard deviation of this average is ± 0.079 g/10 min. from which they compute a reproducibility within ± 0.224 g/10 min, or ± 11% of the mean. The reproducibilities listed in the ASTM tables are 95% confidence interval limits. Since the melt index of this polyethylene used in the ASTM interlaboratory study is closely comparable with the melt index determined for SRM 1473, the results in Table 5 of the ASTM method provide an estimate for the reproducibility of the certificate melt index of SRM 1473 within 1.29 ± 0.14 g/10 min in 95% of the results from a large population of laboratories using different instruments and different operators. This uncertainty due to instrument and operator variability is also given in Table 2 of this report.

4.2.1.1 Die Variability

We did have two different dies. These dies are made of specially hardened steel and are supplied by the Stevens Testing Instrument Co.[7]

We ran the melt flow rate determinations alternately using one die and then the other. The means of the melt flow rates from the two dies differed by considerably less than one standard deviation.

4.2.2 Measurement Errors

An effort is made to estimate the intrinsic error in the measurement . We do this by considering the errors in the measured quantities (mass and time) as well as the errors in the controlled quantities (temperature and the specifications on the instrument). The melt flow rate, F, is given by

$$F = Mass/Time$$

Thus any error in the melt flow rate is then

$$dF/F = dm/m + dt/t + (dF/dT)(dT/T)$$

These terms are : dm/m is the fractional error in the weight of the samples--this is taken to include the possible error in the weighing due to balance error and moisture pickup, and also to extrudate mass errors incurred due to the cutting of the material. dt/t is the fractional error in the timing of the extrudate--this is taken to include only the timing error. The dT/T term is the term arising from the inaccuracy of the

temperature controller and temperature calibration. The causes
of these errors are discussed in the next few paragraphs. These
with the other errors are given in table 2 as well as an estimate
of the overall error resulting from all sources.

4.2.2.1 Weighing Error

The extrudate segments were weighed on a balance with 0.01
mg resolution in mass indication. Replicate weighing of the
segments agreed to within ± 0.01 mg. in general and never varied
beyond ± 0.02 mg at the extreme. Paragraph 9.9 of ASTM Method
D 1238-89 instructs the experimenter to "weigh the extrudate to
the nearest 1 mg when cool." It should be noted that 1 mg of
this polymer occupies very nearly 1 microliter of volume which is
probably a valid estimate of the uncertainty in the cut
considering the technique of cutting the extrudate.
Consequently, the uncertainty in extrudate mass resulting from
the process of cutting the segment is estimated dm= ± 1 mg. The
overall average apparent mass m = 377 mg for SRM 1473 was
calculated for all the extrudate segments in the characterization
of this polymer. Consequently, the relative error in weight
(dm/m) entering into the melt index characterization is

$$dm/m = \pm 1 \text{ mg}/377 \text{ mg} = 0.3\% \quad \text{for SRM 1473}$$

The extrudate segments were routinely weighed within one
hour after having been cut, in compliance with the instruction in
paragraph 9.9 of the ASTM method. Considering the hydrophobic
character of polyethylene it would not be anticipated that the
extrudate would accumulate moisture beyond the initial cooling
stage prior to being weighed. On a few occasions during the
characterization of another polyolefin, extrudate segments, which
had been weighed at the end of a day, were weighed again on the
following day without detecting any statistically valid change of
weight within the groups. All individual changes, either
positive or negative, were much smaller than 1 mg. Consequently,
it may be assumed that there was no detectable error in weight
attributable to moisture adsorption, and that the error in
extrudate weight is overwhelmingly dominated by the volume
uncertainty attending the process of cutting the extrudate.

4.2.2.2 Timing Error

The interval (t) between extrudate cuts for SRM 1473 was
measured with a battery powered stopwatch having a 0.01 sec
resolution in time indication. The extrudate cut was timed to
better than 0.1 sec . Consequently the timing error is 0.1 sec.
as a practical estimate. Hence, the relative error in time
interval may be expressed

$$dt/t = \pm 0.1 \text{ sec}/180 \text{ sec.} = 0.06\%$$

4.2.2.3 Temperature Error

The thermal profile of an undisturbed column of polyethylene melt was scanned along the cylindrical axis of the cylinder bore. This experiment was conducted in another extrusion plastometer during an earlier determination of the melt flow rate of SRM 1475 and SRM 1476. The temperature in the stationary melt column was measured with a thermocouple hot junction stationed at different heights above the top surface of the die, along the cylindrical axis of the bore. Throughout the experiment the indicated cylinder temperature remained at 190.0°C ± 0.1°C in all observations of the mercury column thermometer routinely used to indicate cylinder temperature. The results are listed in Table 3.

Inspection of the tabulated results indicates that the departure of melt temperature from the indicated cylinder temperature is within ± 0.1 deg, at any location in the melt column from 12 mm above the die upward. It may be observed that the 0.7 - 0.8 deg drop in temperature, between the 12 mm and 1 mm levels above the die, occurred in the melt column undisturbed. This temperature drop is probably at least partially erased by the downward flow of melt during an extrusion. It is also possible that the apparent smaller variation of temperature with height from 12 mm upward may be a variation of temperature with time at which the temperature was determined at the different levels. Because of its considerably greater heat capacity and volume displacement, the mercury column thermometer is a very effective temperature averaging device and far less responsive to brief and small changes in temperature, in comparison with a very small and intensively responsive thermocouple junction. Regardless of whether the temperature is changing with time or with height, or both height and time, the maximum temperature error (dT) may be estimated as ± 0.1 deg.

The greater significance of temperature error is its effect on the melt index of this polymer. The effect of temperature error on the melt index of SRM 1473 was determined by conducting a set of five extrusions at 188.4°C and another set of five extrusions at 191.5°C. The two sets of five extrusions at the different temperatures were conducted with charges all taken from the same bottle of polyethylene resin.

The resulting average melt flow rates from the first timed extrudate segments of these extrusions and from those at 190°C are listed in Table 4. Linear regression analysis of melt flow rate versus temperature provided the equation with the coefficients also listed in Table 4. The slope of the resulting equation, 0.040 g/10 min per deg, is the quantitative expression for the temperature dependence of the melt flow rate of SRM 1473

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at temperatures near 190°C. A plot of melt flow rate versus temperature is seen in Figure 1.

Considering the nominal temperature uncertainty, dT = ± 0.1 deg, this result affords an estimate of ± 0.004 g/10 min for the uncertainty in melt index of SRM 1473 due to uncertainty in temperature. The relative uncertainty in melt index of the first timed extrudate due to uncertainty in temperatures, is then 0.3%.

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1. H. P. Frank: "Polypropylene", p.75, Gordon and Breach Science Publishers, N.Y. (1968).

2. S. Matsuoka and T. K. Kwei, in "Macromolecules, an Introd. to Polymer Science", p.346, ed. by F. A. Bovey and F. H. Winslow, Academic Press. N.Y. (1979).

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4. J. L. Throne: "Plastics Process Engineering", p.p. 239-247, 288, Marcel Dekker, Inc., N.Y. (1979).

5. M. G. Natrella: "Experimental Statistics", NBS Handbook 91, Section 1-4, p. 1-6.

6. The Rand Corp.: "A Million Random Digits with 100,000 Normal Deviates", The Free Press, N.Y. (1955).

7. Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily the best available for the purpose.

8. 1990 Annual book of ASTM Standards, Vol. 08.01, pp 395-403.

Table 1
Melt Flow Rate of
SRM 1473 at a Load of 2.16 kg

	Mean(a)	95% Confidence Interval of Mean (a)	Standard Deviation of a Single Measurement (a)
1st timed extrudate(b)	1.287	1.280 to 1.293	0.020
2nd timed extrudate(b)	1.262	1.257 to 1.268	0.018
3rd timed extrudate(b)	1.236	1.231 to 1.241	0.016
Overall data range (a)		1.205 to 1.330	

(a) gm/10 min
(b) mean value for charges

Table 2

Estimates of Errors in Melt Flow Rate of SRM 1473 Polyethylene
Under Condition 190/2.16

1. Overall estimated repeatability
   of experiment   1.6%
   (see Table 1)

2. Instrument Variability   11%
   as estimated from error reported
   in ASTM method

3. dm/m*100   0.3%

4. dt/t *100   0.06%

5. dT/T*dF/dT   0.3%

6. Overall estimated error   12%

Table 3

Variation of Temperature with Height in Undisturbed Melt in Cylinder Bore

Height Above Die, mm	Melt Temp. Degrees C
48	190.09
36	189.93
24	189.97
12	189.94
1	189.23

Table 4

Variation of SRM 1473 Melt Flow Rate with Temperature

Temperature °C	Mean Flow Rate g/10 min	Std. Dev. of a Single Measurement g/10 min
188.4	1.227	0.016
190.0	1.287	0.020
191.5	1.352	0.034

Linear Regression Analysis, Melt Flow Rate = AT+B, T in °C

Coefficient

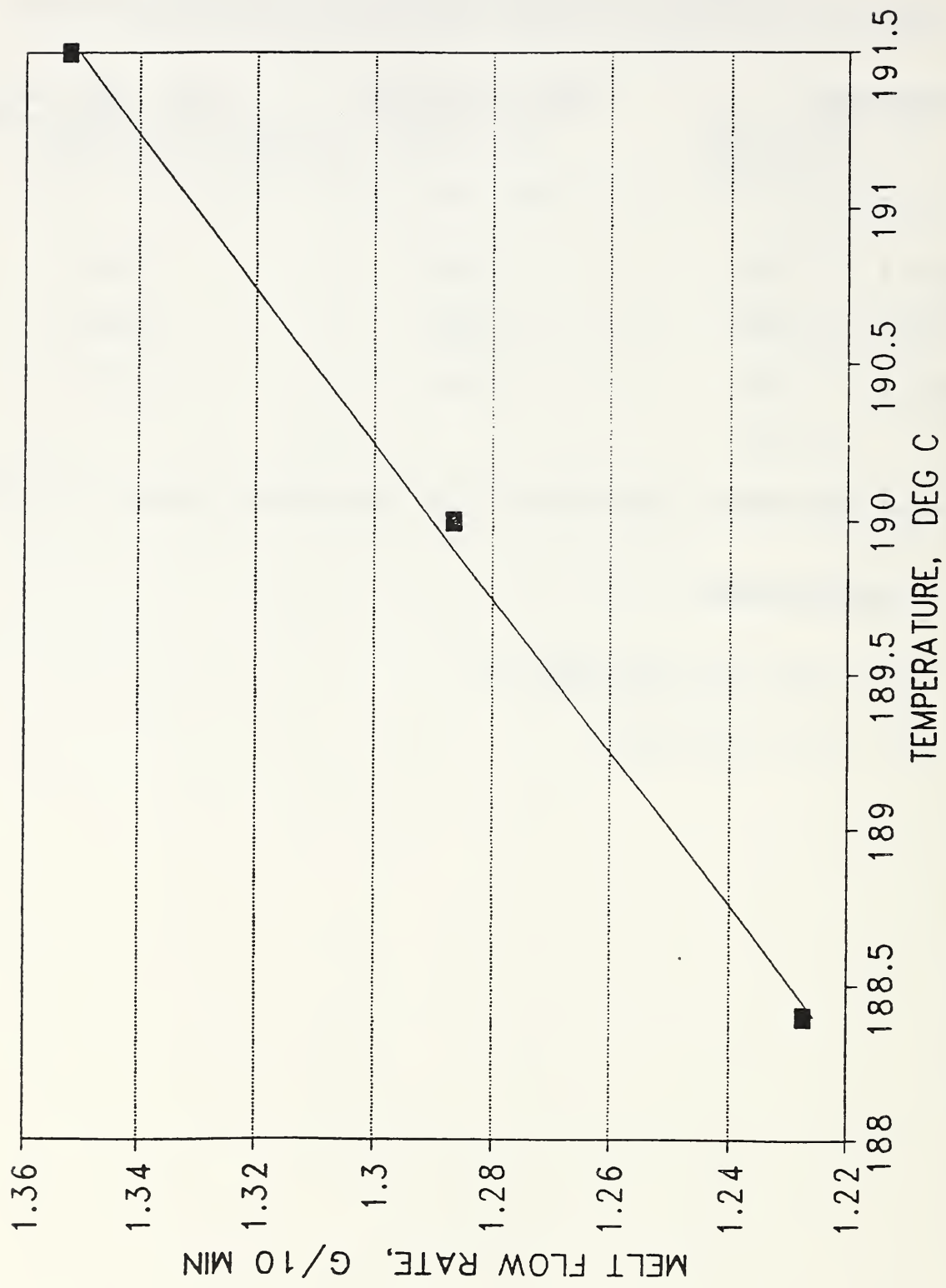A = 0.040 g/10 min per °C

B = -6.39 g/10 min

Figure 1. Temperature Dependence of Melt Flow Rate of SRM 1473 Under 2.16 kg. Load Near 190°C

National Institute of Standards & Technology

Certificate

Standard Reference Material 1473

Low Density Polyethylene Resin

This Standard Reference Material (SRM) is intended primarily for use in calibration and performance evaluation of instruments used in polymer technology and science for the determination of the melt flow rate. The SRM is supplied as white pellets of polyethylene in a 60 gram unit.

This material is certified for melt flow rate using ASTM Method D 1238-89. Standard test condition 190/2.16 was used. Thus, the flow rate was determined at 190.0 ± 0.1°C using a load of 2.16 kg. The flow rate of the melt was measured by a manually operated extrusion plastometer. Under this condition the melt-flow rate for this material is 1.29 g/10 minutes with a standard deviation for a single measurement of 0.020 g/10 minutes and with 41 degrees of freedom. [1]

The supplier for this material was Quantum Chemical Corp., USI Division, Cincinnati, OH.

Notice and Warnings to Users

Expiration of Certification: This certificate will be valid for five years from the date of shipment.

Storage: SRM 1473 should be stored in the tightly closed, original bottle under normal laboratory conditions.

The technical coordination leading to certification of this material was provided by C.C. Han with technical measurement and data interpretation provided by J.R. Maurey and C. M. Guttman of the NIST Polymers Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J. C. Colbert.

REFERENCE

[1]   J. R. Maurey, and C. M. Guttman, Studies on the Melt Flow Rate of SRM 1473, A Low Density Polyethylene Resin, NISTIR 4627.

Gaithersburg, MD 20899
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William P. Reed, Chief
Standard Reference Materials Program

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11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

The melt flow rate of SRM 1473, a low density polyethylene, was determined to be 1.29 g/10 min at 190°C under a load of 2.16 kg using the ASTM Method D 1238-89. The average results from 42 determinations on samples with a standard deviation of a single measurement of 0.020 g/10 min. A small but measurable drift from the first timed extrudate to the third timed extrudate was observed.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

extrudate; extrusion plastometer; melt flow rate; melt index; polyethylene; reference material

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