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Dynamic mechanical properties of an ultra high molecular weight polyethylene reference material SRM 8456

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Abstract The dynamic mechanical analysis storage and loss modulus of a NIST SRM 8456 Ultra High Molecular Weight Polyethylene is determined in 3-point bending in an interlaboratory test. Mean values of (1.18 ± 0.17) GPa for storage modulus and (62.0 ± 9.0) MPa for loss modulus were determined at 21 °C. In addition, the temperature (molecular) spectrum for the material is observed between −100 and +100 °C. These results permit the use of this material for calibration, conformance, and performance demonstration for dynamic mechanical analyzers.

Keywords Calibration · Dynamic mechanical analysis · Loss modulus · Polyethylene · Reference material · Storage modulus

Introduction

Reference materials of known properties are commonly used to calibrate, verify, or validate the performance of test instruments or methods. In dynamic mechanical analysis, spring steel is commonly used to calibrate the apparatus. The value of 192 GPa for carbon steel is commonly taken as a calibration value [1, 2]. Storage modulus is taken to be equivalent to this tensile modulus value for this highly elastic material. No corresponding reference material exists for loss modulus.

The United States National Institute of Standards and Technology (NIST) offers an ultra high molecular weight polyethylene (UHMWPE) reference material SRM 8456 certified for a value of tensile modulus as measured by ASTM International standard D698 [3]. However, polymeric materials such as the UHMWPE are not purely elastic and the tensile modules value may not be taken directly as the storage modulus value.

An interlaboratory test was performed using ASTM International standards E2254 [4] and E2425 [5] to determine the consensus value for storage and loss modulus of the UHMWPE.

Method

The original SRM 8456 sample was purchased from the NIST as a right circular cylinder 7.6 cm in diameter and 150 cm in length. It was machined by Emco Industrial Plastics (Warren, PA) into test specimens approximately 3 mm in thickness, 12.5 mm in width, and 50 mm in length. Each interlaboratory test participant received five test randomly selected specimens. Participants characterized the replicate specimens by ASTM standards E2254 and E2425 at temperatures between 20 and 22 °C and at 1 Hz. All instruments were calibrated for storage and loss modulus according to the manufacturer's recommendation. Three-point bending was the recommended module of testing.

Upon completion of the replicate determinations for storage and loss modulus, the volunteers were asked to perform a single step-and-soak measurement of storage and loss modulus every 10 °C from −100 to +100 °C.

Results were obtained from 15 laboratories described in Table 1. (One volunteer performed tests on two instruments.) All results were coded upon receipt and results were examined blindly using ASTM standard E691 [6]. Table 2 lists the methods of calibration, modes of testing, manufacturer, and model of the instrument for each responding laboratory.

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Table 1 Participating laboratories

Volunteer	Affiliation	Location
Ramon Artiaga	University of Coruna	Ferrol Spain
Tianhong (Terri) Chen	TA Instruments	New Castle DE USA
Antonio Guerreo Conjo	University de Sevilla	Sevilla Spain
Susan Cabral da Fonesceca	National Lab. of Civil Eng.	Lisboa Portugal
John Moyland	Delsen Testing Laboratories	Glendale CA USA
Maria Licher	Polymer Solutions	Blacksburg VA USA
Laura Littlejohn	Ashland	Dublin OH USA
Phuong-Thao Luong	Arkema	King of Prussia PA USA
Kevin Menard	PerkinElmer	Denton TX USA
Sanya Matecic Musanic	Brudarski Institute	Zagreb Croatia
Mike Rich	Michigan State University	East Lansing MI USA
Steve Sauerbrunn	Mettler-Toledo	Newark DE USA
Eric Thompson	Reichhold	Durham NC USA
John Tria	Ascend Performance Materials	Gonzalez FL USA

Results

Results were characterized in four parts. Parts 1 and 2 are quintuplicate replicate measurements at 20–22 °C of storage modulus and loss modulus, respectively. Parts 3 and 4 involve gathering a single set of storage and loss modulus information, respectively, at 10 °C intervals from −100 to +100 °C to create the temperature "molecular" spectrum of the material.

Storage modulus (at 1 Hz and 21 °C)

The quintuplicate determinations of storage modulus were statistically treated by ASTM International standard E691 [6] to determine any within-laboratory *k* precision outliers. (*k* is the ratio of the standard deviation for results from a single laboratory to the pooled standard deviation of all laboratories.) Three laboratories (Labs 3, 10, and 13) were observed to be *k* within-laboratory precision outliers. These results were examined and a single value was observed to exceed the critical *k* value. This single outlying result was discarded and replaced with the mean value of the remaining data points as permitted in E691.

The results presented in Table 3 from 15 laboratories produced a mean storage modulus value of 1.184 GPa, with a within-laboratory repeatability standard deviation of 0.041 GPa and a between-laboratory reproducibility

Table 2 Apparatus

Lab (no)	Calibration method/material	Storage modulus calibration value/GPa	Mode	Instrument
1	Force/displacement	–	3-point bend	TAI^{a} Q800
2	Force/displacement	–	3-point bend	MT^{b} 861
3	Steel		3-point bend	TAI^{a} 2980
4	Force/displacement	–	3-point bend	TAI^{a} Q800
5	Steel		3-point bend	TAI^{1} RSA III
6	Steel	192	Dual cantilever	TAI^{a} Q800
7			Dual cantilever	TAI^{a} 983
8	Force/displacement	–	3-point bend	TAI^{a} Q800
9	Force/displacement	–	Dual cantilever	TAI^{a} Q800
10			3-point bend	Rheo^{c} DMA IV
11	Steel	210	3-point bend	TAI^{a} RSA III
12	Polycarbonate	2.35	3-point bend	TAI^{a} 2980
	Steel	199		
13	Epoxy composite	13	3-point bend	PE^{d} DMA 7E
14	Epoxy composite	13	3-point bend	PE^{d} DMA 7E
15	Steel		3-point bend	PE^{d} DMA 8000

[a] TAI = TA Instruments

[b] MT = Mettler-Toledo

[c] Rheo = Rheometrics Scientific (now TA Instruments)

[d] PE = PerkinElmer

Table 3 Storage modulus experimental values

Lab (no)	Storage modulus/GPa	Loss modulus/MPa
1	1.214 ± 0.029	49.38 ± 0.48
2	1.290 ± 0.024	70.00 ± 1.3
3	1.151 ± 0.066	66.69 ± 2.8
4	1.210 ± 0.014	56.04 ± 1.7
5	1.007 ± 0.065	60.27 ± 1.5
6	1.215 ± 0.017	56.63 ± 0.51
7	1.224 ± 0.029	45.51 ± 1.4
8	1.236 ± 0.057	66.49 ± 2.0
9	1.272 ± 0.050	54.59 ± 2.2
10	1.265 ± 0.021	62.71 ± 2.0
11	1.552 ± 0.045	–
12	1.191 ± 0.017	69.38 ± 1.8
13	0.900 ± 0.032	70.50 ± 4.1
14	0.903 ± 0.032	68.38 ± 3.7
15	1.140 ± 0.055	70.99 ± 4.1
Mean	1.184	61.97
Repeat. std. dev.	± 0.041	± 2.4
Reprod. std. dev.	± 0.16	± 8.6

standard deviation of 0.16 GPa. The within and between-laboratory standard deviations are combined using the root-mean-square method to produce the "gage *R* and *r*" precision value of ±0.17 GPa with 56 degrees of experimental freedom according to ASTM standard E1970 [7].

Loss modulus (at 1 Hz and 21 °C)

The quintuplicate determinations of loss modulus were similarly treated. Labs 3, 10, and 15 were found to be within-laboratory repeatability *k* outliers and were treated by removing the single outlying data point and replacing it with the mean of the remaining four values. Lab 11 was found to be a between-laboratory reproducibility *h* outlier and results from this laboratory were not included in determining the final results. (*h* is the ratio of the deviation from the mean of results for a single laboratory to the standard deviation of all laboratories.)

The results from 14 laboratories presented in Table 3 produced a mean loss modulus value of 62.0 MPa with a within-laboratory repeatability standard deviation of 2.4 MPa and a between-laboratory reproducibility standard deviation of 8.6 MPa. The within and between-laboratory standard deviations were combined as the gage *R* and *r* value of ±9.0 MPa with 53 degrees of experimental freedom.

Comparison to reference storage modulus value

The report of investigation for the Reference Material SRM 8456 lists the Young's modulus (as measured by ASTM standard D638) for the UHMWPE as 1.258 GPa with a within-laboratory repeatability uncertainty of 0.022 GPa and a between-laboratory reproducibility uncertainty of 0.044 GPa [8]. Combining these results as the gage *R* and *r* yields a precision of ±0.049 GPa.

Young's modulus (E) is related to storage (E') and loss modulus (E'') by the equation [9] $E'^2 = E^2 - E''^2$. The storage modulus calculated from the reported Young's and determined loss modulus values, results in (1.26 ± 0.05) GPa, where the standard deviation is determined using the method of propagation of uncertainties. When the storage modulus for the reference material of (1.26 ± 0.05) GPa is compared to the experimentally determined value of (1.18 ± 0.17) GPa, a statistically insignificant small bias of −0.07 GPa or 6.3% is observed (student "*t*" test), i.e., these values may be considered equivalent.

Storage modulus temperature spectrum

Only 13 laboratories reported temperature spectrum information. The storage modulus values at 21 °C in the temperature spectrum data were first compared for consistency with the mean values for the replicate determinations for the same laboratory. All laboratories were in agreement with their corresponding replicated determinations.

The storage modulus temperature spectrum values were initially plotted in overlay using Microsoft Excel® as shown in Fig. 1. The data were then averaged on a temperature point-by-point basis calculating the mean value and standard deviation for each point. The mean storage modulus values along with their respective between-laboratory standard deviations are presented in tabular form in Table 4 and, for ease of interpretation, as a graph Fig. 2. The mean temperature spectrum value at 21 °C of (1.21 ± 0.12) GPa is in agreement with the storage modulus replicated determination mean of (1.18 ± 0.17) GPa linking the temperature spectrum to the reference Young's

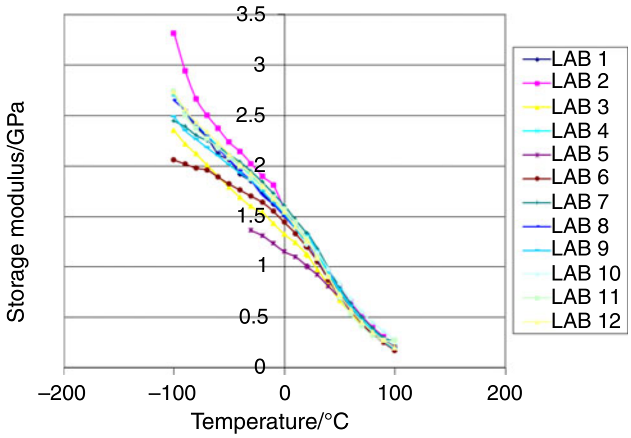

Fig. 1 Storage modulus temperature spectrum for all reported results

Table 4 Mean storage and loss modulus as a function of temperature

Temperature/°C	Storage modulus/GPa	Loss modulus/MPa
−100	2.62 ± 0.33	111 ± 64
−90	2.46 ± 0.24	78 ± 39
−80	2.30 ± 0.22	65 ± 32
−70	2.20 ± 0.19	60 ± 27
−60	2.10 ± 0.18	57 ± 21
−50	2.01 ± 0.17	56 ± 19
−40	1.91 ± 0.16	57 ± 17
−30	1.78 ± 0.21	57 ± 14
−20	1.67 ± 0.18	55 ± 13
−10	1.58 ± 0.17	53 ± 12
0	1.46 ± 0.15	50 ± 10
10	1.34 ± 0.13	49.4 ± 7.9
20	1.20 ± 0.11	58.1 ± 9.7
21	1.21 ± 0.12	60 ± 11
30	1.07 ± 0.073	72.8 ± 9.0
40	0.897 ± 0.055	83.8 ± 7.0
50	0.732 ± 0.049	89.9 ± 9.2
60	0.588 ± 0.044	87.4 ± 8.3
70	0.464 ± 0.038	79.1 ± 7.5
80	0.362 ± 0.034	67.7 ± 6.6
90	0.279 ± 0.028	56.4 ± 5.4
100	0.214 ± 0.034	47.1 ± 5.1

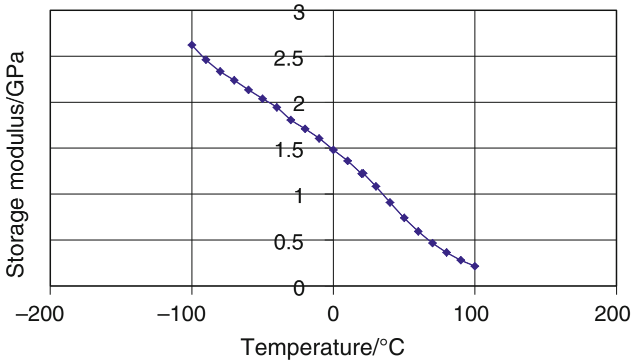

Fig. 2 Mean storage modulus temperature spectrum

modulus value. The overall pooled relative standard deviation from −90 to +90 °C is ±9.1%.

Loss modulus temperature spectrum

Similar to the storage modulus, the loss modulus values were first compared to the mean value of the replicated determinations at 21 °C. One laboratory, Lab 11, showed a different result between the replicate determinations and the loss modulus spectrum. This observation supports the determination above that Lab 11 replicates were a reproducibility *h* outlier. The Lab 11 loss modulus spectrum information was retained and included in the subsequent data treatment.

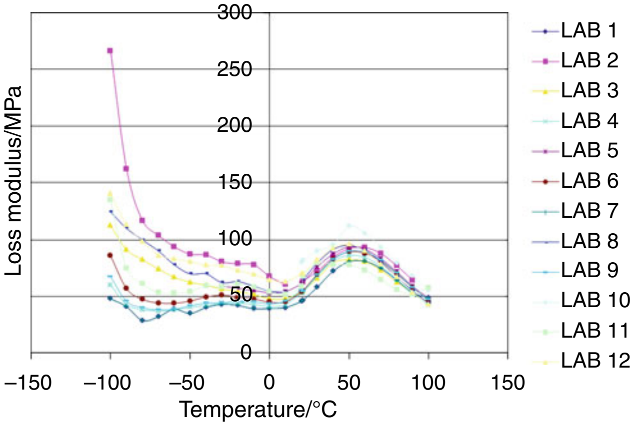

Fig. 3 Loss modulus temperature spectrum for all reported results

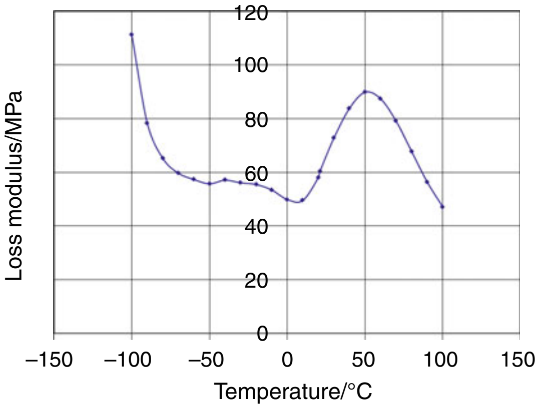

Fig. 4 Mean loss modulus temperature spectrum

For comparison purposes, the loss modulus temperature spectrum information was initially plotted in the overlay shown in Fig. 3. Above ambient temperature, the data show reasonable consistency, but below ambient temperature considerable variation is seen. The data for all 13 laboratories were then averaged on a point-by-point basis. Twelve of the 19 temperature points for Lab 13 showed loss modulus values that were more than two standard deviations from the overall mean value. For this reason, the loss modulus temperature spectrum for Lab 13 was determined to be an outlier and the results were excluded from further consideration.

The loss modulus temperature spectrum for the remaining 12 laboratories was recalculated and the mean values are presented in Fig. 4. The mean temperature spectrum value at 21 °C of (60 ± 11) MPa is in agreement with the mean loss modulus replicated determination of (62 ± 9) MPa. The pooled relative standard deviation for the temperature range from −30 to 100 °C is ±10%.

The loss modulus temperature spectrum shows the anticipated α crystal transition near 50 °C, the side-chain β transition near -40 °C, and the onset to the γ transition crankshaft rotation near -20 °C. Khanna and coworkers discuss the sources of these transitions in detail [10].

Summary

The storage and loss modulus of an ultra high molecular weight polyethylene material was determined by an interlaboratory test using ASTM International standards. The results are consistent with the certified tensile modulus value reported for the material. In addition, a detailed storage and loss modulus temperature spectrum is constructed covering the temperature range from -100 to $+100$ °C. These values permit this material to be used as a calibration, conformance, or performance reference material for dynamic mechanical analysis.

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