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The results of a round-robin study conducted on glass transition temperature determinations using hydroxy-terminated polybutadiene polymers [1]

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Abstract

A round robin study was conducted on glass transition temperature (T_g) measurements performed on a hydroxyl-terminated polybutadiene (HTPB) gumstock and an HTPB inert propellant. The following instruments were used for analysis: rheometrics mechanical spectrometers, differential scanning calorimeters, and thermomechanical analyzers. The objective was to obtain data from several different laboratories using a variety of instruments with comparable methods, and to determine the variance between methods and laboratories. Eight laboratories participated and statistical analyses on T_g data are presented. Results show that the variance between the methods does not differ significantly from the variance between the different laboratories using the same method. Hence data between the different methods from within a laboratory cannot be distinguished from data between laboratories using the same method.

INTRODUCTION

This study was initiated because the sources and magnitude of variations in glass transition temperature (T_g) data between laboratories and between test methods are not well defined. Current analysis is being conducted using several methods with a variety of instrumentation. By sending out a sample with a known sample handling history and having it analyzed by the participating laboratories, the degree of variance within a laboratory using different techniques and the degree of variance between laboratories using the same methods (independent of the manufacturer they use) can be established.

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Three methods were compared in this study: (1) rheometric mechanical spectrometer (RMS), used to measure the viscoelastic properties of a material by applying a controlled sinusoidal deformation to a specimen and measuring the resultant torque; (2) differential scanning calorimetry (DSC), used to measure the differential heat flow into (endothermic) or out of (exothermic) a specimen, compared with an inert reference (usually an empty specimen pan); (3) thermomechanical analysis, used to measure a change in the linear or volumetric dimensions of a specimen as a function of temperature, time of force [1].

Eight laboratories participated in this study, although some laboratories performed only one or two of the methods. Method test parameters were agreed upon by the participating laboratories and were setup to be comparable with existing routine procedures. Two propellant formulations were used for this study: (1) hydroxy-terminated polybutadiene (HTPB) gumstock consisting of R-45M cured with isophorone diisocyanate (IPDI); (2) HTPB inert propellant consisting of R-45M cured with IPDI containing a 70% mixture of aluminum and sodium chloride as filters.

EXPERIMENTAL

Rheometric mechanical spectrometer

A specimen with the approximate dimensions of 60 mm × 6 mm × 12 mm is mounted into a set of torsion rectangular fixtures and clamped in place. The specimen is placed in tension (5%) and allowed to relax. The first test is a rough estimate and is run from high temperature (0°C) to low temperature (−100°C) at increments of 10°C with an equilibrium time of 3 min at each temperature and with a measurement time of 1 min. The T_g is reported when the ratio of the loss modulus to storage modulus (Tan Delta) maximizes. Additional tests are performed using a starting temperature 20°C above the first T_g value calculated. An equilibrium time of 3 min and a measurement time of 1 min are again used but the temperature is lowered at 1.0°C increments during these runs. The spindle is adjusted periodically during the test to zero the normal force and to prevent overstress. Because RMS also calculates the T_g using shear loss modulus G'', these data were also included for comparison.

Differential scanning calorimetry

A specimen of 15–30 mg is placed in a sealed aluminum pan and cooled to −130°C for 5 min. The samples are then heated at 10°C min^{-1} in a nitrogen atmosphere of 50 ml min^{-1} to room temperature. Data analysis is performed using instrumentation software. Temperatures at extrapolated

onset, inflection point and end of transition were reported. Temperature calibration is performed using an indium metal standard. The extrapolated onset temperature is adjusted to within 1.0°C of 156.6°C.

Thermomechanical analysis

A specimen of about 30 mg of gumstock or about 300 mg of inert propellant is cut to approximately 2.3 mm thickness with a flat surface on top and on bottom. The specimen is then placed on the sample platform and the expansion probe lowered onto the surface. The samples are cooled to −130°C for 5 min. A 5g weight is then placed on top of the probes weight tray and the LVDT zeroed. The samples are then heated at 3°C min^{-1} in a nitrogen atmosphere of 50 ml min^{-1} to room temperature. Data analysis is performed using instrumentation software. Temperature calibration is performed using the expansion probe on a indium metal standard. The extrapolated onset temperature is adjusted to within 1.0°C of 156.6°C.

RESULTS

A mean, standard deviation and 95% confidence limit were determined for each set of participating laboratory results. A Q test was used for all suspect laboratory values. A chi-squared test was used to determine whether the observed data differed significantly from the average data. Because the results were drawn from more than two laboratories, an analysis of variance (ANOVA) was performed; a within-sample variation and a between-sample variation were used to determine the degree of variations encountered in the analysis. An F-test was used to determine to what extent the variations had altered the results. A t-test was used to compare the DSC method with the other methods [2,3]. All data passed the Q test and were retained for further statistical analysis. The average T_g value for both the HTPB gumstock and the HTPB inert propellant using all data is −73.8°C. Table 1 lists the laboratories that participated in this study and Table 2 lists the methods performed in each laboratory. (Each laboratory was assigned a

TABLE 1

Laboratory participants

Atlantic Research Corporation, VA	Lockhead Palo Alto, CA
Astronautics Laboratory, CA	Morton Thiokol Inc. UT
Hercules Inc., TX	Naval Ordinance Station, MD
Hercules Inc., MD	United Technologies-CSD, CA

TABLE 2

Methods performed

Lab. no.	RMS	DSC	TMA
1	x	x	
2		x	x
3		x	
6	x		
10	x	x	
13	x	x	x
14	x	x	
15	x	x	x

random identity number; laboratories were contracted privately and informed of that number.)

DISCUSSION

Tables 3 and 4 show 95% confidence intervals for each of the methods performed on the HTPB gumstock and inert propellant. The calculated

TABLE 3

Laboratory methods 95% confidence interval for T_g (°C) of HTPB gumstock

Lab. no.	RMS Tan Delta	RMS G''	DSC	TMA
1	-78.0 ± 0.28	-83.6 ± 0.24	-70.3 ± 1.00	
2			-72.5 ± 3.79	
3			-71.6 ± 1.63	
10			-76.8 ± 0.74	-70.9 ± 0.74
13	-71.5 ± 1.59	-78.9 ± 4.26	-73.4 ± 1.60	-69.1 ± 1.65
14	-60.7 ± 6.25	-73.7 ± 3.80	-71.0 ± 0.00	
15	-78.0 ± 4.30	-85.0 ± 0.00	-70.5 ± 1.76	-72.5 ± 0.76

TABLE 4

Laboratory methods 95% confidence interval for T_g (°C) HTPB inert propellant

Lab. no.	RMS Tan Delta	RMS G''	DSC	TMA
1	-77.0 ± 2.37	-82.3 ± 1.36	-69.9 ± 3.74	
2			-70.5 ± 19.1	-77.2 ± 10.8
3			-73.7 ± 2.83	
6	-76.9 ± 24.8	-82.3 ± 2.88		
10			-76.6 ± 0.25	-65.4 ± 6.54
13	-69.0 ± 6.57	-74.5 ± 2.23	-74.9 ± 1.14	-79.3 ± 2.86
14	-59.3 ± 1.43	-67.3 ± 7.59	-68.7 ± 2.87	
15	-76.5 ± 3.31	-81.5 ± 0.92	-72.0 ± 1.27	-73.5 ± 4.04

TABLE 5

Student t-test HTPB gumstock method comparison

Method	Mean (°C)	Standard deviation (°C)	t-test	
			Calculated	Reference
DSC	−72.3	2.27		
RMS by Tan Delta	−72.1	8.16	0.020	2.260
RMS by G''	−80.3	5.12	1.673	2.260
TMA	−70.8	1.70	0.687	2.130

95% confidence intervals for laboratories 2 and 6 in the inert propellant are high owing to the wide range in data they reported. The inert propellant confidence limits are slightly larger than those of the HTPB gumstock. This can be expected because the inert propellant contains about 70% fillers which can possibly alter the heat capacity or the thermal conductivity of the polymer thus affecting the polymer T_g.

The confidence intervals for DSC and TMA are generally smaller than those for the RMS data; thus T_g by DSC and TMA are more precise than those by RMS. Each analysis method should be very repeatable because the samples were the only variable changed during the analysis.

Results of the chi-squared test indicate that the means for each method do not differ significantly between laboratories at the 95% confidence level. The ANOVA test results show that the within-laboratory mean squares are smaller than the between-laboratory mean squares for all the methods. As a result, the calculated F ratio is higher than the 95% reference value. This indicates that none of the between-laboratory data can be pooled at the 95% confidence level. Data also suggest that the participating laboratories might not be executing the same procedures within each of the methods.

In spite of the ANOVA results, the means from the TMA and RMS methods were compared with the DSC mean using the Student t-test (see Tables 5 and 6). DSC was chosen as the reference method because it was the most performed method in this study and because it had the lowest

TABLE 6

Student t-test HTPB inert propellant method comparison

Method	Mean (°C)	Standard deviation (°C)	t-test	
			Calculated	Reference
DSC	−72.3	2.87		
RMS by Tan Delta	−71.7	7.73	0.061	2.230
RMS by G''	−77.6	6.62	0.688	2.230
TMA	−73.9	6.12	0.227	2.260

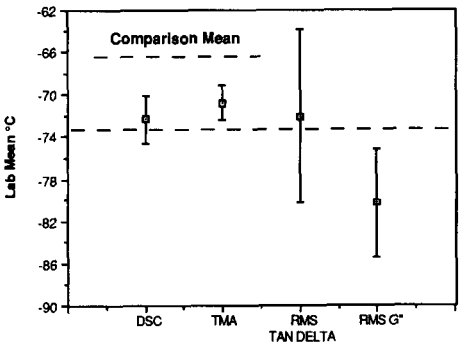

Fig. 1. HTPB gumstock.

scatter for between-method results. Results of this comparison indicate that there is no significant difference in T_g values between DSC, TMA and RMS at the 95% level. However, it must be noted that there was a wide range of variations between the methods performed.

Figures 1 and 2 show the average values and the standard deviations reported for each of the methods. Results show that RMS data reported as Tan Delta correlate better with data from DSC and TMA than the RMS data reported as G''. Owing to the difference in data reduction, it can be expected that one of the two RMS data reduction techniques would correlate better with the thermal analysis data. In the case of RMS by G'', the data were biased lower than the data from the other techniques. The average T_g for both the HTPB gumstock and the HTPB inert propellant was -73.8°C. Because of the large variance reported between the methods, it appears purely by chance that both the HTPB gumstock and the HTPB inert propellant values averaged to -73.8°C.

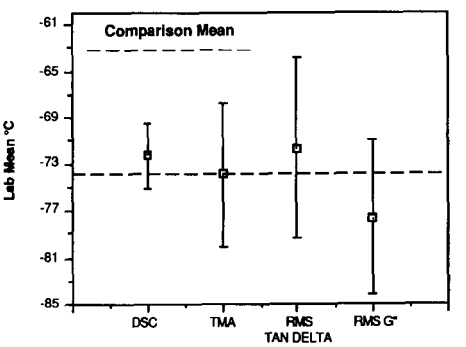

Fig. 2. HTPB inert propellant.

CONCLUSIONS AND RECOMMENDATIONS

The results of this study show that there was no significant difference in the analysis for T_g between methods or between laboratories at these test parameters. No one method proved to be significantly more accurate or precise than any other method although DSC was apparently the preferred method. The RMS results by Tan Delta should be used for T_g determinations if the results are to be compared with results from a thermal method.

In addition, the within-laboratories variation for each of the methods shows that the analyses performed in each of the laboratories was repeatable, but with the range in data reported, it shows that laboratories might not be calibrating the instruments as required or that they might not be performing the same analysis procedures. The between-laboratory variation on any one method indicated that operator experience also played a significant role in the analysis.

In order to reduce further the variances encountered between methods and between laboratories, it is recommended that a stricter set of method parameters be defined and agreed upon prior to specimen testing and that a larger number of laboratories participate in future studies. Careful compliance to these procedures must be emphasized.

ACKNOWLEDGMENTS

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