22
6-2-76
25 copy to HTIS

UCID- 17080

Lawrence Livermore Laboratory

APPLICATION OF YERZLEY MECHANICAL OSCILLOGRAPH TO TESTING OF Y3333

CELLULAR SILICONE (PROGRESS REPORT 1)

W. E. Cady

L. E. Caley

March 12, 1976

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the laboratory.

Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

APPLICATION OF YERZLEY MECHANICAL OSCILLOGRAPH TO
TESTING OF Y3333 CELLULAR SILICONE
(PROGRESS REPORT 1)

ABSTRACT

As part of our long-range goal to improve the properties of weapon cushions, we evaluated the usefulness of the Yertzley mechanical oscillograph in detecting differences among Y3333 cellular silicones. Our interest centered on the Yertzley test method, not the Y3333 cushion material. We measured four properties of Y3333: density, thickness, resilience, and effective dynamic modulus. Test samples came from five lots of standard Y3333 compound and from two lots of experimental Y3333.

Tests of the four properties revealed that individual sheets of Y3333 were homogeneous. Since sheets from the same lot differed little in properties, normal process variations had minimal effect on properties.

Although lot-to-lot variation of standard Y3333 was statistically significant, the coefficients of variation of 5% or less indicated a reasonable consistency among the five lots tested. The two experimental lots of Y3333, made with known material and manufacturing variables, showed a response to the variations but maintained low coefficients of variation.

After evaluating the Yertzley instrument, we decided that it demonstrated its worth for detecting differences among Y3333 cellular silicones.

INTRODUCTION

MASTER

Weapons use cushions to:

- Keep components centered.
- Accommodate variable gaps between components that result from machining tolerances of individual components and temperature changes during weapon life.
- Mitigate the forces from vibration, acceleration, deceleration, and temperature changes.

To accomplish such functions, cushions are assembled in weapons at ambient temperature under compression that must be maintained throughout stockpile life. These cushions consist of porous elastomers that can deform under stress (compression set) with resultant changes in load-bearing properties. There is some concern that current cushion materials (namely, the cellular silicones of Union Carbide Corporation^{*}) may develop large compression set.

Our long-range goal is to improve the properties of cushions used in weapons. We also intend to characterize presently used materials so we can follow their behavior in stockpile and predict future performance. Materials are now defined by bulk density, compression set, and load vs deflection properties. The present compression-set test appears to be so uncontrolled that it yields useless data. The load vs deflection data are too variable to be used for predictive purposes. To meet our goal, we need test methods that yield results related to the functioning of porous elastomers. Such methods must be sensitive to changes in the properties of these materials.

Although the Yerzley mechanical oscillograph is not normally applied to cellular elastomers or thin specimens, we did use it to measure the resilience and effective dynamic modulus (k'_c) of thin specimens of cellular silicone. The American Society for Testing Materials details the use of the Yerzley instrument as a standard test for the mechanical properties of elastomers.¹

In previous work, we modified and adapted the Yerzley oscillograph to test 1.5-mm-thick specimens of Y3333 cellular silicone (0.34 Mg/m^3 bulk density).² Figure 1 shows a typical oscillogram taken during that work. For consecutive repeated tests of a sample, we established average coefficients of variation of 0.7% for resilience and 0.6% for k'_c . For nonconsecutive repeated testing of the same sample at various times over an 8-month time span, we found average coefficients of variations of 2.0% for resilience and 2.5% for k'_c .

For the work reported here, we evaluated the usefulness of the Yerzley oscillograph in detecting differences among Y3333 cellular silicones. We measured four properties of Y3333: density, thickness, resilience,

^{*} Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

Fig. 1. Typical Yertzley oscillogram of 1.5-mm-thick specimen of Y3333 cellular silicone. This curve helps us calculate resilience and k'_c .

NOTICE
 This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PL9

and k'_c . Test samples came from five lots of standard Y3333 compound based on the original W97 gum lot and from two lots of experimental Y3333. We first made independent measurements of density and thickness, then ran the Yerzley oscillograph to measure resilience and k'_c .

Tests of the four properties revealed that individual sheets of Y3333 were homogeneous. Thus, random sampling for testing was valid. Since sheets from the same lot differed little in properties, normal process variations had minimal effect on properties. Sheets molded from the same lot 12 days apart showed no effect of Y3333 shelf aging.

Although lot-to-lot variation of standard Y3333 was statistically significant, the coefficients of variation of 5% or less indicated a reasonable consistency among the five lots tested. The two experimental lots of Y3333, made with known material and manufacturing variables, had much lower k'_c readings than the standard product. These latter lots showed a response to the variations but maintained low coefficients of variation.

After evaluating the Yerzley instrument, we decided that it demonstrated its worth for detecting differences among Y3333 cellular silicones. In particular, the Yerzley test appears to have the required reproducibility to be sensitive to changes in resilience and k'_c .

TEST MATERIAL

The cellular silicone compounds of Union Carbide Corporation form a family of porous elastomers that differ from each other primarily in bulk density. Table 1 presents a short history of the Y3333 end product as it emerges from the manufacturing and fabrication processes.

We tested Y3333, which is the lowest-density cellular silicone in use (0.34 Mg/m^3 bulk density). This silicone is the most difficult one to formulate and fabricate. It also is most suspect in its long-term retention of load-bearing properties.

All the numerous steps in forming cellular silicone compounds can contribute to variations in the Y3333 material. To date, only two lots of W97 gum have been used in the preparation of many lots of Y3333.

The fabrication process consists of these main steps:

- Compression die molding at 106°C for a short time (e.g., 15 min).
- Washing in boiling water for about 5 h.

Table 1. Raw-material manufacturing and end-product fabrication of cellular silicone.

Sequence of development	Product name	Product definition
Raw-material manufacturing (Union Carbide Corporation)	Gum	Polysiloxane terpolymer (W97 or Y3976)
	Y1668	Gum + SiO ₂ (Cabosil) + additive, prior to heat treatment
	Base compound Y3219	Y1668 after heat treatment to remove volatiles
End-product fabrication (Bendix Corporation)	Cellular silicone compound Y3333	Y3219 + curing agent ^a + void-former (urea)
	Y3333 cellular silicone	Cellular silicone compound Y3333 after press cure, removal of urea, and postcure

^a2,4-dichlorobenzoyl peroxide (CADOX TS-50 paste of 50% peroxide with silicone fluid).

- Drying in air at 149°C for 4 h.
- Postcuring in air at 249°C for 24 h.

Normal variations in processing controls could cause variations in end-product properties. Bendix Corporation fabricated the seven lots of Y3333, each of which consisted of 1.5-mm-thick sheets of varying dimensions.

TEST PROCEDURE

We tested 29-mm-diameter disk specimens from 1.5-mm-thick Y3333 sheets to establish:

- Sheet uniformity.
- Variation among sheets from the same lot.
- Baseline data for standard Y3333.
- Data for some nonstandard (experimental) Y3333 lots with known variations.

For sheet uniformity, we tested three sheets for thickness, density, percent resilience, and k'_c : one 20-cm-square (sq) sheet from cellular-silicone compound lot P-22-1 in 18 places, one 20-cm-diam sheet from lot Z-18-1 in 13 places, and a 15-cm-sq sheet from the same lot in nine places.

For variation among sheets from the same lot, we tested the two sheets from lot Z-18-1 as just described. We also tested three 20-cm-sq sheets from lot D-29-1 in three places per sheet for thickness, resilience, and k'_c ; we did the same for two sheets from lot Y-6-3.

For baseline data on standard Y3333, we tested lots P-22-1 and D-29-1 plus three samples each from 20-cm-sq sheets of lots L-3-1, L-11-1 and Y-6-2 for a total of five lots of standard Y3333.

Standard Y3333 is based on W97 gum, DuPont urea, and the catalyst 2,4-dichlorobenzoyl peroxide. The first variation from standard that we checked was lot Z-18-1, which once contained Nipak urea and was made from the second and current lot of W97 gum. The second variation we tested was lot Y-6-3, which was based on DuPont urea and Y3976 gum (an ethyl-end-blocked variation of W97 gum). We tested three samples from each of two 20-cm-sq sheets of lot Y-6-3. These two sheets of lot Y-6-3 were molded 12 days apart. Since standard Y3333 base compound may have a shelf life of 15 days, the two sheets of lot Y-6-3 give an insight into the shelf aging characteristics of a modified Y3333 compound.

RESULTS

Sheet Uniformity

Because sheets are large in area compared to our sample size of 29 mm diam, it is essential to know if our sample is representative of the sheet. Thickness depends on flow of material and uniformity of the mold cavity. Density depends on the uniformity of mix in the Y3333 compound and on uniformity of compaction of the materials in the mold. Resilience and effective dynamic modulus depend on the uniformity of heat distribution throughout the sheet during time of press cure.

Sheet uniformity is illustrated by the data in Table 2 for the 18 samples taken from the 20-cm-sq sheet of lot P-22-1 according to the sampling pattern of Fig. 2. We sampled the 20-cm-diam sheet and the 15-cm-sq sheet from lot

Fig. 2. Sample positions for 20-cm-sq sheet from lot P-22-1 (Y3333 cellular silicone).

Z-18-1 in a similar manner. Table 3 summarizes the data for all three sheets. In these sheets, there is no significant variation of properties with respect to position in the sheet. Within the range of variations of properties (Table 2), we unsuccessfully tried to correlate these properties with each other. The scatter of data appear to be purely random with a coefficient of variation of around 2% (except for k'_c) as shown by the data in Table 3. Samples taken anywhere in a sheet are representative of the sheet.

Table 2. Measurements on standard Y3333 samples from lot P-22-1 sheet.

Sample	Resilience (%)	Effective dynamic modulus (kPa)	Thickness (mm)	Density (Mg/m ³)
1	64.56	162.07	1.494	0.355
2	63.63	154.50	1.514	0.341
3	63.55	157.13	1.494	0.352
4	61.63	154.13	1.542	0.342
5	61.25	153.87	1.547	0.341
6	62.80	153.73	1.506	0.348
7	63.49	163.20	1.529	0.349
8	62.87	166.43	1.534	0.349
9	61.14	151.77	1.547	0.338
10	62.72	158.83	1.554	0.341
11	62.31	149.93	1.539	0.332
12	63.61	168.25	1.549	0.343
13	63.54	168.43	1.534	0.348
14	62.39	171.73	1.532	0.357
15	61.01	163.78	1.547	0.346
16	64.16	168.93	1.532	0.350
17	61.67	156.03	1.529	0.347
18	60.37	172.36	1.527	0.352
Average	62.59	160.84	1.531	0.3461
Standard deviation	1.20	7.29	0.018	0.0063
Coefficient of variation (%)	1.92	4.53	0.18	1.82
Range	60.37 to 64.56	149.93 to 172.36	1.494 to 1.554	0.332 to 0.357

Table 3. Average measurements for three Y3333 sheets from two lots.

Lot	Dimension (cm)	Average	Standard deviation	Coefficient of variation (%)	Spread
Resilience (%)					
P-22-1	20 sq	62.59	1.20	1.92	4.19
Z-18-1	15 sq	66.15	1.42	2.15	3.79
	20 diam	66.87	0.707	1.06	2.55
Effective dynamic modulus (kPa)					
P-22-1	20 sq	160.84	7.29	4.53	22.43
Z-18-1	15 sq	116.53	1.38	1.19	3.47
	20 diam	119.79	2.43	2.03	7.97
Thickness (mm)					
P-22-1	20 sq	1.531	0.018	1.18	0.060
Z-18-1	15 sq	1.567	0.014	0.895	0.038
	20 diam	1.528	0.032	2.11	0.109
Density (Mg/m ³)					
P-22-1	20 sq	0.3461	0.0063	1.82	0.025
Z-18-1	15 sq	0.3380	0.0051	1.53	0.014
	20 diam	0.3369	0.0076	2.28	0.023

Variations Among the Sheets from the Same Lot

Each sheet or part of cellular silicone is an entity because it is formed and press cured by itself and, so, is subject to the effects of molding variables. We checked variation among sheets on three lots of cellular silicone compound (Table 4). For all three lots, percent resilience is consistent from sheet to sheet. For two of the three lots, k'_c is consistent from sheet to sheet, but the coefficients of variation are surprisingly large.

For lot Z-18-1, where the coefficient of variation is around 2%, the two sheets are statistically different in k'_c , but it is not clear that the difference is important. The effective dynamic modulus appears to be more sensitive to processing variations than resilience is. Probably, normal variations in the production process have little effect on the properties of the product.

The two sheets of Y-6-3 also represent the results of shelf-aging the Y3333 compound. We assume this compound has a short shelf life of 15 days before it becomes risky to process. The two sheets of Y-6-3 that were molded 12 days apart are alike. So shelf-aging of Y3333 may not be such a severe problem.

Table 4. Average measurements for Y3333 sheets from same lot.

Lot	Resilience (%)			Effective dynamic modulus (kPa)		
	Average	Standard deviation	Coefficient of variation (%)	Average	Standard deviation	Coefficient of variation (%)
Z-18-1	1	66.15	1.42	116.53	1.38	1.19
	2	66.87	0.707	119.79	2.43	2.03
	Sheet av	66.51		118.16		
D-29-1	1	62.41	1.14	148.66	1.34	0.90
	2	63.58	0.92	158.11	11.28	7.13
	3	63.05	0.81	160.54	8.88	5.53
	Sheet av	63.01	0.586	155.77	6.28	4.03
Y-6-3	1	62.29	0.65	123.13	3.90	3.17
	2	62.68	0.54	126.38	3.03	2.39
	Sheet av	62.49		124.76		

Baseline Data on Standard Y3333

To interpret the effect of material and processing variables on the properties of Y3333 and to evaluate aging effects, one must have baseline values of the properties of Y3333 that reflect the normal lot-to-lot variations expected and the normal processing variations that occur. We measured resilience and k'_c of five lots of standard Y3333 (Table 5) based on the first lot of W97 gum. The values of k'_c vary more than percent resilience, but the lots are reasonably consistent. However, the lot-to-lot variations in both percent resilience and k'_c are statistically significant. There is no trend

of values with the age of the gum. We have already observed that normal processing variations have little effect on the properties of Y3333 compound.

The gum used for these lots changed with time to the point where the production agency would no longer accept Y3333 compound from that gum. Union Carbide formulated a second W97 lot of gum that is still in use. Y3333 cellular silicone, based on the current gum, has slightly different load vs deflection properties than those based on the old gum. The data of Table 5 may not be representative of production material from January 1973 on. We will check current production material.

Variations from Standard Y3333

The study of variations from standard Y3333 was not a planned program but a happenstance one since we had on hand two materials, each with known variations from Y3333. Because the coefficients of variation in Yertzley results on Y3333 are small, it was suggested that perhaps the Yertzley test is not sensitive. Testing of known variations gave us a chance to evaluate the sensitivity of the test.

The substitution of Y3976 gum for W97 gum updates the state of the art in polymerization of silicone gums. This should result in improved processing and mechanical properties according to Union Carbide Corporation. The change in polymerization process presumably alters the gum in two ways: by substituting $(C_2H_5)_3Si-$ groups on the ends of polymer chains for $HO(CH_3)_2Si-$ or $KO(CH_3)_2Si-$ groups and by narrowing the range of molecular weights.³ Bendix studied the processing of Y3333 based on end-blocked gum in detail and reported that the new material processed more readily than standard material, but the properties (e.g., load vs deflection) of the end product were not equivalent.⁴ Table 6 compares the results of our testing of Y3333 (based on end-blocked gum) to standard Y3333. Changes in the gum did not affect the resilience of the Y3333 but did significantly decrease the effective dynamic modulus. A change in gum did alter the processibility, conventional properties, and k'_c as measured by the Yertzley test.

Table 5. Measurements on sheets from five standard lots of standard Y3333.

Lot (production date)	No. of sheets	Disks per sheet	Total disks	Resilience (%)			Effective dynamic modulus (kPa)		
				Aver- age	Standard deviation	Coefficient of variation (%)	Aver- age	Standard deviation	Coefficient of variation (%)
P-22-1 (4/71)	1	18	18	62.59	1.20	1.92	160.84	7.29	4.53
P-29-1 (6/72)	3	3	9	63.01	0.98	1.55	155.77	6.28	4.03
P-3-1 (12/70)	1	3	3	60.53	0.21	0.35	149.17	5.30	3.55
P-11-1 (12/70)	1	3	3	64.55	0.21	0.33	145.10	2.44	1.68
Y-6-2 (1/72)	1	3	3	61.05	1.12	1.83	145.14	8.23	5.67
All 5 Lots				62.35	1.61	2.58	151.20	6.93	4.58

Table 6. Comparison of known variations in Y3333 to standard Y3333.

	Resilience (%)			Effective dynamic modulus (kPa)		
	Aver- age	Standard deviation	Coefficient of variation (%)	Aver- age	Standard deviation	Coefficient of variation (%)
Standard with first gum lot	62.35	1.61	2.58	151.20	6.93	4.58
End- blocked gum (lot Y-6-3)	62.49	0.28	0.44	124.76	2.30	1.84
Second gum lot and Nipak urea (lot Z-18-1)	66.51	0.51	0.77	118.16	2.31	1.95

In the second variation from standard Y3333, two changes were made. Nipak urea was substituted for Dupont urea and the gum used was the second lot of W97. Bendix had evaluated this same material and found no significant differences in either processing or conventional properties from the standard Y3333 based on the first W97 gum lot.⁵ In our Yertzley testing of this variation (Table 6), we found a significantly higher resilience and lower k'_c than the standard Y3333. Also, as shown in Table 3, experimental lot Z-18-1 has a significantly lower density than standard lot P-22-1, although both were compounded to give the same nominal density. Because lot Z-18-1 consists of two variables, significant changes in properties cannot be interpreted. We will evaluate standard Y3333 based on the second W97 gum lot and then be able to interpret the changes in lot Z-18-1.

The significance of this brief study of two experimental lots of Y3333 is that the Yertzley test showed a response to the variations but maintained low coefficients of variation.

CONCLUSION

After evaluating the Yertzley mechanical oscillograph, we decided that

it demonstrated its worth for detecting differences among Y3333 cellular silicones. In particular, the Yertzley test appears to have the required reproducibility to be sensitive to changes in resilience and k'_c .

FUTURE WORK

A great deal of work remains to fully establish the use of the Yertzley in testing porous elastomers of varying densities and differing chemical composition in a range of practical applications. This work includes:

- Establishing baseline values for standard Y3333 made from the new gum lot.
- Evaluating the effect of thickness variations on test results.
- Testing Y8197, a new Y3333 based on Y3976 gum and NH_4Cl temporary filler.
- Applying the Yertzley test to samples of Y3333 being aged at 20% relative humidity and 74°C at both 20% and 65% deflection.
- Correlating the measurements of the Yertzley test with other standard measurements such as load vs deflection, compression set, and impurity levels.
- Applying the Yertzley test to Y3260 cellular silicone, which is also extensively used in weapons.
- Testing Y3260-5PNH₄, a new Y3260 based on Y3976 gum and NH_4Cl temporary filler.
- Applying the Yertzley test to shaped parts for homogeneity.
- Establishing the significance of resilience and k'_c to cushion performance in a weapon.
- Evaluating the effect of density variations on test results.
- Correlating the Yertzley test with compression-set testing by the improved closed-die method we are trying to develop.
- Applying the Yertzley test to other than cellular-silicone porous elastomers (e.g., room-temperature-vulcanizing-blown silicone foams).

We base the priority of these tasks on order of need for information and increasing difficulties, complexity, and time consumption. The first task is currently in progress.

REFERENCES

1. "ASTM P945-68: Rubber, Carbon Black, Gaskets," *Standards of the American Society for Testing Materials* (American Society for Testing Materials, Philadelphia, Pa., April 1969), part 28, p. 455.
2. J. K. Lepper and H. L. Lentzner, *Organic Materials Division Quarterly Report - January through March 1975*, Lawrence Livermore Laboratory, Rept. UCRL-50019-75-1 (1975), pp. 3-4.
3. S. A. Aspey, *Improved Cellular Silicone*, Lawrence Livermore Laboratory, Rept. UCID-16225 (1972).
4. G. W. Edman, IV, *Process Evaluation of New Cellular Silicone Material*, Bendix Corporation, Kansas City, Rept. BDX-613-1082 (1974).
5. Letter from D. J. Fossey (Bendix Corporation, Kansas City) to P. Naillon (Lawrence Livermore Laboratory), *Spherical Urea Stockpile for Cellular Silicone Parts* (October 18, 1974).

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$ ____*; Microfiche \$2.25

~~*Pages~~

~~1-50
51-150
151-325
326-500
501-1000~~

~~NTIS
Selling Price~~

~~\$4.00
\$5.45
\$7.60
\$10.60
\$13.60~~

Technical Information Department

LAWRENCE LIVERMORE LABORATORY

University of California | Livermore, California | 94550