DETERMINATION OF DEGREE OF CURE OF
ISOTHERMALLY AGED LX-13

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DEVELOPMENT DIVISION

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ABSTRACT

An isothermal aging study of uncured LX-13 was undertaken to gain some insight into the chemical and physical cure of this material as a function of temperature.

Uncured LX-13 samples were isothermally aged at 3.5, 22, 52, and 68 C, for various elapsed times. The resultant isothermal residues were analyzed for degree of chemical cure and for hardness as a function of time and temperature through NMR spectrometry and Shore durometer measurements.

EXPERIMENTAL

Samples were prepared by rolling an LX-13 patty to relatively uniform thickness(1). Individual samples in the form of right circular cylinders (cores) were made by use of a stainless steel cork borer, and were approximately 4 mm in diameter and 7-8 mm in length. Sufficient number of these cores were made such that three samples were available for each selected elapsed time. The sample cores were placed in petri dishes and stored in covered containers at 3.5, 22, 52, and 68 C. Durometer measurement samples were approximately 7-8 mm thick and 15-18 mm square. These also were placed in petri dishes and stored as the others. Only one square per elapsed time measurement was required for durometer data due to the sufficient area for several measurements on each surface.

At various elapsed times, core samples were removed, weighed, and placed in a septum vial along with 1 ml of a 50/50 (V) mixture of d^6 benzene/ d^6 acetone. A weighed amount of tetramethoxysilane (TMOS) was also added to each sample to serve as an internal quantitative standard. After closure with a septum, they were placed on a Kahn mechanical shaker for several hours until complete dissolution of PETN and unbound Sylgard was effected. As the degree of cure increases with time, a soft gelatinous core remains undissolved. Previous studies have shown that all the PETN has been removed and is in solution along with the Sylgard extractables. This solution is placed in a standard 5 mm NMR tube, along with 0.05 ml of benzene to serve as an internal lock material, and analyzed on a Varian HA-100 through routine integration techniques. All three species are single peak systems, thus placing the integration results at an optimum point. Physical cure (hardness) is monitored by durometer measurements taken at various locations on the LX-13 squares. The Shore durometer used was a Model "A-2" (ASTM 2240) as the size of the sample squares required a smaller measurement contact surface than normally used.

(1) PX Lot 20-76-0127-217. This material was not deaerated after milling, to eliminate the lengthy room temperature contact.

LX-13 AGING AT 3.5 C (38 F)

Table I and Fig. 1 present the results of chemical aging of the material at 3.5 C, as outlined in the previous section. Table II and Fig. 2 contain the results of Shore durometer measurements of this system. Fig. 3 displays the relative trends of hardness cure and chemical cure, the latter shown as percent of original polydimethylsiloxane unextractable.

LX-13 AGING AT 22 C (72 F)

The chemical analysis and hardness measurement results for the 22 C system are presented in Table III and Fig. 4, and in Table IV and Fig. 5, respectively. Behavioral comparison of the two is presented in Fig. 6.

LX-13 AGING AT 52 C (126 F)

Chemical and hardness data for this system are presented in Table V and Fig. 7 and Table VI and Fig. 8, respectively. Behavioral comparison is presented in Fig. 9.

LX-13 AGING AT 68 C (154 F)

Chemical and hardness data for this system are presented in Table VII and Fig. 10, and in Table VIII and Fig. 11, respectively. Comparison of cure curves is presented in Fig. 12.

Fig. 13 presents comparison of the chemical cure curves for the four temperatures studied (3.5, 22, 52, and 68 C).

Fig. 14 presents comparison of the hardness curves obtained in the four systems.

In considering the four isothermal systems, at a common percent polydimethylsiloxane retention point, there should exist a linear relationship between the reciprocal temperature (K) and the log of the elapsed time. In previous studies of the Sylgard system, an arbitrary retention point of 50% was chosen. However, in this study, the 3.5 C system was monitored only up to 1273 hours, with a final polydimethylsiloxane retention of 37.5%; in order to include the 3.5 C system data, an arbitrary retention point of 30% was chosen. The results are presented in Fig. 15. The data show a relatively good linear adherence for the four isothermal systems, at least up to this point.

COMMENTS

This completes the data gathering portion of the LX-13 cure study. Determination of system kinetics parameters will be completed by J. Holovka, Sandia Laboratories, Albuquerque, New Mexico.

Table I. Polydimethylsiloxane Extractables (LX-13) 3.5.C

Elapsed Time (hrs)	Percent Polydimethylsiloxane					Percent Extractables
	1	2	3	Average	σ	
0	19.9	20.0	19.9	19.9	0.06	99.5
50	19.8	19.8	20.0	19.9	0.12	99.5
98	19.7	19.6	19.7	19.7	0.06	98.5
165	19.2	19.2	19.1	19.2	0.06	96.0
215	18.6	18.5	18.7	18.6	0.10	93.0
260	18.4	18.6	18.4	18.5	0.12	92.5
332	17.8	17.8	17.8	17.8	0.00	89.0
380	17.5	17.6	17.5	17.5	0.06	87.5
428	17.1	17.0	17.0	17.0	0.06	85.0
600	15.9	15.9	16.0	15.9	0.06	79.5
769	14.5	14.5	14.6	14.5	0.06	72.5
840	14.0	14.1	13.9	14.0	0.10	70.0
937	13.6	13.6	13.8	13.7	0.12	68.5
1009	13.4	13.3	13.5	13.4	0.10	67.0
1105	12.9	13.0	13.0	13.0	0.06	65.0
1273	12.6	12.6	12.4	12.5	0.12	62.5

Fig. 1. LX-13 Polydimethylsiloxane Extractables (3.5 C)

Table II. Durometer Measurements (LX-13) 3.5 C

Elapsed Time (hrs)	<u>1</u>	<u>2</u>	<u>3</u>	<u>Average</u>	<u>σ</u>
0	0	0	0	0	-
50	0	0	0	0	-
98	0	0	0	0	-
165	0	0	0	0	-
215	0	0	0	0	-
260	0	0	0	0	-
332	0	0	0	0	-
380	0	0	0	0	-
428	3	3	2	2.7	0.6
600	11	11	12	11.3	0.6
625	14	15	14	14.3	0.6
673	21	21	20	20.7	0.6
769	31	30	30	30.3	0.6
840	37	36	36	36.3	0.6
937	43	42	43	42.7	0.6
1009	48	48	46	47.3	1.2
1105	50	50	50	50.0	0.0
1273	54	54	55	54.3	0.6
1500	59	59	58	58.7	0.6

Fig. 2. LX-13 Durometer Measurements (3.5 C)

Fig. 3. LX-13 Comparison of Durometer Measurements with Percent Extractables (3.5 C)

Table III. Polydimethylsiloxane Extractables (LX-13) 22 C

Elapsed Time (hrs)	Percent Polydimethylsiloxane					Percent Extractables
	<u>1</u>	<u>2</u>	<u>3</u>	<u>Average</u>	<u>σ</u>	
0	19.9	19.9	19.9	19.9	0.00	99.5
4.5	19.8	19.9	19.8	19.8	0.06	99.0
20.3	19.3	19.4	19.4	19.4	0.06	97.0
26.5	18.3	18.3	18.5	18.4	0.12	92.0
45	16.6	16.5	16.5	16.5	0.06	82.5
50	15.5	15.3	15.3	15.4	0.12	77.0
68	13.5	13.5	13.3	13.4	0.12	67.0
74	12.8	12.8	12.8	12.8	0.00	64.0
92	11.6	11.7	11.6	11.6	0.06	58.0
165	6.2	6.4	6.4	6.3	0.12	31.5
189	5.1	5.1	5.3	5.2	0.12	26.0
215	4.5	4.6	4.6	4.6	0.06	23.0
260	3.9	4.1	4.1	4.0	0.12	20.0

Fig. 4. LX-13 Polydimethylsiloxane Extractables (22 C)

Table IV. Durometer Measurements (LX-13) 22 C

<u>Elapsed Time (hrs)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>Average</u>	<u>σ</u>
0	0	0	0	0	-
4.5	0	0	0	0	-
20.3	0	0	0	0	-
26.5	0	0	0	0	-
45	4	5	4	4.3	0.6
50	8	8	8	8.0	0.0
68	29	30	29	29.3	0.6
74	37	37	39	37.7	1.2
92	49	51	50	50.0	1.0
165	69	70	70	69.7	0.6
189	73	73	72	72.7	0.6
215	76	76	74	75.3	1.2
260	77	78	78	77.7	0.6

Fig. 5. LX-13 Durometer Measurements (22 C)

Fig. 6. LX-13 Comparison of Durometer Measurements with Percent Extractables (22 C)

Table V. Polydimethylsiloxane Extractables (LX-13) 52 C

Elapsed Time (hrs)	Percent Polydimethylsiloxane					Percent Extractables
	<u>1</u>	<u>2</u>	<u>3</u>	<u>Average</u>	<u>σ</u>	
0.0	19.9	19.9	19.9	19.9	0.00	99.5
1.0	18.6	18.5	18.5	18.5	0.06	93.0
1.5	10.7	10.6	10.6	10.6	0.06	53.0
2.0	8.7	8.8	8.8	8.8	0.06	44.0
3.0	6.0	6.0	5.8	5.9	0.12	29.5
4.0	4.7	4.7	4.8	4.7	0.06	23.5
5.0	4.1	4.1	4.1	4.1	0.00	20.5
5.8	3.7	3.6	3.6	3.6	0.06	18.0

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Fig. 7. LX-13 Polydimethylsiloxane Extractables (52 C)

Table VI. Durometer Measurements (LX-13) 52 C

<u>Elapsed Time (hrs)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>Average</u>	<u>σ</u>
0.0	0	0	0	0	-
1.0	4	4	4	4	0.0
1.5	15	15	13	14.3	1.2
2.0	37	37	39	37.7	1.2
3.0	57	57	55	56.3	1.2
4.0	70	70	69	69.7	0.6
5.0	77	77	77	77.0	0.0
5.8	79	79	79	79.0	0.0

Fig. 8. LX-13 Durometer Measurements (52°C)

Fig. 9. LX-13 Comparison of Durometer Measurements with Percent Extractables (52 C)

Table VII. Polydimethylsiloxane Extractables (LX-13) 68 C

Elapsed Time (hrs)	Percent Polydimethylsiloxane					Percent Extractables
	1	2	3	Average	σ	
0.00	19.9	19.8	19.9	19.9	0.06	99.5
0.17	15.2	15.4	15.4	15.3	0.12	76.5
0.33	12.3	12.5	12.3	12.4	0.12	62.0
0.50	8.6	8.6	8.8	8.7	0.12	43.5
0.67	5.4	5.4	5.5	5.4	0.06	27.0
0.83	3.9	3.8	3.8	3.8	0.06	19.0
1.00	3.5	3.6	3.6	3.6	0.06	18.0
1.50	3.3	3.5	3.3	3.4	0.12	17.0
2.00	3.3	3.2	3.2	3.2	0.06	16.0

Fig. 10. LX-13 Polydimethylsiloxane Extractables (68 C)

Table VIII. Durometer Measurements (LX-13) 68 C

<u>Elapsed Time (hrs)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>Average</u>	<u>σ</u>
0.00	0	0	0	0	-
0.17	0	0	0	0	-
0.33	7	7	7	7	0.0
0.50	30	31	31	30.7	0.6
0.67	55	55	53	54.3	1.2
0.83	65	67	65	65.7	1.2
1.00	69	71	71	70.3	1.2
1.50	78	78	77	77.7	0.6
2.00	81	81	83	81.7	1.2
3.50	84	84	84	84.0	0.0

Fig. 11. LX-13 Durometer Measurements (68 C)

Fig. 12. LX-13 Comparison of Durometer Measurements with Percent Extractables (68 C)

Fig. 13. Elapsed Time Versus Percent Non-Extractables

Fig. 14. Elapsed Time Versus Durometer Hardness

Fig. 15. Time Versus Reciprocal Temperature at 30% Extractables Cure Point