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Isothermal Aging of Three Polyurethane Elastomers

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ISOTHERMAL AGING OF THREE POLYURETHANE ELASTOMERS

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ABSTRACT

Two polyurethane systems, EN-7 and L-100, have a long history as encapsulants and coatings in Sandia programs. These materials contain significant amounts of toluene diisocyanate (TDI), a suspect human carcinogen. As part of efforts to reduce the use of hazardous materials in the workplace, PET-90A, a polyurethane with less than 0.1% free TDI, was identified as a candidate for new applications and as a replacement for the more hazardous polyurethanes in selected programs. This report documents the results of a two-year accelerated aging study of PET-90A, EN-7, and L-100 polyurethane elastomers to characterize the effect of 135°F isothermal aging on selected physical, electrical, mechanical and thermal properties. In general, there was very little change in properties over the two year period for the three elastomers. The largest changes occurred in EN-7, which is the polyurethane with the longest service history in Sandia applications.

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INTRODUCTION

Polyurethane elastomers are used as encapsulants and coatings to mitigate harsh environments in numerous DOE and industrial applications. For example, EN-7 polyurethane is used in firing sets. Uncured EN-7 contains about 12% free (potentially airborne) toluene diisocyanate (TDI), a suspect human carcinogen. DOE has funded environmentally conscious manufacturing (ECM) programs to eliminate or reduce many chemically hazardous materials by identifying replacement materials to substitute for the more hazardous ones. One effort is to qualify low TDI polyurethane systems to replace high TDI materials.

In May 1990 an Alternate Polyurethane Systems Working Group was established with members from SNL, AS/FM&T, Y-12, LLNL, LANL, Mound, and Pinellas. One of the group's accomplishments was to identify PET-90A/Ethacure 300 (referred to as PET-90A in this report), a polyurethane with low levels of free TDI ($<0.1\%$), as a potential replacement for high TDI polyurethane systems. SNL and AS/FM&T initiated programs to characterize and qualify the PET-90A system for WR applications. AS/FM&T has released material standards and process specifications for PET-90A and is currently studying its adhesion characteristics. SNL has performed statistical experiments to optimize processing parameters [1] and completed an accelerated isothermal aging study of PET-90A.

This report describes the two-year isothermal aging program. Specimens were fabricated, thermally aged in a temperature chamber and periodically withdrawn for measurements of hardness, tear strength, glass transition temperature, modulus, electrical properties and outgassing products. In addition to the PET-90A system, two other polyurethane systems were included in the study as controls to provide direct comparison of aging characteristics between materials in use and the replacement candidate. The two controls are EN-7 and L-100 polyurethane systems.

PROGRAM PLAN

The plan was to evaluate material responses throughout the thermal aging study in which polyurethane samples were subjected to 135°F isothermal exposure for a period of 2 years. Rationale for this temperature and time interval is a historical one [2]. According to former Sandian Ray Gott, historical aging parameters for polyurethane studies at Sandia are 135°F for 2 years. This exposure for accelerated aging was thought to be equivalent to 20 years aging at ambient temperature. Even though no documentation stating this premise is known to exist, Gott recalled having seen such a memo. Gott and Ramona Myers felt that aging at higher temperature for periods shorter than 2 years could cause thermal degradation in polyurethane; i.e., a different degradation mechanism than in normal aging. Therefore, they recommended the 135°F isothermal exposure for a period of 2 years as the environmental condition for the thermal aging study.

Various tests were scheduled at selected time intervals relative to the start of thermal aging. Hardness, tear strength, glass transition temperature, modulus, and gas analysis tests were performed at the 0-month, 1-month, 3-month, 6-month, 9-month, 12-month, 15-month, 18-month, 21-month, and 24-month intervals. Electrical property measurements for dielectric constant, dissipation factor and volume resistivity were taken every six months and for dielectric strength every 12 months.

MATERIALS

The polyurethanes in this study were 2-part, castable elastomer systems. Material standards and processing parameters used to fabricate plaques for test specimens are listed in Table 1.

The polyurethane samples were made by hand-mixing the degassed prepolymer and the curative, evacuating the mixture, pouring it into four stainless steel plaque molds (molds designated A, B, C, and D), degassing the material again, and placing the molds in an oven to cure. Each batch produced four 4"× 6"× 0.120" plaques (dimensions in inches). One operator fabricated all of the plaques for this study; 26 plaques of each polyurethane were required for the program. After removal from the oven, all plaques were stored in a desiccator for a minimum of seven days. At that time, 0-month Shore A hardness measurements were made on all plaques before cutting out tear strength, glass transition temperature, and electrical property samples.

One electrical test coupon or six tear strength specimens were cut from each plaque. Glass transition temperature specimens and material for outgassing experiments were taken from excess material remaining after tear and electrical specimens were removed from a plaque. With the guidance of E. V. Thomas, a strategy was developed for systematically mixing tear samples throughout all test sets to be used in the 2 year study. This was done by tracking the pour date and mold ID associated with each specimen. It was assumed that the six tear specimens from a single plaque are identical. Samples from every plaque were in the initial (0-month) and final (24-month) test sets. This strategy was aimed at removing any bias that may exist due to pour date and/or the individual molds.

Plaques were poured and test specimens cut out during the first quarter of FY94. The 0-month control tests were performed the first week of January 1994. Materials to be checked for outgassing were placed in stainless steel canisters that were evacuated then backfilled with argon gas. Specimens for the other tests were placed in glass jars, along with desiccant to ensure a dry atmosphere. A separate glass jar was used for each of the three polyurethane systems. On January 10, 1994, the eight stainless steel canisters and three glass jars containing samples for thermal aging were placed in a 135°F oven.

EXPERIMENTAL PROCEDURES AND RESULTS

All measurements in this study were made at a nominal temperature of 72°F.

HARDNESS

Each polyurethane's indentation hardness was measured in tests that follow the guidelines in ASTM D-2240 "*Standard Method of Test for Indentation Hardness of Rubber and Plastics by Means of a Durometer*". This method is based on the penetration of a specified indenter forced into the material under specified conditions. This method is an empirical test intended primarily for control purposes. The Type A Shore indenter was used in this program. Each Shore A hardness value reported is an average of a minimum of three measurements. Measurements are made within 1 second after the indenter is pressed into the sample.

Hardness of the control (0-month) specimens were measured on the 4 inch by 6 inch plaques of material once they had been removed from the molds and aged at room temperature for a

minimum of 7 days. Hardness measurements of thermally aged material were done on the ends of tear strength specimens prior to the strength tests.

Hardness data for the control and thermally aged specimens are summarized in Table 2 and displayed in Figure 1. Data in Table 2 includes the number of test specimens and the mean value, standard deviation (stdev) and coefficient of variation [$cv = (stdev/mean) \times 100$] of hardness. A minimum of three hardness measurements are taken on each specimen. The Shore A hardness of the EN-7 and L-100 polyurethane systems are about equal (≈ 94) and somewhat higher than the PET-90A hardness (≈ 88). The hardness of each polyurethane is basically unaffected during the 24 months of 135°F thermal aging in an atmosphere of dry air.

TEAR STRENGTH

The tear resistance of each polyurethane was measured in tests that follow the guidelines in ASTM D-624 "*Standard Test Method for Rubber Property - Tear Resistance*". Elastomeric materials often fail in service applications due to the generation of a type of rupture called a tear. This test method measures the resistance to tearing action. Five un-nicked 90° angle specimens were punched from each 4 inch by 6 inch polyurethane plaque using the Die C geometry defined in ASTM D-624. A schematic of the specimen and its dimensions are shown in Figure 2. These specimens were loaded in tension in an 1125 Instron test machine at a crosshead speed of 20 inches per minute. The tear strength (resistance) was calculated from the maximum load divided by the thickness of the specimen; tear strength has units of pounds per linear inch of thickness (pli).

Tear strength data for the control and thermally aged specimens are summarized in Table 3 and displayed in Figure 3. Data in Table 3 includes the number of specimens and the mean value, standard deviation and coefficient of variation of tear strength. The 0-month tear strength of the L-100 material is the highest (≈ 640 pli), followed by PET-90A (≈ 590 pli) and EN-7 (≈ 400 pli). The data suggests that the tear strength of both PET-90A and L-100 increases slightly with thermal aging at 135°F; whereas, the tear strength of EN-7 decreases from about 400 pli to approximately 300 pli. Most of the strength decrease in the EN-7 occurred within the first month of thermal aging.

The tear strength of PET-90A as a function of hardness is discussed in the Appendix.

GLASS TRANSITION TEMPERATURE

The glass transition temperature T_g and apparent flexural modulus, E' , as a function of temperature were measured using a Polymer Laboratories' Dynamic Mechanical Thermal Analyzer (DMTA). Flexural non-resonant forced vibration tests on dual cantilever specimens were performed at 1 Hz frequency over the temperature range of -80°C to 0°C. The heating rate was 3°C/min. Typical E' and $\tan \delta$ (the loss tangent) curves for L-100 polyurethane are shown in Figure 4. For the purposes of this study, T_g is defined as the temperature at which the $\tan \delta$ curve reaches its maximum value. One to three specimens of each polyurethane was evaluated for T_g at the different thermal aging intervals.

Glass transition temperature data for the control and thermally aged specimens are listed in Table 4 and displayed in Figure 5. The 0-month T_g of L-100 is about 20°C higher ($\approx -34^\circ\text{C}$) than

the values for PET-90A ($\approx -55^{\circ}\text{C}$) and EN-7 ($\approx -55^{\circ}\text{C}$). The data in Figure 5 suggests that the T_g of all three polyurethanes are only minimally affected by 24 months of aging; the observed overall changes in T_g are less than 5°C after 24 months.

FLEXURAL MODULUS

Flexural modulus data as a function of test temperature were obtained from the DMTA tests performed to measure T_g . These values are considered apparent moduli since specimen geometry can influence the absolute values measured. However, these moduli values illustrate the effect of test temperature on the stiffness of the materials at temperatures below and above the glass transition temperature. There is very little change in the response of the L-100 and PET-90A materials due to thermal aging for two years, see Figure 6. However, the moduli of these two materials change more than an order of magnitude over the -80°C to 0°C range. Additionally, there were some changes in the modulus curves of the EN-7 polyurethane, Figure 7. At higher temperatures, the modulus increased in the thermally aged specimens. Very little change was observed after 12 months of aging.

ELECTRICAL PROPERTIES

The electrical properties of dielectric constant, dissipation factor, and volume resistivity were measured by Paul Beeson. These measurements were made on two each 4 inch by 4 inch polyurethane plaques of each material at 0-, 6-, 12- 18-, and 24-months thermal aging time intervals. Dielectric constants and dissipation factors were measured at four frequencies following the guidelines in ASTM D-150 "*Standard Methods of Test for A-C Loss Characteristics and Dielectric Constant (Permittivity) of Solid Electrical Insulating Materials*". Results are listed in Tables 5 and 6; the 0- and 24 month data are plotted as a function of frequency in Figures 8 and 9. The dielectric constant appears to be independent of the thermal aging parameters (Figure 8).

Volume resistivity was measured following the guidelines in ASTM D-257 "*Standard Methods of Test for D-C Resistance or Conductance of Insulating Materials*". Measurements were made 1 minute after the application of 1000 volts to the polyurethane specimen; results are listed in Table 7 and plotted as a function of thermal aging time in Figure 10. Volume resistivity of PET-90A appears to decrease slightly with aging time; whereas, the slight changes in volume resistivity of L-100 and EN-7 indicate that they are probably independent of aging time.

Dielectric strength measurements were provided at time intervals of 0-, 6-, 12-, and 24-months by Mark Wilson of Allied Signal/Federal Manufacturing & Technologies Division. Tests were performed on one plaque of each material in dielectric strengths tests that followed the guidelines in ASTM D-149 "*Standard Methods of Test for Dielectric Breakdown Voltage and Dielectric Strength of Electrical Insulation Materials at Commercial Power Frequencies*". Tests were conducted with alternating (AC) voltage at 1000 volts/second using a 0.25 inch electrode; a total of 10 measurements are made on one sample of each polyurethane plaque. The dielectric strength data are listed in Table 8 and plotted in Figure 11. Changes in the AC voltage dielectric strengths vary by less than 5% over the two year thermal aging time interval. The dielectric strength of EN-7 is more than 10% higher than the other two elastomers.

At the 24-month interval, additional samples were tested for dielectric strength using dc voltage at 1000 volts/second. The results, which are listed in Table 8, show that the direct current (DC) voltage dielectric strengths of the polyurethanes are significantly higher than the AC voltage dielectric strengths. The test equipment has a maximum voltage output of 100 kilovolts, a level insufficient to cause DC voltage dielectric breakdown in the EN-7 sample. Direct current dielectric breakdown occurred in all L-100 samples and in about one-half of the PET-90A samples.

GAS ANALYSIS

Gas analyses were used in an attempt to detect specific inorganic gases that might be produced due to thermal degradation of the polyurethane systems during the accelerated thermal aging process. A total of 8 stainless steel canisters were prepared for the study; each sealed and backfilled with argon gas. Two canisters contained samples of EN-7, two contained L-100, two contained PET 90A and two were 'blanks' or controls having no materials inside other than the argon fill gas. These canisters were kept in the same oven in which all other specimens were thermally aged at 135°F. At each test interval, the 8 canisters were removed from the oven, transported to Department 1823 where gas samples were taken; the canisters were then returned to the 135°F oven. The canisters were out of the oven for less than 8 hours at each test interval. No gas analysis tests were done at the 21-month interval because the equipment was being moved to a different building.

Gas samples from the canisters were analyzed using a Finnigan MAT271 magnetic sector mass spectrometer. The gases measured were N₂, O₂, Ar, CO, CO₂, CH₄, and H₂. Estimated uncertainties for measurements are ±5% of reading with a detection limit around 10-50 parts per million (ppm) depending on the gas species. Summaries of the results are listed in Table 9. The data suggests that there was been no thermal degradation of the L-100 and PET 90A materials that resulted in reaction products of the inorganic gases listed. However, the 18-month and 24-month data for EN-7 showed a significant decrease in argon gas content and large increase in the presence of nitrogen gas. These changes were measured for both canisters containing EN-7. The increase in N₂ was probably not caused by an air leak into the canisters since there was no accompanying increase in O₂ content. The increase in N₂ content in the EN-7 canisters is not understood at this time. It is of interest to note that the changes in gas analyses over the 24 months of thermal aging occurred only in the EN-7 material which has been successfully used in a long service history. There was no change in gas products for PET-90A, the low TDI material, or for the L-100 polyurethane.

SUMMARY

EN-7, L-100 and PET-90A polyurethane elastomers were subjected to a 2-year study to determine the effect of accelerated isothermal aging on selected physical, mechanical, thermal and electrical properties. Specific properties measured were Shore A hardness, tear strength, glass transition temperature, flexural modulus, dielectric constant, dissipation factor, volume resistivity, dielectric strength and outgassing products. An overall comparison of these properties at the beginning of the study and after the 24-months of isothermal aging at 135°F is summarized in Table 10. In broad terms, the following trends were observed over the 2-year period:

- **Hardness**- No changes in EN-7 and L-100. Perhaps a slight increase in the hardness of PET90-A.
- **Tear Strength**-About a 20% decrease in the strength of EN-7 and increases of approximately 8% and 12% in the strengths of L-100 and PET-90A, respectively.
- **Glass Transition Temperature**- Less than 10% change in T_g of each of the materials.
- **Flexural Modulus**- Overall, the changes are negligible. The biggest indication of change is near 0°C for EN-7 and PET-90A.
- **Dielectric Constant**- For tests at 1,000 Hz, there are essentially no changes for any of the materials.
- **Dissipation Factor**- For tests at 1,000 Hz, there are small increases for EN-7 and L-100 and a decrease for PET-90A.
- **Volume Resistivity**-For tests at 1,000 Hz, there is no change for EN-7, a 36% decrease for L-100 and an 80% decrease for PET-90A. Even though the resistivity of PET-90A dropped 80%, it is still superior to L-100.
- **Dielectric Strength**-For tests using ac voltage, there is less than a 4% change in any of the materials.
- **Gas Analysis**- No changes were observed except for the EN-7 polyurethane. In this material, the percentage of argon gas decreased significantly ($\approx 13\%$) and the percentage of N_2 increased. The reason for this change is not known.

In general, there did not appear to be significant degradation of properties in the three polyurethanes due to accelerated isothermal aging at 135°F for a period of two years. The biggest changes were in the modulus of EN-7 (-20%), the volume resistivity of L-100 (-36%) and PET-90A (-80%), and the outgassing products of EN-7.

REFERENCES

- [1]. Myers, R. L., and Thomas, E. V., **Characterization of Polyurethane Systems which Contain Low Levels of Free TDI**, Sandia National Laboratories report SAND94-2031, printed 1995.
- [2]. Myers, R. L., Personal communication, September 1993.

ACKNOWLEDGMENTS

Ramona Myers helped in the initial planning of this study. and in obtained FY94 ECM funding for it prior to returning to graduate school. Johnson Morgan fabricated the polyurethane plaques from which test specimens were cut. Mark Stavig performed tear strength and DMTA experiments. Electrical properties tests were done by Paul Beeson and Mark Wilson (AS/FM&T). Lane Harwell prepared and sealed the metal canisters containing samples for the gas analysis experiments that were performed by Steve Reber, Steve Thornberg and Sharon Metzger.

TABLE 1. Polyurethane Systems in the Thermal Aging Study

	EN-7	L-100	PET-90A
Material Standard	2519603	2526812	2502800
Process Specification	9927087	9927104	9927116
Prepolymer	EN-7 Part A	Adiprene L-100	Airthane PET-90A
Curative	EN-7 Part B	Cyanacure	Ethacure-300
Mix Ratio (pbw)	100:18.8	100:11.5	100:9.0
Cure Schedule	1. 16 h @ 72°F 2. 16 h @ 160°F 3. 7 days @ 72°F	1. 16 h @ 160F 2. 7 days @ 72°F	1. 16 h @ 160F 2. 7 days @ 72°F
Free TDI (%)	12.4 ¹	0.2 ²	0.04 to 0.08 ¹

¹ Value measured by Mark Wilson of Allied Signal Inc., FM&T.

² Value from manufacturer's material safety data sheet (MSDS).

TABLE 2. Summary of Shore A Hardness Data

MATERIAL	AGING TIME (months)									
	0	1	3	6	9	12	15	18	21	24
<u>EN-7</u>										
NO. SPECIMENS	18	9	9	9	9	9	9	9	9	18
MEAN	94.6	94.1	94.7	93.9	95.0	94.0	94.6	94.6	94.8	94.8
STDEV	0.4	0.6	0.2	0.2	0.0	1.0	.5	.4	.3	.4
CV (%)	0.4	0.6	0.2	0.2	0.0	1.1	.5	.4	.3	.5
<u>L-100</u>										
NO. SPECIMENS	18	9	9	10	9	8	9	9	9	16
MEAN	94.1	94.2	94.3	93.7	94.2	93.9	94.2	94.4	94.4	94.2
STDEV	0.8	1.0	0.6	0.7	0.4	0.6	.6	.2	.3	.4
CV (%)	0.8	1.0	0.6	0.7	0.4	0.6	.7	.2	.3	.5
<u>PET-90A</u>										
NO. SPECIMENS	18	8	10	12	12	11	12	12	12	24
MEAN	87.7	87.6	87.6	87.2	88.1	88.5	88.8	88.8	88.7	89.0
STDEV	1.0	1.4	1.1	1.0	0.5	0.5	.4	.3	.4	.3
CV (%)	1.1	1.7	1.2	1.1	0.6	0.6	.5	.4	.4	.3

TABLE 3. Summary of Tear Strength Data

MATERIAL	AGING TIME (months)									
	0	1	3	6	9	12	15	18	21	24
EN-7										
NO. SPECIMENS	18	9	9	9	9	9	9	9	9	18
MEAN (pli)	397	335	322	334	308	295	298	324	305	314
STDEV (pli)	16.7	11.6	9.8	20.8	18.4	13.9	19	12	13	25
CV (%)	4.2	3.5	3.0	6.2	6.0	4.7	6.3	3.8	4.3	7.9
L-100										
NO. SPECIMENS	18	9	9	10	9	8	9	9	9	16
MEAN (pli)	642	659	675	672	698	666	688	718	691	694
STDEV (pli)	42.1	24.8	29.8	18.3	14.2	15.5	43	38	26	30
CV (%)	6.6	3.8	4.4	2.7	2.0	2.3	6.3	5.3	3.7	4.3
PET-90A										
NO. SPECIMENS	18	8	10	12	12	11	12	12	12	24
MEAN (pli)	586	624	616	612	630	620	630	659	652	654
STDEV (pli)	54.8	26.8	32.2	20.9	42.9	16.3	28	29	33	27
CV (%)	9.4	4.3	5.2	3.4	6.8	2.6	4.4	4.4	5.1	4.2

TABLE 4. Summary of Glass Transition Temperature Data

AGING TIME (months)	T _g (C)		
	EN-7	L-100	PET-90A
0	-56.5	-34.0	-55.0
1	-51.0	-32.5	-55.5
3	-50.5	-33.0	-51.0
6	-51.0	-34.0	-55.0
9	-50.0	-33.5	-56.0
12	-53.5	-34.2	-58.0
15	-52.0	-35.2	-57.5
18	-52.2	-36.0	-58.5
21	-54.0	-35.0	-59.0
24	-51.0	-33.0	-58.0

TABLE 5. Summary of Dielectric Constant Data (average of data from 2 samples)

MATERIAL	FREQUENCY (Hz)	AGING TIME (months)				
		0	6	12	18	24
<u>EN-7</u>	1,000	2.74	2.83	2.83	2.85	2.83
	10,000	2.71	2.79	2.79	2.80	2.79
	100,000	2.68	2.74	2.74	2.75	2.74
	1,000,000	2.65	2.71	2.71	2.71	2.70
<u>L-100</u>	1,000	6.05	6.20	5.97	6.05	5.99
	10,000	5.71	5.80	5.61	5.68	5.62
	100,000	5.30	5.37	5.21	5.27	5.21
	1,000,000	4.89	4.96	4.84	4.87	4.83
<u>PET-90A</u>	1,000	5.42	5.48	5.33	5.32	5.28
	10,000	5.30	5.39	5.25	5.25	5.21
	100,000	5.14	5.24	5.12	5.12	5.08
	1,000,000	4.95	5.07	4.97	4.96	4.93

TABLE 6. Summary of Dissipation Factor Data (average of data from 2 samples)

MATERIAL	FREQUENCY (Hz)	AGING TIME (months)				
		0	6	12	18	24
<u>EN-7</u>	1,000	0.011	0.013	0.014	0.015	0.015
	10,000	0.009	0.011	0.012	0.013	0.012
	100,000	0.008	0.010	0.011	0.012	0.011
	1,000,000	0.010	0.011	0.012	0.013	0.012
<u>L-100</u>	1,000	0.039	0.045	0.044	0.044	0.044
	10,000	0.045	0.050	0.048	0.049	0.049
	100,000	0.052	0.054	0.051	0.052	0.052
	1,000,000	0.058	0.056	0.053	0.055	0.053
<u>PET-90A</u>	1,000	0.017	0.014	0.013	0.012	0.012
	10,000	0.019	0.016	0.015	0.014	0.014
	100,000	0.024	0.021	0.020	0.019	0.019
	1,000,000	0.028	0.028	0.025	0.026	0.024

TABLE 7. Summary of Volume Resistivity Data (ohm-cm)

MATERIAL	FREQUENCY (Hz)	AGING TIME (months)				
		0	6	12	18	24
<u>EN-7</u>	1,000	5.76×10^{15}	5.69×10^{15}	6.10×10^{15}	5.34×10^{15}	5.77×10^{15}
<u>L-100</u>	1,000	10.85×10^{11}	4.87×10^{11}	7.64×10^{11}	6.81×10^{11}	6.92×10^{11}
<u>PET-90A</u>	1,000	17.5×10^{12}	11.1×10^{12}	7.85×10^{12}	4.64×10^{12}	3.39×10^{12}

TABLE 8. Summary of Dielectric Strength Data

MATERIAL	AGING TIME (months)				24 ¹
	0	6	12	24	
EN-7					
NO. MEASUREMENTS	10	10	10	10	10
MEAN (volt/mil)	445	440	467	458	>790 ²
STDEV (volt/mil)	17.2	29.1	19.6	12.9	
CV (%)	3.9	6.6	4.2	2.8	
L-100					
NO. MEASUREMENTS	10	10	10	10	10
MEAN (volt/mil)	387	393	356	389	550
STDEV (volt/mil)	16.5	14.1	14.2	7.2	13.1
CV (%)	4.3	3.6	4.0	1.8	2.4
PET-90A					
NO. MEASUREMENTS	10	10	10	10	10
MEAN (volt/mil)	391	394	416	407	>790 ²
STDEV (volt/mil)	14.5	8.2	14.6	14.5	
CV (%)	3.7	2.1	3.5	3.6	

¹ Data in this column are from dc voltage measurements; all other data in this table are from dielectric strength tests using ac voltage.

² The strength of these specimens have to be greater than 790 volts/mil based on specimen thickness of about 0.126 inch (126 mils) and an equipment limitation of 100,000 volts.

TABLE 9. Gas Analysis Data (averages from 2 canisters; materials placed in canisters then backfilled with argon)

POLYURETHANE/ GAS PRODUCT	AGING TIME (months)								
	0	1	3	6	9	12 ¹	15	18	24
<u>NONE (CONTROL)</u>									
Argon (%)	99.8	99.7	99.6	99.9	99.9	99.9	99.8	98.6	98.5
N ₂ (%)	0.2	0.3	0.4	0.4	0.5	0.1	0.7	0.4	0.9
O ₂ (%)	0.0	0.0	0.5	0.2	0.2	0.0	0.2	0.4	0.3
H ₂ (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.3
CH ₄ (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
CO ₂ (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<u>EN-7</u>									
Argon (%)	99.0	99.3	99.3	99.3	99.0	98.0	98.9	95.9	87.2
N ₂ (%)	0.9	0.3	0.2	0.2	1.1	1.0	1.6	2.4	11.3
O ₂ (%)	0.2	0.0	0.2	0.0	0.2	0.2	0.0	0.2	0.1
H ₂ (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.05
CH ₄ (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.05
CO ₂ (%)	0.0	0.0	0.6	0.7	0.9	0.8	1.1	1.1	1.3
<u>L-100/Cyanacure</u>									
Argon (%)	99.8	99.9	98.4	98.6	98.8	97.1	98.8	98.0	97.9
N ₂ (%)	0.2	0.3	0.2	0.2	0.2	1.4	0.3	0.2	0.6
O ₂ (%)	0.0	0.0	0.4	0.1	0.0	0.3	0.1	0.2	0.15
H ₂ (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0
CH ₄ (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.05
CO ₂ (%)	0.0	0.0	1.3	1.3	1.3	1.2	1.1	1.2	1.2
<u>PET-90A/Ethacure</u>									
<u>300</u>									
Argon (%)	99.9	99.9	99.5	99.7	99.7	99.3	99.6	99.0	99.1
N ₂ (%)	0.1	0.1	0.2	0.1	0.2	0.4	0.2	0.1	0.1
O ₂ (%)	0.0	0.0	0.4	0.1	0.0	0.05	0.1	0.3	0.2
H ₂ (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.1
CH ₄ (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
CO ₂ (%)	0.0	0.0	0.2	0.3	0.3	0.3	0.3	0.3	0.4

¹The 12-month gas data were analyzed with a Tracor gas chromatograph which has an estimated uncertainty of +/- 15% of the reading. All other gas samples were analyzed with a Finnigan MAT271 magnetic sector mass spectrometer that has an estimated uncertainty of +/- 5% of the reading.

TABLE 10. Comparison of Data Measured at the Beginning (0-Month) and at the End (24-Month) of the 135°F Isothermal Aging Study.

135°F Aging Time	<u>EN-7</u>		<u>L-100</u>		<u>PET-90A</u>	
	0-Month	24-Month	0-Month	24-Month	0-Month	24-Month
Hardness (Shore A)	94.6	94.8	94.1	94.2	87.7	89.0
Tear Strength (pli)	397	314	642	694	586	654
Glass Transition Temperature- (C)	-56.5	-51	-34.0	-33.0	-55.0	-58.0
Flexural Modulus at -80°C (10 ⁶ psi)	275,000	285,000	230,000	270,000	176,000	180,000
at 0°C (10 ⁶ psi)	22,000	35,000	14,000	14,000	7,000	4,800
Dielectric Constant at 1,000 Hz	2.74	2.83	6.05	5.99	5.42	5.28
Dissipation Factor at 1,000 Hz	0.011	0.015	0.039	0.044	0.017	0.012
Volume Resistivity at 1,000 Hz (ohm-cm)	5.76x10 ¹⁵	5.77x10 ¹⁵	10.85x10 ¹¹	6.92x10 ¹¹	17.5x10 ¹²	3.39x10 ¹²
AC Voltage Dielectric Strength (volts/mil)	445	458	387	389	391	407
Gas Analysis Argon Content (%)	99.0	87.2	99.8	97.9	99.9	99.1

Fig. 1. Hardness as a function of time for three polyurethane elastomers aged at 135°F in air. Error bars represent one standard deviation.

Dimension	Value (in)	Tolerances (in)
A	4.000	± 0.020
B	0.750	± 0.002
C	0.750	± 0.002
D	0.500	± 0.002
E	1.000	± 0.002
F	1.061	± 0.002
G	1.118	± 0.002
H	2.000	± 0.010

Fig 2. Schematic of tear strength test specimen and its dimensions.

Fig. 3. Tear strength as a function of time for three polyurethane elastomers aged at 135°F in air. Error bars represent one standard deviation.

Fig. 4. Representative DMTA data showing the apparent flexural modulus E' and $\text{Tan } \delta$ curves for the L-100 polyurethane after 24- months of isothermal aging at 135°F in air. The glass transition temperature is taken as the temperature at which the $\text{Tan } \delta$ curve reaches its maximum value.

Fig. 5. Glass transition temperature as a function of time for three polyurethane elastomers aged at 135°F in air.

Fig. 6. Apparent flexural modulus as a function of temperature at two aging times for L-100 and PET-90A polyurethane elastomers aged at 135°F in air.

Fig. 7. Apparent flexural modulus as a function of temperature at four aging times for EN-7 polyurethane elastomer aged at 135°F in air.

Fig. 8. Dielectric constant as a function of frequency at two aging times for three polyurethane elastomers aged at 135°F in air.

Fig. 9. Dissipation factor as a function of frequency at two aging times for three polyurethane elastomers aged at 135°F in air.

Fig. 10. Volume resistivity as a function of time for three polyurethane elastomers aged at 135°F in air. Measurements at a frequency of 1000 Hz.

Fig. 11. Dielectric strength as a function of time for three polyurethane elastomers aged at 135°F in air. Tests conducted using alternating current voltage

APPENDIX

PET-90A: Tear strength as a function of Shore A hardness

The PET-90A test data reported in the main body of this report were from measurements on material having Shore A hardness values of 87 to 89. When plaques of PET-90A were processed at the beginning of the study, a few of them had Shore A hardness values ranging between about 82 and 86. The low hardness values of these plaques may have been the result improper polymer to curative mix ratio [1], lot-to-lot variation, out-of-date materials, or moisture-contaminated material. Based on the data reported in [1], the low hardness and strengths of some plaques was most likely due to off ratio mixes. Whatever the cause for the plaques to have the wide range of hardnesses, their availability provided an opportunity to measure the influence of hardness on tear strength.

The results of tear strength tests as a function of hardness are plotted in Figure A1. These measurements were made on 0-month specimens; i.e., specimens that had not been thermally aged. Note that the tear strength appears to have a strong linear dependence on hardness for hardness values between 82 and 86 and to be independent of hardness for values greater than 86.

Fig. A1. PET-90A polyurethane tear strength as a function of hardness.

These results suggest that checking hardness of PET-90A polyurethane could provide a quality control to indicate whether processed material has its expected tear strength. The tear strength of PET-90A would be severely compromised if its Shore A hardness is less than 86.

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