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EFFECTS OF STRESS ON PERMEATION AND POLYURETHANE
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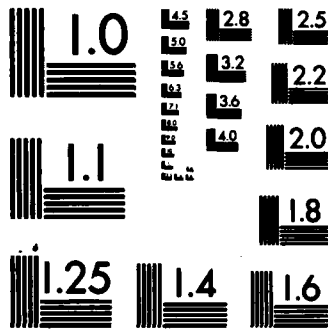
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EFFECTS OF STRESS ON PERMEATION
AND
POLYURETHANE DEGRADATION

FINAL REPORT

NRL Contract N00014-82-C-2208

Submitted to:

Naval Research Laboratory
Underwater Sound Reference Detachment
P.O. Box 8337
Orlando, Florida 32806
Attn: Dr. R. W. Timme,
Code 5970
Program Manager
Sonar Transducer Reliability
Improvement Program

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Submitted by:

Patrick E. Cassidy, Ph.D.
Texas Research Institute, Inc.
9063 Bee Caves Road
Austin, Texas 78746
512/263-2101

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1.0 INTRODUCTION AND BACKGROUND

1.1 Permeation and Stress

Water permeation through elastomers and plastics has been studied for many years. The past ten years have witnessed increased interest in this phenomenon in regard to failure modes and expected lifetimes of sonar transducers. The basis of this concern lies in the fact that transducer design often calls for rubber to be the primary barrier to seawater penetrating into the electroacoustic spaces of the transducer.

A seemingly very important consideration that has been overlooked up to now is the effect of stress on the permeability of the rubber barrier. Two types of stress are commonly present when rubber is used in transducers: (1) a static stress due to the rubber being stretched; and (2) a dynamic stress resulting from the rubber being subjected to acoustic vibration. If these factors affect water permeation, then the behavior and lifetime of the transducer will differ from that expected.

Very little work has appeared in the literature regarding stress effects on permeability. One report of low frequency cycling in an elongation mode considered water diffusion in polymers [1]. A more recent paper discussed effects of tensile deformations on gas transport in glassy polymers [2]. The permeability (P) and diffusion (D) coefficients increased with strain for nitrogen in a polycarbonate but decreased with time at constant strain. Increasing strain (up to 2%) on a polyimide increased P and D; above 2% P and D decreased, and at 6% strain they became less than the unstrained control values.

1.2 Polyurethane Stability

About 15 years ago polyurethane displayed poor stability by reverting to

a gummy substance when exposed to water and heat [3]. Since then, extensive changes in chemical composition have resulted in stable, tough elastomers. However, the consequences of long time exposures are not well defined.

Very recently an extremely stable polyurethane was reported which was subjected to short-term high temperature testing [4]. Polyisobutylene glycols were used in place of polyether or polyester glycols and were cross-linked with triphenylmethane triisocyanate. Four days exposure to 85°C high humidity resulted in tensile strength losses of only 0.4 to 4.8%. Air-oven aging at 128°C for two days resulted in tensile strength losses of 6.5 to 7.3%.

1.3 Accelerated Aging

TRI is experienced in conducting and evaluating accelerated tests for lifetime estimation. Numerous materials have been subjected to temperatures higher than those seen in ordinary duty in order to accelerate aging. Maximum temperatures of 70-80°C are used on rubber to evaluate permeability, bonding, leaching of components, change in hardness, dimension, etc.

2.0 RESULTS AND DISCUSSION

2.1 Permeation and Stress

Two rubber samples were formulated for this program by Burke Rubber Company, San Jose, CA. These were identical zinc oxide/magnesium oxide-cured WRT Neoprenes except that one (designated NXA 1883) had 30 phr black while the other (designated NSA 1938) had 15 phr black and 15 phr hydrated silica. Total filler loading of both materials was therefore the same.

The gum stock was molded into a flat-end cup configuration, 0.030 in. thick on face, 0.070 in. thick on side. The rubber cup was then fitted over the open end of a glass cup and secured with a hose clamp. For

static stressing of the rubber the face of the glass cup was made 10% larger in area than the face of the rubber cup so that the latter was stretched to fit.

For dynamic stressing the cup sizes (rubber and glass) were equal. The closed end of the glass cup was ground flat and an acoustic transducer was coupled to this end via a thin slab of silicone elastomer. Two transducers were used, one resonant at 52 kHz, the other at 99 kHz. The transducer was driven at its resonant frequency with a power input to the glass cup of nom. 0.08 W/cm^2 . The entire assembly, cup with attached transducer, was placed in a desiccator in a circulating air oven at 60°C . To weigh the permeation cell the transducer and silicone slab were removed and the cell was brought to room temperature in a desiccator. Weight was determined to 0.01 mg. When the weight loss became linear with time (2 days to 1 week) the experiment was terminated.

Results are reported in Table I as permeability coefficients. Determinations were made before, during and after ensonification and with a static stress (stretched membrane). Percent changes in permeability coefficients, vis-a-vis nonstressed controls, are also given in Table I.

TABLE I
PERMEATION
Salt Water

<u>Control Samples (60°C)</u>	<u>Permeability Coefficient</u> <u>(mg cm/cm² day mmHg) x 10³</u>	<u>% of</u> <u>Control</u>
NXA-1883 Silica Filled	14.62	—
NXA-1938 Non-silica Filled	14.15	—
<u>Statically Stressed Samples (60°C)</u>		
NXA-1883 Silica Filled	14.15	97
NXA-1938 Non-silica Filled	14.15	100
<u>Dynamically Stressed Samples</u> <u>(Ensonified at 99 kHz; temperature</u> <u>unknown, approx. 75°C)</u>		
NXA-1883 Silica Filled	52.6	360
NXA-1938 Non-silica Filled	52.6	372
<u>After Dynamic Stress (60°C)</u>		
NXA-1883 Silica Filled	12.18	83
NXA-1938 Non-silica Filled	11.92	84

It is apparent that the presence of silica caused no difference in permeability, nor did the static stress of 10% stretch (when corrected for the 10% decrease in thickness which occurred). However, a very striking result was that ensonification yielded a 370% increase in permeability coefficient.

Subsequent tests performed using a thermistor attached to the permeation cell revealed that although the cell was in a desiccator in a 60°C oven, heat generated by the sound source raised the temperature of the cell to 75°C due to the slow rate of heat dissipation through the desiccator. To determine whether this increased temperature would account for some of the increased permeability, similar tests were run using the transducer resonant at 52 kHz. These tests again showed an increase in cell temperature to 70-72°C, even though the

oven chamber was at 60°C. Evidently, the energy generated by the transducer cannot be rapidly dissipated through the desiccator.

Therefore, permeation rates were measured for the ensonified material in a 60°C oven (70-72°C cell temperature) and for a control at 72°C. The results are shown in Table II.

TABLE II

Permeation Through Neoprene
3.5% NaCl Solution; 50 kHz Ensonification

<u>Control (72°C)</u>	<u>(mg/hr)</u>	<u>Permeability</u> <u>(mg cm/cm²day cm Hg) x 10³</u>	<u>% of</u> <u>Control</u>
NXA-1883 Silica Filled	3.94	23.2	
NXA-1938 Non-Silica Filled	3.17	18.5	
<u>Ensonified (70-72°C)</u>			
NXA-1883 Silica Filled	4.08	23.9	+3.4%*
NXA-1938 Non-Silica Filled	2.92	17.1	-8.7%*

*due probably to temperature variation (2°C) during ensonification

2.2 Polyurethane Stability

Because of delayed receipt of specified test materials TRI ran preliminary screening tests on PRC-1538 to assess polyurethane degradation rates. A slab of PRC-1538 0.070-0.079 in. thick was used from which six 1 in. diameter discs and 24 mini-dogbone tensile test specimens (2-1/2 in. long by 1/8 in. wide in the center test portion) were cut. These specimens were aged in a 3.5% salt water bath.

Table III gives the results of the tensile strength measurements. Some experimental error is evident in the irregular variation of the strength over the test duration. This may have been due to the small size of the test samples or to the limited number (three) of specimens per data point. The variability of the elongation measure renders it of little value. The most significant result is an immediate (less than

one day) loss in strength which plateaus for the balance of the exposure period until severe breakdown between 42 and 72 days.

TABLE III

Tensile Data, PRC-1538
Salt Water Aging, 60°C

<u>Elapsed Time</u> <u>(Days)</u>	<u>Average</u> <u>(psi)</u>	<u>% of</u> <u>Original</u>	<u>Average</u> <u>Elongation</u> <u>(%)</u>
0	1,170	--	392
1	800	68	300
3	743	64	287
9	785	67	325
42	822	70	287
72	445	38	--

Table IV lists changes in weight and thickness of the disc specimens at three different temperatures.

TABLE IV

Weight and Dimensional Changes of PRC-1538 at 23, 40 and 60°C
Salt Water Exposure

<u>Temperature</u> <u>(°C)</u>	<u>Weight (%)</u>		<u>Thickness (%)</u>	
	<u>Day 1</u>	<u>Day 43</u>	<u>Day 1</u>	<u>Day 43</u>
23	1.9	2.2	1.3	1.3
40	2.2	2.2	1.4	1.4
60	2.1	2.2	1.3	1.3

Clearly any change is insignificantly small, immediate, and temperature insensitive.

It has been reported [5] that the tensile strength of specimens cut before aging is lower than that of specimens cut after aging the parent slab. This was examined as follows using samples of the test polyurethanes.

Mini-dogbone tensile specimens (2-1/2 in. long, 1/8 in. wide at the center test area) were cut and aged in salt water at 60°C as were whole sheets

of parent material, from which the same size mini-dogbone specimens were cut after aging. The results of tensile strength measurements on these samples are shown in Table V.

TABLE V

Tensile Strengths of Polyurethane Samples
Aged at 60°C in Salt Water

<u>Material/Sample</u>		<u>Baseline (preaged)</u>	<u>Aged</u>	
			<u>1 Day</u>	<u>3 days</u>
L-83	Precut	4,250	3,120	2,920
	Whole	4,250	2,860	2,850
L-167	Precut	6,110	4,520	3,710
	Whole	6,110	4,460	4,240
M-483	Precut	5,280	4,700	4,760
	Whole	5,280	4,090	4,060
L-83-21	Precut	3,280	2,470	1,980
	Whole	3,280	2,220	2,430

Tabulated values are averages for three specimens. Deviations ranged from 5 to 32% of mean value.

Because there is no clear-cut trend evident in the results in Table V all specimens used in the TRI experiments were cut prior to aging.

The four test urethanes were received in two shipments. There were visible differences between these. Material L-83 in the first batch received was dark around the edges, while in the second lot it was a lighter yellow. Material L-83-21 in the second shipment was a darker yellow than that received in the first shipment and had dark edges.

Since darkening may be caused by a postcure or degradation, which may affect material strength, and since all of both shipments were required for testing, these sample differences may prove significant.

To permit efficient use of large tensile specimens (4-1/2 in. long x 1/4 in. thick, ASTM D412 Die C), mini-dogbones were cut for screening. Aging of these started five weeks in advance of the large specimens. Decomposition occurring in the screening specimens flags use of the large dogbones for more accurate measurements.

Table VI shows the results of tensile strength measurements on the small dogbone screening specimens over 85 days of aging at 60°C. All of the materials show an immediate (less than one day) decrement in tensile strength, with some (L-83, L-167) exhibiting continued loss and others (M-483, L83-21) evidencing apparent recovery. Some of this variation may be due to the material differences noted earlier.

TABLE VI

Tensile Strength of Small Dogbone Screening Specimens
Aged at 60°C

<u>Time</u> <u>(days)</u>	<u>Material</u>			
	<u>L-83</u>	<u>L-167</u>	<u>M-483</u>	<u>L83-21</u>
0	4250 psi	6110 psi	5280 psi	3280 psi
1	3120	4520	4700	2470
3	2920	3710	4760	1980
42	3050	2790	void*	2950
64	3180	2880	void*	3590
85	914	2560	5700	2530

*Samples slipped in grips of testing machine.

Tensile strength measurements for the large dogbone specimens aged at 23, 40 and 60°C are listed in Table VII. Material L-83 shows a severe loss at 98 days and 60°, a result predicted from the small dogbone screening results (Table VI). This begs the question, will the specimens aged at 23 and 40°C show comparable losses at longer aging times?

TABLE VII

Tensile Strength of Large Dogbone Specimens
Entries are psi

<u>Material</u>	<u>Time</u> (Days)	<u>Aging Temperature</u> (°C)		
		23	40	60
L-83	0	4,570	4,570	4,570
	1	2,970	3,430	3,340
	2	2,420	2,650	2,790
	16	2,190	2,150	3,020
	98	2,285	2,550	1,460
L-83-21	0	2,750	2,750	2,750
	1	2,780	2,090	2,140
	2	2,060	2,360	2,040
	16	2,140	2,450	2,170
	98	2,340	2,200	2,360
M-483	0	5,290	5,290	5,290
	1	4,660	4,180	4,710
	2	4,340	3,700	4,550
	16	void*	4,130	void*
	98	4,920	4,710	5,180
L-167	0	5,850	5,850	5,850
	1	4,560	4,210	4,910
	2	4,270	4,150	4,210
	16	4,270	3,570	3,570
	98	3,690	3,980	3,220

*Samples slipped during tests; material difficult to grip

Material L-83-21 evidences some recovery of tensile strength at the longest aging time. This is probably due to a postcure or to crosslinking. This material's strength retention is somewhat surprising in view of its high water uptake (see Table IX).

Material M-483 also evidences recovery and retention, better, in fact, than any of the other materials. However, M-483 is the most difficult material to test because of its slippery surface--it is difficult to grip in the tensile tester.

Other parameters being monitored are thickness (Table VIII), weight, i.e., solubility of water in the elastomer (Table IX), and Shore A hardness (Table X).

Materials L-83 and L-83-21 show appreciable changes in thickness after one day of aging. Material L-83-21 continues to change, while L-83 does not. The other two materials evidence no essential change in thickness.

Material L-83-21 shows significantly more water uptake than the others (Table IX). The weight gain was 8, 10 and 14% after 75 days aging at 23, 40 and 60°C, respectively, compared to approximately 1% for the other materials. Interestingly, however, swelling in this material was quite small (+2.7%). (Of course, the other materials showed even less.) Material L-83-21 also manifested slightly greater loss of hardness than the other materials at 54 days aging.

Material L-167 showed least change in hardness, -2%, compared to -5 and -7% for the other three materials.

Aging of materials will continue for one year total time with data collected quarterly. Present conclusions are that material L-83 lacks long-term tensile strength, and material L-83-21, even though it retains strength well may be unsatisfactory due to its high water uptake.

There are three processes, one physical and two chemical in nature, which can cause property changes. The simplest is the physical process of water absorption and subsequent plasticization of the polymer. This will lead to elongation with weight gain and a softer material. The chemical process with the same results plus a loss of tensile strength is hydrolysis of the backbone causing a decrease in molecular weight and crosslink density. The chemical process which would lead to a toughening of the elastomer is increased cure brought about by the aging at increased temperature. All three processes probably occur simultaneously but at different rates.

TABLE VIII

Thickness

	Time (days)	Cumulative Percent Change in Thickness		
		23°C	40°C	60°C
L-83	1	+6.6	+6.5	+1.2
	2	0.0	0.0	0.0
	4	0.0	0.0	-1.2
	8	0.0	0.0	0.0
	26	0.0	-1.3	0.0
	54	0.0	-1.3	0.0
L-83-21	1	+7.9	+8.1	+7.5
	2	+1.3	+2.7	+1.4
	4	+1.3	+2.7	+1.4
	8	+1.3	+2.7	+1.4
	26	+1.3	+2.7	+1.4
	54	+1.3	+2.7	+2.7
M-483	1	0.0	+1.1	+1.3
	2	0.0	0.0	0.0
	4	0.0	0.0	0.0
	8	-1.5	0.0	0.0
	26	-1.5	0.0	0.0
	54	-1.5	+5.4	0.0
L-167	1	+1.3	+1.3	0.0
	2	0.0	0.0	0.0
	4	0.0	0.0	0.0
	8	0.0	0.0	0.0
	23	0.0	0.0	-1.0
	54	0.0	0.0	-1.0

Samples were 0.070 to 0.080 in. thick so that a change of 0.001 in. = 1.4%.

TABLE IX

Solubility

	Time (days)	Cumulative Percent Increase in Weight		
		23°C	40°C	60°C
L-83	1	1.10	1.08	1.26
	2	1.14	1.13	1.28
	4	1.13	1.20	1.36
	8	1.10	1.12	1.25
	26	1.04	1.01	1.10
	54	0.85	0.98	0.91
	L-83-21	1	3.49	5.10
2		5.18	6.71	8.06
4		6.75	7.89	9.46
8		7.55	8.21	9.25
26		7.98	8.53	11.18
54		7.79	8.66	12.88
M-483		1	0.82	1.05
	2	1.05	1.23	1.32
	4	1.12	1.22	1.52
	8	1.10	1.22	1.38
	26	1.03	1.12	1.23
	54	0.96	1.10	1.18
	L-167	1	0.92	1.18
2		1.17	1.27	1.26
4		1.27	1.24	1.36
8		1.25	1.12	1.26
26		1.19	1.19	1.17
54		1.11	1.12	1.09

TABLE X

Hardness
(SHORE A)

	Time (days)	Cumulative Percent Change in Hardness		
		23°C	40°C	60°C
<hr/>				
L-83 (H ₀ = 84-89)	1	+1.2	-2.3	-3.4
	2	+1.2	-2.3	-3.4
	4	+3.6	-1.1	-2.2
	8	+3.6	0.0	-2.2
	26	0.0	-4.6	-5.6
	54	+1.2	-4.6	-5.6
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L-83-21 (H ₀ = 82-86)	1	-2.3	+1.2	-3.5
	2	-2.3	+1.2	-3.5
	4	0.0	+3.7	-3.5
	8	-1.1	+3.7	-3.5
	26	-5.8	0.0	-5.8
	54	-4.7	-1.2	-7.0
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M-483 (H ₀ = 92)	1	-1.1	-1.1	-1.1
	2	-1.1	0.0	-1.1
	4	-1.1	-1.1	0.0
	8	-1.1	0.0	-1.1
	26	-2.2	-2.2	-4.3
	54	-2.2	-2.2	-5.4
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L-167 (H ₀ = 96-97)	1	0.0	-1.0	-1.0
	2	0.0	-2.0	-1.0
	4	0.0	-1.0	-1.0
	8	0.0	-1.0	-1.0
	26	0.0	-1.0	-2.0
	54	0.0	-2.0	-2.0
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3.0 SUMMARY AND CONCLUSIONS

Two Neoprene formulations (with and without silica filler) were tested for deionized and salt permeation under static (10% area stretch) and dynamic (52 and 99 kHz ensonification) stress. Silica filler did not affect permeation. Ensonification caused no significant changes in permeability after compensation for temperature rise caused by the ultrasonic energy input.

Four polyurethane elastomers are being exposed to 23, 40 and 60°C salt water and are being monitored for changes in tensile strength, weight, dimension and hardness. Very little change in hardness or thickness has been observed. Only one material (L-83-21) has shown significant water uptake (13% at 60°C over 54 days). Tensile strength data showed immediate (<1 day) losses with subsequent stabilization at 65-90% of original values up to 98 days of aging. At 60°C L-83 begins to show serious loss (to 32% of original value) at 98 days test time.

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