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# Effect of saline exposure on the surface and bulk properties of medical grade silicone elastomers

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J. J. Kennan,<sup>1</sup> Y. A. Peters,<sup>1</sup> D. E. Swarthout,<sup>1</sup> M. J. Owen,<sup>1</sup> A. Namkanisorn,<sup>2</sup> M. K. Chaudhury<sup>1,2</sup>

<sup>1</sup> Dow Corning Corporation, Mail #C03101, Midland, Michigan 48686-0994

<sup>2</sup> Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

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**Abstract:** Medical-grade silicone elastomers were subjected to accelerated aging in saline to verify the hydrolytic stability of the elastomer. Tensile strength, elongation at break, and the elastomer stress measured at 100% or 200% elongation did not change significantly for peroxide-cured sheeting aged in 37°C or 100°C saline for 45 h. Under similar condition, hydrosilylation cured sheeting behaved similarly; however, increases in stresses measured at 100% and 200% elongation were observed after the first hour of treatment. After the first hour, the physical properties remained relatively constant. On either elastomer, initial liquid drop advancing contact angles for water ranged from 110° to 115°, and in no case was a change of >6° observed as a result of aging in saline for 45 h at temperatures up to 97°C. The high advancing angles indicated that the surface remained largely hydropho-

bic. Initial liquid drop receding contact angles ranged from 48° to 64°, with receding contact angles being more sensitive to accelerated aging, in one case decreasing to 14°. Similar decreases in receding contact angle were observed on polyethylene subjected to the same accelerated aging conditions. Decreases in receding contact angle were not considered to be indicative of extensive hydrolysis. The observed contact angle phenomena are consistent with current views of contact angle hysteresis being caused by surface heterogeneity. There was no evidence of significant surface or bulk siloxane hydrolysis under these accelerated aging conditions. © 1997 John Wiley & Sons, Inc. *J Biomed Mater Res*, **36**, 487–497, 1997.

**Key words:** silicone elastomer; hydrolytic stability in saline; tensile strength and contact angle hysteresis

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## INTRODUCTION

Elastomers play a key role in numerous medical devices, yet only a few elastomers are suitable for long-term implantation in a biological environment. Classes of polymeric material in use include polyurethanes, polyolefins, and silicones.<sup>1</sup> Although silicones have long been considered one of the premier materials, they have come under increasing scrutiny owing to litigation surrounding breast implants and the proliferation of anecdotal reports of illnesses associated with silicone implants.

Recently, exposure to saline was reported to cause changes in the surface chemistry of silicone elastomers.<sup>2,3</sup> The reported changes were based on a study in which peroxide-cured silicone sheeting was exposed to saline at temperatures of 60°C, 70°C, 80°C, and 100°C for 45 h.<sup>4</sup> Saline exposure caused decreases in the captive bubble contact angles that were assumed to be

caused by surface hydrolysis of the elastomer. X-ray photoelectron spectroscopy (XPS) determinations of nitrogen uptake on the elastomer following reaction with 3-aminopropyltriethoxysilane were taken as confirmation of the surface hydrolysis. A kinetic analysis led the authors to conclude that a silicone elastomer surface would reach a 12% coverage of surface hydroxyls within 12 h in saline at 37°C. The implication was that surface hydrolysis changes the biocompatibility of silicones following implantation.

In view of the suggestion that biocompatibility may be compromised, it becomes important to clarify whether physical or chemical processes occurring in saline compromise the integrity of the elastomer or change its surface chemistry. Examination of the original experimental work<sup>4</sup> revealed that the silanol concentration estimates were based on receding contact angle measurements. Use of receding contact angles to determine the concentration of surface species is without precedent and potentially misleading. Unfortunately, advancing contact angles were not reported.

The purpose of this work was to look at the effect of accelerated aging in saline on the surface and bulk properties of medical grade silicone elastomers. To assess whether cure residues affect the hydrolytic stabil-

Correspondence to: J. J. Kennan

ity, both peroxide- and hydrosilylation-cured samples were evaluated. Changes to the surface were monitored by measuring both advancing and receding contact angles. Contact angle is a very sensitive technique for monitoring changes on a surface, but assigning the cause of time-dependent contact angle phenomenon is a subject of continued debate. To give perspective to the contact angle observations, a comparison was made with a nonsilicone subjected to the same accelerated aging conditions. Bulk properties were monitored by measuring the tensile properties of the elastomers.

## MATERIALS ANDS METHODS

### Materials

Deionized water with a resistivity of 17.8 M $\Omega$ -cm or better was used for all the experiments. Saline was prepared as 0.9% biological-grade sodium chloride in deionized water. Two silicone elastomers were evaluated. The hydrosilylation cured elastomer, Silastic<sup>®</sup> Rx Medical-Grade Sheeting NRV 7-5202 (Lot HX114069), was crosslinked by platinum-catalyzed hydrosilylation chemistry. The peroxide-cured elastomer, Silastic<sup>®</sup> Rx Medical-Grade Sheeting Nonreinforced, Catalogue No. 500 (Lot HX114070), was prepared by peroxide-initiated, free-radical crosslinking chemistry. Both materials are described as silica-reinforced polydimethylsiloxane silicone rubbers and were received in the form of 0.051-cm-thick sheeting. The peroxide-cured elastomer was received with an NaHCO<sub>3</sub> coating that was removed prior to the accelerated aging experiments. Additive-free, injection molding-grade, low-density polyethylene (Dow LDPE 5004IM) was obtained as pellets having  $M_n = 18,500$ ,  $M_w = 105,800$ , and  $d = 0.923$  g/cc.

Tables I and II describe the elastomer formulations using generic descriptors for the proprietary siloxane components. These components are high-molecular-weight gums, low-molecular-weight fluid plasticizers, and crosslinkers.

### Material pretreatment

The elastomer sheeting was cut into 2.54  $\times$  15.24-cm samples for the physical property studies or 1.5  $\times$

4 cm for the contact angle studies. The samples were rinsed with water and placed in a sonic bath to remove the NaHCO<sub>3</sub> coating. Samples were dried and then extracted with toluene for 48–50 h in a Soxhlet extractor. After air drying, residual toluene was removed at room temperature in vacuum overnight. Tensile specimens were stored in a desiccator for 2 h prior to measuring the weights and dimensions. For the hydrosilylation- and peroxide-cured elastomers, extractables averaged 3.0% and 2.3%, respectively.

Polyethylene pellets were extracted with hexane for 4 h in a Soxhlet extractor. The pellets were dried at room temperature and then transferred to a vacuum oven and dried at room temperature in vacuum overnight. Extractables averaged 1.0%. A Boy 15S injection molder was used to prepare the 12.7  $\times$  1.3  $\times$  0.32-cm polyethylene bars. In the injection-molding process, the pellets were passed through a barrel in which they were melted and compressed at 240°C and then passed through a 200°C nozzle into a mold maintained at 46°C. Mold release agents were not used in preparation of the polyethylene bars.

### Accelerated aging treatment

The extracted samples were suspended from glass hooks on a modified glass stirrer. An air motor was used to stir the samples in a saline-filled resin kettle maintained at the desired treatment temperature, typically for periods of 1, 5, 10, 20, and 45 h. The samples were rinsed with water and then soaked in water for 1 h.

### Tensile measurements

Tensile properties were measured on die C dumbbell-shaped tensile bars as specified in ASTM test D412. Stress-strain curves were recorded on a Instron<sup>™</sup> model 55R1122US outfitted with an extensometer and a 200-lb load cell. The crosshead speed was 20 in/min. Reported tensile properties were based on the mean of five samples.

### Statistical analysis of tensile data

The experimental design was treated as a completely randomized trial with three factors (elastomer type, exposure time, and exposure temperature) using a general linear model. The data were analyzed to determine if there were any changes in the tensile strength, elongation at break, stress at 100% elongation, or stress at 200% elongation of the two elastomers when heated over a 45-h period in either 37°C or 100°C saline. The probability of type I error was set at 5% using a two-tailed test. The effect of duration of exposure was tested

TABLE I  
Formulation for Peroxide-Cured Silicone Sheeting

Chemical Name	Description	%
Dimethylsiloxane, methylvinylsiloxane, dimethylvinyl terminated	Gum	65.50
Dimethylsiloxane, hydroxy terminated	Fluid (low $M_n$ )	6.55
Silica, amorphous	Filler	26.85
bis-(2,4-Dichlorobenzoyl) peroxide		1.10

TABLE II  
Formulation for Hydrosilylation-Cured Silicone Sheeting

Chemical Name	Description	%
Dimethylsiloxane, dimethylvinyl terminated	Gum	62.36
Dimethylsiloxane, hydroxy terminated	Gum	5.13
Dimethylsiloxane, hydroxy terminated	Fluid (low <i>Mn</i> )	5.43
Dimethyl, methylvinylsiloxane, hydroxy terminated	Fluid (low <i>Mn</i> )	0.22
Silica, amorphous	Filler	25.65
Platinum-siloxane complex	Catalyst	0.20
Dimethyl, methylhydrogen siloxane	Fluid (crosslinker)	0.99
Inhibitor		0.025

using Dunnett's method to compare the mean response at each time of exposure to saline to that of the time zero control. In addition, where significant effects were observed, Tukey's test was used to make all possible comparisons over time. This was done to determine whether an observed effect was due to a gradual or step change.

#### Contact angle measurements

Contact angles were measured by both liquid drop and captive bubble methods. After accelerated aging in saline, the elastomer sample was immediately cut into a 0.5 × 0.5-cm piece and placed on a glass slide. A liquid or air bubble was advanced or withdrawn across the surface by slowly changing the volume dispensed through a syringe needle. The needle remained in the drop during measurements to avoid vibration or distortion of the drop. Advancing or receding contact angles were measured when the liquid was brought to rest after being slowly advanced or withdrawn across the surface respectively. Contact angles were measured directly using a microscope fitted with a goniometer eyepiece. For each sample, the average of about eight measurements was reported.

## RESULTS

Prior to saline treatment, elastomers were extracted with toluene to remove low-molecular-weight species that might interfere with the contact angle measurements. Elastomer slabs were then immersed in saline for various times at the specified temperatures. The properties monitored as a function of exposure were the contact angle and the tensile properties of the elastomer.

Tables III and IV show the tensile strength, elongation at break, and stresses measured at several elongations for peroxide-cured sheeting aged in saline at 37°C and 100°C, respectively. The stresses at 100% and 200% elongation and the tensile strength are plotted as a

function of saline immersion time and temperature in Figure 1. After 45 h treatment in 100°C saline, the tensile strength was observed to decrease by 4.2% from the initial value, while the elongation increased by <1%. The effect of duration of exposure was tested using Dunnett's method to compare the mean response at each time of exposure against the time zero control. There was no consistent effect of either temperature or duration of exposure on the bulk properties of the peroxide-cured silicone elastomer. For example, using the aforementioned statistical test, the stress at 100% elongation at 10 h and the stress at 200% elongation at 20 h gave statistically significant values higher than the control, but at no other times were the measured stresses significantly different from the control. Similar observations were made for the tensile strength and the elongation. In view of these results, changes in the peroxide-cured elastomer due to saline exposure were deemed slight.

Tables V and VI show the tensile strength, elongation at break, and stresses measured at several elongations for the hydrosilylation-cured sheeting aged in saline at 37°C and 100°C, respectively. Figure 2 shows the stresses at 100% and 200% elongation and the tensile strength plotted as a function of saline immersion time and temperature. After 45 h at 100°C, the tensile strength was observed to undergo a 0.9% decrease from the initial value, while the elongation was observed to decrease by 4.4%; these changes were not statistically significant. A statistical analysis of the data using Dunnett's method showed that only the stresses at 100% and 200% elongation had statistically significant sustained increases of <10% and 5% of the control, respectively. The data were further analyzed using Tukey's test to make all possible comparisons over time. It was concluded that the change in the stresses at 100% and 200% elongation occurred over the first hour of exposure, and that no further statistically significant changes occurred over the duration of the experiment.

A separate set of samples was examined for changes in contact angles as a function of exposure to saline at 60°C, 70°C, and 97°C. Contact angles were examined using both the captive bubble and liquid drop techniques. Standard deviations for captive bubble contact

**TABLE III**  
**Tensile Properties of Peroxide-Cured Sheeting Aged in Saline at 37°C**

Time Aged in Saline (hr)	0	1	5	10	20	45
Tensile (MPa)						
Ave.	11.78	10.83	11.64	11.58	11.67	11.48
SD	0.70	0.45	0.66	0.69	0.56	0.61
Elongation (%)						
Ave.	479	455	470	470	455	482
SD	24	25	12	16	18	27
Stress at 100% (MPa)						
Ave.	1.46	1.46	1.50	1.48	1.64	1.43
SD	0.04	0.06	0.12	0.03	0.06	0.04
Stress at 200% (MPa)						
Ave.	3.32	3.32	3.45	3.41	3.74	3.23
SD	0.12	0.15	0.26	0.08	0.14	0.12
Stress at 300% (MPa)						
Ave.	6.03	5.97	6.20	6.14	6.58	5.85
SD	0.20	0.26	0.41	0.12	0.24	0.19
Stress at 400% (MPa)						
Ave.	9.12	9.05	9.36	9.29	9.81	8.89
SD	0.28	0.33	0.54	0.19	0.33	0.26

angle measurements averaged 2.1 and 3.0 for advancing and receding angles, respectively. Standard deviations for liquid contact angle measurements averaged 1.7 and 2.7 for advancing and receding angles, respectively.

Captive bubble advancing contact angles for peroxide- and hydrosilylation-cured elastomers as a function of saline immersion conditions are summarized in Table VII and Figures 3 and 4. Analogous liquid drop measurements are shown in Table VIII and Figures 5 and 6. In most cases, the advancing angles are stable, especially those measured by the more reproducible liquid drop technique. For either elastomer, liquid drop advancing angles were not observed to change by  $>6^\circ$  as a result of saline immersion. Regardless of immersion time, temperature, or measurement tech-

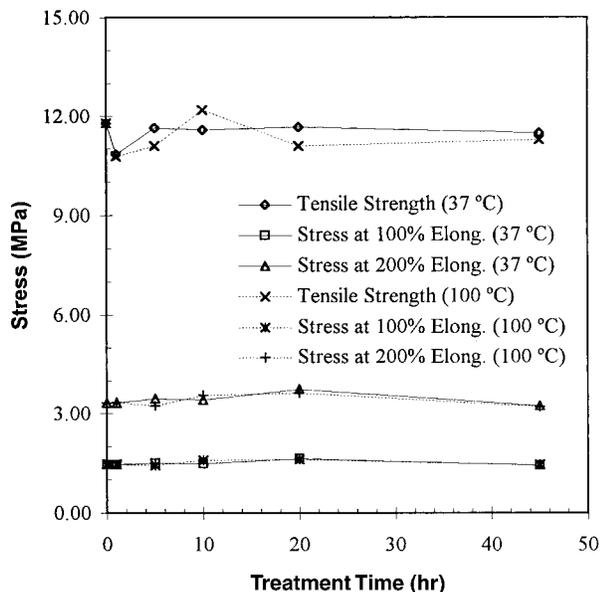
nique, all measured advancing angles exceeded  $100^\circ$ , indicating that the surfaces retained a significant hydrophobic component.

Captive bubble receding contact angles are shown in Table IX and Figures 3 and 4, whereas the analogous liquid drop measurements are shown in Table X and Figures 5 and 6. The initial receding angles were as much as  $50^\circ$  lower than the analogous advancing angles; thus, there was a significant amount of hysteresis in the contact angle measurement.

Saline immersion caused a significant decrease in the receding angles; however, the scatter in results makes it impractical to attempt a kinetic analysis such as that reported in Reference 4. The worst case decrease in the liquid drop contact angle was observed on the hydrosilylation-cured elastomer that showed a de-

**TABLE IV**  
**Tensile Properties of Peroxide-Cured Sheeting Aged in Saline at 100°C**

Time Aged in Saline (hr)	0	1	5	10	20	45
Tensile (MPa)						
Ave.	11.78	10.78	11.09	12.19	11.09	11.29
SD	0.70	0.88	1.01	0.32	0.59	0.44
Elongation (%)						
Ave.	479	453	472	488	446	481
SD	24	30	41	12	19	18
Stress at 100% (MPa)						
Ave.	1.46	1.46	1.43	1.58	1.61	1.44
SD	0.04	0.06	0.10	0.02	0.04	0.03
Stress at 200% (MPa)						
Ave.	3.32	3.33	3.23	3.55	3.63	3.21
SD	0.12	0.14	0.21	0.07	0.12	0.06
Stress at 300% (MPa)						
Ave.	6.03	6.00	5.83	6.25	6.40	5.76
SD	0.20	0.23	0.29	0.11	0.19	0.10
Stress at 400% (MPa)						
Ave.	9.12	9.08	8.83	9.34	9.57	8.74
SD	0.28	0.32	0.37	0.14	0.27	0.14



**Figure 1.** Tensile strength, stress at 100% elongation, and stress at 200% elongation values for peroxide-cured silicone elastomer following saline exposure for various times at 37°C or 100°C.

crease in receding contact angle of 43° upon immersion in saline for 45 h at 100°C.

It was of interest to determine if the surface phenomenon observed was unique to silicone. For comparison, polyethylene bars were subjected to the 97°C aging conditions, and the advancing and receding contact angles were monitored using the liquid drop contact angle technique. The contact angles are summarized in Table XI and Figure 7.

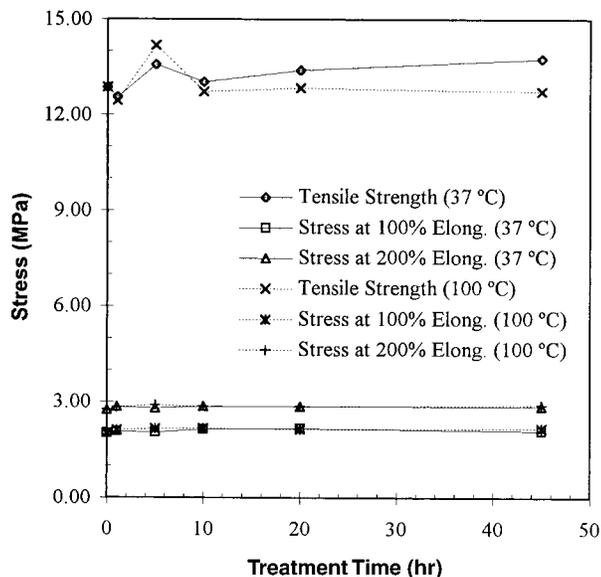
## DISCUSSION

Tensile strength, elongation, stress at 100% elongation, and stress at 200% elongation of silicone elastomers were measured as a function of time of exposure in 37°C or 100°C saline. Analysis of the data using Dunnett's method revealed that no sustained changes in tensile strength, elongation at break, or stresses measured at 100% or 200% elongation of peroxide-cured silicone elastomers occurred during immersion for 45 h at 37°C or 100°C. In the case of the hydrosilylation-cured elastomer, temperature or time of exposure had no sustained effect on tensile strength and elongation during the entire experiment. Increases in the stresses measured at 100% and 200% elongation were observed over the first hour of exposure, after which the material remained unchanged. The reason for the increase in the stresses at 100% and 200% elongation of the hydrosilylation-cured material is not clear; however, it is unlikely to be due to ongoing degradation of the elastomer, since the material remained stable after the first hour. The observed stability of the elastomers is consistent with literature reports showing that a 70-h exposure of a silicone rubber to water at 100°C led to 10% losses in tensile strength and elongation at break, whereas a 70-h exposure at 149°C led to a 10% loss in tensile strength and a 10% increase in elongation at break.<sup>5</sup> Given the small amount of change in the properties, it would be difficult to discern any slight degradation of the rubber from plasticizing that might occur due to moisture pickup. It is reasonable to conclude that no extensive degradation of the rubber occurred under these conditions.

Concerning the elastomer surface, advancing contact angles with water were reproducible and did not ap-

**TABLE V**  
Tensile Properties of Hydrosilylation-Cured Sheeting Aged in Saline at 37°C

Time Aged in Saline (hr)	0	1	5	10	20	45
Tensile (MPa)						
Ave.	12.85	12.55	13.58	13.02	13.40	13.76
SD	0.49	0.49	1.41	0.38	0.70	1.12
Elongation (%)						
Ave.	812	761	804	769	800	802
SD	25	24	50	10	43	53
Stress at 100% (MPa)						
Ave.	2.02	2.08	2.05	2.14	2.17	2.10
SD	0.03	0.10	0.05	0.02	0.09	0.06
Stress at 200% (MPa)						
Ave.	2.76	2.85	2.81	2.86	2.86	2.86
SD	0.02	0.12	0.04	0.02	0.09	0.06
Stress at 300% (MPa)						
Ave.	3.43	3.61	3.55	3.63	3.60	3.63
SD	0.04	0.19	0.08	0.03	0.19	0.10
Stress at 400% (MPa)						
Ave.	4.47	4.81	4.70	4.85	4.78	4.81
SD	0.08	0.32	0.15	0.06	0.37	0.17



**Figure 2.** Tensile strength, stress at 100% elongation, and stress at 200% elongation values for hydrosilylation-cured silicone elastomer following saline exposure for various times at 37°C or 100°C.

pear to undergo significant change over the range of times and temperatures examined. For example, 45-h exposures to 97° saline led to decreases of 3° and 6° in the liquid drop advancing angles on the peroxide- and hydrosilylation-cured elastomers. Contact angle hysteresis was observed, with initial receding angles ranging from 47° to 64° lower than the corresponding advancing angles. Receding contact angles exhibited more scatter than the advancing angles. At moderate temperatures (60°C and 70°C), the receding contact angles decreased over the first 10–20 h and then either leveled out or underwent a slow decline. Saline expo-

sure caused larger changes to the receding angles than the advancing angles. For example, exposing peroxide cured elastomers to 70° and 97° saline for 45 h caused the liquid drop receding angles to decrease by 13° and 37°, respectively.

Despite observed changes to the receding angles, it seems unlikely that the extensive surface hydrolysis is occurring. Even under the most severe treatment conditions, advancing contact angles remain high, suggesting that the surface is still largely hydrophobic.

The reason for the observed decreases in receding contact angles would be a subject for considerable debate. Although it is impossible to eliminate limited surface hydrolysis as a contributor to the effect, it is also impossible to eliminate many other possible contributing factors. For example, Figure 7 shows that the contact angle of water on polyethylene is also affected by immersion in 97°C saline. Following a 48-h exposure, the advancing angle was observed to drop by 21°, while the receding angle was observed to decrease by 53°. Since polyethylene does not contain readily hydrolyzable bonds, the surface changes are probably the result of mechanisms other than surface hydrolysis.

Closer examination of the surface hydrolysis claim reported in References 2 and 4 shows that their kinetic analysis and reported silanol concentrations are based on a number of questionable assumptions regarding the relationship between surface silanol and the receding contact angle. The main criticism of the work must be the assumption that the change in the receding contact angle is attributable to a single mechanism, i.e., surface hydrolysis.

Beyond the mechanism issue, since only receding contact angles with water were reported, there is no way to convert this measurement into a meaningful thermodynamic quantity that can be related to the con-

**TABLE VI**  
Tensile Properties of Hydrosilylation-Cured Sheeted Aged in Saline at 100°C

Time Aged in Saline (hr)	0	1	5	10	20	45
Tensile (MPa)						
Ave.	12.85	12.45	14.18	12.73	12.84	12.74
SD	0.49	0.92	0.25	0.70	0.75	0.32
Elongation (%)						
Ave.	812	768	810	778	763	776
SD	25	44	16	39	53	19
Stress at 100% (MPa)						
Ave.	2.02	2.12	2.15	2.17	2.14	2.16
SD	0.03	0.03	0.05	0.04	0.08	0.06
Stress at 200% (MPa)						
Ave.	2.76	2.83	2.90	2.86	2.85	2.90
SD	0.02	0.03	0.05	0.04	0.07	0.06
Stress at 300% (MPa)						
Ave.	3.43	3.56	3.67	3.59	3.63	3.63
SD	0.04	0.08	0.09	0.08	0.13	0.08
Stress at 400% (MPa)						
Ave.	4.47	4.71	4.87	4.74	4.87	4.80
SD	0.08	0.15	0.18	0.14	0.27	0.14

**TABLE VII**  
**Captive Bubble Advancing Contact Angles (deg) on Silicone Samples following Aging in Saline**

Exposure Time (h)	Angle (deg) following Exposure at Specified Temp.					
	Peroxide Cured			Hydrosilylation Cured		
	60°C	70°C	97°C	60°C	70°C	97°C
0	119	122	120	123	121	123
1	120	112	116	121	121	123
5		118	111	121	120	118
5.5	114					
10	118		109	122	118	104
11		122				
20	114		112	118	122	111
21		106				
34		117				
44		112				
45	114		114	124	119	101

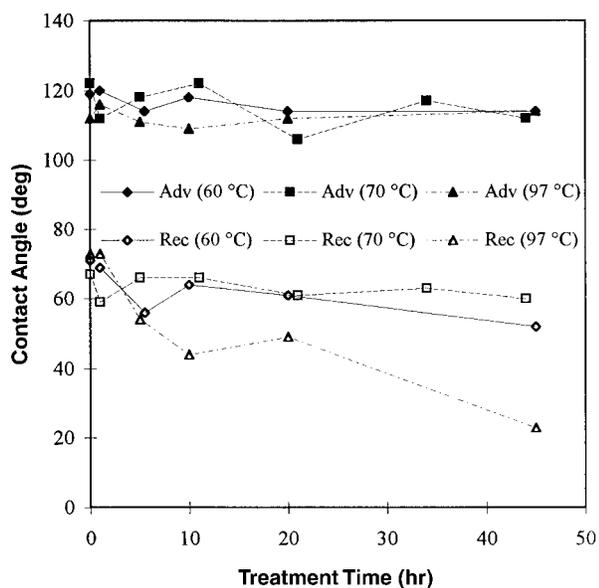
centration of surface species. In the original work, the Young Equation (1) was used to convert the receding contact angles to liquid–solid surface tensions ( $\gamma_{SL}$ ) which were then assumed to be linearly related to the percent silanol<sup>4</sup>:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (1)$$

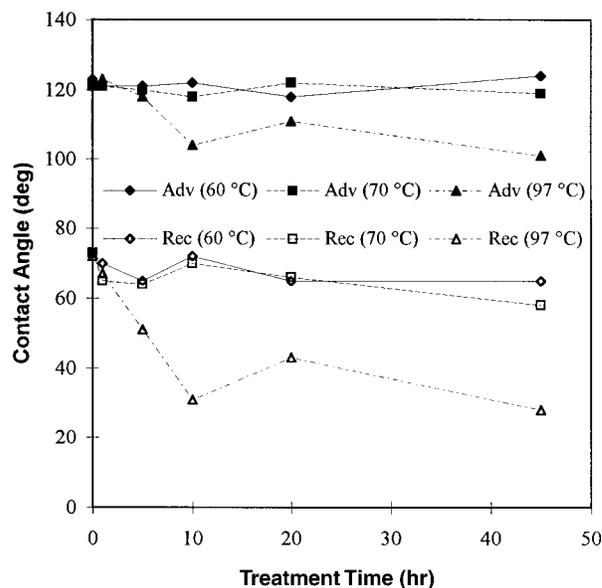
These calculations are potentially bad approximations, for a number of reasons. First, with systems that exhibit contact angle hysteresis it is usual to apply Young's equation only to the quasi-equilibrium advancing contact angles. Indeed, in the form presented above,  $\gamma_{SV}$  is defined as the surface tension of the solid in equilibrium with the vapor of the wetting liquid (not the liquid of the wetting liquid), and thus the advancing contact angle of water must be used, not the receding

angle. Second, the Young equation cannot be directly used to estimate the solid–liquid surface tension in a single measurement, since the solid–vapor surface tension is also unknown. Third, for the purposes of calibrating the relationship between  $\gamma_{SL}$  and silanol coverage, in Reference 4 the most heavily treated elastomer was assumed to have a fractional silanol concentration of 50%. A coverage of 50% seems unlikely since in this study, similarly treated surfaces exhibit advancing contact angles  $>100^\circ$ . In view of these points, any attempt to quantify the amount of silanol through a receding contact angle measurement must be questioned.

Contact angle hysteresis is commonly observed in polymer systems. Numerous polymer solids were shown to exhibit contact angle hysteresis with water,



**Figure 3.** Captive bubble advancing and receding contact angles on peroxide-cured silicone elastomer following saline exposure for various times at 60°C, 70°C, or 97°C.



**Figure 4.** Captive bubble advancing and receding contact angles on hydrosilylation-cured silicone elastomer following saline exposure for various times at 60°C, 70°C, or 97°C.

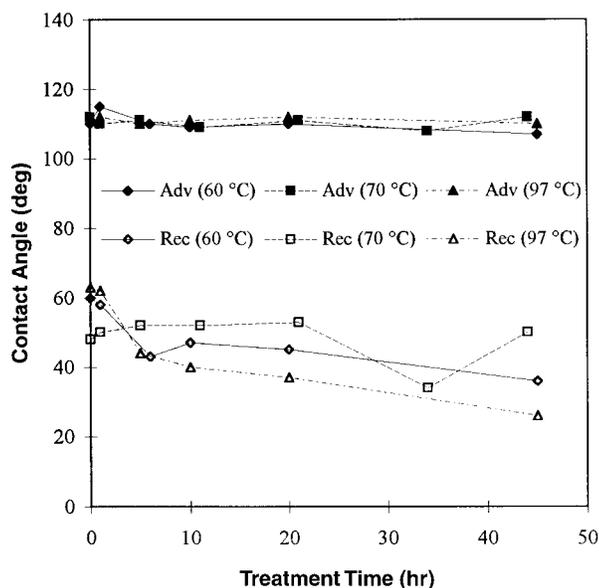
**TABLE VIII**  
**Liquid Drop Advancing Contact Angles (deg) on Silicone Samples following Aging in Saline**

Exposure Time (h)	Angle (deg) following Exposure at Specified Temp.					
	Peroxide Cured			Hydrosilylation Cured		
	60°C	70°C	97°C	60°C	70°C	97°C
0	110	112	112	115	114	112
1	115	110	112	115	114	112
5		111	110	113	114	110
6	110					
10	109		111	111	112	110
11		109				
20	110		112	111	112	112
21		111				
34		108				
44		112				
45	107		110	111	111	106

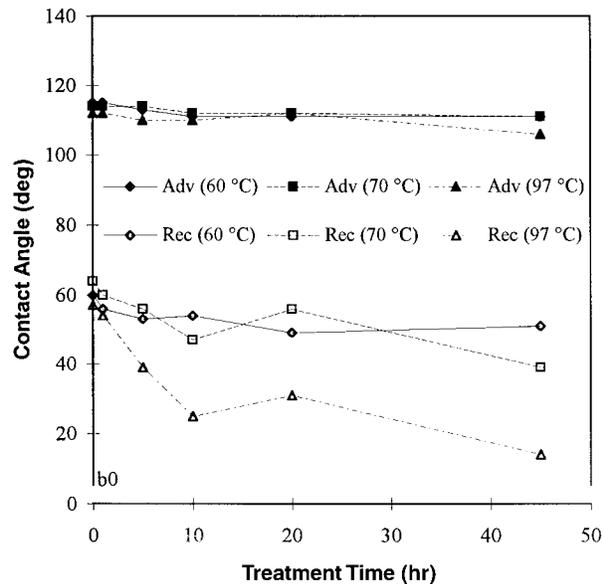
formamide, methylene iodide, ethylene glycol, bromonaphthalene, dimethylacetamide, and hexadecane.<sup>6</sup> Significant hysteresis of water contact angles was recently reported for polytetrafluoroethylene, polyethylene, polypropylene, poly(ether urethane), poly(ethylene terephthalate), nylon 6, poly(vinyl alcohol), and cellulose.<sup>7</sup> In the latter study, time-dependent changes in the receding contact angle during relatively short immersion times in water were noted for several of the polymers studied. Generally, hysteresis phenomena are associated with chemical or physical heterogeneity of the surface. Chemical heterogeneity might imply a surface with high- and low-energy regions due to different chemical moieties present at the surface, whereas physical heterogeneity might concern surface roughness. There are many things which cause surface

heterogeneity. In a recent review, kinetic or time-dependent hysteresis phenomena were attributed to surface heterogeneity caused by surface deformation/relaxation, liquid penetration of the surface, and surface reorientation effects.<sup>8</sup>

Concerning liquid penetration of surfaces, contact angle hysteresis on a monolayer of 17-(perfluorheptyl)heptadecanoic acid was particularly severe when the contacting liquid had a low molecular volume.<sup>9</sup> Liquid water appeared to behave as though it was associated in clusters of six water molecules, but even in this state, water's low molecular volume allows it to readily penetrate polymer surfaces. For example, dynamic contact angle measurements and relaxation studies on silicones show that water causes time-dependent surface phenomena, whereas glycerol and for-



**Figure 5.** Liquid drop advancing and receding contact angles on peroxide-cured silicone elastomer following saline exposure for various times at 60°C, 70°C, or 97°C.



**Figure 6.** Liquid drop advancing and receding contact angles on hydrosilylation-cured silicone elastomer following saline exposure for various times at 60°C, 70°C, or 97°C.

**TABLE IX**  
**Captive Bubble Receding Contact Angles (deg) on Silicone Samples following Aging in Saline**

Exposure Time (h)	Angle (deg) following Exposure at Specified Temp.					
	Peroxide Cured			Hydrosilylation Cured		
	60°C	70°C	97°C	60°C	70°C	97°C
0	71	67	73	73	73	72
1	69	59	73	70	65	67
5		66	54	65	64	51
5.5	56					
10	64		44	72	70	31
11		66				
20	61		49	65	66	43
21		61				
34		63				
44		60				
45	52		23	65	58	28

mamide that have larger molar volumes did not.<sup>10</sup> In a recent review, water penetration was proposed as a contributing factor to changes in contact angles observed during water immersion of films of polydimethylsiloxane, polystyrene, and poly(isobutyl methacrylate).<sup>11</sup> Adam and Elliot reported that a 16.5-h room temperature water immersion of low-density polyethylene caused a 10° decrease in the advancing angle and a 47° decrease in the receding angle.<sup>12</sup> They attributed the changes to water penetration of the surface.

In the current study, if water penetration was a contributing factor, then the effects of immersion time and temperature on contact angle may have been the result of the time and temperature dependence of water penetration into polyethylene and polydimethylsiloxane. The saturation concentration of water in polyethylene at 60°C was reported as approximately 150 ppm, whereas at 100°C the saturation concentration was above 1000 ppm.<sup>13</sup> Unfilled crosslinked polydimethylsiloxane absorbed between 0.15% and 0.30% water at 65°C.<sup>14</sup> Furthermore, silica-filled elastomers absorbed higher concentrations of water than unfilled polymer,

with the amount of absorbed water increasing at higher temperature.<sup>15</sup> Direct observation of the time dependence of water penetration into a siliconized glass slide was made by observing decreases in the contact angle and droplet size over the course of a 300-h experiment.<sup>16</sup>

Apart from the possible effects of water penetration, receding angles on hydrophobic surfaces are very sensitive to the presence of trace hydrophilic species. These hydrophilic species can originate from within the polymer. For example, 1 h immersion in water induced changes in the water contact angles on films of poly(tetrafluoroethylene-co-perfluoropropylvinylether) containing only 3 mol % perfluoropropylvinylether. Despite the low concentrations of the ether moiety, the changes in contact angle were attributed to a reorganization of the surface to include more of the polyether oxygen.<sup>17</sup> Aside from polymer reorientation, sources of hydrophilic species that might be present in any polymer system include hydrophilic chain ends, plasticizers, antioxidants, crosslinkers, oxidized groups arising during high temperature processing,

**TABLE X**  
**Liquid Drop Receding Contact Angles (deg) on Silicone Samples following Aging in Saline**

Exposure Time (h)	Angle (deg) following Exposure at Specified Temp.					
	Peroxide Cured			Hydrosilylation Cured		
	60°C	70°C	97°C	60°C	70°C	97°C
0	60	48	63	60	64	57
1	58	50	62	56	60	54
5		52	44	53	56	39
6	43					
10	47		40	54	47	25
11		52				
20	45		37	49	56	31
21		53				
34		34				
44		50				
45	36		26	51	39	14

TABLE XI  
Liquid Drop Contact Angles (deg) on Polyethylene  
following Aging in 97°C Saline

Exposure Time (h)	Advancing (deg)	Receding (deg)
0	107	87
1	107	90
4	100	72
24	83	37
48	86	34

and catalysts or polymerization initiator residues. During immersion in water, these species will diffuse to the surface. It is also possible that hydrophilic contaminants may originate from external sources.

For example, during the course of this work, it was determined that boiling saline for 45 h in a Pyrex flask led to a concentration of 3.3 ppm silicon (probably as silicate) in the saline. Under these conditions, deposition of trace quantities of silicates on the polymer surfaces cannot be precluded.

Finally, the derivitization technique employed for the XPS measurements in Reference 4 is suspect, since the derivatizing agent, aminopropyltriethoxysilane, was applied from a 95% ethanol/water solution. This indirect measure of silanol concentration required that the derivatizing agent react in a 1:1 fashion with surface silanol. No reference for this treatment procedure was provided; however, product literature suggests that the treatment procedure can lead to depositions of three to eight molecular layers owing to polymerization of the treating agent.<sup>18</sup> Deposition of aminopropyltriethoxysilane on glass from benzene solution leads to five to 10 monolayers of a strongly chemisorbed

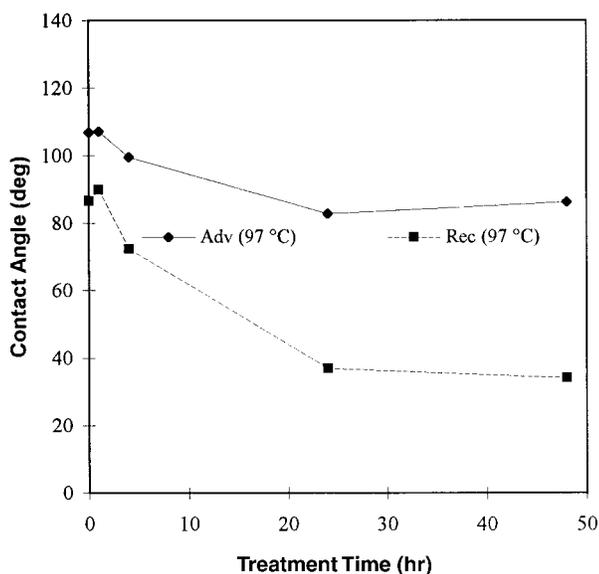


Figure 7. Liquid drop advancing and receding contact angles on low-density polyethylene following saline exposure for various times at 97°C.

layer and a much thicker physisorbed layer.<sup>19</sup> It is not known whether the deposition of the silane would be influenced by water present in a swollen surface layer. An experiment of this type is difficult, especially if the silane has any solubility in the polymer. The experiment would have been better performed using a mono-functional treating agent applied from the vapor phase.

## CONCLUSIONS

After 45 h exposure to saline at 37°C or 100°C, it was noted that for the peroxide-cured silicone elastomer, no changes in elastomer tensile strength, elongation, stress at 100% elongation, or stress at 200% elongation were sustained over time. It was thus impossible to reliably distinguish small changes in the elastomer properties. In the case of the hydrosilylation-cured elastomer, it was noted that small but statistically significant increases in the stresses measured at 100% and 200% elongation occurred over the first hour of exposure, but afterward, the material remained stable. Such changes occurring over a short period of time might suggest some sort of postcure phenomenon; however, it was concluded that degradation of the material did not occur, since the material did not change further with time. It was concluded that at moderate temperatures and in the absence of catalytic species, silicone elastomers are stable against hydrolysis in saline.

Water contact angle measurements showed hysteresis behavior typical of polymeric materials. Such hysteresis is frequently explained by surface heterogeneity and reorganization of the surface upon exposure to the wetting liquid. Following exposure to saline at elevated temperatures, advancing contact angles remained high, indicative of a largely hydrophobic surface. Saline exposure at elevated temperatures had a greater impact on receding contact angles. Others have attributed these decreases in receding angle to extensive surface hydrolysis; however, advancing contact angles were never reported.<sup>4</sup> In this work, it was shown that advancing angles remain high; thus, extensive hydrolysis is unlikely. From this work it is impossible to determine the cause of the decreases in receding angle; however, it may be that observed decreases in receding angle cannot be attributed to a single cause. Decreases in receding angle may be the result of several phenomena including penetration of water into the surface, reorientation of the siloxane backbone, and/or migration of polar groups (e.g., preexisting silanol chain ends) to the surface, resulting in surface heterogeneity which may be reflected in substantial contact angle hysteresis. It was concluded that there was no indication of significant surface or bulk hydrolysis under these accelerated aging conditions.

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## References

1. C. R. McMillin, "Elastomers for biomedical applications," *Rubber Chem. Technol. Rubber Rev.*, **67**, 417–446 (1994).
2. J. Marotta, D. DePalma, and C. Batich, "Surface changes in 'silicone' elastomer upon exposure to saline," in *20th Annual Meeting of the Society for Biomaterials*, Boston, MA, April 5–9, 1994, p. 148.
3. C. Batich, D. DePalma, J. Marotta, G. Latorre, and N. S. Hardt, "Silicone degradation reactions," in *Immunology of Silicones*, M. Potter and N. R. Rose (eds.), Springer-Verlag, New York, 1996, pp. 13–23.
4. D. DePalma, "Surface hydrolysis of polydimethylsiloxane (silicone elastomer)," Masters thesis, College of Engineering, University of Florida at Gainesville, 1992.
5. F. Lewis, "Science and technology of silicone rubber," *Rubber Chem. Technol.*, **35**, 1222–1275 (1962).
6. L. S. Penn and B. J. Miller, "A study of the primary cause of contact angle hysteresis on some polymeric solids," *J. Colloid Interface Sci.*, **78**, 238–241 (1980).
7. O. N. Tretinnikov and Y. Ikada, "Dynamic wetting and contact angle hysteresis of polymer surfaces studied with the modified Wilhelmy balance method," *Langmuir*, **10**, 1606–1614 (1994).
8. J. D. Andrade, "Contact angle analysis of biomedical polymers: From air to water to electrolytes," in *Polymers in Medicine II: Biomedical and Pharmaceutical Applications*, E. Chiellini, P. Giusti, C. Migliaresi, and L. Nicolais (eds.), Plenum Press, New York, 1986, pp. 29–40.
9. C. O. Timmons and W. A. Zisman, "Effect of liquid structure on contact angle hysteresis," *J. Colloid Interface Sci.*, **22**, 165–171 (1966).
10. M. C. Phillips and A. C. Riddiford, "Dynamic contact angles: II. Velocity and relaxation effects for various liquids," *J. Colloid Interface Sci.*, **41**, 77–85 (1972).
11. J. D. Andrade, L. M. Smith, and D. E. Gregonis, "The contact angle and interface energetics," in *Surface and Interfacial Aspects of Biomedical Polymers*, Vol. 1, J. D. Andrade (ed.), Plenum Press, New York, 1985, pp. 249–292.
12. N. K. Adam and G. E. P. Elliott, "Contact angles of water against saturated hydrocarbons," *J. Chem. Soc. London*, **2**, 2206–2209 (1962).
13. E. Ildstad, "Water migration and water treeing in cross-linked polyethylene cables," Ph.D. dissertation, Electrical Engineering Department, University of Trondheim, Norway, 1982.
14. J. A. Barrie and B. Platt, "The diffusion and clustering of water vapour in polymers," *Polymer*, **40**, 303–313 (1963).
15. J. A. Barrie and D. Machin, "Sorption and diffusion in silicone rubbers: II," *J. Macromol. Sci. Phys.*, **B3**, 673–692 (1969).
16. S. H. Lee and E. Ruckenstein, "Surface restructuring of polymers" *J. Colloid Interface Sci.*, **120**, 529–536 (1987).
17. H. Yasuda, T. Okuno, Y. Sawa, and T. Yasuda, "Surface configuration change observed for Teflon-PFA on immersion in water," *Langmuir*, **11**, 3255–3260 (1995).
18. B. Arkles, "Silane coupling agent chemistry," in *Silicon Compounds Register and Review*, 5th ed., Huls America, Inc., Piscataway, NJ, 1991, pp. 59–64.
19. M. Schrader, "Radioisotope studies of coupling agents at the interface," *Compos. Mater.*, **6**, 109–129 (1974).