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Wettability, water sorption and water solubility of seven silicone elastomers used for maxillofacial prostheses

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Abstract The wettability, water sorption and solubility of silicone elastomers used for maxillofacial prostheses were studied. The hypothesis was, that a material that has absorbed water would show an increase in the wettability and thus also the surface free energy of the material.

Seven silicone elastomers, both addition- and condensation type polymers, were included. Five specimens of each material were subjected to treatment according to ISO standards 1567:1999 and 10477: 2004 for water sorption and solubility. The volumes of the specimens were measured according to Archimedes principle. The contact angle was measured with a contact angle goniometer at various stages of the sorption/solubility test.

Wettability changed over the test period, but not according to theory. The addition type silicones showed little or no sorption and solubility, but two of the condensation type polymers tested had a significant sorption and solubility. This study showed that condensation type polymers may show too large volumetric changes when exposed to fluids, and therefore should no longer be used in prosthetic devices. The results of this study also suggests that it might be of interest to test sorption and solubility of materials that are to be implanted, since most of the materials had some solubility.

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Introduction

There are many factors that are important concerning the life expectancy and serviceability of a maxillofacial prosthesis. Many authors have over the years suggested what they thought were the most crucial factors—chemical stability, dimensional stability, and minimal to no water absorption are a few of the factors mentioned [1–4].

When discussing chemical stability in a maxillofacial prosthesis, many authors refer to the materials' ability to withstand degradation by sunlight. Likewise, factors like elasticity and elongation have been mentioned when dimensional stability has been discussed [2, 3]. However, if a material absorbs liquid to such an extent that it loses the original dimensions, or shows solubility, then the prosthesis may have lost it's functionality.

The ISO standard on requirements for medical silicones for implants states that they must be tested for solubility in hexane [5]. How a silicone reacts to an organic solvent and how it reacts to water may not be the same. It was shown in an earlier study that water could affect the appearance of some silicone materials [6]. If that change in appearance was caused by sorption of water, it would be very interesting to test the materials for sorption. If they can absorb water, then there might also be a solubility in water.

Another important factor that has been discussed in the literature is the surface wettability [7–12]. By determining the wettability of a material, one can also determine the surface free energy. It has been reported that a material with a high surface free energy more readily promotes bacterial- and cell growth on its surface [13–15]. This is an important quality for a material that also is used as implants, sometimes custom made, e.g. to lift up the orbital floor, and as a material used in close contact with the mucosa.

There have been no previous studies regarding the water sorption and solubility of silicones used for medical purposes, and thus also no studies linking the effects of water sorption with the wettability of the materials.

The purpose of this investigation was to study the wettability, water sorption and solubility of commercially available silicone elastomers used for maxillofacial prostheses. The hypothesis was, that a material that has absorbed water would show an increase in the wettability and thus also in the surface free energy of the material.

Methods and materials

The materials

Seven commercially available silicone elastomers were chosen, either because of their long standing use as a material for maxillofacial prostheses, or because they are advertised as such a material (Table 1).

Five circular specimens of each material with a diameter of 40 mm and a thickness of 3 mm were made. The materials were mixed according to the manufacturers instructions and the specimens were prepared in dental stone moulds (Vel Mix, Kerr Europe AG, Switzerland) treated with an alginate separation fluid (Ivoclar Vivadent AG, Schaan, Lichtenstein), as previously described [6].

Water sorption and water solubility

The water sorption and water solubility were determined according to the ISO standards 1567:1999 and 10477:2004 [16, 17]. The volumes of the specimens were measured according to Archimedes principle.

Wettability

The theories behind measurement, and calculation of the surface free energy have developed, ever since Young first formulated a way to calculate the surface tension. In Young's equation one assumes that the solid is chemically homogeneous, rigid and completely flat. Further, it is assumed that there is no chemical interaction of the liquid face or gases with the solid. Several researchers have over the years shown that there are interactions between liquid, solid and the gaseous atmosphere. They have also shown that no solid is chemically homogeneous, rigid and completely flat, therefore it is recommended that both advancing and retreating angles of the drop are measured [18]. The advancing angle is defined as the equilibrium angle on the lower-free energy areas of the surface, and it is the highest value observed. The retreating angle is defined as the equilibrium angle on the higher-energy areas, and that is the lowest value the angle can take on [18].

There are several methods that can be used, but in this case a technique developed by RJ. Good was used. "There the liquid drop is introduced by means of a micrometer syringe with a fine needle, and is held captive while additional liquid is added to the drop until a steady value of the contact angle is achieved. This value is the advancing angle. To measure the retreating angle, liquid is withdrawn from the drop with the help of the micrometer syringe" [18].

It has been found that the surface free energy consists of several components acting together. One such component, the Lifshitz-van der Waals, "yields a value of the surface free energy that is the consequence of all the electromagnetic interactions taken together, whether due to oscillating temporary dipoles or permanent dipoles or induced dipoles" [18]. The other components of the surface free energy are the acid and base components, where the Lewis acid component is the electron acceptor, and the Lewis base component is the electron donor [18].

The surface tension of the materials was determined with a contact angle goniometer (Ramé-Hart Inc., Mountain Lakes, NJ, U.S.A.). Five different liquids were used (Table 2). The advancing and retreating angles were determined and the surface tension was calculated according to the equations [18]:

Table 1 Silicone elastomers used

No	Type	Brand name	Code	Manufacturer
1	Condensation	Cosmesil Regular	CR	Principality Medical Ltd., Rogerstone Newport, Wales, United Kingdom
2	Condensation	Cosmesil High Compliance	CH	Principality Medical Ltd., Rogerstone Newport, Wales, United Kingdom
3	Condensation	R&S 330 T-RTV[a]	RS	Ringsted & Semler, Copenhagen, Denmark.
4	Addition	Wacker RTV-ME 625	RT	Wacker Chemie GmbH, Munich, Germany
5	Addition	A-2186	A2	Factor II, Lakeside, Arizona U.S.A.
6	Addition	LSR 30-10:1	LS	Applied Silicone Corp. Ventura, California, U.S.A.
7	Addition	SEN 240	SE	Shin-Etsu Silicones Europe B.V, AV Almere, the Netherlands

[a] Synonymous with Wacker M-539, Wacker Chemie GmbH, Munich, Germany

Table 2 Liquids used for contact angle measurements

	Liquid	Polarity
1	Di-iodmethane	Apolar
2	Chemically pure water	Polar
3	Ethylene glycol	Polar
4	Formamide	Polar
5	Glycerol	Polar

$$\gamma_s^{LW} = \gamma_1^{LW} \text{ apolar liquid } \frac{(1 + \cos\Theta)^2}{4}$$

and

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB}$$
$$\gamma_s^{AB} = 2\sqrt{\gamma_s^{\oplus}\gamma_s^{\ominus}}$$

$$\sqrt{\gamma^{\oplus}} = \frac{AF - BC}{CF - DE} \qquad \sqrt{\gamma^{\ominus}} = \frac{BC - AE}{CF - DE}$$
$$A = \gamma_2\,(1 + \cos\Theta) - 2\sqrt{\gamma_s^{LW}\,\gamma_2^{LW}}$$
$$B = \gamma_3\,(1 + \cos\Theta) - 2\sqrt{\gamma_s^{LW}\,\gamma_3^{LW}}$$
$$C = 2\sqrt{\gamma_2^{\ominus}} \quad D = 2\sqrt{\gamma_2^{\oplus}}$$
$$E = 2\sqrt{\gamma_3^{\ominus}} \quad F = 2\sqrt{\gamma_3^{\oplus}}$$

γ^{LW} = Lifshitz-van der Waals component of γ; $\gamma^{\oplus}$ = (Lewis) acid component of γ; $\gamma^{\ominus}$ = (Lewis) base component of γ; γ_s = surface tension

To be able to calculate these different components, one need to measure the dynamic contact angles of several different liquids on the surface of the solid. To determine the Lifshitz van der Waals component, an apolar liquid is used, and for the acid and base components, polar liquids are used. It is recommended that no less than three liquids must be used for these equations; one apolar and two polar liquids. Water is one of the polar liquids. In this study five liquids were used.

To determine the Lifshitz-van der Waals component of the surface-free-tension the apolar liquid diiodmethane was used. The reason why diiodmethane was used rather than the more commonly used alpha-bromonaphtalene is that alpha-bromonaphtalene is an "effective" solvent and it affects the surface of the silicones. Diiodmethane was the only one of the recommended apolar liquids that was found to leave the surface of the materials unaltered when it was used, as was found when the liquids were tested on the silicones before the study was started.

The other four liquids: chemically pure water, ethylene glycol, formamide, and glycerol are all polar. It has been found that water in pair with ethylene glycol or formamide works well together in determining the surface free energy. Glycol is also a useful liquid provided that care is taken to provide for the viscosity of the glycerol [18]. This means that in these equations water was used as liquid 2 in pair with one other polar liquid, and that water was used to calculate the coefficients A, C and D, while each of the other polar liquids were used to calculate B, E and F. Thus, three equations were obtained and a mean result of these three equations was used as the surface free energy of the materials. All liquids were measured five times.

The contact angles for the materials were determined at four different states of treatment: (i) when the specimens were newly made (start); (ii) when they had been dried to a constant weight (conditioned); (iii) after three days in water (three days) and finally; (iv) when the specimens were saturated with water (saturated). This was done with the hypothesis that water adsorbed in the materials could alter the surface free energy of the materials.

Statistical analysis was made using SPSS 11 for Macintosh using paired t-tests and Bonferroni ANOVA.

Results

Wettability

Condensation polymers

For the condensation silicone CR, there were significant differences in wettability between the newly made specimens and specimens at the three other states of treatment ($p < 0.0001$) (Fig. 1). However, no such difference was found at a comparison between the CR-specimens at these three states (conditioned, three days and saturated).

The material CH showed no significant difference between any of the four states of treatment (Fig. 1).

The RS material showed significant differences between the newly made specimens and the conditioned specimens ($p < 0.02$), and between the newly made and the three days specimens ($p < 0.0001$). No other significant differences could be seen when comparing the four states of treatment (Fig. 1).

Addition polymers

For the addition silicone SE, there were no significant differences found between any of the groups (Fig. 2). The silicone LS showed significant differences between the newly made specimens and the conditioned specimens, and between the newly made specimens and the saturated specimens ($p < 0.0001$). Furthermore, a significant difference was found between the conditioned specimens and the

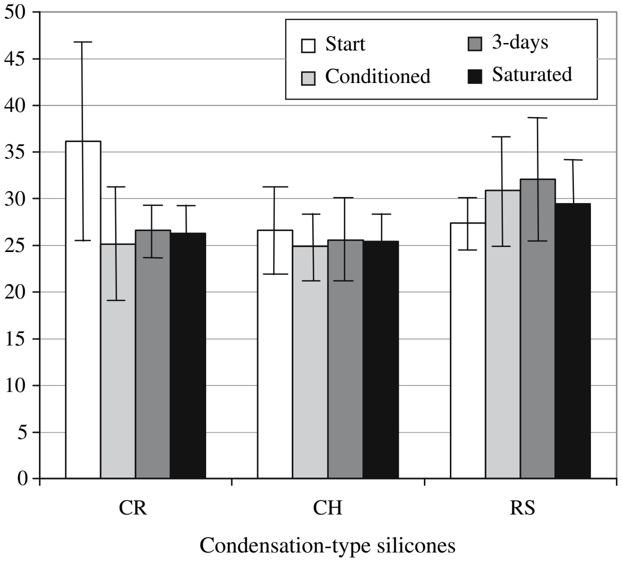

Fig. 1 Mean values and standard deviation for the surface free energy of the condensation silicones. Each bar represent five specimen and five measurements for each specimen

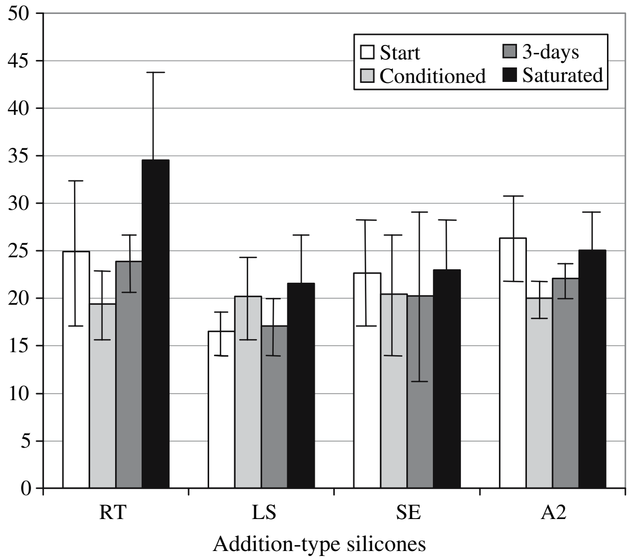

Fig. 2 Mean values and standard deviation for the surface free energy of the addition silicones. Each bar represent five specimen and five measurements for each specimen

specimens after three days in water ($p < 0.01$), and between the three days specimens and the saturated specimens ($p < 0.0001$).

The silicone RT showed significant differences between all states of treatment ($p < 0.01$) except between the starting point and the measurement on day three where there was no significant difference, and between the conditioned specimens and those that had been three days in water.

As regards the material A2, a significant difference was found between all groups of specimens ($p < 0.01$), except between the newly made specimens and the saturated specimens, and the conditioned specimens and after three days in water.

Sorption

All materials had little sorption with values below the requirements of the standards ISO 1567:1999 and ISO 10477:2004, except two materials that differed considerably from the others. The condensation silicones CR and RS showed much higher sorption than the other materials (Fig. 3).

However, there were significant differences between all materials, between A2 and LS ($p < 0.02$), and A2 and RT ($p < 0.003$), while the value for the other comparisons was $p < 0.0001$ (Table 3).

Solubility

The values for the solubility in water are shown in Fig. 4.

Two materials differed from the others, the condensation silicones CR and RS (Fig. 4).

There were highly significant differences between all materials ($p < 0.0001$), except between SE and A2, and CH and SE ($p < 0.05$). However, between SE and RT, and SE and LS no significant differences were found.

The results of the solubility test for the addition silicone SE deviated from the others. Some specimens showed solubility while others showed a weight increase after the final conditioning. This irregularity was found strictly

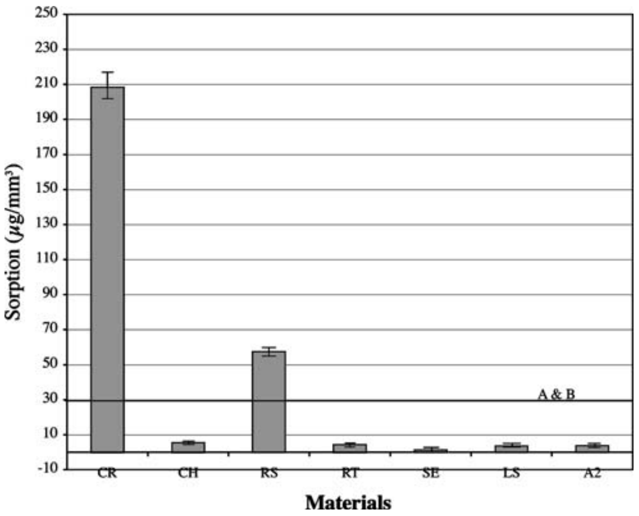

Fig. 3 Sorption of water. Each bar represent five specimen and five measurements for each specimen. **A**. ISO 1567 Heat and light curing denture base resin, the water sorption shall not exceed 32 µg/mm^3. **B**. ISO 10477 Polymer based crown- and bridge materials, the water sorption shall not exceed 32 µg/mm^3

Table 3 Differences in water sorption between the materials tested ($p < 0.05$)

	CR/CS	CHC/CS	RS/CS	RT/AS	A2/AS	LS/AS	SE/AS
CR/CS	–	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$
CH/CS	$p = 0.000$	–	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$
RS/CS	$p = 0.000$	$p = 0.000$	–	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$
RT/AS	$p = 0.000$	$p = 0.000$	$p = 0.000$	–	$p = 0.020$	$p = 0.000$	$p = 0.000$
A2/AS	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.020$	–	$p = 0.003$	$p = 0.000$
LS/AS	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.003$	–	$p = 0.000$
SE/AS	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$	$p = 0.000$	–

AS: addition silicone

CS: condensation silicone

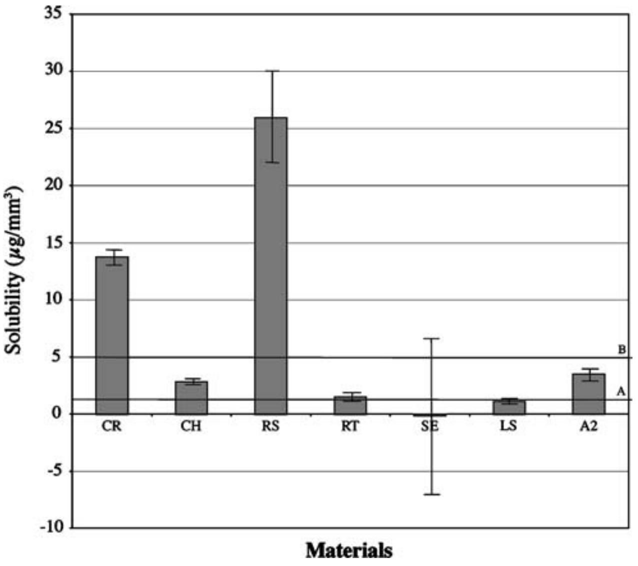

Fig. 4 Solubility in water. Each bar represent five specimen and five measurements for each specimen. **A**. ISO 1567 Heat and light curing denture base resin, the water solubility shall not exceed 1.6 μg/mm³. **B**. ISO 10477 Polymer based crown- and bridge materials, the water solubility shall not exceed 5.0 μg/mm³

between the different specimens and not between the different measurements of the individual specimens.

Discussion

Wettability

The hypothesis of the present study was that a material that has absorbed water would show an increase in the wettability and thus also the surface free energy of the material. Our results did not support the hypothesis, since only two of the seven materials reacted in this manner. Wettability is a complex phenomenon dependent on several surface components. The theory of contact angle measurements, as it was first formulated, considers the drop as stable and the surface of the solid as smooth and homogenous. This is, however, not the case. A liquid drop has many different stable angles on a solid surface. This phenomenon has been given the name hysteresis [19] and there are many causes for this behavior. Surface roughness is one cause for this behavior. Other causes can be microscopic heterogeneities of the solid, and rate effects due to viscous flow of the fluid phase [18]. Another cause of hysteresis is a behavior seen with some polar solids, where there is a reorientation of molecules or groups in the surface of the solid under the influence of the liquid phase. An example of this is when the hydroxyl groups on a polymer chain, which are normally tuned away from the surface, will in contact with water turn over so that they can form hydrogen bonds with the water [18]. A commonly used way to deal with the hysteresis is to use a technique with a dynamic contact angle, *i.e.* measure the angle both when it is advancing and when it is retreating. The method employed in this study was a method described by Good [18].

The surface free energy is separated into components where the acid–base interaction between the molecules of the liquid and the molecules of the solid surface is one component and the Lifshitz-van der Waals component is the other.

To be able to calculate these different components one need to measure the dynamic contact angles of several different liquids on the surface of the solid. In this study we used five. This may be an overkill, but it was done with the knowledge in mind that ethylene glycol, although recommended, can give slightly erratic results. It is also always possible to exclude a liquid that has been found inadequate in a latter stage, but it is more difficult to include a substitute liquid at that stage. Glycerol is among the recommended liquids, and was included in the five that was used. Provided that it is given time to ‘set’ because of its high viscosity, it is a useful liquid [18].

The silicone elastomers in the present study, three condensation type silicones and four hydrosilylation (so called addition type) silicones, were all processed in stone molds. Since silicones are good impression materials, which would have given the specimens a rough surface.

Hysteresis was also evident on all specimens which might explain some of the standard deviations of the materials. Another part of the explanation is that the mean values for the surface free energy were composed from all the measurements of both the advancing and the retreating angles.

The addition type materials RT and LS were the only materials to react according to the hypothesis. RT was the only material where you clearly could see bubbles of hydrogen gas forming on the surface of the material when it was immersed in water, and LS was the only material to be so sensitive to humidity that it had to be processed in dry molds. The Platinum-catalyzed addition reaction is a hydrosilation (addition of silicon hydride) of the olefinic group (double bond). The group silicon hydride is very reactive towards water: the negative hydride reacts with a proton from water and hydrogen gas is formed, and the hydroxide anion reacts with the “positive silicon” and a polar silicon hydroxide group is formed, Si-OH. This “silisic acid” group is available for hydrogen bonding to water molecules. Thereby an increase in the surface energy is possible.

There is no standard dealing with water sorption and solubility of silicone elastomers. Therefore, standards on dental acrylate based materials were used [16, 17]. On the whole, the addition-type silicones had a lower sorption and solubility than the condensation-type silicones. This may be explained by their different curing chemistries. The addition type polymers cure without any byproducts forming, while the condensation type polymers form byproducts that later leaves the polymeric structure. This would probably lead to a more porous polymeric structure than in the addition type polymers, and could be an explanation to why the condensation type silicones showed a larger sorption and solubility.

Sorption

All materials except two of the condensation silicones had a sorption that was below what is recommended in the ISO standards 1567:1999 and 10 477:2004. The deviant materials, CR and RS, had a sorption that was 1.8 and 6.5 times larger than recommended. Condensation-type materials are not used as implant materials, but they are used in obturators and as such, they are exposed to saliva and other body fluids. This may lead to an unwanted dimensional change of the prosthesis.

Solubility

All addition-type silicones and one condensation-type silicone had solubilities lower than the recommended upper limit in ISO 10477:2004, whereas two condensation-type silicones, CR and RS, exceeded this value with 2.8 and 5.2 times, respectively. When the solubility values for those two materials were compared with the recommended limit in ISO 1567:1999 it was found that they exceeded the recommended limit with 8.6 and 16.2 times, respectively. One reasonable explanation for this behavior might be that the amount of polymerization by-product in these materials may be fairly high, products that may be released from the material.

Bacteria grow on silicone, this is a common problem for those who use silicone implants in a non-sterile surrounding [20–23]. It is also known that sorption and solubility is associated with odor and the growth of bacteria on soft denture liners [24].

The solubility results for the addition-type polymer SE were rather odd. Some specimens showed an increase in weight, i.e. an apparent sorption, after reconditioning, while other specimens showed a loss in weight, i.e. solubility. The mass increase after water storage and reconditioning can be due to hydrolytic reactions, i.e. reactions of water with components in the silicone material such as inorganic fillers and the silicone itself. Such reactions may lead to addition of water and after reconditioning the result is the presence of additional hydroxide and oxide. Considering the results obtained in this study, perhaps it would be prudent to include tests on water sorption and solubility for silicone materials that are to be implanted in the human body.

One material that was included in a previous study on changes in appearance [6], and previously has been the most commonly used on the USA market, was omitted since it no longer is in production [25].

It is reasonable to assume that the sorption of liquids may facilitate the transport of bacteria into a material, and if this sorption is large enough, it ought to be able to change the physical properties of the material. Important properties for a maxillofacial prosthesis such as tear- and tensile strength might be affected and this will be examined in a future study.

Conclusion

This study showed that condensation type polymers may show too large volumetric changes when exposed to fluids, and therefore should no longer be used in prosthetic devices. The results of this study also suggest that it might be of interest to test sorption and solubility of materials that are to be implanted, since most of the materials had some solubility.

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