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Characterisation of some experimental silicones

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Abstract Release of antimicrobials/antibacterials like chlorhexidine diacetate (CHD) has proved successful in inhibiting Candidal colonisation of silicone-based biomaterials. However, their addition will increase water uptake and may compromise the mechanical integrity. Two experimental silicones (S1 and S2) differing only in the surface treatment of the filler, were investigated. Ultimate tensile strength (UTS), % elongation at break (Eb), Shore A hardness and, when doped with 1% CHD, water uptake and CHD release were measured. Elastic modulus (E) was calculated from the hardness measurements. There was no significant difference in UTS and Eb between the two materials. However S1 had a higher hardness (30.6 ± 0.97) and thus E (0.76 MPa) than S2 (hardness $= 23.8 \pm 0.48$, E $= 0.45$ MPa). Water uptake for S2 (0.6%) was higher than for S2 (0.1) and addition of CHD dramatically increased the uptake of both (S1 = 3.1%, S2 = 4.0%). Release of CHD was higher for S2 (30%) than S1 (27%). Equating osmotic pressure within the droplets with elastic restraining force gave an extension ratio of 1.95 for S1 and 5.39 for S2. Thus, addition of a hydrophilic agent can compromise the mechanical integrity of low modulus silicones.

1 Introduction

The flexibility, ease of processing and low reactivity of silicones elastomers have led to them being the most widely used polymers in biomedical applications [1], uses include heart valves, central venous catheters, urological catheters, maxillofacial prostheses, finger joints etc. A common problem with implanted silicone-based materials is colonisation and biofilm formation by Candida which can lead to local infection and ultimate failure [2]. There have been several approaches made to prevent the initial biofilm formation including use of materials with inherent resistance and surface modification such as coatings [3]. An alternative is the release of antimicrobials/antibacterials like chlorhexidine diacetate (CHD) which has proved successful in inhibiting colonisation [4]. However, incorporation of a hydrophilic component into a silicone elastomer will increase water uptake and, if at a sufficient level, may compromise the mechanical integrity [5].

In an aqueous environment all polymeric materials will absorb water. If there are water soluble or hydrophilic components within the matrix uptake is increased. The theory of water uptake in elastomers was developed in a series of papers by Muniandy and Thomas [6, 7]. Water is attracted to the hydrophilic sites and droplets are formed. These droplets grow driven by the chemical potential gradient between the droplet and the external solution. Growth will continue until the gradient equalises, until restrained by the elastic forces of the material or (where restraining forces are low) mechanical failure occurs. The latter occurrence will obviously depend on the osmotic pressure acting to expand the droplet and the modulus and strain at break of the material.

It was the aim of this study to characterise the mechanical properties of two experimental silicone formulations and investigate the effect of adding CHD.

2 Materials and methods

The two experimental materials were formulated as two pastes. Details of the components are listed in Table 1 and

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Table 1 Components

Component	Abbreviation	Supplier
H-siloxane VXL	HS	Crompton, OSi Specialities, Switzerland
Vinyl siloxane V60K	VS	“
Organo-platinum catalyst	VCAT1	“
Fumed silica treated with methacrylsilane	R711	Degussa, Cheshire, UK
Fumed silica treated with hexamethyldisilane	R812S	“
Chlorhexidene diacetate	CHD	Sigma-Aldrich Co, Dorset, UK

Table 2 Base silicone formulation

Component (g)	Paste 1	Paste 2
VS	5	–
HS	45	50
VCAT1	–	0.01

the base silicone formulation is detailed in Table 2. Then 45 g base silicone (paste 1 and 2) was mixed with 5 g filler. S1 contained R711 as filler and S2 contained R812S.

2.1 Sample preparation

Sheets of material (1 mm thick for water uptake/release, 2 mm thick for tensile testing, 6 mm thick for hardness) were prepared by mixing equal weights of the two pastes and sandwiching between metal plates lined with acetate sheets and containing a spacer of appropriate thickness. The whole was then clamped and placed under pressure (100 bar) in a hydraulic press for 2 h, until the material was cured. All specimens were cut from these sheets.

2.2 Tensile testing

Tensile specimens were then cut from the prepared 2 mm thick sheets with a dumb-bell shaped die specified by the standard test method for rubber properties in tension (ASTM D412-87). A minimum of seven specimens was cut for each material. Specimens were tested on an Instron MK30 using a cross-head speed of 500 mm/min at ambient temperature (23 ± 2°C) according to ISO 37: 1994. The extension was measured continuously using a video extensometer. Ultimate tensile strength (UTS) and %elongation at break (%Eb) were determined. Results were subjected to one way ANOVA and ranked using Mann-Witney.

2.3 Hardness testing

Shore A hardness testing was carried out in accordance with ASTM D 2240-86 and ISO 868 using a H17A Shore A Hardness Tester with Congenix data control software (Wallace, Kingston, England). The minimum dwell time of 1-second was used in order to minimise creep effects and tests were carried out at 23°C ± 1°C. Measurements were taken at regular intervals at least 12 mm from the edge of the specimen and 10 mm apart (as outlined by ASTM D 2240-86. A minimum of six readings was taken for each specimen and the mean calculated. Elastic modulus was calculated from the hardness values using the relationship between Shore and ISO Hardness and Young’s Modulus [8] as given by:

$$S = 100\,\mathrm{erf}(\mathrm{k}\mathrm{E}^{1/2})$$

Where $S =$ hardness, and $k = 3.186 \times 10^{-4}\ \mathrm{Pa}^{1/2}$.

2.4 Water uptake and CHD release

Four specimens of each formulation (20 mm × 40 mm × 2 mm) were conditioned to minimum weight at 37°C in an oven containing a desiccant. They were then immersed in 100 ml of deionised water at 37°C and weighed at regular intervals up to 24 weeks. Percentage weight change with time was calculated. Parallel CHD release was monitored using a UV/Vis Spectrophotometer (ATI Unicam). 5 ml aliquots of immersion liquids were taken at the same intervals as the weight measurements and absorbance at 254 nm measured. CHD content was calculated using a calibration curve constructed from measurement of known concentrations. The 5 ml aliquot was replaced by 5 ml of fresh water at 37°C and was found not to have an effect on uptake. Cumulative percentage CHD release with time was calculated.

3 Results

Table 3 shows the tensile properties, hardness values and calculated elastic moduli for both experimental materials. There was no significant difference in the UTS and percentage elongation but S1 has a higher hardness and modulus. Figure 1 shows the percentage weight change for S1 and S2 with and without CHD and Fig. 2 the percentage CHD release both as a function of square root time. Table 4 shows a summary of the water uptake and CHD release data. S2 has the highest uptake both with and without CHD and also releases at a higher level.

Table 3 Mechanical properties

Formulation	UTS (MPa)	%Eb	Shore A hardness	*E* (MPa)
S1	1.6 ± 0.3	560 ± 43	30.6 ± 1.0	0.76
S2	1.5 ± 0.2	554 ± 14	23.8 ± 0.5	0.45

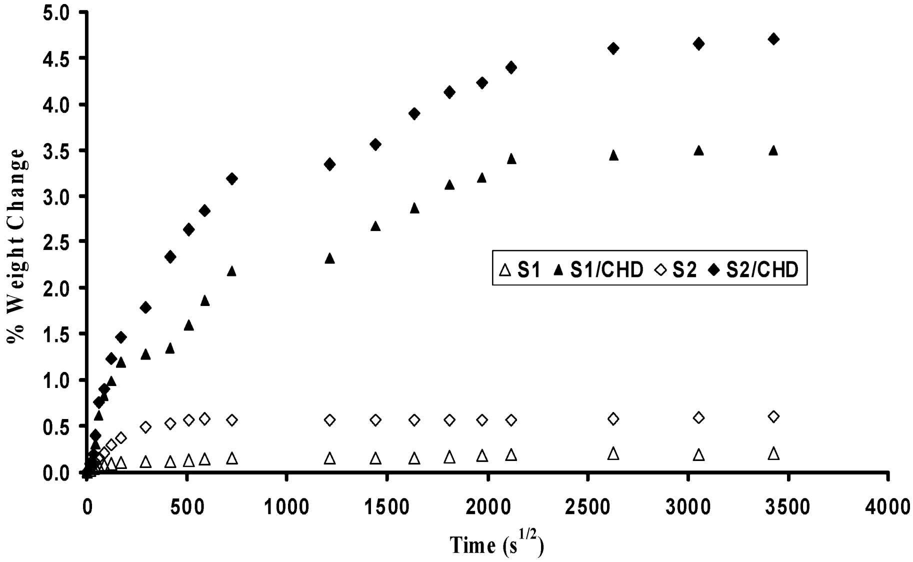

Fig. 1 Percentage weight change as a function of square root time for S1 and S2 with and without CHD

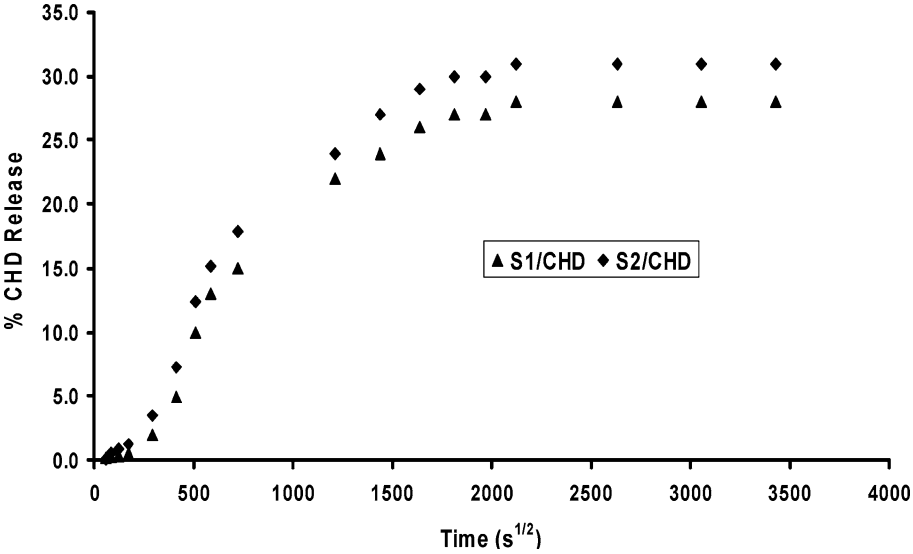

Fig. 2 Percentage CHD release as a function of square root time for S1/CHD and S2/CHD

4 Discussion

As can be seen from Table 3, there was no significant difference in the ultimate tensile strength and elongation at break of the two formulations however, S1 had a higher hardness and thus elastic modulus than S2. The only difference in formulation between the two materials is the surface treatment of the filler with that used in S2 being surface treated with a higher molecular weight, longer chain silane. This may lead to a more flexible linkage between the filler and the siloxane matrix resulting in a material that is more easily deformed and thus having a lower modulus.

Figure 1 shows that both materials reach apparent equilibrium both with and without CHD addition with S2 having the higher water uptake. The lower modulus of S2 results in a lower restraining force so facilitating droplet growth and hence higher water uptake. S2 also released CHD at a slightly higher level as shown in Fig. 2, although in both materials only ∼30% was released in total. Other authors [9–11] have found release levels in the range 8–64% depending on the

Table 4 Summary of water uptake and CHD results

Formulation	% Weight change	% CHD release
S1	0.1	–
S1/CHD	3.1	27
S2	0.6	
S2/CHD	4.0	30

type of material and level of drug loading. It is suggested that there is some association between the positively charged CHD and the siloxane matrix.

In each material the addition of CHD dramatically increased %water uptake as shown in Fig. 1. On immersion, water is attracted to CHD and solution droplets are formed. These droplets will grow, driven by the chemical potential gradient between the droplet and the external solution, until restrained by the elastic properties of the material. Thus, at equilibrium, the osmotic pressure Π within the droplets must equal the elastic pressure P exerted round the droplet. Raoults Law:

$$\Pi = cRT(1+\alpha)/M$$
$$= 0.320\,\text{MPa}$$

Where $c = 20 \times 103$ g/m^3, $R = 8.314$ JK^{-1}mol^{-1}, $T = 310$ K $M = 643.56$ $\alpha = 3$.

From rubber elasticity theory [12]:

$$P = E/6(5 - 1/\lambda^4 - 4/\lambda)$$

Where λ = extension ratio.

If $P = \Pi$ and $E = 0.76$ MPa then $\lambda \sim 1.95$ and for $E = 0.45$ MPa then $\lambda \sim 5.39$. For S1 this is a lot lower than the uniaxial λ measured in this study, but the circumferential λ values are biaxial and could well occur at lower λ values. However, for S2 the value is close to the measured Eb which equates to an extension ratio of 6.54. However for more soluble, lower molecular weight additives Π would be a lot higher thus leading to potential failure round the droplets. In some silicone [13] and other polymeric [9] drug delivery systems this is used as the release mechanism. However, where the silicone has a mechanical function it could result in degradation and failure. Additionally, in polymers with a low yield point this phenomenon would lead to creep round the droplets and protracted water uptake as found by Riggs et al. [14] for the PEM/THFM system. Thus mechanical properties are an important factor in the control of release and also in ensuring the successful function of silicone-based and other polymeric biomedical materials *in vivo*.

5 Conclusions

Addition of CHD to the experimental silicone formulations increased the level of water uptake.

Elastic modulus can affect the level of uptake.

The addition of a hydrophilic agent to silicone-based materials can compromise the mechanical integrity, especially those with low modulus.

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