JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **14** (2003) 497–502

The effect of resin/crosslinker ratio on the mechanical properties and fungal deterioration of a maxillofacial silicone elastomer

R. L. TAYLOR*, C. M. LIAUW, C. MARYAN
The Manchester Metropolitan University, Department of Chemistry and Materials, John Dalton Building, Chester Street, Manchester, M1 5GD, UK
E-mail: r.taylor@mmu.ac.uk

Variation of the crosslinker/resin ratio of a room temperature condensation cure maxillofacial silicone elastomer has caused considerable changes in the mechanical properties and deterioration by *Candida albicans*. Increasing the crosslinker/resin ratio caused a decrease in the tensile strength and stiffness of the elastomer. However, tear strength appeared to show an optimum value at the recommended crosslinker/resin ratio. These effects were due to the low molar mass silicone polymer that acts as a carrier for the actual crosslinking additive. The general decrease in mechanical properties was accompanied by an increase in the hexane extractables content and an increase in the Si–H content of the elastomer. The unbound polymer (extractable material) content of the elastomer was found to influence the colonization of the material by *C. albicans*. An increase in the unbound polymer content corresponded to an increasing number of hyphae and blastospores observed penetrating into the elastomer. The data obtained in this study have significant implications concerning the degree of control of elastomer formulation and the deterioration of maxillofacial appliances.

Introduction

Maxillofacial silicone elastomers are used for a variety of medical applications, replacing tissues that have been lost through trauma and disease (voice, ocular, nose, ear, digit and partial facial). Such elastomers are generally of the condensation cure type in which the resin component consists of hydroxyl terminated poly(dimethylsiloxane) (PDMS) of sufficient molar mass to be a viscous liquid. The crosslinker component is usually an oligomeric poly(hydromethylsiloxane) (PHMS). The chain extension/crosslinking therefore, proceeds via reaction of the Si–H and Si–OH groups, accompanied by elimination of H_2 [1]. This reaction is catalyzed either by an amine or tin octoate. The Prestige ''Premium'' system used in this study employs a crosslinker that consists of a PHMS that is diluted in a low molar mass silicone fluid. Therefore when adding this crosslinker to the resin, a plasticizer is being added together with the PHMS. This ultimately causes the crosslink density increasing effect of PHMS to be overshadowed by plasticization. From discussions with people in the industry, the authors have learned that dental technicians may abuse this feature in order to tailor the flexibility of an appliance. Very often production of the correct texture is the only objective with no consideration of the effect of the excess PHMS, and the reactive Si–H bonds, on the mechanical properties and the susceptibility to microbial colonization. It is envisaged that a fraction of the excess PHMS will not be bound to the hydroxyl terminated PDMS and, together with the low molar mass PDMS plasticizer, will contribute to increased free volume. These factors are likely to render the elastomer more susceptible to microbial colonization and ingrowth. *In vitro* [2, 3] and *in vivo* [4, 5] studies have shown that *Candida albicans* has a predilection for silicone elastomers, which can result in the loss of aesthetic quality and function of the prosthesis.

The aim of this paper is to examine the effect of excess crosslinker (i.e. excess plasticizer) on the curing behvior, the level of unreacted Si–H bonds and the amount of extractable PHMS. The effect of crosslinker levels on mechanical properties and colonization by *C. albicans* will also be investigated.

Experimental

Materials

The maxillofacial silicone elastomer was supplied by Prestige and consists of a resin and crosslinker component. The crosslinker/resin ratios shown in Table I were used for initial infrared studies. The ratio

* Author to whom all correspondence should be addressed.

TABLE I Crosslinker/resin ratios investigated. Sample C is based on the recommended ratio

Sample	% w/w crosslinker
A	3
B	6
C	10
D	15
E	30

recommended by the supplier is 10% w/w crosslinker to 90% w/w.

Investigation of curing kinetics

Elastomer formulations shown in Table I were made up and smeared on to KBr discs such that the elastomer layer was of sufficient thickness to give a maximum C–H stretch infrared absorbance of ca 0.4. The infrared spectra were recorded, at appropriate time intervals, in transmission using a Nicolet 510 P, spectra were made up of 32 scans with resolution set to $4\,cm^{-1}$. In order to allow for small variations in thickness, measurements of the Si–H stretching band were normalized, by taking the area of the C–H stretching bands as an internal standard. The relative level of Si–H was therefore taken as the peak area ratio of the Si–H bands ($A_{(Si-H)s}$, 2260–2080 cm^{-1}, with two-point base line using the same limits) to the C–H stretching bands ($A_{(C-H)s}$, 3031–2757 cm^{-1}, with two-point base line using the same limits).

Analysis of hexane extractable fraction

The amount of this fraction in the elastomer samples was determined by 24 h Soxhlet extraction with hexane. After extraction the bulk of the hexane was removed from the highly swollen samples by evaporation at ambient temperature in the draught of a fume cupboard, the remaining hexane was removed by drying to constant mass at 70 °C. The hexane extract was isolated by rotary evaporation. The extractables content was determined both from the mass loss of the samples before and after extraction and from the mass of extract obtained. The Si–H content of the extracted samples was assessed by attenuated total reflectance (ATR) (germanium crystal) infrared spectroscopy.

Determination of mechanical properties

BS903 Pt A2 type 2 tensile dumbbells and ISO 34 angle tear test pieces were cut from the molded sheets and the tensile properties determined using a Hounsfield M series tensometer fitted with a laser extensometer. The crosshead speed was $500\,mm\,min^{-1}$. Angle tear strength (without nicking) was determined in accordance with ISO 34 using the same equipment. In addition to the tear strength expressed as force per unit thickness, the energy to tear was also measured using the area under the load-deflection curve.

Colonization of elastomer by *C. albicans*

Elastomer formulations A, C and E (Table I) were processed against perspex to ensure a consistent surface finish. The 3 mm elastomer sheets were cut into eight 20×10 mm test pieces and placed into universals containing 10 ml artificial saliva. The composition of the artificial saliva ($g\,l^{-1}$) was as follows; Lab-Lemco powder (1.0); yeast extract (2.0); protease peptone (5.0); hog gastrin mucin type III (2.5), sodium chloride (0.3); potassium chloride (0.2); calcium chloride (0.2). All components of the latter were supplied by Oxoid Limited, Hampshire, UK. The universals were autoclaved and then inoculated with 0.1 ml of an overnight culture of *C. albicans* GDH 2346. Universals were placed in an orbital incubator at 37 °C for 6 weeks. Test pieces were aseptically removed from their universals on a weekly basis and placed in new universals containing fresh artificial saliva.

Upon completion of the incubation period, test pieces were rinsed in phosphate buffered saline and placed in 4% gluteraldehyde for 2 h. Test pieces were then dehydrated in an alcohol series (30–100%) for 10 min each.

Thin (0.1 mm) transverse sections of the test pieces were cut manually using a scalpel blade and rinsed thoroughly with distilled water. Sections were then stained with crystal violet for 2 min, rinsed and viewed using light microscopy (Nikon Eclipse E600) ($\times$ 100 magnification) and image analysis (Lucia Measurement on Corona).

Results and discussion

Cure characteristics

As chain extension/crosslinking proceeds via condensation of the terminal hydroxyl groups with the Si–H groups on the PHMS; the curing reactions can thus be followed using infrared spectroscopy to record the decrease in relative concentration of Si–H. Spectra of samples A to E immediately after incorporation of the crosslinker are shown in Fig. 1, where the measured absorptions (C–H stretch and Si–H stretch) are indicated. The silanol (Si–O–H) stretching region of the spectra (4000–3000 cm^{-1} [6]) was examined but did not afford data suitable for quantification, as the absorptions were weak and broad due to hydrogen bonding. Absorbed water would have almost certainly caused errors if attempts were made to quantify these bands. The extent of reaction was therefore followed by monitoring the reduction of the far more clearly defined Si–H absorption band at 2160 cm^{-1} [6].

Plots of $A_{(Si-H)s}/A_{(C-H)s}$ are shown in Fig. 2(a). It is immediately apparent that the raw area ratio plotted against time yields data of limited use for kinetic analysis due to the shift in the data up the y-axis as the level of crosslinker increases. However, unreacted Si–H can be observed in Fig. 1 even in the sample containing the lowest level of crosslinker. In order to obtain data for kinetic analysis the difference in area ratio ($\Delta(A_{(Si-H)s}/A_{(C-H)s})$) between the area ratio at zero time and that at the time of recording was plotted against time (Fig. 2(b)). At all crosslinker levels, a change in slope was observed between 5 and 7 h, after which Si–H

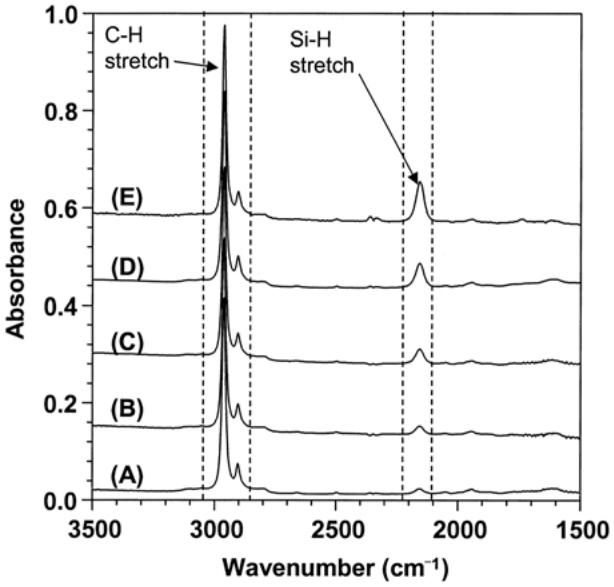

Figure 1 Infrared spectra of elastomer samples immediately after incorporation of catalyst. The letters correspond to the crosslinker/resin ratios given in Table I.

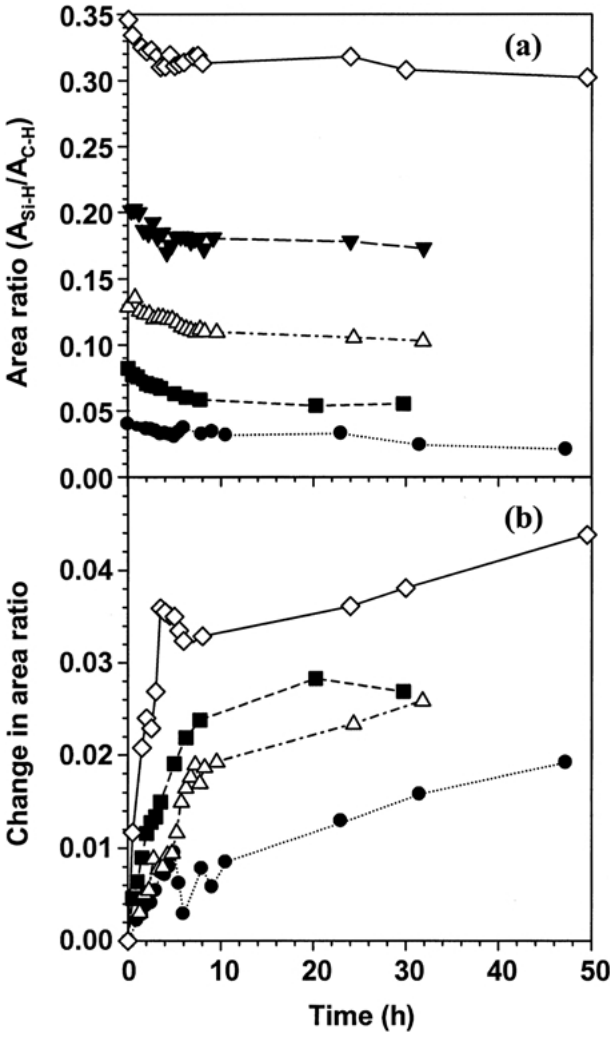

Figure 2 (a) Integrated peak area ratio $(A_{(Si-H)s}/A_{(C-H)s})$ and (b) change in peak area ratio $\Delta(A_{(Si-H)s}/A_{(C-H)s})$ (relative to peak area ratio at zero time) as a function of time at ambient temperature; ● A, ■ B, △ C, ▼ D and ◇ E, letters correspond to the crosslinker/resin ratios given in Table I.

reactions continued at a slower rate that was similar for all samples. The time at which the change in slope occurred coincided with gelation and hence is related to a decrease in molecular mobility. Increasing the level of crosslinker from 3 to 6% w/w brings about a step increase in the data that is not observed as a result of further increasing the crosslinker level to the recommended amount of 10% w/w, and beyond to 15 w/w. Large excesses of crosslinker (30% w/w) do, however, give rise to a further overall increase in $(\Delta(A_{(Si-H)s}/A_{(C-H)s}))$, though the slope after the initial rise is largely independent of crosslinker level. The latter sample was extremely tacky and flexible and thus can be considered much over plasticized. It therefore appears that there is some margin of error (of approximately 4–5% w/w) for crosslinker addition, at least as far as cure characteristics are concerned. Although some technicians probably go over this margin to achieve the degree of flexibility required for some applications. For further investigations samples A, C and E only were produced on a larger scale.

Hexane extractable content

The hexane extractables content of samples A, C and E are given in Table II. Here it is evident that the percentage mass loss for all samples was greater than the amount of crosslinker added, therefore indicating that not all the chains in the resin component become incorporated into the crosslinked network. Predictably, the extractable content increases as the level of crosslinker increases, as there are only a finite number of chain ends to tie together. ATR analysis of the dried extracted samples indicated (Fig. 3) a large fall in Si–H level, though as the level of crosslinker increased the amount of residual Si–H also increased. Only in the case of sample A (containing the lowest crosslinker level) did the level of Si–H reduce to zero, indicating complete reaction of all Si–H groups of the incorporated crosslinker. The manufacturer's recommended level of crosslinker certainly seems to be far in excess of the level required for reaction of all Si–OH groups. However, at this recommended crosslinker level a significant number of PHMS chains are tied in to the network via reaction of a fraction of their Si–H groups, and a smaller number of PHMS chains are not involved in any reaction and hence are extractable. A threefold increase in the crosslinker level (over the recommended amount) results in a sharp increase in the concentration of unbound PHMS, and only a small increase in the level of bound PHMS.

FTIR analysis of the isolated hexane extractable fraction from samples A, C and E, showed a progressive

TABLE II Hexane extractable content for samples A, C, and E

Sample	Hexane extractable content (% w/w)	
	From mass loss of sample	From mass of extract isolated
A	10.2	9.1
C	15.4	14.4
E	37.5	36.2

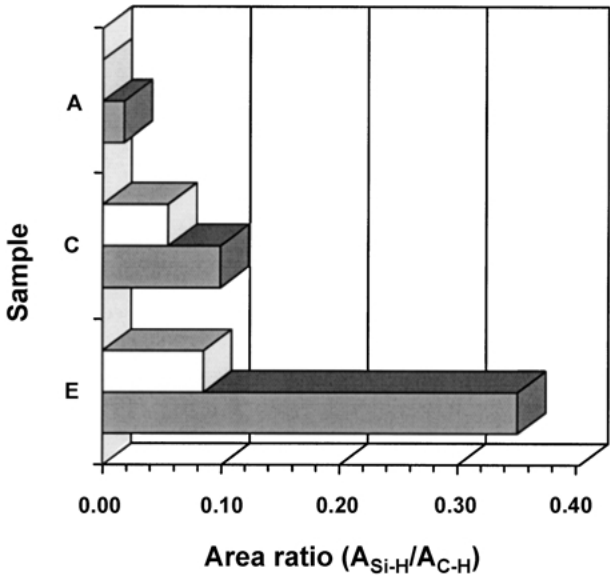

Figure 3 Effect of 24 h hexane extraction on Si–H content of samples A, C and E; ■ before extraction, □ after extraction.

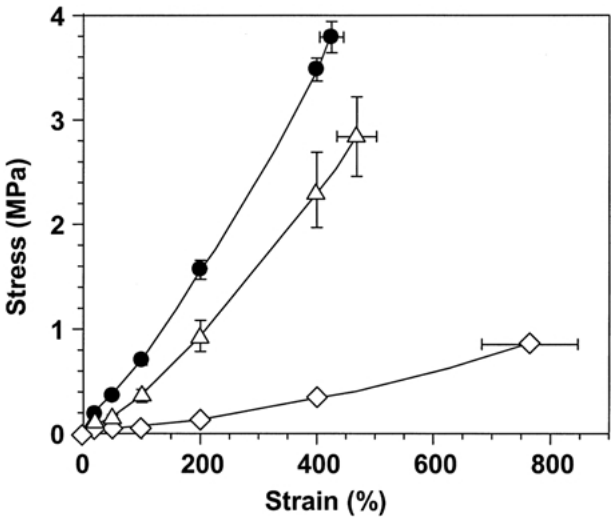

Figure 4 Average stress–strain curves for samples: ● A, △ C, and ◇ E.

increase in Si–H content (Table III). This is entirely consistent with the behavior shown in Fig. 3. $A_{(Si-H)s}/A_{(C-H)s}$ data for the crosslinker itself and pure PHMS are also shown in Table III and from this data it is estimated that the PHMS content of the crosslinker component is approximately 12% on a molar basis.

Mechanical properties

Average stress-strain curves for the elastomers are shown in Fig. 4 and angle tear strength data is given in Fig. 5. The stress–strain data effectively illustrates the plasticization effect of the excess crosslinker. The tear strength of samples A and C are very similar if the spread of data is considered, sample E, however, has seemingly useless tear strength for all but the least demanding applications. Tear strength, as defined by ISO 34, has to be considered carefully in the context of maxillofacial usage, as no mention of the elongation or energy to tear is required.

With this point in mind, both these parameters were obtained from the raw data and are displayed in Fig. 6. The figures for energy to tear were based on the initial cross sectional area of the test pieces. Elongation to tear predictably increases as the level of plasticization increases, though only a small increase is observed with Sample E. Of the three crosslinker levels evaluated, the recommended level (Sample C), gave the highest energy to tear and therefore provides the best all round property profile.

TABLE III Si–H content of hexane extracts

Sample	$A_{(Si-H)s}/A_{(C-H)s}$
A	0.04
C	0.18
E	0.33
Crosslinker	1.04
PHMS#	8.93

Dow Corning DC1107.

Colonization of elastomer by *C. albicans*

In order to determine the extent of colonization and ingrowth by *C. albicans*, microscopy was performed on all sections with emphasis on the edges and center of sections. Blastospores and hyphae were observed in all sections, but the extent of colonization and ingrowth varied between elastomer formulations. Due to the dimorphic nature of this fungus, tangled masses of both blastospores and hyphae were observed within the material. Therefore it was not always possible to quantify the number of *C. albicans* present in each section. Sections from formulation A (Fig. 7(a)) had the least amount of *C. albicans* colonizing the outer surface of the material and blastospores and hyphae were observed sparsely within the sections (Fig. 7(b)).

Sections from formulation E (Fig. 8(a)) had the most extensive colonization of *C. albicans* on the outer surface

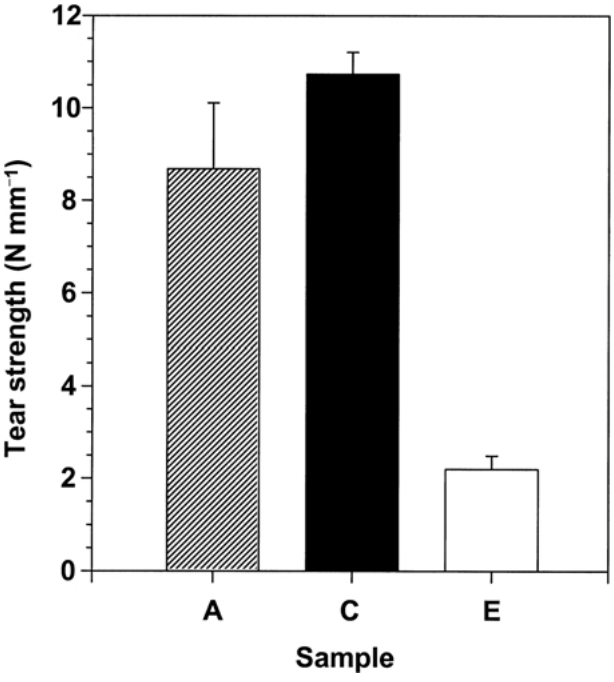

Figure 5 Angle tear strength of samples A, C and E.

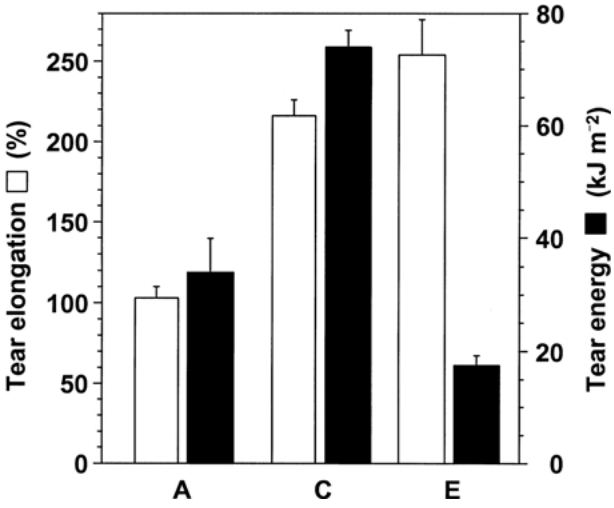

Figure 6 Energy (■) and elongation to tear (□) for samples A, C, and E.

of the material, which correlated with increased numbers of blastospores and hyphae penetrating within the elastomer (Fig. 8(b)). Sections from formulation C (Figs. 9(a) and (b)) showed levels of colonization and ingrowth of *C. albicans* between the two extremes of A and E.

The means by which *C. albicans* deteriorates silicone elastomers is not fully understood. Two modes of attack have been suggested; chemical, involving enzyme degradation of polymeric compounds [7]; or mechanical, whereby firm adhesion of the fungus is required to generate sufficient turgor pressure to penetrate the material [8]. The hydrophobicity of a material has been shown to influence microbial adhesion [9]. However, the Si–H bond is not particularly polar and will not in itself significantly increase the hydrophilicity of the surface. Hydrolysis of some of the Si–H bonds to Si–OH (silanol groups) [10, 11] may, however, modify the level of hydrophilicity due to the ability to form hydrogen bonds. Such hydrolysis may have occurred as a result of exposure to the artificial saliva during autoclaving and/or during extended exposure at body temperature. Whilst the overall pH of artificial saliva is very close to neutral, the basic components such as urea and the possible presence of residual silicone curing catalysts may have served to catalyze the hydrolysis. The silanol hydroxyl group can participate in hydrogen bonding with the proteins present in the artificial saliva, thereby resulting in protein adsorption and ultimately formation of the conditioning film. It is therefore envisaged that an increased concentration of Si–H will result in an increased concentration of Si–OH and hence faster and more prolific protein adsorption, thus promoting build up of an effective conditioning film. Such conditions are more conducive to extensive colonisation by *C. albicans* than when formation of the conditioning film is

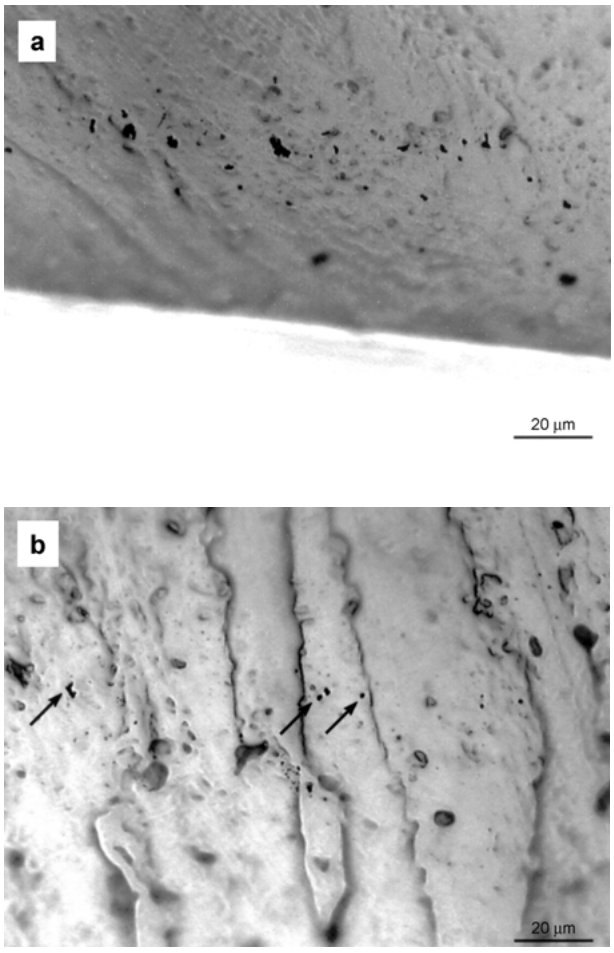

Figure 7 Light micrographs of sections from formulation A, (a) edge and (b) center (arrows denote the presence of blastospores) (scale bar represents 20 µm).

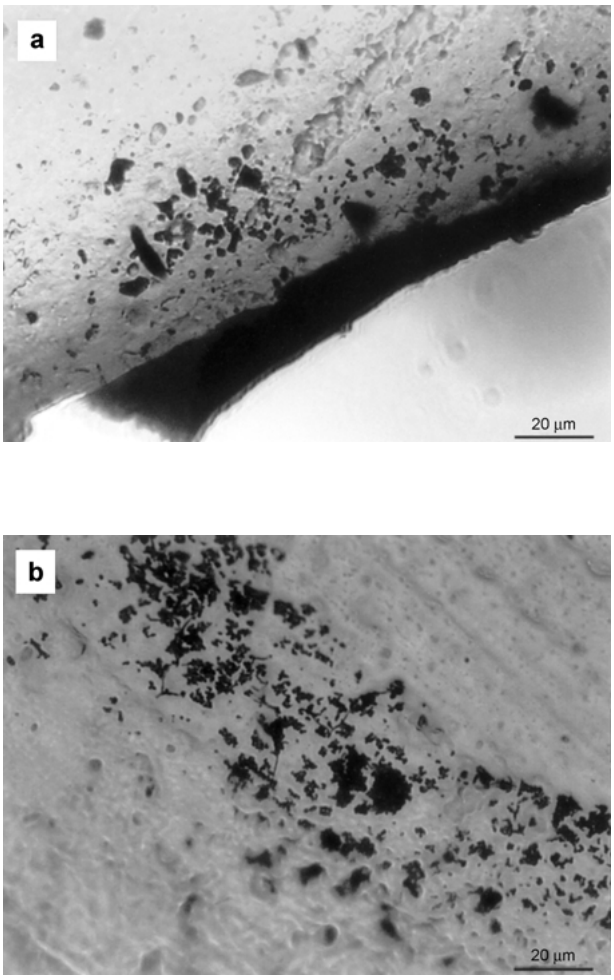

Figure 8 Light micrographs of sections from formulation E, (a) edge and (b) center (scale bar represents 20 µm).

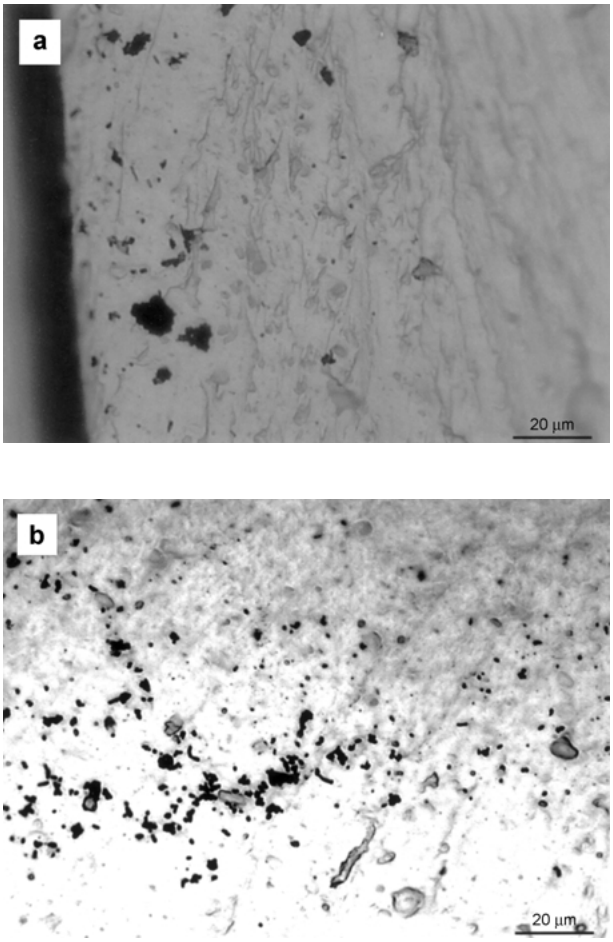

Figure 9 Light micrographs of sections from formulation C, (a) edge and (b) center (scale bar represents 20 μm).

hampered by a lack of protein adsorption sites, as is the case when the crosslinker level (i.e., Si–H concentration) is low. Further work is necessary to verify this idea and will form the basis of a future publication.

In addition, the high level of low unbound molar mass PDMS and PHMS in sample E significantly increased free volume and caused this sample to be very tacky. This property could facilitate more artificial saliva being imbibed into the material and reduce the turgor pressure necessary for yeast cells and hyphae to penetrate into silicone. The results indicate an association between the level of crosslinker used in the production of elastomer formulations and the extent of colonization and ingrowth by *C. albicans*, which will subsequently impact on the rate of silicone deterioration.

Conclusions

A possible link between incorrect formulation and susceptibility to fungal deterioration of a maxillofacial silicone elastomer has been found. Use of excessive levels of a PHMS crosslinking additive in a hydroxyl terminated liquid PDMS resin results in prolific growth and penetration of *C. albicans* into the elastomer. Such high levels of PHMS also result in very poor tensile and tear strength but high elongation to failure; this is due to excessive plasticization, possibly associated with the low molar mass PDMS carrier for the PHMS. A large proportion of the excess crosslinking additive is extractable. This feature, together with possible basic hydrolysis of the Si–H bonds of PHMS to Si–OH, is considered to be the cause of increased colonization by *C. albicans*. The increased free volume may reduce the turgor pressure needed for penetration of hyphae, and the possible increase in the hydrogen bonding component of surface energy may result in an increase in the level of protein adsorption and hence facilitated formation of the conditioning film.

References

1. K. J. SAUNDERS, ''Organic Polymer Chemistry'' (Chapman and Hall, New York, USA, 1985) p. 360.
2. H. J. BUSSCHER, C. E. DEBOER, G. J. VERKERKE, R. KALICHARAN, H. K. SCHUTTE and H. C. VAN DER MEI, *Int. Biodeter. Biodegr.* **33** (1994) 383.
3. J. VERRAN and C. MARYAN, *J. Prosthet. Dent.* **77** (1997) 535.
4. T. R. NEU, G. J. VERKERKE, I. F. HERRMAN, H. K. SCHUTTE, H. C. VAN DER MEI and H. J. BUSSCHER, *J. Appl. Bacteriol.* **76** (1994) 521.
5. S. R. ELL, *J. Laryngol. Otol.* **110** (1996) 240.
6. A. L. SMITH, ''The Analytical Chemistry of Silicones'' (Wiley, New York, 1991).
7. T. R. NEU, H. C. VAN DER MEI, H. J. BUSSCHER, F. DIJK and G.J. VERKERKE, *Biomaterials* **14** (1993) 459.
8. H. F. MAHIEU, H. K. F. VAN SAENE and H. K. SCHUTTE, *Arch. Otolaryngol. Head Neck Surg.* **112** (1986) 321.
9. E. P. J. M. EVERAERT, H. C. VAN DER MEI and H. J. BUSSCHER, *Colloids Surf. B: Biointerf.* **10** (1998) 179.
10. W. NOLL, ''Chemistry and Technology of Silicones'' (Academic Press, New York, USA, 1968) p. 90.
11. E. G. ROCHOW, ''An Introduction to the Chemistry of the Silicones'' 2nd edn. (John Wiley, New York, 1951) p. 5.

Received 28 March
and accepted 29 October 2002