

Swelling Properties of Cross-Linked Maxillofacial Elastomers

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SYNOPSIS

Silicone specimens cross-linked with various amounts of cross-linking agent were studied in terms of mechanical and swelling behavior. The measured tensile modulus allowed calculation of the average molecular weight between cross-links (\bar{M}_c). Equilibrium swelling data were also used, in combination with the determined \bar{M}_c values, to obtain the interaction parameter χ of various silicone-solvent systems at 25°C. Part of this work was also the study of swelling of silicone samples with varying network density in selected solvents such as toluene, ethyl acetate, *n*-butanol, and methyl ethyl ketone.

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INTRODUCTION

Among other materials, silicones have been used for long for maxillofacial prostheses because of their excellent properties.¹ These materials can be cross-linked at room temperature and are based on dimethylsiloxane polymers. Cross-linking can be carried out by condensation or an addition reaction, depending on the specific chemical structure of the base polymer and the consistency of the cross-linking system. Condensation of hydroxy groups (Si—OH) via dehydration catalyzed by stannous octoate can lead to a network structure. Similarly, addition of silane groups (Si—H) to silicone vinyl units, catalyzed by platinum compounds, is an alternative route leading to products with lower shrinkage and better dimensional stability.^{2,3}

Maxillofacial prosthetic materials are based on suitable formulations of elastomeric compounds with various additives. Rubber-base materials have been used for a long time in prosthodontics, but application in the field of maxillofacial prostheses introduces an increased list of property requirements.^{4,5} Thus, an ideal material has to be soft, pliable, and capable of adapting to facial movement. It also must be light in weight so that it may be supported without risks of detachment during wear-

ing. Special attention has to be paid into the hygiene of the prosthesis, which requires a nonporous, capable-of-being-washed-and-disinfected material that does not irritate the tissues in contact. In addition, a nontoxic, nonallergenic, and noncarcinogenic response is necessary. Durability, i.e., resistance to aging, is another important requirement accompanied by aesthetic characteristics, ease of manipulation, and reasonable cost.

The above complicated requirements are due to the fact that maxillofacial prosthetics, in the effort to restore missing parts of the face, encounter the problem of replacing tissues with different properties, e.g., hardness, elasticity, and pliability. The ear, for instance, consists of a folded cartilaginous skeleton covered by thin skin and the fatty lobe is slung from its lower and posterior margin, while the skin of the nose is draped over a skeleton that is bony above and cartilaginous below. In such cases, the construction of a prosthesis simulating the missing tissues as closely as possible is an imperative and demanding task. Such a prosthesis will be composed of parts presenting different mechanical properties attempting to simulate facial tissues.

Many studies have already been made on the properties and performance characteristics of silicones as maxillofacial prosthetic materials.⁶⁻¹⁰ Emphasis has been given to mechanical properties, such as tensile characteristics and tear resistance, as a function of the cross-linker concentration.¹¹ Shore hardness, wettability in terms of surface tension,

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and weatherability after accelerated aging have also been studied.¹² However, little attention has been placed on the network characteristics that play an important role on the final properties of the cross-linked product.

The network characteristics can be described by parameters such as the average molecular weight between cross-links, \bar{M}_c . A method for the determination of \bar{M}_c for a polymer network is based on equilibrium swelling measurements that must be inserted into the Flory formula:¹³

$$-\left[\ln(1 - v_2) + v_2 + \chi v_2^2\right] \\ = (V_1/\bar{v}\bar{M}_c)(1 - 2\bar{M}_c/\bar{M}_n)(v_2^{1/3} - v_2/2) \quad (1)$$

where v_2 is the polymer volume fraction at equilibrium swelling; χ , the interaction parameter; V_1 , the molar volume of the solvent; \bar{v} , the polymer specific volume at the unswollen state; and \bar{M}_n the primary molecular weight of the polymer. It is obvious that the interaction parameter χ is an important factor for fast determination of the average molecular weight between cross-links (\bar{M}_c) via swelling experiments in a suitable solvent.^{14,15}

\bar{M}_c can also be determined by mechanical tests. Assuming that (a) the statistical theory of rubber elasticity is valid and (b) the material is above its glass transition temperature (T_g), i.e., in the rubbery state, we can use the following equations:

$$G = \rho RT/\bar{M}_c \quad (2)$$

$$G = E/3 \quad (3)$$

where G the equilibrium shear modulus; R , the gas constant; ρ , the density; T , the absolute temperature; and E , the Young's modulus.¹⁶

In this work, an attempt was made to combine swelling and mechanical data obtained from experiments with silicone rubber samples cross-linked with varying cross-linker concentrations. In this way, it is possible to determine \bar{M}_c for each specimen and then the interaction parameter χ of the silicone-solvent system. This approach intends to correlate structure parameters with property characteristics and is believed to be a contribution to basic knowledge about these materials and promising the prediction of performance. In addition, the interaction parameter, once determined for a specific silicone-solvent system, can be inserted into the Flory formula, which becomes a tool for fast determination of the \bar{M}_c of silicone samples swollen in the same solvent.

EXPERIMENTAL

The silicone material used in this study was Cosmesil SM4 (Cosmedica Ltd, Cardiff, South Wales, U.K.), which is the trade name of a silicone tissue replacement material developed by the University of Wales Institute of Science and Technology and the Institute of Maxillofacial Technology. It consists essentially of a high molecular weight hydroxy functional polydimethylsiloxane, which is known as the silicone elastomer base. Vulcanization takes place at room temperature by a polycondensation reaction and the elimination of alcohol. The cross-linking system consisted of a mixture of trifunctional alkoxy silanes, called X-Linker M, and the catalyst, an alkyl tin dicarboxylate, which acts as an accelerator of the cross-linking reaction.

The material was cross-linked to various extents by altering the amount of X-Linker M added. The ratio of catalyst to the elastomer base was kept constant for all specimens.

Tensile characteristics were determined using specimens according to ISO-37, Determination of Tensile Stress-Strain Properties of Vulcanized Rubber (equivalent to ASTM D 412, Standard Test Methods for Rubber Properties in Tension). Molded dumbbell specimens of Type 2 (ISO 37) with a thickness of 1.8 mm were tested. Tensile modulus at 100% elongation was measured at 25°C, using a Monsanto testing machine (Model T 10, Monsanto Ltd., Swindon, UK) equipped with a TEO 44 automatic extensometer. The extensometer grips were preset to a standard length of 20 mm using a setting gauge. Tests were performed at a crosshead speed of 50 mm/min and the cross-sectional area of each specimen was entered into the program of the testing machine.

For the swelling experiments, discs 2 mm thick and 25 mm in diameter were immersed in various solvents at 25°C, and the weight increase was recorded. The following aromatic and oxygen-containing solvents were used: toluene, ethyl acetate, *n*-butanol, and methyl ethyl ketone.

RESULTS AND DISCUSSION

The swelling behavior of silicone samples in various solvents at room temperature is shown in Figures 1-4. In these graphs, the ratio of the amount of solvent sorbed at time t (M_t) to the amount sorbed at equilibrium (M_∞) was plotted vs. the square root of

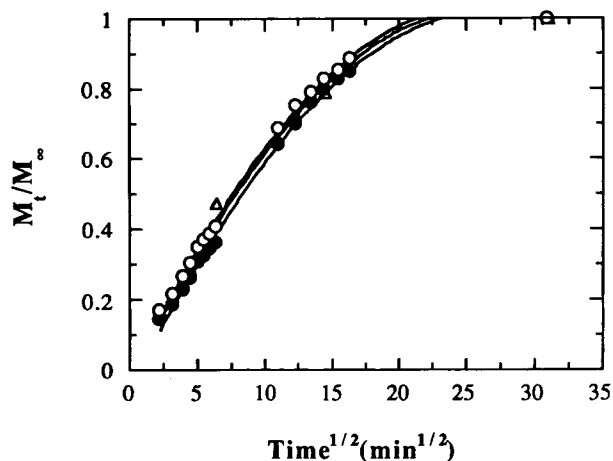


Figure 1 Swelling of silicone samples with varying cross-linker concentrations in toluene, at 25°C: (●) 0.02%; (○) 0.04%; (△) 0.06%.

time. These expressions were selected in order to examine the applicability of the Fick's law, i.e.,

$$M_t/M_\infty = 4/\pi[Dt/l^2]^{1/2} \quad (4)$$

where M_t and M_∞ are the amount of solvent sorbed at time t and equilibrium, respectively; D , the diffusion coefficient; and l , the specimen thickness. Equation (4) is useful for the determination of the diffusion coefficient of materials such as membranes and was applicable to the specimens and solvents tested at least up to a swelling ratio of about 0.70. Swelling then became parabolic with the square root

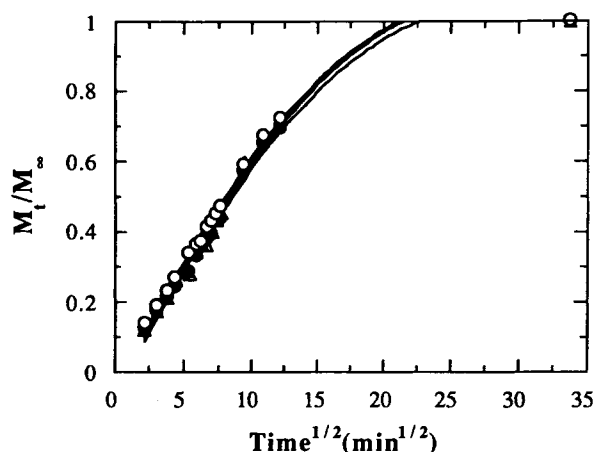


Figure 2 Swelling of silicone samples with varying cross-linker concentrations in ethyl acetate at 25°C: (●) 0.02%; (○) 0.04%; (△) 0.06%.

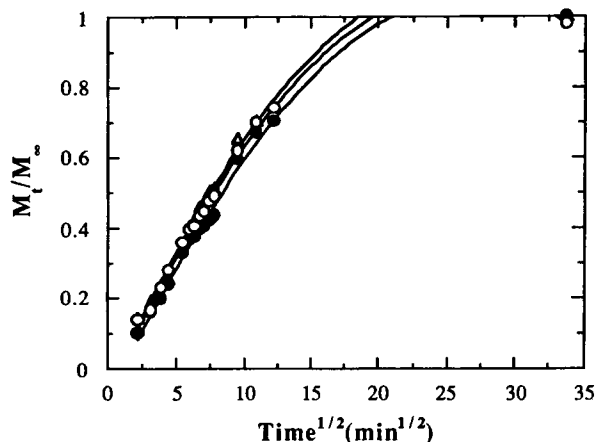


Figure 3 Swelling of silicone samples with varying cross-linker concentrations in methyl ethyl ketone at 25°C: (●) 0.02%; (○) 0.04%; (△) 0.06%.

of time, which probably means a change in diffusion coefficients of highly swollen specimens. Very interestingly, the absorption behavior for the silicone specimens with varying cross-linker concentration is essentially the same, as can be seen from the curves of Figures 1–4. Similarly, the percent equilibrium swelling, presented in Table I, shows a small decrease as the network density increases by increasing the cross-linker concentration. Similarly, the moduli of elasticity for the same samples, shown in Table II, increase with cross-link density, as expected from the above-mentioned eqs. (2) and (3). However, for the cross-linker concentration exceed-

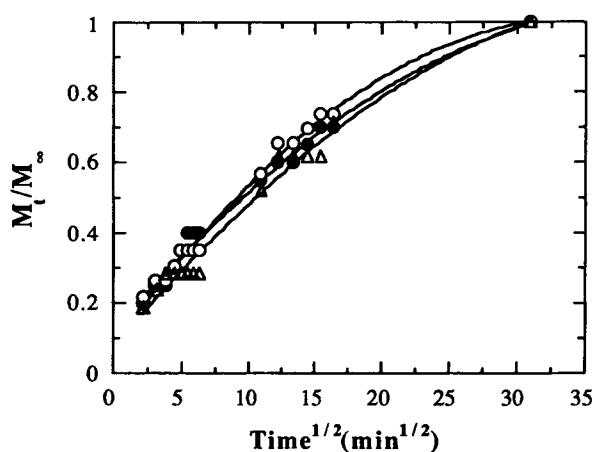


Figure 4 Swelling of silicone samples with varying cross-linker concentrations in *n*-butanol at 25°C: (●) 0.02%; (○) 0.04%; (△) 0.06%.

Table I Equilibrium Swelling (%) of Silicone Samples in Various Solvents at 25°C

Sample	Cross-linker (%)	Solvent			
		Toluene	E/A	<i>n</i> -Butanol	MEK
A	0.020	184	118	13.3	68
B	0.04	157	106	10.7	61
C	0.06	130	92	11.0	54

E/A: ethyl acetate; MEK: methyl ethyl ketone.

ing 0.04%, which is also the recommended concentration by the manufacturer, a rather modest increase in modulus occurs. From the independence of absorption behavior and cross-link density, the small reduction in equilibrium swelling as we increase the cross-link density, and the small increase in modulus with cross-linker concentration above 0.04%, we infer that the cross-linking density of the network is not linear with cross-linker concentration. Concentrations higher than 0.04% appear to further advance cross-linking to a small extent, probably because of restricted chain mobility.

These results along with the swelling data suggest that the silica particles present as a filler contribute to the formation of the network. As a matter of fact, such a contribution would be expected by the surface chemistry of the silica particles.¹⁷ One can find hydroxyl groups on that surface that can chemically combine with siloxane molecules via condensation reactions similar to those taking place during cross-linking. Also, the surface porosity of silica may adsorb silicone chains and act as a multifunctional cross-link.

Based on the moduli of elasticity, the average molecular weight between cross-links (\bar{M}_c) was calculated for samples studied in this work. Furthermore, these \bar{M}_c values inserted into Flory's formula [eq. (1)] along with swelling data allowed us to determine interaction parameters (χ) for silicone/

solvent at room temperature for all four solvents used. The results presented in Table III are similar for toluene, ethyl acetate, and methyl ethyl ketone, which appear to be good solvents, whereas *n*-butanol gave the lowest swelling and the obtained χ value is unusually high. This may be correlated with a lower value of the diffusion coefficient of *n*-butanol, as can be seen from a comparison of the slope of the curves in Figure 4, with those of Figures 1–3.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. Within the range 0.02–0.06%, cross-linker concentration affects the network density of maxillofacial silicone compounds in terms of equilibrium swelling. The effect on the modulus appears to be strong for concentrations up to 0.04%
2. Silica particles incorporated as a filler probably produce additional multifunctional cross-links in reinforced silicone elastomers.
3. Cross-linked silicone samples swell in toluene, ethyl acetate, methyl ethyl ketone, and *n*-butanol according to Fick's law up to a swelling ratio of about 0.7. The highest equi-

Table II Modulus of Silicone Samples with Varying Amounts of Cross-linker

Sample	Cross-linker (%)	Modulus (at 100% Elongation 25°C, 50 mm/min) (MPa)
A	0.02	0.46
B	0.04	0.80
C	0.06	0.90

Table III Calculated Interaction Parameters for Various Silicone/Solvent Systems at 25°C

Solvent	Interaction Parameter (χ)
Toluene	0.610
Ethyl acetate	0.667
Methyl ethyl ketone	0.695
<i>n</i> -Butanol	1.252

librium swelling takes place in toluene, followed by ethyl acetate and methyl ethyl ketone. Swelling in *n*-butanol is considerably lower.

4. The interaction parameter value is in the range 0.6–0.7 for good solvents, whereas a value of 1.252 was determined for the system silicone/*n*-butanol.

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