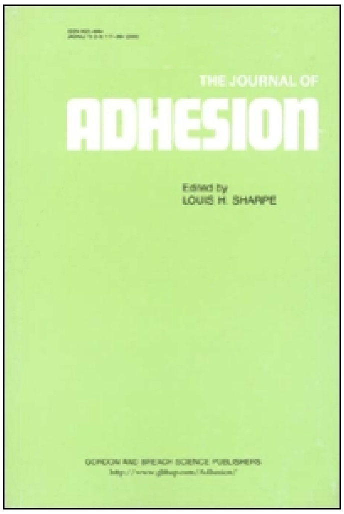

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The Structure and Properties of Films of Siloxane Coupling Agents

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The structure of a free film of hydrolysed gamma-glycidoxypropyl-trimethoxy-silane is examined by various techniques. It is particulate rather than continuous in structure and there are residual hydroxy and methoxy groups. These hydroxyl groups are largely inaccessible to exchange with deuterium oxide. The structure suggested is mainly six-membered rings joined by short lengths of —SiO— chains and crosslinked by fusion of rings. The free hydroxyl groups on connected chains are protected by a spiral structure and probably from hydrogen bonds.

INTRODUCTION

Alkoxy silane coupling agents have achieved wide recognition and acceptance in the glass-reinforced plastic industry particularly for their part in producing satisfactory and durable composites resistant to water. These compounds have only been adopted in adhesive technology much more slowly and over a restricted range of applications in spite of the well-known sensitivity to moisture of metal/metal joints made with structural adhesives.

With essentially silica substrates the reaction has been firmly established as a primary chemical bond between the silicon of the siloxane and the hydroxyl of the silanol group in the surface.[1] The nature of the link with the hydrated oxide surface of metals is more problematical although a similar bonding to the hydroxyl groups is usually assumed. The particular case of aluminium surfaces does not appear to have been investigated.

W. D. Bascom[2] adsorbed fluoro and chloro carbon trialkoxy silane films from aqueous solution on a number of surfaces including α-alumina.

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Generally these films were only resistant to removal by washing if they had been initially deposited at elevated temperatures and in the presence of a catalyst, acid or base. It was shown by ellipsometry that the layer was ten or more molecules thick for some of the substrates, although not on alumina. There is here, as elsewhere, a *prima facie* case that the hydroxyl groups of the siloxane are bound to the surface although not necessarily by primary bonds. Similar results for the thickness of siloxane films adsorbed from aqueous solution on glass are reported by D. J. Tutas, R. R. Stromberg and E. Passaglia.[3]

Mild steel surfaces from which acrylic coatings containing 1% siloxanes had been stripped have been examined[4] by Fourier transform infra-red spectrometry and have shown frequencies characteristic of the siloxanes but none indicative of the character of the adsorption.

F. J. Boerio and J. E. Greivenkamp[5] examined the adsorption of γ amino propyl triethoxy silane on highly polished iron using plane polarised reflectance infra-red spectroscopy. Adsorption from aqueous solution gave a thick layer most of which was easily removed by extraction with water. The material removed was polysiloxane and it appeared that the remaining, firmly held, thin film had been adsorbed as dimers with the amino group chelated to the iron.

It is known[6] in the case of glass reinforced plastics that the extent of protection against moisture which the coupling agent confers is dependent upon the "degree of cure" which the siloxane polymer attains before the matrix polymer is applied to the fibre. This suggests a certain hydrolytic sensitivity of the siloxane after it has cured.

Further, if a thin film of a siloxane is formed on and then removed from a non-adherent surface, the isolated material is rather brittle as would be expected for a highly cross-linked substance. However, the strength of neither GRP nor metal–metal adhesive joints appear to be adversely affected by this potentially weak layer. By analogy with R. E. Robertson's[7] work with polystyrene this may be due to the relative thinness of the layer.

There are, it would seem, a number of aspects of the use of siloxane coupling agents which are imperfectly understood. Among these is the fact that as applied technologically, a film of finite thickness and of uncertain properties is interposed between the adhesive and the metal surface.

The properties of this film would be expected to influence the joint strength and behaviour irrespective of the nature of the bond between it and either the substrate or the adhesive. This present work investigates the structure of this film and attempts to relate this to its properties and those of joints. Essentially films of polysiloxane have been prepared in isolation and examined by various physical techniques in order to elucidate the properties and nature of the polymer.

EXPERIMENTAL

Hydrolysis and polymerisation of alkoxysilane

Throughout this work the silane coupling agent used was γ-glycidoxypropyl trimethoxy silane. This monomer is available from Dow Corning as Z6040 or from Union Carbide as A187.

The hydrolysis was carried out by adding slowly and with constant stirring to one gram-mole (236 g) of monomer three gram-mole (54 g) of distilled water containing 0.5 ml of concentrated hydrochloric acid. This took 20 minutes during which time some heat was evolved but the flask was not cooled. The pH was adjusted to 3.85 by the addition of dilute hydrochloric acid and the mixture was allowed to stand for an hour. This solution of hydrolysed siloxane was then diluted by the slow addition of 500 ml of methanol and the mixture was refluxed for 30 minutes. Then aqueous methanol was removed by distillation at 65 ~ 70°C and a viscous, colourless liquid of refractive index 1.446 remained. It was poured into a Perspex mould lined with very thin polyethylene to act as a release film and a sheet of material 15 × 15 × 0.5 cm was prepared by heating the mould in an air oven at 40°C for 24 hours; roughly the time taken for the liquid to gel and for the gel to acquire sufficient strength for it to be removed from the mould without breaking. This stage was regarded as the base from which further curing was measured.

Infra-red spectra were obtained of (i) the original monomer, (ii) the mixture after hydrolysis but before addition of methanol and (iii) the final viscous liquid. Comparison of the second and third with the first showed the appearance of a strong bond at 1650 cm^{-1} which suggests that some of the epoxide rings have been hydrolysed to a glycol which has then been dehydrated to give a terminal vinyl group.

It will be recognised that this procedure would be expected to give a completely hydrolysed product with all the methoxy groups replaced by hydroxy groups. The characteristic absorbances at 2840 cm^{-1} and 1190 cm^{-1} identified by Haslam, Willis and Squirrel[6] are evident in the original monomer as expected; but, surprisingly, remain in the final product. There is little room for doubt about the ascription of these bonds and it is clear that some unhydrolysed methoxy groups remain. Boerio and Greivenkamp[5] similarly report the continuing occurrence of ethoxy groups in films of the coupling agent which they employed, although they did not use a catalyst to accelerate hydrolysis.

Extent of condensation of cured material

Condensation of contiguous silanol groups eliminates water and produces Si—O—Si bonds. It was decided to follow the extent of this condensation by

TABLE I

IR peak heights for polysiloxane KBr disc specimens

	Cure time hour	Peak heights (cm)					Ratio of peak heights				
		A	B	C	D	E	D/E	B/D	B/E	$2C/(D+E)$	$2A/(D+E)$
	approx. wave number	(O—H) 3370	(C—H) 2900	(epoxy) 900	(Si—C) 840	(Si—C) 770					
Before rigorous drying	0	1.9	1.8	2.1	1.5	1.4	1.07	1.20	1.29	1.45	1.31
	2	1.9	2.1	2.6	1.4	1.1	1.27	1.50	1.91	2.08	1.52
	4	2.2	2.5	2.6	1.9	1.8	1.06	1.32	1.39	1.41	1.19
	8	2.6	3.1	2.9	2.2	1.8	1.22	1.41	1.72	1.45	1.30
	12	2.0	2.6	2.3	1.9	1.5	1.27	1.37	1.73	1.35	1.18
	24	2.1	2.9	3.8	3.4	3.0	1.13	0.85	0.97	1.19	0.66
	48	1.7	2.6	3.5	2.8	2.5	1.12	0.93	1.04	1.32	0.64
	168	0.5	0.9	1.0	0.9	0.8	1.13	1.00	1.13	1.18	0.59
						Mean	1.15	1.20	1.40	1.42	—
						S.E.M.	0.03	0.09	0.12	0.10	—
After rigorous drying	0	1.7	1.9	2.2	1.9	1.5	1.27	1.00	1.27	1.29	1.00
	2	1.1	1.4	1.5	1.25	1.25	1.00	1.12	1.12	1.20	0.88
	4	1.25	1.6	1.45	1.15	0.9	1.28	1.39	1.78	1.41	1.22
	8	1.6	2.3	1.85	1.7	1.35	1.26	1.35	1.63	1.21	1.05
	12	1.4	2.05	1.7	1.45	1.43	1.00	1.41	1.41	1.17	0.97
	24	1.15	1.7	1.45	1.3	1.0	1.30	1.31	1.70	1.26	1.00
	48	1.4	2.15	1.9	1.7	1.35	1.26	1.26	1.59	1.85	0.92
	168	1.8	2.55	2.65	2.35	2.3	1.02	1.09	1.11	1.14	0.77
						Mean	1.17	1.24	1.45	1.32	—
						S.E.M.	0.05	0.05	0.09	0.08	—

examining the infra-red spectra of specimens cured for increasing periods of time. Discs 15 mm in diameter were punched from the original sheet and were cured in air at 70°C for varying periods. Between completion of curing and testing the discs were stored in a desiccator.

Spectra were measured with a Perkin Elmer double beam grating spectrometer Model 457. Two techniques were used to prepare specimens; in the first the comminuted sample was mixed with potassium bromide and pressed into a disc in a die to which vacuum could be applied. The die containing powder was evacuated for two minutes before pressure was applied for 2 minutes. This was followed by two cycles of evacuation/pressure.

Better spectra were, on the whole, obtained by coating films of the original viscous liquid directly on to rock salt plates and curing them *in situ.*

The peak heights of the selected absorption peaks were made by the tangent line method.

Instrumental limitations decided the selection of the OH stretching frequency at about 3330 cm^{-1} to follow the dehydroxylation and several frequencies were examined to establish the best to use as an internal standard. Since the free hydroxyl frequency was being used it implied complete absence of moisture from the samples and to verify this a second series was examined after they had been extracted with sodium-dried ether to remove any traces of residual water.

Results of the measurements with KBr discs are given in Table I. Of the frequencies chosen as possible internal standards the two arising from the same Si—C valency bond, D and E, would be expected to show a constant ratio in all samples and indeed the standard error of the mean of this ratio is lower than any other. The best internal standard is therefore the mean of these two and the absorbance corresponding to the epoxy group tested against this is reasonably constant. There is almost nothing to choose between the dried and the ether-extracted, rigorously dried samples although overall the latter show a very slightly lower hydroxyl content which is consistent with the ether extract being relatively rich in unreacted silanol groups.

The results from the later measurements with films cast and cured directly on rock salt plates are given in Table II. These gave spectra of somewhat better quality as is indicated by the lower Standard Error for the ratio of the two Si—C frequencies.

All the values for the ratio $2A/(D+E)$ are shown plotted against time of cure in Figure 1 which shows the difficulty of drawing quantitative conclusions. However it is clear that the hydroxyl content decreases but a considerable amount remains even after a long period at 70°C and if it is assumed that the freshly gelled material is essentially linear then the fully cured material is not very highly cross-linked.

If the ratios based on the films cast on rock salt alone are considered, being

TABLE II

IR peak heights for polysiloxane cured on rock salt plates

Cure time hour	Peak heights (cm)			Ratios	
	A	D	E	D/E	$2A/(D+E)$
0	1.95	2.7	1.8	1.50	0.87
15	2.3	3.3	2.3	1.43	0.82
25	1.5	2.7	1.8	1.50	0.67
45	1.05	2.15	1.4	1.54	0.59
60	1.7	3.45	2.2	1.51	0.60
192	1.75	3.0	1.95	1.54	0.71
			Mean	1.50	
			SEM	0.02	

the more accurate and consistent, then the hydroxyl content has decreased during cure by a third (from a value proportional to 0.9 to one proportional to 0.6). This implies that for linear polysiloxanes crosslinking, one in three of the pendant hydroxyl groups is eliminated.

Deuteration of siloxane film

An attempt was made to effect an exchange with deuterium of the hydrogen of the hydroxyl groups remaining after cure. Fully cured material which had been

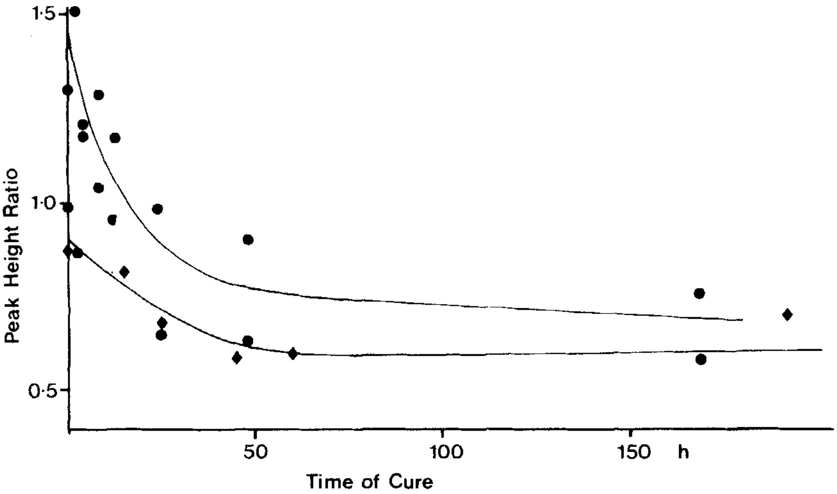


FIGURE 1 Quantitative estimation of hydroxyl concentration from infra-red data.
● Results from KBr disc specimens
♦ Results from films cast on rock salt

rigorously dried with sodium dried ether was ground to a fine powder and shaken overnight with 99.8% D_2O in a sealed tube. The powder was carefully dried before incorporation into KBr discs. The infra-red spectra showed no change from those previously obtained indicating that only a negligible amount of exchange could have occurred.

An attempt was then made to see if deuterium exchange could be detected purely on the surface of the film. A Techmation Multiple Internal Reflectance Unit with nine reflections at an angle of 45° was used. Spectra were obtained before and after a specimen had been immersed in deuterium oxide for twelve hours. The relevant section of the spectra are shown in Figure 2. The appearance of the broad peak due to OD is very obvious and if the two spectra are correlated via the height of the C—H peak the hydroxyl absorption is found to have completely vanished.

Thus it appears that only the hydroxyl groups which are actually at the surface of the film are accessible to exchange with deuterium oxide.

Surface polarity of siloxane film

A fully condensed polysiloxane resulting from the oxidation of all the available hydroxyl groups of a trihydroxy monomeric silane would be expected to have a surface with properties characterised by the properties of the fourth substituent group of the monomer. In the present case this will be the gamma-glycidoxy propyl group. Some polarity would arise from the terminal epoxy group but as this does not usually take part in hydrogen bonding pairs, the cured material would not be expected to show highly polar interaction with glycerol or water.

Contact angles were measured for drops of a range of liquids on the smooth surface of discs of fully cured materials using a reflection goniometer.[9] Mean values of cosine θ are given in Table III from which it is immediately apparent that there is no significant change in the property with time of curing.

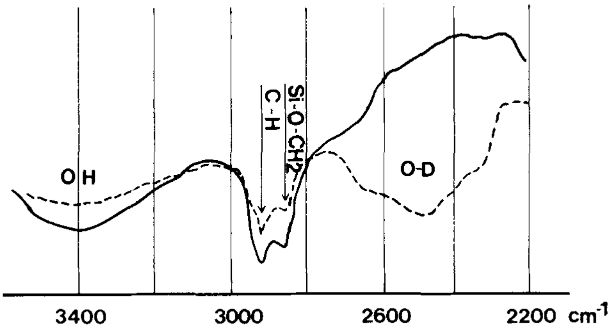


FIGURE 2 Effect of deuteration on infra-red spectrum.

TABLE III

Cosines of contact angles for liquids on siloxane film

Liquid	Time of cure/hour							Mean	Surface components of liquid		
	2	4	8	12	24	48	170		γ_l	γ_l^d	γ_l^p
Water	0.59	0.59	0.74	0.61	0.63	0.56	0.59	0.62 ± 0.06	72	22	50
Glycerol	0.48	0.82	0.47	0.66	0.50	0.55	0.54	0.57 ± 0.11	65	35	30
Formamide	0.87	0.86	0.88	0.87	0.72	0.78	0.85	0.83 ± 0.11	58	32	26
Di-iodomethane	0.82	0.83	0.79	0.79	0.82	0.81	0.78	0.80 ± 0.03	49	47	2
Bromonaphthalene	1.00	0.93	0.97	0.91	0.95	0.97	0.97	0.96 ± 0.07	50	50	0
Tritolylphosphate	1.00	0.97	0.96	0.93	1.00	0.97	0.97	0.97 ± 0.06	44	42	2

Each mean value of cosine θ arises from six independent estimates of θ.

It may be assumed that the surface free energy of the siloxane film comprises two components, one due to polar forces and the other due to dispersion forces and that with non-polar liquids the interaction and the work of adhesion is expressible in terms involving the dispersion component. Fowkes[10] combined the Girifalco–Good equation with the Young equation to give:

$$\gamma_s^d = \frac{(\gamma_l)^2 (1+\cos\theta)^2}{4\gamma_l^d}$$

which assumes that the spreading pressure of the liquid upon the solid (π) is small and may be neglected.

This assumption is commonly made when considering liquids which form finite contact angles with organic solids. It may not be strictly valid in the present case but it is unlikely to introduce any considerable error.

The last three liquids in the table may be regarded as non-polar and if the values given on the table are inserted into the aforementioned equation, the value for γ_s^d calculated is 43.0 mJ $\cdot$ m^{-2} with a standard error of the mean of 1.7. For all the liquids the work of adhesion may be derived either by calculation from the dispersion component of the surface free energy of the solid and liquid or from the observed total surface free of energy of the liquid and cosine θ. The values resulting from these calculations are given in Table IV.

It will be immediately obvious that for the liquids with some degree of polarity the work of adhesion observed is considerably more than that calculated from the dispersion forces alone. Since these excess energies particularly occur with liquids capable of hydrogen bonding it is reasonable to deduce that the solid surface does contain a group capable of forming hydrogen bonds. It may be noted in passing that a consistent value for γ_s^p cannot be calculated from a polar analogue of the expression when dispersion forces alone operate.

If from this data cos θ is plotted against γ_l and the line is extrapolated to cos $\theta = 1$, following Zisman,[11] then a value of γ_c of about 40 mJ $\cdot$ m^{-2} is

TABLE IV

Comparison of calculated and observed work of adhesion (mJ $\cdot$ m^{-2})

Liquid	Work of adhesion derived from $2(\gamma_l^d \gamma_s^d)^{1/2}$	$\gamma_l(1+\cos\theta)$	Difference
Water	61.5	117.6	56.1
Glycerol	79.8	99.5	19.7
Formamide	82.4	106.5	24.1
Di-iodomethane	89.9	88.2	−1.7
Bromonaphthalene	92.7	99.0	6.3
Tri-tolyl phosphate	85.0	85.9	0.9

derived. This is in agreement with the accepted values for surfaces containing the more polarized groups.

Interaction of siloxane film with liquids

The cured polysiloxane films were, unexpectedly, flexible solids of low extension, easily torn and quite friable. For example films of a thickness of 5 mm broke extremely easily when twisted between the fingers. This suggested that they were rubbery in nature rather than being brittle solids of low strength and extensibility. It is well-known that the strength of rubbers increases with increasing cross-linking, passes through a maximum and then decreases sharply. A vulcanisate of natural rubber and sulphur with about 7% sulphur is weak and friable; very much like the polysiloxane films which had been made. Attempts were therefore made to use the technique of swelling in solvents and measuring the modulus of the swollen material, which is successful with rubbers, to derive information on the degree of cross-linking of the polymers, their solubility parameters and hence their structure.

Swelling in liquids

Cylinders of uncured but gelled siloxane were cut from the cast sheet and placed, in pairs, in the solvents. They were left for six days by which time the swelling had reached equilibrium. Uncured material was used in order to maximise the swelling obtained. The extent of swelling was measured by weighing the cylinders before and after immersion. For a number of the solvents it was not possible to measure the swelling achieved because the samples became so fragile that they disintegrated as they were removed from the liquid. The data on swelling together with the solubility parameters of the liquids and an indication of their hydroxyl generated hydrogen bonding character are given in Table V.

An exact analogy for this behaviour was reported by Humphreys and Wake[12] in their study of rubber vulcanisates made from rubber latex which was vulcanised while still an emulsion. This latex when dried gave a rubber sheet with the usual strength and extensibility of gum rubber, but on swelling in benzene it disintegrated on touch presumably into particles derived from the original latex emulsion. The explanation then advanced and subsequently confirmed by Voyutskii[13] was that a rubber film prepared by the usual methods is randomly cross-linked virtually throughout its entirety. When this is swollen in a solvent a continuous molecular network remains, sufficient to provide cohesion. With a vulcanised latex the cross-linking is restricted to being within each particle and the cohesion of the dried film depends upon secondary, Van der Waals' forces between the surfaces of these vulcanised

TABLE V

Swelling of polysiloxane film in liquids

Liquids	Solubility parameter $(\mathrm{mJ} \cdot \mathrm{m}^{-3})^{1/2}$	Hydrogen bonding character	% increase in weight-mean of 2
n-Hexane	14.9	Poor	0.8
Diethyl ether	15.1	Moderate	13.5
Petroleum ether (100–120)	~15.5	Poor	7.2
Cyclohexane	16.7	Poor	2.0
Carbon tetrachloride	17.6	Poor	45.0
n-Butyl acetate	17.7	Moderate	52.0
Ethyl acetate	18.6	Moderate	57.5
iso-Propan-2-ol	20.4	Strong	22.5
n-Butan-1-ol	23.7	Strong	16.0
Ethanol	26.1	Strong	24.5
Methanol	29.6	Strong	33.0
Water	47.9	Strong	51.5
Triochloro ethylene	19.0	Poor	One sample only, other disintegrated
Xylene	18.0	Poor	Samples disintegrated
Toluene	18.2	Poor	
Benzene	18.7	Poor	
Chloroform	19.0	Poor	
Dichloromethane	19.8	Poor	
Dichloro ethane	20.0	Poor	
Acetone	20.4	Moderate	

Solubility parameters from Brydson, *Rubber Chemistry* (London, 1978), or K. L. Hoy, *J. Paint Tech.* **42**, 547 (1970).

particles. When this structure is swollen in a good solvent this cohesion is lost and the film becomes exceedingly fragile.

The data on swelling are plotted against the solubility parameters of the solvent in Figure 3 where the liquids for which the swelling could not be measured are indicated by arrows. The swelling depends very markedly upon the hydrogen bonding characteristics of the liquids and separate curves are indicated for those with poor or moderate and for those with strong hydrogen bonding character.

From the curve with liquids which do not show hydrogen bonding, a solubility parameter of the silicone of about $19(\mathrm{mJ} \cdot \mathrm{m}^{-3})^{1/2}$ can be deduced. This puts the polymer far away from the usual silicone rubbers in its behaviour (solubility parameter about $15(\mathrm{mJ} \cdot \mathrm{m}^{-3})^{1/2}$) and into the class of nitrile rubbers, polyvinylacetate and polycarbonate. Polycarbonate which is derived from bis-phenol A like most of the epoxy resins, has a solubility parameter of 19.4 and this similarity suggests a compatability between the siloxane and epoxy resins with the possibility of mutual solubility and interdiffusion before curing brings such processes to a halt.

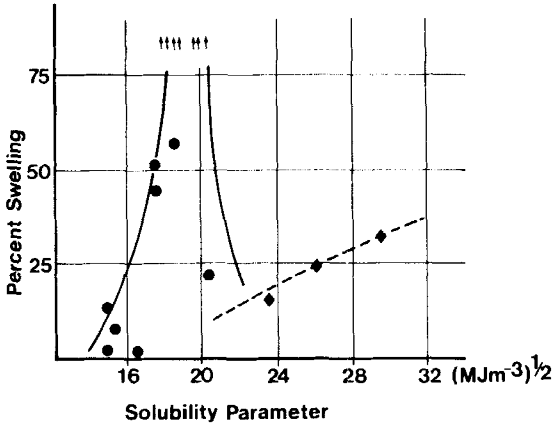


FIGURE 3 Swelling of polymer in liquids. Amount of swelling vs solubility parameter.

Modulus after swelling in ethanol

None of the non-hydrogen bonding liquids are absorbed by the siloxane polymer in sufficient quantity to overcome the secondary valence forces without at the same time rendering the polymer friable even if still capable of being handled. Obviously the modulus in extension of the swollen material could not be measured but it was possible to measure it in compression.

Four cylindrical test pieces for each of seven different periods of cure, including the gelled samples considered as zero cure, were swollen in ethanol and the compression moduli measured. Then the test pieces were immediately weighed, the ethanol removed and they were reweighed. Thus the volume fraction of polymer in the swollen sample was determined independent of any extraction of polymer by the solvent. In fact, reference to initial dry weights showed that on average about 5% of the polymeric material diffused out into the ethanol. A typical set of experimental results are shown in Figure 4 and the final results of these measurements are given in Table VI. From the figure it is obvious that the first cycle of loading/unloading is atypical but that subsequent cycles are reproducible and the figure for the modulus was taken from these. There is hysteresis occurring which implies that an equilibrium modulus is strictly unobtainable but the slope on loading was taken to represent the time equilibrium modulus.

The theory relating the compression modulus of a swollen sample to the constants of the Mooney–Rivlin equation (C_1 and C_2) was worked out by L. D. Loan[14] and gives:

$$\frac{f \cdot h_0}{6\Delta h \cdot A_0} = (C_1 + C_2)$$

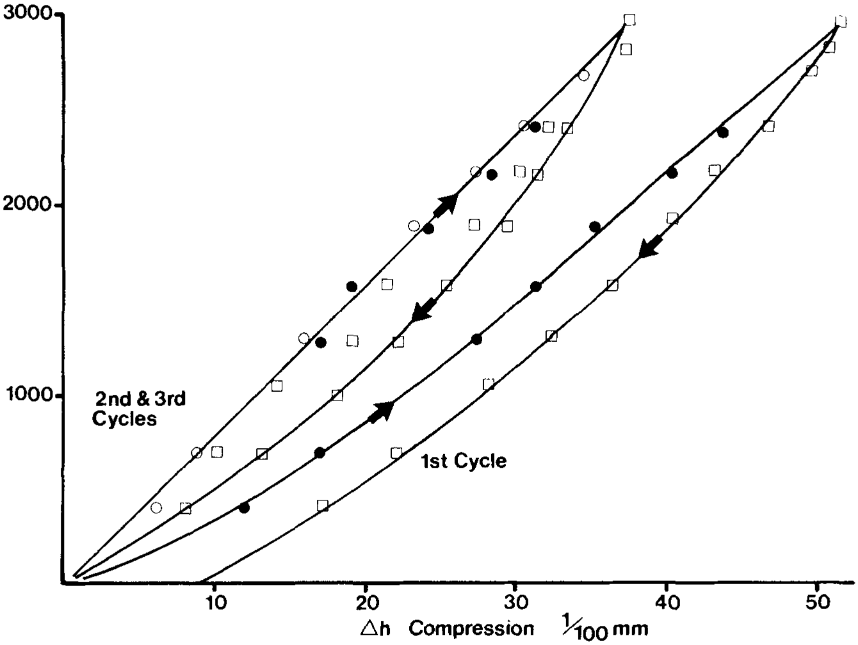


FIGURE 4 Typical stress-strain curves of polymer in compression.

where f is the force applied; h_0 is the initial height of the specimen; Δh is the change in height and A_0 is the initial cross-sectional area of a cylindrical specimen. In the Mooney–Rivlin equation, C_1 is directly related to the network structure and C_2 is a function of secondary forces and entanglements. It follows that the dependence of $(C_1 + C_2)$ upon the degree of swelling of the polymer should be wholly dependent upon C_2. The degree of swelling is represented by V_r the volume fraction of polymer in the swollen sample and linear extrapolation of $(C_1 + C_2)$ against V_r to $V_r = 0$ should enable C_1 to be calculated.

The experimental results are plotted in Figure 5 and should appear as a series of parallel straight lines, one for each set of test pieces with the same degree of cure, rising from left to right. What is found is a series of very scattered results which with one exception shows no clear trend, but which, so far as any pattern can be discerned, generally show a slope in the opposite direction to that expected.

While this has not been explained it must indicate that the essential requirements for a valid application of the theory are distorted in some way. These essential requirements are for a homogeneous network uniformly swollen by this liquid, and for the degree of swelling to be great enough substantially to reduce the interchain attractive forces. If, as has begun to be

TABLE VI

Compression experiments with swollen test pieces
$6A_0 = 10.61\ \text{cm}^2$. Temp. 298 °K. Gradient $= f/\Delta h$

Cured time hour	Gradient $N \cdot m^{-1}$	h_0 mm	$\frac{f}{\Delta h} \cdot \frac{h_0}{6A_0} = C_1 + C_2$ $kN \cdot m^{-2}$	Volume fraction polymer
0	639	5.48	3.30	0.717
	477	5.69	2.56	0.738
	598	5.06	2.85	0.727
2	518	5.34	2.61	0.730
	522	5.51	2.71	0.710
	546	5.19	2.67	0.726
4	463	5.29	2.31	0.725
	493	5.16	2.40	0.726
	539	5.73	2.91	0.722
	493	5.55	2.58	0.728
6	623	4.99	2.93	0.717
	458	5.53	2.39	0.731
	810	5.10	3.90	0.727
	698	4.94	3.25	0.722
8	648	4.98	3.04	0.711
	500	5.03	2.37	0.720
	592	5.01	2.80	0.728
	450	5.59	2.37	0.733
18	357	5.29	1.78	0.727
	652	4.91	3.02	0.729
	467	4.98	2.19	0.738
	499	5.37	2.57	0.728
24	366	5.53	1.91	0.734
	486	5.15	2.36	0.736
	553	5.10	2.66	0.732
	592	5.01	2.80	0.727
	457	5.32	2.29	0.726

Note: volume fraction calculated from weights and densities.

suggested, the polymer is particulate rather than homogeneous then the first requirement is not met and the extent to which the second is satisfied is rather dubious since the swelling amounted to any about 25% rather than the 80 ~ 100% which is usually attained.

Molar refractivity of siloxane films

Molecular refractivity as defined by the Lorentz–Lorentz equation is an additive quantity which has been used in assisting to determine structures. For the usual compounds of organic chemistry the precision of the available data coupled with the high purity of the compounds involved enable agreement to within a few percent or less to be achieved between values based on

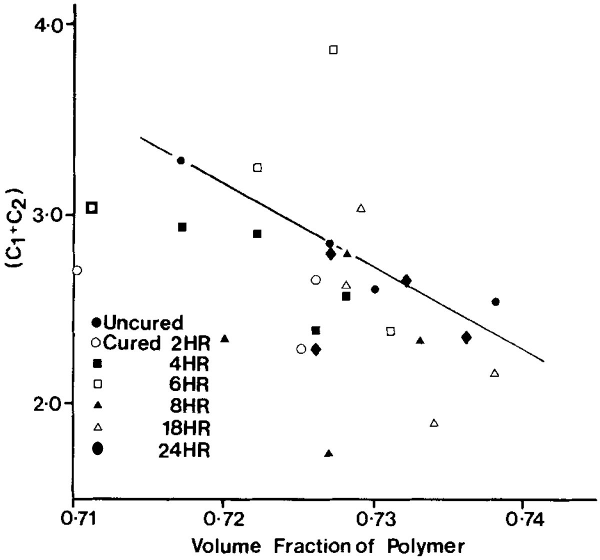


FIGURE 5 Attempted determination of $(C_1 + C_2)$.

experimental measurements of refractive index and density and those calculated from the sum of the contribution from various atoms and groups.

While this method has been used with siloxane compounds it is less satisfactory; purities are commonly lower and in any case many of the compounds are susceptible to hydrolysis, and more fundamentally because of uncertainty and disagreement upon the proper values for contributions arising from silicon-containing groups to the molecular refractivity. It is now clear[15] that the atomic refraction of silicon varies widely depending upon the compound in which it is involved. Comparatively small changes in the radicals to which the silicon is bonded may involve quite significant changes in the atomic refractivity (*e.g.* 7.12 in $(C_2H_5)_3SiR$ to 7.47 in $(CH_3)_3SiR$).

Nevertheless it was considered useful to explore the molar refractivities of the silicones of different degrees of cure. Since the molecular weight of the polymerised material is not established, nor is that of the (unknown) repeating unit in the polymer which would be the relevant value, the molecular refractivity cannot be directly calculated but only the ratio of molecular refractivity to molecular weight.

Densities of the cylindrical samples were measured in triplicate with a hydrostatic balance using water as the immersion liquid. Refractive indices were measured in duplicate by determining the real and apparent depths of the specimens with a travelling microscope. For specimens cured up to eight hours this was comparatively straightforward and the standard error of the means

TABLE VII

Effect of cure time on molar refraction of siloxane film

Cure time hour	Density at 20°C	Refractive index	$\frac{MR}{MWT} = \frac{(n^2-1)}{(n^2+2} \cdot \frac{1}{d}$
0	1.075	1.441	0.246
2	1.081	1.460	0.254
4	1.077	1.478	0.263
6	1.077	1.489	0.268
8	1.083	1.496	0.270
18	1.089	1.543	0.290
24	1.092	1.584	0.307
168	1.086	1.585	0.319

was 0.0085. Specimens cured for longer times cracked and were not uniformly transparent so the determination was more difficult and less accurate; the standard error of the means rising to 0.06.

The results of these measurements are given in Table VII. The relationship between cure time and refractive indices is extraordinarily regular and all the points lie on a straight line well within twice their standard error. The relationship between cure time and density is certainly not linear but its exact form is uncertain. The relationship between the cure time and the ratio of molecular refractivity to molecular weight is shown in Figure 6 and indicates a regular rise in molecular complexity up to 24 hours, approaching a constant value indicative of a final state of cross linking although all the experimental values for 168 hours cure are less reliable than the others.

Mechanical properties of siloxane films

For polymer materials which can be produced in a rod or bar of moderate strength, investigation via a torsional pendulum is a well-known and convenient technique for exploring the variation of shear modulus with temperature and the loss angle. For weaker materials the technique has been modified[16] so that the inertia mass is supported by a fine braid of fibres (fabric or glass) impregnated with the polymer.

This technique of torsional braid analysis was applied to two siloxane polymers, one which had only just gelled (*i.e.* uncured), and another which had been cured at 70°C for 120 hours. In each case the modulus was high at very low temperature, as expected, then fell as the glass transition temperature was passed and reached a very low value from about -60°C. The plot of tan δ enabled the T_g to be determined as about -80°C for the gelled, uncured material and -60°C for the material which after 120 hours at 70°C must be as fully cross-linked as it is likely to be.

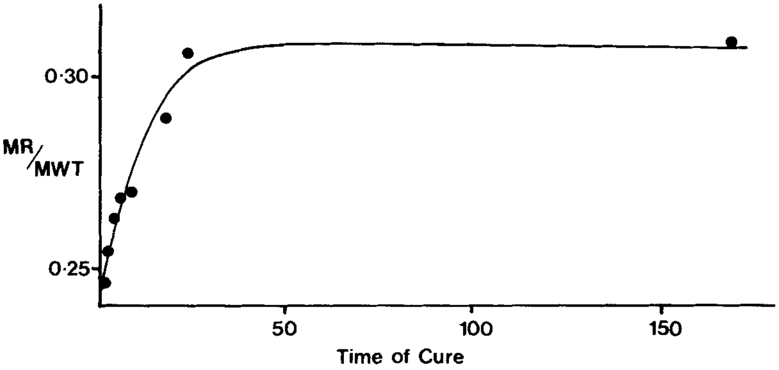


FIGURE 6 Relationship of time cure to the ratio between molecular refractivity and molecular weight.

The only other mechanical property which it proved possible to measure was the compression modulus. Load/deflection curves were plotted for samples after various periods of cure. These curves were non-linear overall but most showed an initial low modulus linearity followed by a fairly linear section of higher modulus before "barrelling" of the test piece became appreciable and added to the apparent modulus. Moduli were calculated from the slopes of both parts of these curves together with the dimensions of the samples and the results are given in Table VIII. The stage at which the initial linear part of the stress/strain curve gave way to the higher modulus section corresponded to about 27 kN • m^{-2}. This appears to represent a compacting or consolidation of the test piece after which a true compression modulus is demonstrated.

TABLE VIII

Compression moduli of polysiloxane films

Time of cure at 70°C	Compression modulus MN • m^2 Initial	Compression modulus MN • m^2 Over major part of curve
Uncured	1.72	2.60
2 hours	2.19	3.70
5	2.88	4.75
10	3.45	11.61
15	3.23	10.3
25	4.52	12.5†
50	5.06	14.0†

† Based on apparent slope of a very irregular set of data.

STRUCTURE OF FREE SILOXANE FILM

In spite of the vigorous hydrolysis conditions employed, there is evidence from the infra-red spectra that hydrolysis is not complete and that the cured film still contains some unknown quantity of methoxy groups. This quantity is unlikely to be substantial but there is no evidence that cross-linking further reduces it as the appropriate infra-red frequencies appear in the fully cured just as in the uncured material. Condensation with the elimination of methyl alcohol from methoxy and hydroxyl groups therefore does not occur during the curing. It seems fairly certain that the hydroxyl content of the condensed polymer falls during the cure, and that when fully cured, the hydroxyl content remains substantial but accessible to deuteration only on the surface. Contact angle measurements of various liquids show that the surface contains functional groups capable of forming hydrogen bonds with suitable liquids. The water absorption value of 28% found for the fully cured material would be expected for a substantially hydroxylated material but does not fit with the failure of deuteration. An explanation of this paradox is offered later.

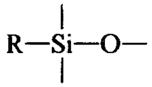
Attempts to determine the hydroxyl content in some absolute manner failed and it is only possible to speculate on the amount likely to be present. If it is assumed that the methoxy groups are few and may be ignored, and that the viscous liquid obtained by hydrolysis and removal of methanol consists of linear oligomers which cross-link only very lightly when gelling occurs (*i.e.* in the material referred to as uncured) then at that stage one hydroxyl group per silicon atom would remain, that is a third of those originally present. If so and only about 30% of these are consumed during the subsequent curing at 70°C, there is left 25% of the original fully hydrolysed hydroxyl groups in the cross-linked structure. This would not be unexpected as the reactivity of the silanol group towards condensation reactions decreases as the compound proceeds from $RSi(OH)_3$ through $RSi(OH)_2$ to RSiOH. The residual uncondensed groups are most likely to be held within fixed ring or spiral structures since they are not accessible to deuterium oxide, although the more open structure obtained when the material is first gelled can imbibe water up to 50% and the fully cured material up to 28%. The rise observed in the ratio of molecular refractivity to molecular weight as curing proceeds would be expected if ring structures were introduced, but not to the extent observed if due merely to chain extension or branching.

The behaviour of the cross-linked material in a liquid shows the gel behaviour to be that of an assembly of particles. This leads to the very weak tensile strength and the crumbling behaviour observed on compression. No fully extended network could be so weak unless very swollen by liquid, and the apparent break into two substantially linear portions of the compression stress/strain relationship suggests a packing of particles. Such a structure would also explain the failure of attempts to measure the cross-linking via the swollen modulus, and account for the erratic densities recorded in spite of the regular refractive indices.

If the surface properties of the bulk material are those of the individual particles, then it is possible to conceive that the large absorption of water is due to adsorption on the surface of the particles and hence between them. Deuteration would occur similarly but viewed by transmission spectroscopy the total surface area would not be equivalent to a sufficient concentration in depth to show against the hydroxyl concentration. A layer of water 0.5 nm thick would be equivalent to a water absorption of 28% if the particles on which it was absorbed were about 5 nm diameter. Several monolayers of water would lead to much larger particles being postulated.

The actual value of the compression modulus, increasing with increasing cure, is much lower than would be expected of a silicate-like structure. This also supports the idea that the degree of cross-linking between chains is not high but that the chains contain ring or spiral structures.

Torsional braid analysis shows the —Si—O—Si— flexible chain to be present and to remain as the cure proceeds; although the rise in T_g shows this flexibility to be hindered somewhat in the fully cured material. There is, however, no question but that rotational freedom around Si—O—Si bonds still exists, and this implies that there is a substantial proportion of



$$\mathrm{R{-}\overset{|}{\underset{|}{Si}}{-}O{-}}$$

units which are neither cross-linked nor participating in ring structures. Since these "free"

$$\mathrm{R\overset{|}{\underset{|}{Si}}O{-}}$$

groups must also contain the hydroxyl groups; it suggests that they form parts of a spiral, proceeding from one ring structure or cross-linking site to another. A spiral configuration is a reasonable assumption to preserve the inviolability of the hydroxyl by enclosing it without it actually forming part of a ring. Ring structures of either six or eight atoms, the smallest capable of formation, are only possible with the hydroxyl groups on the surface where, presumably, they would be accessible to deuterium exchange. Spiral structures with included hydroxyl groups have been suggested by J. D. Birchall, J. G. Carey and A. J. Howard[17] for silanol terminated poly-oxymethylenes, the silanol in the centre of a spiral of oxymethylenes.

If an overall average of 25% silicon atoms occurs not necessarily together but between rings and/or cross-links, leaving 75% to participate in ring structures; it can be seen that such rings must be fused if a reasonable length of —Si—O— chain is to exist to confer the flexibility indicated by the T_g of −60°C from torsional braid analysis. The picture that emerges is of mainly six-membered rings joined by short lengths of —Si—O— chains and cross-linked by fusion rings, with the free hydroxyl groups on connecting chains protected by a spiral —Si—O—Si—O structure in which adjacent hydroxyl groups probably form hydrogen bonds. An amorphous untidy structure.

CONCLUSION

It seems likely that the thick films prepared by prolonged hydrolysis, removal of solvent and curing which have been considered here are different in structure from the relatively thin films normally deposited on metals when using siloxanes as coupling agents. With the latter it seems likely that the particulate gels as they condense may extend across the whole depth of the film giving it greater strength than is apparent in the thicker, cast material. However, they must have many features in common including the residual hydroxyl groups although their importance to the performance of a joint in adverse environments is lessened by the discovery that they are not accessible to deuterium oxide and by analogy to water.

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