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The dependence of the rate of crosslinking in poly(dimethyl siloxane) on the thickness of coatings

T.R.E. Simpson[a], B. Parbhoo[b], J.L. Keddie[a,*]

[a]Department of Physics, School of Electronics and Physical Sciences, University of Surrey, Guildford, Surrey GU2 7XH, UK
[b]New Ventures R&D, Dow Corning Ltd., Cardiff Road, Barry, S. Glamorgan CF63 2YL, UK

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Abstract

We consider reasons why the crosslinking reaction rate in poly(dimethyl siloxane) (PDMS) network coatings might differ from the rate found in the bulk and specifically examine the influence of coating thickness. Infrared spectroscopic ellipsometry (IRSE) is employed as an in situ probe of the reactions between vinyl (–CH=CH$_2$) end groups on PDMS and SiH groups in a crosslinker and between unreacted SiH groups and hydroxyl/silanol groups within PDMS coatings, all on silicon substrates. Measurements of the concentrations of SiH groups (using the characteristic vibration at 2160 cm^{-1}) were obtained from coatings between 1 and 27 μm in thickness, over temperatures ranging from 25 to 120 °C. First-order kinetics are exhibited in the consumption of SiH groups. The reaction rate constant is found to decrease with increasing coating thickness. Although there is evidence that the Pt catalyst segregates to the interface with the substrate, this phenomenon does not appear to have an impact on the thickness dependence. The diffusion of water into the silicone might be the rate-limiting step in the reactions, however, and therefore lead to the observed thickness dependence of the reaction rate.

Keywords: Silicone coatings; Hydrosilylation; Infrared ellipsometry

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1. Introduction

Polysiloxanes, usually referred to as silicones, find numerous applications in the form of coatings and thin films. Common examples are silicone release liners for dispensing pressure-sensitive adhesives used in tapes and labels [1,2], oxygen-resistant coatings for spacecraft [3], and biocompatible coatings used on stents [4,5] and catheters [6]. All of these applications rely on the unique physical and chemical properties of silicones in the bulk form and at interfaces. A three-dimensional silicone network is formed by the crosslinking of linear silicone molecules, usually poly(dimethyl siloxane) (PDMS). The crosslinking rate of a silicone formulation and its extent of reaction are important factors that determine its performance in a coating. For instance, the extent of cure strongly affects the release and adhesion properties of silicone coatings. Although various methods exist to measure the reaction rates in crosslinking polymer networks, their use is mainly restricted to bulk samples or thick coatings. This present work concerns coatings formed by catalytically crosslinking vinyl-functionalised PDMS chains with hydridosilane-functionalised poly(siloxane). Infrared ellipsometry is used as an in situ monitor of the crosslinking and curing reactions in thin coatings, and the primary objective is to determine the effect of coating thickness on the reaction rates.

Crosslinking reactions in bulk silicones have been characterised via a number of well-established techniques: nuclear magnetic resonance relaxation [7], differential scanning calorimetry [8–10], rheological analysis [10], vibrating needle curemeter [11,12], and IR spectroscopy [13]. Various authors have studied the kinetics of the hydrosilylation reaction catalysed by a platinum complex [8,13]. Batch et al. [8] have developed a model for the bulk reaction between vinyl-terminated PDMS and silane crosslinkers. They used differential scanning calorimetry and determined that the reaction is first order in vinyl concentration and is limited by the consumption of vinyl

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[*] Corresponding author. Tel.: +44-1483-686803; fax: +44-1483-686781.

E-mail address: j.keddie@surrey.ac.uk (J.L. Keddie).

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groups. In coatings, the crosslinking density has been determined via gravimetric measurements of swelling [1].

When a silicone is confined to a thin film or coating, the kinetics of the crosslinking reactions might be expected to differ from the bulk behaviour. Four possible physicochemical reasons are considered below.

1. *Surface segregation*. A reactive component of the coating might segregate to the interface with either the substrate or the atmosphere, driven by thermodynamics, and thereby lower the interfacial energy [14]. There will be a depletion of the component in the bulk and an excess concentration at the interface. The segregation and consequent increased concentration of an inhibitor, catalyst or a crosslinker at an interface is likely to affect the overall observed reaction kinetics of a coating.
2. *Altered molecular mobility*. Theory developed by Semenov [15] has predicted that the viscosity and self-diffusivity of polymers confined to films differ from the bulk. There is experimental evidence that the diffusivity of polymers in the bulk differs from that in thin films [16,17]. There is also experimental evidence that the short-range mobility of polymers can be enhanced near a free surface [18], but it is likely that this effect extends to distances of only tens of nanometers. Chain confinement effects on mobility might be seen when the film thickness is of the same order of magnitude as the polymer's radius-of-gyration. None of these interfacial or confinement effects are expected to be operative in thicker coatings (>1 μm). Nevertheless, in thin films, enhanced or impeded diffusivity of reactive polymer segments would affect the rate of the crosslinking reaction.
3. *High surface area-to-volume ratio*. Because of the large surface area-to-volume ratio in films and coatings, a greater fraction of the components of the formulation is near the interface with the atmosphere. There is, therefore, a shorter average diffusion distance for oxygen and water diffusing in from the atmosphere. The catalytic role of oxygen on the hydrosilylation reaction has been recognised by Lewis [19]. In his model, molecular oxygen interacts with colloidal platinum catalyst. Radical polymerisation reactions in silicone coatings are highly susceptible to oxygen inhibition for this reason [20]. Silicone coatings are very permeable to water vapour. It is thus likely that hydrolysis will occur readily near the top surface of a coating and interfere with the crosslinking chemistry.
4. *Chemical reactions with a substrate*. The presence of an interface with a substrate opens up the possibility of additional reactions other than the polymer's crosslinking reactions. In silicones, it has been found that reactive groups such as Si–OH chain ends will bond to surface hydroxyl groups [21]. Of particular relevance to the current study, SiH groups can react with silanol or hydroxyl groups on a substrate [22].

For these various reasons, the kinetics of reactions in coatings cannot be assumed to be the same as in the bulk material. Rather surprisingly, there are very few publications in the open literature that describe the crosslinking kinetics in silicone coatings, despite their important uses. This can be partly be explained by the difficulty of monitoring a physical or chemical property of the coating while the reaction process occurs. Moreover, the fast reaction rates of such systems and the high temperature at which industrial processes are run add to the experimental difficulty.

Any study of thermally-initiated crosslinking in silicones requires a technique that can probe molecular changes within thin films and coatings over a range of temperatures. Some analytical techniques probe only the surface, but the crosslinking throughout the depth of the film is of most interest. Spectroscopic ellipsometry using visible light is sensitive to the refractive index depth profile of a material. As such, it can provide information on structure and composition. This technique has been used to obtain accurate values of the thickness of silicone coatings up to 2 μm [23]. A primary strength of ellipsometry is that it offers great flexibility to use a variety of substrates and ambient conditions. A limitation of visible-light ellipsometry is that it offers little chemical sensitivity, unless there is a large difference in refractive index between chemical compounds.

When IR radiation is used for ellipsometry, information about the nature of the chemical groups present can be obtained from the study of the characteristic absorption bands [24]. IR spectroscopic ellipsometry (IRSE) combines the chemical information provided by IR spectroscopy with the depth resolution and high sensitivity provided by ellipsometry. It is a well-established technique for semiconductor analysis but has not been heavily used in the study of polymers [25]. IRSE has previously been used to identify the chemical groups in silicones that are created during treatment in oxygen plasmas [3,26]. Although, there are a few examples of IRSE being used to characterise the surface chemistry of polymers [24,25], it has never before been used to follow polymerisation or crosslinking reactions in polymer systems.

The principles of ellipsometry have been described elsewhere [27], and the applications of ellipsometry to the study of polymer films [28] and organic interfaces [29] have been reviewed recently. The technique relies on the reflection of polarised light from an interface. A measurement determines the values of two parameters, Ψ and Δ, at a particular wavelength and angle, where Ψ is related to the change in amplitude of the light caused by the reflection, and Δ is related to the change in its phase relationship. The two ellipsometry parameters constitute a complex number, known as the ellipticity, ρ :

$$\rho = \tan \varphi e^{i\Delta}. \tag{1}$$

For a reflection from a single interface at an angle-of-incidence, ϕ_0, with respect to the normal to the sample, the complex refractive index, $\bar{n}$, can be extracted from the measured ellipticity, ρ, by the relation:

$$\bar{n} = \bar{n}_0 \tan(\phi_0) \left[1 - \frac{4\rho}{(1+\rho)^{1/2}} \sin^2(\phi_0) \right]^{1/2}, \tag{2}$$

provided that the refractive index of the ambient medium, $\bar{n}_0$, is known. In the case of air, $\bar{n}_0 = 1$. The complex refractive index consists of a real component, n, and an imaginary component, k, which is also referred to as the extinction coefficient.

One objective of this work is to demonstrate the applicability of IRSE in determining the rate of crosslinking and curing in thin silicone coatings at temperatures up to 120 °C. We then explore the effects of confinement by determining how the rate of the consumption of SiH groups depends on coating thickness. The silicone formulations are models of those used in industrial production.

2. Experimental materials and methods

2.1. Materials

The crosslinked networks were created from the reaction of vinyl-terminated PDMS (hereafter designated as SiVi) with a trimethylsilyl-terminated poly(hydrogen methyl siloxane) crosslinker in the presence of a Pt catalyst and inhibitor. The SiVi [CH_2=CH–Si(CH_3)$_2$–O–{Si(CH_3)$_2$–O}$_{150}$–Si(CH_3)$_2$–CH=CH_2] (average degree of polymerisation of 150), the crosslinker [(CH_3)$_3$Si–O–{SiH(CH_3)–O}$_{25}$–Si(CH_3)$_3$], and the Pt catalyst complex were all provided by Dow Corning Ltd. (Barry, UK). The polymer contained 0.15% of a catalysis inhibitor: 1-ethynylcyclohexanol [CH ≡ C-C(OH)-(CH_2)$_5$]. The structures of the SiVi, crosslinker and inhibitor are shown in Fig. 1.

Silicone formulations were prepared by adding the crosslinker to the SiVi, after which the mixture was shaken vigorously for 1 min to ensure thorough mixing. The catalyst was next added to the mixture and thoroughly mixed. The weight ratios of crosslinker to SiVi polymer were varied over the range from 1:0.012 to 1:0.038. These ratios give a molar ratio of SiH:–CH=CH_2 (vinyl) groups ranging from 1:1 to 3.2:1. The mass ratio of formulation to catalyst was always 1:0.024 in order to maintain the Pt metal concentration at 120 ppm (wt/wt).

2.2. Film deposition

The polymer films were deposited by spin coating fresh formulations using a photoresist spin-coater (Cammax Precima Ltd., Colchester, UK). The substrates for all experiments were IR-reflective, p-doped silicon wafers with an orientation of < 100 > and used as received. Two methods were used to vary the thickness of the spin-cast films: by dilution or by adjusting the angular velocity and spin time. The polymer mixture was diluted in analar-grade toluene to concentrations of 20, 40 or 70 vol.%. The angular velocities and spin times used were 1900 rpm for 10 s, 2000 rpm for 30 s, 3000 rpm for 60 s, or 4000 rpm for 60 s. Silicone films with a thickness range from 1.5 to 27 μm were thereby deposited.

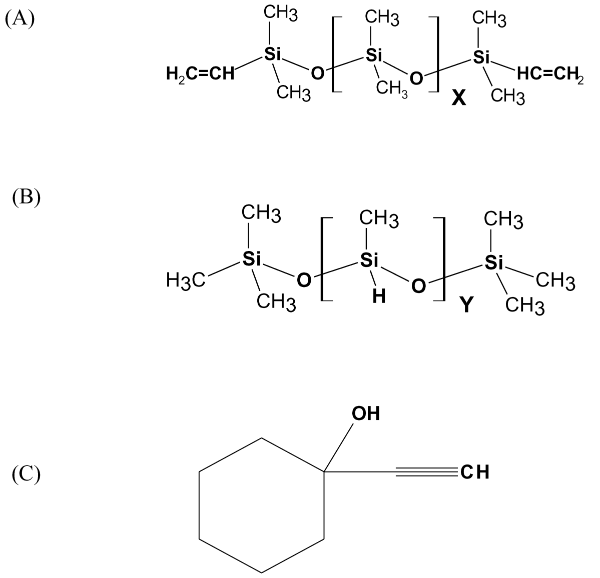


Fig. 1. Chemical structures of (A) silicone polymer, SiVi ($X = 150$), (B) crosslinker ($Y = 25$), and (C) inhibitor.

2.3. In situ ellipsometry analysis of crosslinking reactions

The silicone films and silicon substrates were analysed using an FTIR spectroscopic ellipsometer (Model GESP5-FTIR, SOPRA Sa., Bois-Colombes, France). A silicone film was spin-coated onto the Si substrate, and a series of IRSE spectra were recorded over time until no further reduction in the Si–H peak could be observed. A hot-stage (Linkam Scientific Instruments Ltd, Tadworth, Surrey, UK) was used when performing measurements above room temperature. The Si substrate was aligned on the hot-stage, and then a series of IRSE spectra were recorded. The measurement time for each IRSE spectrum was 30 s. Spectra were recorded sequentially over the first 15 min of the experiment, with an increasing time delay between subsequent spectra.

The state of either (a) the hydrosilylation reaction (when the number ratio of SiH groups to vinyl groups in the mixture was 1:1) or (b) the so-called ‘post-cure’ reaction (when the number of SiH groups per vinyl group in the mixture was greater than unity) was determined by analysing the changes in the SiH characteristic absorption

(2150 cm^{-1}) as a function of time and temperature. (Details of the relevant reactions are given in the next section.) The thickness of thinner films was determined using spectroscopic ellipsometry in the visible range (VASE, J.A. Woollam Co., Inc., Lincoln, NE, USA).

3. Results and discussion

The hydrosilylation reaction of SiVi with a hydridosilane polysiloxane crosslinker creates a three-dimensional network. This addition reaction is represented as

$$(\mathit{Crosslinker})\text{–Si–H} + \mathrm{CH_2{=}HC}\text{–Si–}(\mathit{Polymer}) \xrightarrow[\text{heat}]{\text{Pt Catalyst}} \text{–Si–}\mathrm{CH_2}\text{–}\mathrm{CH_2}\text{–Si–}(3D\,\mathit{network}) \quad (3)$$

The rate of the reaction is a complex function of the catalyst nature and concentration, of inhibitor nature and concentration, and on the concentration of vinyl and SiH groups [8,22]. At high temperature (*ca.* 150 °C) with a catalyst concentration of 120 ppm (Pt) and in thin films (*ca.* 1 μm or less) the reaction can be completed within seconds.Secondary reactions also occur [22,30], and are especially favoured with an excess of crosslinker and when in the so-called 'post-cure' stage. The first of the secondary reactions is the catalysed hydrolysis of SiH groups, as follows:

$$\sim \text{–Si–H} + \mathrm{H_2O} \xrightarrow[\text{heat}]{\text{Pt catalyst}} \sim \text{–Si–}\mathrm{OH_2} + \mathrm{H_2} \quad (4)$$

The newly-formed silanol group (SiOH) then catalytically reacts with remaining SiH groups to form a type of crosslinking via Si–O–Si bonds:

$$\sim \text{–Si–H} + \text{HO–Si} \sim \xrightarrow[\text{heat}]{\text{Pt catalyst}} \sim \text{–Si–O–Si–} \sim + \mathrm{H_2} \quad (5)$$

Another secondary reaction is the condensation of two silanol groups (formed via reaction 4).

$$\sim \text{–Si–OH} + \text{HO–Si} \sim \xrightarrow[\text{heat}]{} \sim \text{–Si–O–Si} \sim + \mathrm{H_2O} \quad (6)$$

The platinum catalysed reactions in Eqs. (4) and (5) are slower than the primary crosslinking reaction (Eq. (3)). It is expected that the silanol condensation reaction (6) is even slower than the SiH reactions (4) and (5). Reactions (4)–(6) are jointly referred to as post-cure reactions. These reactions produce crosslinks in a siloxane network when they occur between different molecules [22]. To distinguish Eq. (3), we will refer to it as a crosslinking reaction.

This work concerns crosslinking and post-cure reactions in systems and conditions similar to those in industrial manufacturing. In Section 3.1, we describe the development of IRSE to determine the extent of crosslinking and post-cure through the analysis of changes in the characteristic SiH stretching absorption of the crosslinker. In Section 3.2, we consider the kinetics of a system in which the SiH:SiVi ratio is 1:1, and in Section 3.3, we consider the case when SiVi is in excess of what is needed by stoichiometry for the reaction. Finally, in Section 3.4 we determine the effect of interfaces on the rate of crosslinking and curing by examining the thickness dependence of the reactions.

3.1. Development of in situ IRSE analysis of silicone reactions

Modelling of IR ellipsometry Ψ and Δ data requires that the optical constants (refractive index) of the film material as a function of wavelength are known. Using Eq. (2), the complex refractive index $\bar{n}$ can be determined directly from a measurement of ρ provided that the reflection occurs from a single interface, without reflections from a back surface or underlying interfaces. An IRSE scan was performed on a 2 mm thick fully-cured silicone layer (SiH:SiVi ratio of 3.2:1) to obtain ρ as a function of wavenumber (cm^{-1}). This spectrum was inverted to yield the optical constants (n and k) as a function of wavelength λ (in μm) and wavenumber (cm^{-1}), as shown in Fig. 2. The extinction coefficient k is indicative of the IR radiation absorption, as it is related to the absorption coefficient, $\mu = 2\pi \boldsymbol{k}/\lambda$. The inset figure clearly shows absorption bands at the expected characteristic frequencies for silicones [31]: $\mathrm{CH_3}$ (1250 cm^{-1}); SiOSi (1000–1100 cm^{-1}); and $\mathrm{CH_3}$/SiC (749 cm^{-1}). These optical constants are used subsequently in data modelling to determine the thickness of silicone films. (As an aid to other researchers, tabulated values of the optical constants of the silicone will be provided on request.) It is seen that the silicone is essentially transparent to IR radiation ($k \approx 0$) for $\lambda < 7.8$ μm.

Typical Ψ and Δ ellipsometry spectra of a silicone film on a Si substrate are shown in Fig. 3. The spectra from the bare substrate are shown for comparison. For both Ψ and Δ, the spectrum for the silicone film is quite distinct from that of the bare substrate. In the spectral regions, where the silicone film is transparent (>1500 cm^{-1}), oscillations in the spectra (also referred to as fringes) are observed. These are caused by interference between reflections from the air/film interface and from the film/substrate interface. The spacing of the fringes is highly sensitive to film thickness. Note that in spectral regions where $k > 0$, features in the spectra are the result of IR absorption. The model that fits best to the experimental data (using the optical constants shown in Fig. 2) indicates that the film thickness is 7.1 μm. The initial thickness of all films studied was determined in a similar way. The thickness of thinner films (below 2 μm) was determined by visible ellipsometry.

IRSE was used to monitor the film thickness during the silicone curing process. Fig. 4 shows the Ψ and Δ spectra (in the transparent region of silicone) obtained from a silicone film before and after crosslinking at 120 °C. Fitting the data to the model determined that the film was initially 27.24 μm thick. This thickness decreased by approximately 130 nm

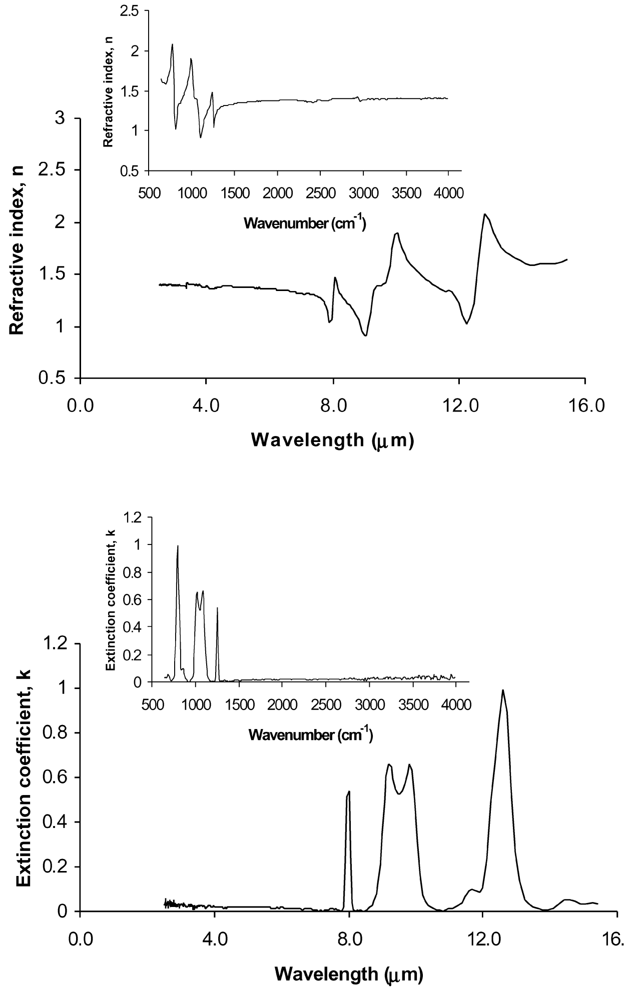


Fig. 2. Refractive index, *n*, and extinction coefficient, *k*, as a function of wavelength (nm) and (inset) wavenumber (cm^{-1}) for a silicone network, as determined from IR ellipsometry.

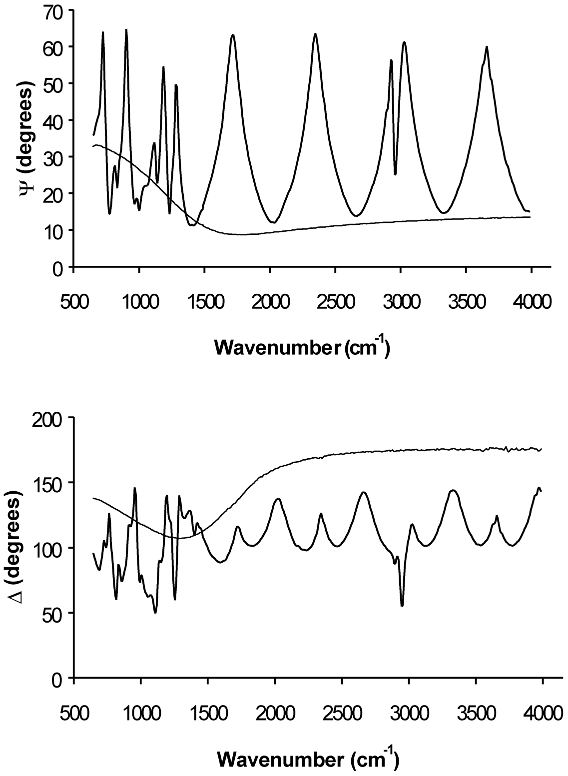


Fig. 3. Ellipsometry spectra (Ψ and Δ) for a silicone coating cast on a doped-Si substrate. The heavy line represents the raw data. The light line shows the spectra obtained from a clean substrate, for comparison.

during a curing time of 78 min. This amount of shrinkage of 0.5 % was typical of all films studied.

Fig. 5 shows the ellipsometry spectra obtained from a thick silicone film at 80 °C immediately after film deposition. The relatively short spacing of fringes in the data is the result of the relatively large film thickness (14.6 μm). Examination of the data (Δ in particular) throughout the subsequent crosslinking reaction revealed no significant change in the spectra over time with the exception of the absorption band centred around 2150 cm^{-1}. This frequency is characteristic of the SiH stretching mode [31]. During the curing process, the SiH groups react and the degree of absorption at this frequency decreases. The change in the optical constants of the silicone is apparent in the ellipsometry spectra.

Fig. 6 shows a series of spectra obtained over time in the SiH spectral range (2100–2200 cm^{-1}) for the same coating analysed in Fig. 5. At times longer than 182 min after the start of crosslinking, there were no changes observed in the spectra. After this time, no further reactions involving the SiH group took place. The first data set represents the unreacted state; its reaction was defined as being ‘0% complete’. A reaction was deemed to be ‘100% complete’ at the point when the spectra did not change within the uncertainty of the measurement and the SiH was fully consumed. Optical constants were obtained from the (Ψ, Δ) pairs at each wavelength for the 0 and 100% complete data. A Bruggeman effective medium approximate (EMA) [32] was then applied to relate the optical constants at intermediate times to the extent of SiH consumption. An EMA model predicts the optical constants for a blend (or composite) of two or more substances by considering the optical constants of each of the constituent substances. In this case, the silicone is considered to be a blend of unreacted silicone (containing SiH) and fully-cured silicone (without any SiH). Note that the optical constants of a composite are not merely a numerical average of the constituents, but they must be calculated via an EMA model.

Note that IR ellipsometry spectra are not the same as IR transmission spectra. There is no flat baseline in ellipsometry spectra, because the spectra do not represent reflectivity or transmission. Instead, Ψ and Δ are a function of film thickness as well as concentration of absorbing group. Fig. 6 shows the curves of best fit obtained using an EMA model to describe the spectra that are intermediate between 0 and 100% complete. Note that the ‘V-shape’ of the final spectrum is attributed to an underlying thickness

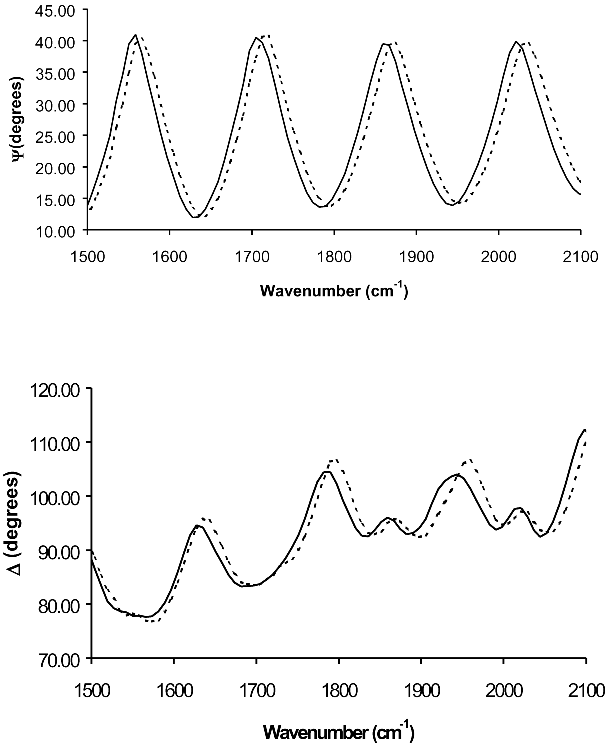


Fig. 4. Ellipsometry spectra (*Ψ* and *Δ*) obtained from a silicone coating at the start of crosslinking at 120 °C (solid line) and after reacting for 78 min (dashed line). The best fits to the data correspond to an initial thickness of 27.24 μm and a final thickness of 27.11 μm. The coating shrinks by about 0.5% during the crosslinking reaction.

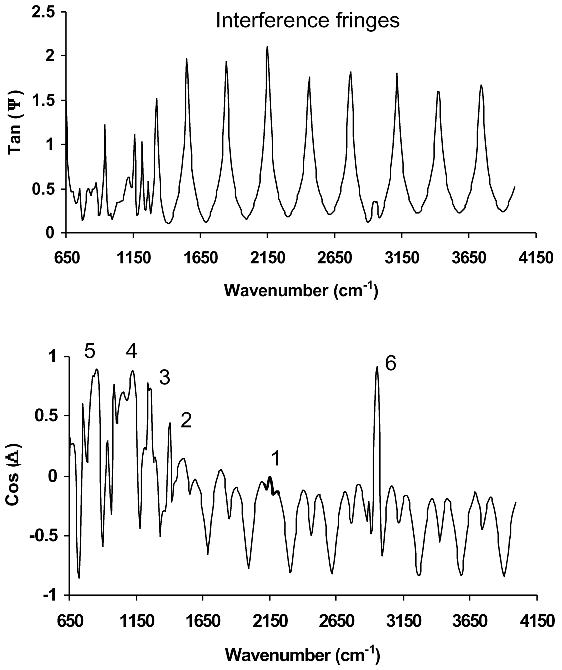


Fig. 5. Ellipsometry spectra (tan *Ψ* and cos *Δ*) obtained from a 14.6 μm silicone coating at the start of crosslinking at 80 °C. Interference fringes are clearly seen in the tan *Ψ* spectrum. The SiH stretching mode (1) is apparent in the spectrum at about 2150 cm^{-1} as indicated with the heavy line. The other bands in the spectrum are the asymmetric (2: 1400 cm^{-1}) and symmetric (3: 1250 cm^{-1}) CH_3 deformations, Si–O–Si stretch (4: 1000–1100 cm^{-1}), CH_3 rock/Si–C stretch (5: 750–870 cm^{-1}) and asymmetric CH_3 stretch (6: 2954 cm^{-1}).

fringe that is expected for a transparent film. In the initial film, the *Δ* value is higher in the same region because of the SiH absorption band. From the fitted values of the fraction of 100% reacted silicone, a value for the extent of SiH consumption (i.e. cure) was obtained as a function of time. A measurement of the cure completion time can be found, with an uncertainty that is set by the time interval between measurements. This same method of data analysis was applied to coatings of various thicknesses and over a range of crosslinking temperatures.

3.2. *Crosslinking when SiH and SiVi are stoichiometric (1:1 ratio)*

For a silicone formulation in which the molar ratio SiH:SiVi is 1:1 and the thickness is 14.6 μm, it was found that the cure rate is fast and the consumption of SiH groups takes *ca.* 4 min at a temperature of 80 °C. At this temperature, the reaction conversion rate was such that the IRSE data sampling time (30 s per spectrum) made a detailed kinetic study impossible to perform. Instead, experiments on a series of coatings were performed at room temperature where the reaction rate is slower. The time to complete the cure at room temperature, as evidenced by the disappearance of the SiH absorption bands, was found to be linearly and strongly dependent on the film thickness, as shown in Fig. 7. In bulk silicones, the crosslinking reaction is known to be exceedingly slow at room temperature. Measurements were not performed on films greater than 25 μm thick, and so it is not known when the bulk behaviour is approached. Reasons for the observed thickness dependence of the reaction will be considered in Section 3.4.

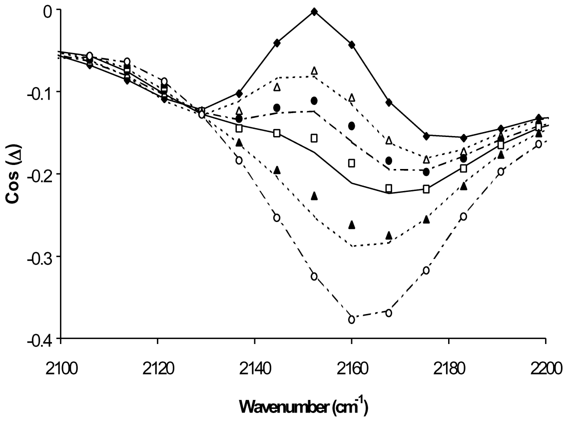


Fig. 6. A series of *Δ* spectra obtained after various times of crosslinking of a 14.6 μm coating at 80 °C. The times shown are 0 (◆), 1.2 (△), 3.7 (●), 4.9 (□), 13.7 (▲), and 182 min. (○). The lines show the best fit to the data using an EMA model, corresponding to 0, 19, 29, 42, 64 and 100% completion (in chronological order).

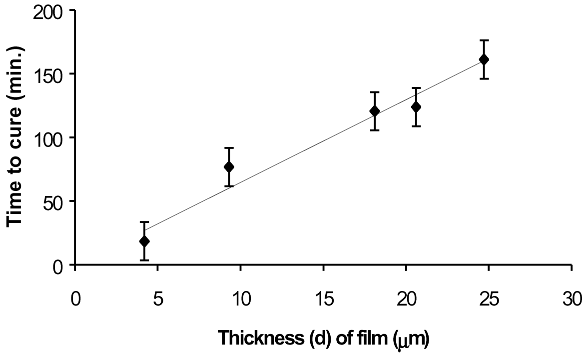


Fig. 7. The dependence of the time for the complete reaction of SiH as a function of coating thickness when the SiH:SiVi ratio is 1:1. Measurements were made at 25 °C.

3.3. Reaction kinetics when SiH is in excess relative to SiVi

From a practical standpoint, silicone formulations with excess SiH can be used in industrial applications to improve performance properties such as adhesion. The data in Fig. 8 show the effect of increasing the SiH concentration when curing silicone coatings at 80 °C (with a fixed coating thickness). The SiH:SiVi ratio was systematically varied over these ratios: 1:1, 1.5:1, 2:1, 2.5:1 and 3.2:1. On increasing the concentration of crosslinker's SiH reactive group relative to the reactive vinyl end group, the overall cure time was seen to increase significantly. It is clear from Section 3.2 that the reactions are completed very rapidly at 80 °C when SiH is not in excess, and it is assumed that the SiH groups are mainly consumed in the primary crosslinking reaction (i.e. hydrosilylation as in Eq. (3)). The consumption of the excess SiH with high SiH:SiVi ratios must rely on the slower post-cure reactions (Eqs. (4)–(6)), and hence the reaction times increase as shown in Fig. 8.

This slowing down in the cure rate with excess SiH allowed us to monitor the reactions at higher temperatures with IRSE. The extent of conversion of SiH groups was determined as a function of time under a variety of conditions. The data corresponding to the post-cure reactions were corrected to take into account the initial time elapsed during which the hydrosilylation reaction primarily occurred. From measurements on films in which the SiH:SiVi ratio was 1:1 (Section 3.2), an approximate completion time for the crosslinking reaction was obtained for a given temperature and film thickness. This crosslinking-completion time was then subtracted from the data for films where the SiH was in excess in order to obtain a reaction zero point for the post-cure reactions. As an example, our data show that for a 14.6 μm film, the crosslinking reaction is complete after about 4 min, whereas the curing reaction takes over 100 min. This difference in rate enables us to effectively separate the processes in time and independently study the cure kinetics.

As representative data, Fig. 9(A) shows the extent of cure conversion obtained at 80 °C as a function of time for three coatings of different thickness. Fig. 9(B) shows similar data obtained at two temperatures (25 and 80 °C) for 4 μm thick coatings. Several trends are observed which apply to all of the experiments performed. The overall cure rate at 80 °C is faster in thinner coatings, as seen when comparing the data for 1.5, 7.1 and 14.6 μm thick coatings. The overall rate of the reactions is also significantly faster at higher temperatures, as expected for a thermally-activated process.

In order to understand the reaction kinetics better, we

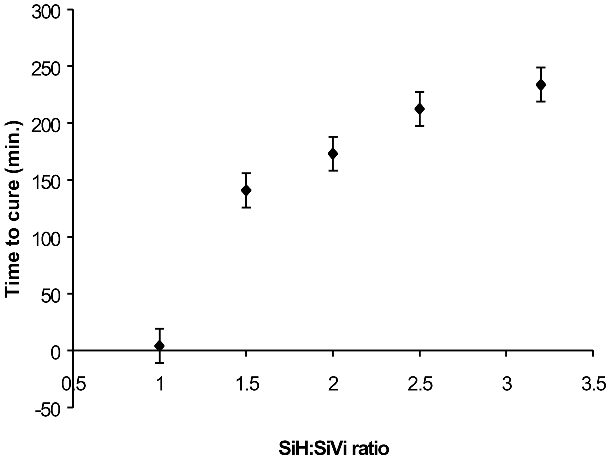


Fig. 8. The time for the complete reaction of SiH at 80 °C as a function of the ratio of SiH groups to vinyl groups in the formulation for 14.6 μm coatings.

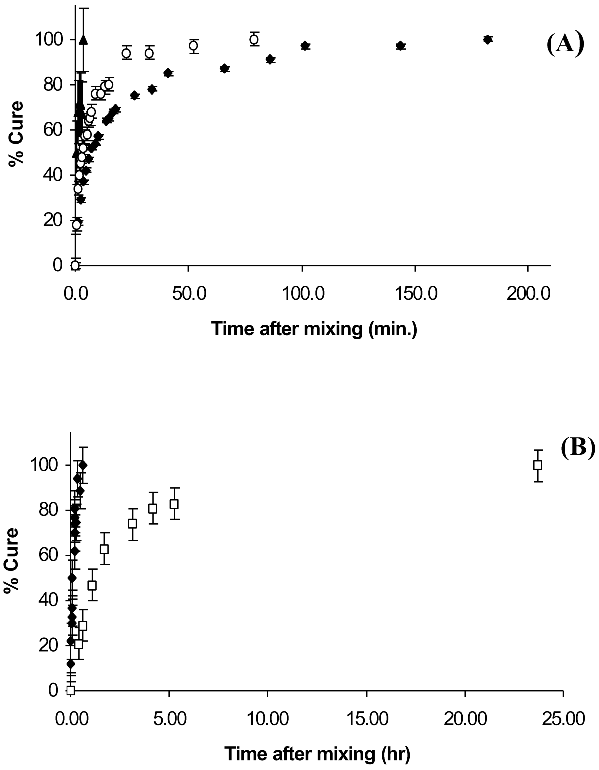


Fig. 9. The extent of SiH reaction as a function of time (A) at a temperature of 80 °C for coatings with thicknesses of 1.5 (▲), 7.1 (○) and 14.6 μm (◆) and (B) for coatings with a thickness of 4 μm at temperatures of 25 °C (□) and 80 °C (◆). In all cases, the SiH:Vi ratio is 3.2:1.

examined the order of the reaction in consuming SiH. If the reaction follows first-order kinetics of the form:

$$\frac{\mathrm{d[SiH]}}{\mathrm{d}t} = -k_1[\mathrm{SiH}], \tag{7}$$

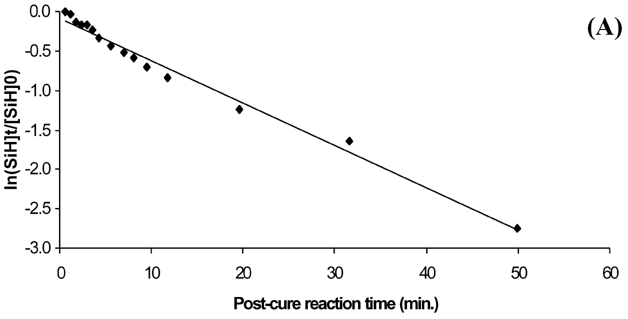
where [SiH] represents the concentration of SiH groups and k_1 is a reaction coefficient, then a plot of $\ln[\mathrm{SiH}]_t/[\mathrm{SiH}]_0$ (where the subscripts indicate time) as a function of post-cure time t will be linear. On the other hand, if the reactions follows second-order kinetics of the form:

$$\frac{\mathrm{d[SiH]}}{\mathrm{d}t} = -k_2[\mathrm{SiH}]^2 \tag{8}$$

with k_2 being a second-order reaction coefficient, then a plot of $[\mathrm{SiH}]_t^{-1}$ as a function of t will be linear. Typical results are shown in Fig. 10(A) and (B) for a 14.6 μm thick coating that was crosslinked at 80 °C. These data, as well as the data from experiments on coatings of various thicknesses and crosslinked at other temperatures, are more consistent with first-order reaction kinetics for the consumption of SiH. In a study of the reaction rate of water with SiH in siloxane, it was likewise found that the consumption of SiH followed first-order reaction kinetics [30].The first-order reaction coefficients k_1 obtained for silicone films of varying thickness and at different temperatures are listed in Table 1. Note that the first-order reaction coefficient k_1 at 120 °C is about two orders of magnitude greater than at a temperature of 25 °C. Assuming that k_1 follows an Arrhenius behaviour, then its temperature dependence will be given by

$$k_1 = A\exp\left(\frac{-E_a}{RT}\right), \tag{9}$$

where E_a is an activation energy, R is the gas constant, and A is an Arrhenius coefficient. The data in Table 1 are consistent with Eq. (9) having $E_a = 22.2\ \mathrm{kJ\ mol^{-1}}$ and $A = 1.004\ \mathrm{s^{-1}}$. (As the thicknesses are within 2 μm of each other, any effect of the coating thickness is neglected in this analysis.) This value for E_a is of the same order of magnitude as a value for E_a obtained previously for the secondary reactions (Eqs. (4)–(6)) in bulk material [30].



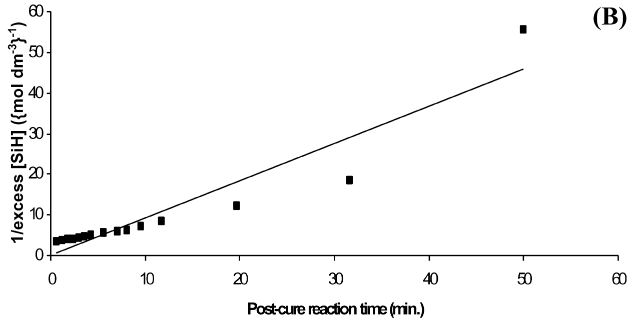


Fig. 10. The time dependence of the SiH concentration plotted to test (A) first-order kinetics and (B) second-order kinetics for a 9.1 μm thick coating at 80 °C. The correlation coefficient R^2 for the linear fit is 0.986 for (A) and is 0.887 for (B).

Table 1
First-order reaction coefficients (k_1) for the loss of SiH in silicone coatings at different temperatures

Temperature (°C)	Thickness, d (μm)	k_1 ($\times 10^{-5}\ \mathrm{s^{-1}}$)
25	13.5	1.8
65	14.8	23.2
80	14.6	37.2
120	15.7	174.2

3.4. Thickness dependence of crosslinking and curing rates

The most intriguing aspect of our results is that k_1 was found to vary inversely with coating thickness. For instance, at a temperature of 80 °C, k_1 is more than four times greater in a thin film (4.1 μm) than in a thick film (25.7 μm). Although workers in the field expect such an effect, there has been hitherto no published data to support its existence. As a summary of the kinetics results, the first-order reaction coefficient for the consumption of SiH (k_1) is plotted as a function of coating thickness for three different temperatures (65, 80 and 120 °C) in Fig. 11. At all three temperatures, k_1 decreases linearly with increasing thickness of these coatings having an excess of SiH compared to SiVi (SiH:SiVi of 3.2:1). Regardless of temperature, k_1 approaches a constant value in coatings greater than about 15 μm in thickness.

Several possible physicochemical reasons were proposed in the Section 1 for why the reaction kinetics in films might differ from the bulk. One explanation for the dependence of k_1 on thickness could be the segregation of Pt to the interface with the substrate, thus depleting the amount of Pt remaining to catalyse the SiH reactions in the bulk of the film. Preliminary experiments using Rutherford backscattering spectrometry (RBS) to determine the depth profile of Pt in the silicone coatings have confirmed that there is indeed a build-up of Pt at the interface with the silicon substrate. The interfacial concentrations are significantly higher than the concentrations in the bulk of the coatings. From this Pt segregation, however, one might predict that the reaction rates would be faster in thicker films in which depletion of Pt would be proportionally less. As an example, if a monolayer of Pt was segregated at the interface of a

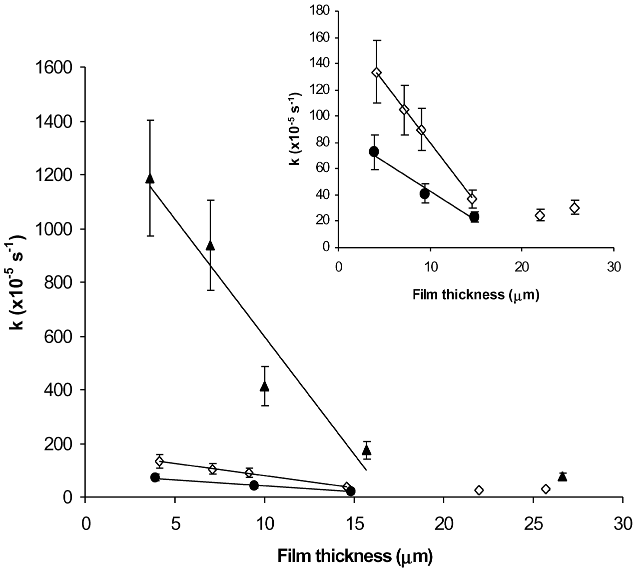


Fig. 11. The thickness dependence of the first-order reaction coefficient for the consumption of SiH in silicone coatings. The SiH:SiVi molar ratio is 3.2:1. Data were obtained at three different temperatures: 65 °C (●); 80 °C (◇); and 120 °C (▲). The lines are guides to the eye.

2.5 μm film, 37% of the Pt is estimated to remain in the bulk. In contrast, in a thicker 20 μm film, about 92% of the Pt would remain in the bulk. The curing would then be expected to be slowed down more in a thinner film, because the Pt depletion would be greater. Thus, we conclude that the Pt segregation does not explain the observed thickness dependence of reaction rates.

Pt segregation to the interface could, however, explain why the substrate (or more specifically, the surface energy of the substrate) plays a role in influencing the kinetics of the SiH reactions. Other work in our laboratory has found that the composition of a silicone coating's substrate has a strong influence on the SiH reaction rates. Experiments have found that the SiH reaction rate in silicone films on poly(ethylene terephthalate) and poly(styrene) substrates is faster than on silicon substrates, possibly because there is less Pt segregation to the interface with a polymer substrate. Regardless of the substrate, however, there is a thickness dependence in the SiH reaction rate, which suggests that another factor is relevant.

Such a factor could be that the silicone coatings have high surface area-to-volume ratios leading to short diffusion distances. As the majority of the SiH groups (when in excess) are consumed via secondary reactions with water, it might be expected that the diffusion of water vapour into the film would be the controlling factor on the kinetics of the reaction. In a thicker film, the diffusion distances are greater, and so the time for diffusion of water throughout the film is greater.

If the time for completion of the curing is taken as a characteristic diffusion time, an order-of-magnitude estimate of the diffusion coefficient of water D_w in the curing silicone can be obtained from data such as presented in Fig. 9. Our results lead to an estimate for D_w of 10^{-14} m^2 s^{-1} at a temperature of 80 °C. (This estimate uses the simplification that D_w is independent of concentration.) This value is three orders of magnitude slower than values estimated elsewhere for D_w in cured silicone films at room temperature [33]. In our experimental set-up, however, the silicone temperature is higher than that of the ambient atmosphere. The resulting gradient in temperature will alter the chemical potential gradient that drives diffusion of water into the film and might, therefore, lead to a decreased diffusion rate. This effect is deserving of further study. A further complication is that water is being consumed (via Eq. 4) as it diffuses into the coating. This reaction would thereby decrease the inward flux of water.

Incidentally, we had some concern that in order to prepare coatings of various thicknesses, we were adjusting the conditions of film deposition. There was the possibility that the observed thickness-dependence of the reaction coefficient was in fact the result of either the dilution of the starting formulation in solvent or the variation of the speed and time of spin deposition. To explore whether the method of film deposition was influencing the times for complete consumption of SiH, we compared the results when films were prepared with and without dilution in toluene. It was found that the SiH reaction times follow an identical dependence on coating thickness, regardless of the method of film deposition.

4. Conclusions

We have used infrared ellipsometry as an in situ probe of crosslinking and post-cure reactions in coatings of PDMS. Experiments were performed at temperatures ranging from 25 to 120 °C in coatings between 1 and 27 μm thick. With an excess of SiH (SiH:SiVi ratio of 3.2:1), as well as when there is a 1:1 ratio of SiH:SiVi, the total time for the reactions increases linearly with film thickness. The post-cure reaction follows first-order reaction kinetics in the consumption of SiH. The first-order reaction coefficient decreases linearly with increasing coating thickness up to a value of about 15 μm, where a constant value is approached. Although there is evidence from RBS analysis for the segregation of the Pt catalyst at the coating/substrate interface, the depletion of Pt in the bulk of the film would not be expected to cause slower reactions in thinner films. Another possibility is that the diffusion of water into silicone might be the rate-limiting step in the curing reaction.

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