Oxidizable coupling agents: Introduction of surface functionality

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OXIDIZABLE COUPLING AGENTS: INTRODUCTION OF SURFACE FUNCTIONALITY

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*The synthesis and grafting to glass or quartz of alkylalkoxysilane coupling agents (RSi(OR′)$_3$) that are susceptible/responsive to oxidation is described. Hydrosilylation of the inexpensive polyolefin squalene occurred efficiently once or twice with the silane HMe$_2$SiOSiMe$_2$(CH$_2$)$_2$Si(OEt)$_3$ to give a silane coupling agent **3** that possesses several alkene groups. Once grafted to a silica surface **Q-Sq** using traditional means, the coupling agent was oxidized and further processed in several different ways. First, epoxidation using soluble peracids led to polyepoxides that could be further hydrolyzed to give polyalcohol surfaces **Q-Sq-PAA-H$_2$O**. Alternatively, ozonolysis with gaseous O$_3$ led to the ozonides **Q-Sq-O$_3$**, which could be decomposed to give either aldehyde/ketone **Q-Sq-O$_3$-redu**, or ketone/carboxylic acid groups **Q-Sq-O$_3$-H$_2$O$_2$**, respectively, bound to the surface. The aldehyde/ketone groups were characterized by condensation with dinitrophenylhydrazine to give the highly colored hydrazones **Q-Sq-O$_3$-redu-DNPH**. These studies demonstrate the ready portability of organic chemistry to silica (or related) surfaces using judiciously chosen silane coupling agents and the possibility of controlling surface functionalization by postgrafting oxidation.*

INTRODUCTION

Silane coupling agents are widely used to change surface properties and promote the adhesion of substances to modified surfaces. For example, one of the major uses of silane coupling agents is the surface modification of glass fibers for use in composites. Glassfiber-resin composites are very strong, but the loss in laminate strength following prolonged exposure to moisture is problematic [1] unless the glass is first sized with silane coupling agents. Such changes lead to a reduction in moisture sensitivity and an enhanced adhesion of the resin to the glass fibers.

Improved adhesion can result even when the surface is modified with agents that have no residual organofunctional groups. However, the best silane coupling agents in composites are generally those where an organofunctional group on silicon can efficiently react with thermosetting resins during curing [2]. In such systems, the coupling agent acts as a bidirectional "glue" between the surface and the matrix.

Coupling agents that are responsive to specific stimuli are rare. The advantages that such compounds would give are related to the ability to change, on demand, the surface energy of the surface and thus the effective adhesion of materials to the modified surface. Simultaneously, the modification of the surface would provide new functional groups and thus new opportunities to surface graft compounds *only after* the surface modification.

Our attention was drawn to the work of Puskas, in which the efficiency of epoxidized squalene as a highly functional crosslinker was demonstrated (Scheme 1A) [3]. It is apparent that the hydrophobicity of the epoxy compound is very different from that of the starting squalene. Furthermore, squalene can be oxidized using ozone (Scheme 1B) [4] to give either aldehydes/ketones or ketones/carboxylic acids. If it were possible to bind such an alkene-rich molecule to the surface, we reasoned, it would be possible to surface modify the compound to produce these new groups on demand using traditional chemistry.

In this work, we describe the preparation of a coupling agent, derived from squalene, that can be bound to quartz. The subsequent behavior of the surface to oxidizing conditions, both with respect to surface energy and chemical reactivity, will be described.

EXPERIMENTAL

Materials

We used quartz slides (PSI® Supplies) of at least 85% UV transmittance at 254 nm. Also, vinyltriethoxysilane (Gelest), 1,1,3,3,-tetramethyldisiloxane (Gelest), hydrogen-terminated polydimethylsiloxane
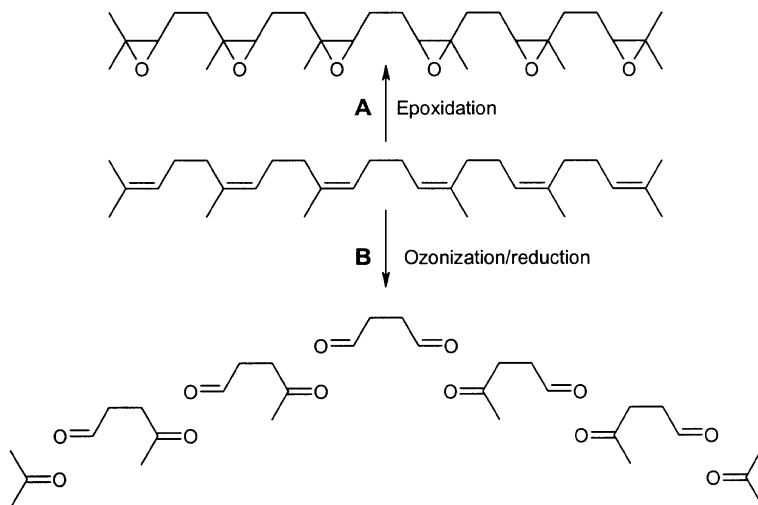
SCHEME 1

$(HSiMe_2(OSiMe_2)_nSiMe_2H$, $n \approx 230$ [500 cSt.], Gelest), platinum divinyltetramethyldisiloxane complex (Karstedt's catalyst, Gelest), squalene (Aldrich), boron trifluoride diethyl etherate (Aldrich), anhydrous magnesium sulphate (BDH), potassium permanganate crystals (BDH), anhydrous calcium chloride (BDH), 30% hydrogen peroxide solution in water (BDH), peracetic acid (32 wt% solution in diluted acetic acid, Aldrich), dinitrophenylhydrazine (Eastern), metal zinc (Fisher), hydrochloric acid (BDH), glacial acetic acid (BDH), cyclohexane (Caledon), pentane (Caledon), acetonitrile (Caledon), and acetone (Caledon) were used as received.

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC-200 and AV-200 Fourier transform spectrometers, respectively (at 200 MHz for proton and 50.3 MHz for carbon, respectively). ^{29}Si NMR spectra were recorded on a Bruker AV-300 spectrometer (at 59.6 MHz for silicon). Chemical shifts were recorded with respect to $CDCl_3$ as an internal standard and set at 7.24 ppm and 77 ppm for ^{1}H NMR and ^{13}C NMR, respectively. Coupling constants (for ^{1}H NMR) were recorded in ppm. The abbreviations—s = single, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, st = septet, m = multiplet—are used to report the spectra.

Electron impact (EI) and chemical ionization (CI, NH$_3$) mass spectra were recorded at 70 eV with a source temperature of ca. 200°C on a Finnigan 4500 Mass Spectrometer. Electrospray ionization mass spectroscopy was performed using a Micromass Quattro LC. LC-MS was performed using Waters 2690 equipped with YMC-Pack C-8 column (100 × 4.6 mm i.d.) and the Micromass Quattro LC.

Infrared spectra were recorded using a BIO RAD FTS-40 Fourier spectrometer, and UV transmittance was measured using Varian Cary-300 and Cary-50 spectrophotometers, respectively.

Gas Chromatographic-Mass Spectral (GC-MS) analysis was carried out using a Hewlett-Packard model 5890 series II gas chromatograph equipped with DB-17 capillary column (30 m × 0.25 mm i.d. × 0.15 μm film, J&W Scientific). The detection system was a Hewlett-Packard model 5971A mass selective detector operated in full scan mode. The temperature gradient was from 50°C to 200°C at rates of 5°C/min and an injector temperature of 200°C.

Ozone gas was generated through electric discharge using a Welsbach ozonizer (Welsbach Corporation) adjusted to 80 volt and 6895 mmHg pressure with output flow rate adjusted to ≈ 5 l/min.

An argon plasma glow discharge system from Picotron™ (Park Dental Research Corp.) was used to clean the glass and quartz slides. Measurements of the contact angle were carried out using a contact angle goniometer (model 100-00, Ramé Hart Inc.) using deionized distilled water (milliQ water), and the samples were placed in a special chamber (provided by the manufacturer) to provide a humid environment during the measuring process.

Preparation of Coupling Agents

Synthesis of 1,1,3,3-Tetramethyl-1((2-triethoxysilyl)ethyl) disiloxane:1,1,3,3-Tetramethyl-1((2-triethoxysilyl)ethyl) disiloxane:1/2

1,1,3,3-Tetramethyldisiloxane (10.72 g, 0.08 mol) was dissolved in dried pentane (30 mL dried over anhydrous magnesium sulfate). After cooling to 0°C, Karstedt's catalyst (≈ 2 drops) was added to the solution and then vinyltriethoxysilane (3.8 g, 0.02 mol) was added dropwise over 30 min under a nitrogen atmosphere. After 30 min, the reaction was allowed to warm to room temperature and left overnight. The solvents and excess reagents were removed from the crude mixture by rotary evaporation, and the product was collected by vacuum distillation at 75−76°C/1 mm Hg (yield: 5.28 g, 81.5%).

GC-analysis indicated that the product was actually a mixture of two compounds (25% R$_t$ = 16.8 min and 75% R$_t$ = 17.5 min). GC-MS

indicated that the two compounds are isomers. From ^{1}H NMR analysis, the two products were identified as the regioisomers **1** (75%) and **2** (25%, Scheme 2). The distilled mixture was used directly in the subsequent reactions.

1: HSiMe$_2$OSiMe$_2$CH$_2$CH$_2$Si(OEt)$_3$
^{1}H NMR (CDCl$_3$): $\delta = 0.02$ (s, 6H, Si(CH_3)$_2$CH$_2$CH$_2$Si(OEt)$_3$); 0.13 (d, 6H, $J = 2.8$ Hz, H(CH_3)$_2$SiOSi; 0.53 (s, 4H, Si(CH$_3$)$_2$CH_2CH_2-Si(OEt)$_3$); 1.202 (t, 9H, $J = 7.0$ Hz, O(CH$_3$)$_2$SiCH$_2$CH$_2$Si(OCH$_2$CH_3)$_3$); 3.79 (q, 6H, $J = 7.0$ Hz, SiCH2CH2Si (OCH2CH3); 4.65 (st, 1H, $J = 2.7$ Hz, H-Si). ^{13}C NMR (CDCl$_3$): $\delta = -0.7$ (HSi(CH_3)$_2$OSi); 0.8 Si(CH3)2CH2CH2Si(OEt)$_3$); 5.9 Si(CH$_3$)$_2$CH_2CH$_2$Si(OEt)$_3$); 9.0 Si(CH3)2CH2CH2Si(OEt)$_3$); 18.3 (CH_3CH$_2$O); 58.4 (CH$_3$CH_2O); ^{29}Si NMR: $\delta = -45.4$ (SiCH$_2$CH$_2$Si(OEt)$_3$); -7.1 (HSi(CH$_3$)$_2$OSi); 10.1 Si(CH$_3$)$_2$CH$_2$CH$_2$Si(OEt)$_3$).

2: H(CH$_3$)$_2$SiOSi(CH$_3$)$_2$CH(CH$_3$)Si(OEt)$_3$
^{1}H NMR (CDCl$_3$): $\delta = 0.10$ (d, 6H, $J = 1.9$ Hz, H(CH_3)$_2$SiOSi(CH$_3$)$_2$CH (CH$_3$)Si(OEt)$_3$); 0.15 (s, 6H, OSi(CH_3)$_2$CH(CH$_3$)Si(OEt)$_3$); 0.01–0.15 (m, 1H, OSi (CH$_3$)$_2$CH(CH$_3$)Si(OEt)$_3$); 1.05 (d, 3H, $J = 7.5$ Hz OSi (CH$_3$)$_2$CH(CH_3)Si(OEt)$_3$); 1.18 (t, 9H, $J = 7.0$ Hz, SiCH(CH$_3$)Si (OCH$_2$CH_3)$_3$); 3.79 (q, 6H, $J = 7.0$ Hz, SiCH(CH$_3$)Si(OCH_2CH$_3$)$_3$). ^{13}C NMR (CDCl$_3$): $\delta = -0.7$ (HSi(CH_3)$_2$Si); -0.2 (SiCH(CH$_3$)Si); 1.7 (OSi (CH$_3$)$_2$CH(CH$_3$)Si; 7.6 (SiCH(CH_3)Si); 18.3 (CH_3CH$_2$O); 58.4 (CH$_3$CH_2O). ^{29}Si NMR: $\delta = -46.4$ (SiCH$_2$CH$_2$Si(OEt)$_3$); -7.9 (HSi(CH$_3$)$_2$OSi); 9.7 (OSi(CH$_3$)$_2$CH(CH$_3$)Si(OEt)$_3$).

1 + 2: IR: v (cm^{-1}) 2975, 2927, 2888, 2121, 1408, 1390, 1255, 1167, 1144, 1106, 1082, 958, 912, 840, 813, 785; MS (EI): m/z = 323 (M$^-$ $-$ 1, 10); 309 (M$^+$-CH$_3$, 38); 279 (M$^+$-OCH$_2$CH$_3$, 100); 249 (M$^+$- H(CH3)2 SiO, 48).

Hydrosilylation of Squalene: 3

To a 5 ml round-bottomed flask was added squalene (2.05 g 5.0 mmol) and **1/2** (75/25 mixture, 1.62 g, 5.0 mmol). Karstedt's
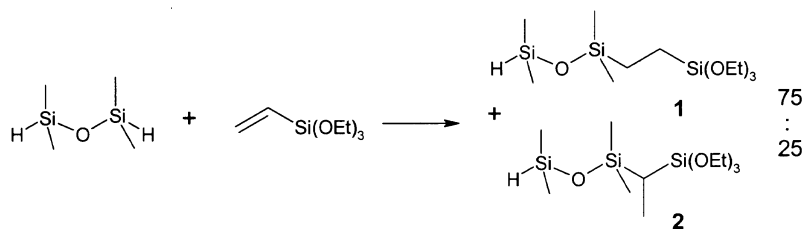
SCHEME 2

catalyst (one drop) was added and the oil bath temperature was set to 85°C. The reaction mixture was stirred with heating under nitrogen for 4 h, after which ^{1}H NMR indicated a complete consumption of Si-H and the appearance of a new CH_2 peak ($\delta = 0.85$ ppm. The product **3** was dissolved in dried pentane (≈ 10 ml), following which activated charcoal (≈ 1 g) was added and the mixture was stirred for 2 h to adsorb the Pt catalyst. After the solids were removed by filtration over Celite, the solution was rotary evaporated to remove pentane, and the oily product was collected (yield: 3.1 g, 85%).

The ^{1}H NMR spectrum of the product indicated that, on average, the reaction product comprised a 1:1 adduct of the two starting materials. The integration of the H-C $=$ C peak of squalene at $\delta = 5.08$ ppm dropped in intensity from ≈ 6H to ≈ 4.8H. Also, a new CH_2 peak at $\delta = 0.85$ ppm appeared as a consequence of the hydrosilylation of the double bond. Similarly, the ^{1}H NMR spectrum revealed the presence of the triethoxysilyl group. As all 6 double bonds are, in principle, capable of reacting with silane compounds, several structural and regioisomers are possible constituents of a 1:1 adduct. For comparison the ^{1}H NMR of squalene is provided: ^{1}H NMR (CDCl$_3$): $\delta =$ **1.58 (bs, 18H), 1.66 (bs, 6H), 2.00 (bs, 20H), 5.1 (bs, 6H)**. The NMR and LC-MS are consistent with the formation of 63%, 16%, and 1% of the mono-, di- and trihydrosilylated squalenes, respectively, and 20% of the recovered squalene starting material (Table 1).

^{1}H NMR (CDCl$_3$): $\delta = -0.01-0.10$ (m, 12H, SiMe), 0.52 (s, 3.2 H), 0.83$-$0.88 (m, 6H), 1.07 (d, 1.2 H), 1.16$-$1.25 (two overlapped triplets, 12 H), 1.34 (bm, 3H), **1.58 (s, 12H)**, **1.66 (s, 4.2 H)**, 1.71 (s, 1H), **1.99 (m, 12H)**, 3.80 (q, 6H), **5.08 (m, 3.7 H)**, 5.20$-$6.20 (m, 1.3H). IR: v

TABLE 1 Product Distribution Following the Hydrosilylation of Squalene

Structure	Squalene	Mono-silylated squalene	Di-silylated squalene	Tri-silylated squalene	
Molecular weight range[a]	517$-$522	841$-$846[b]	1165$-$1171[b]	1489$-$1496[c]	Total
Retention time of peaks (min)	2.58	4.36, 5.47	9.46, 12.35	21.70	
Area	5.6×10^5	1.8×10^6	4.5×10^5	2.3×10^4	2.8×10^6
Area %	20	63	16	1	100

[a] Peaks were observed within these the molecular weight "brackets". Mass spectral data for the sample was collected in an LC-MS from m/z $= 0-1500$.

[b] Two discrete peaks.

[c] Broad peak.

(cm $^{-1}$) 2969, 2925, 1660 (weak), 1445, 1386, 1255, 1167, 1139, 1106, 1082, 960, 840, 789. UV: $\lambda_{max} = 256$, $\varepsilon = 35035$ mol $^{-1}$ cm $^{-1}$. MS-ESI: (AgNO$_3$ in MeCN 5×10^{-4} M) m/z $= 841.5$ (M[734] $+$ Ag[107.5]) $^+$; 843.5 (M-15[734] $+$ Ag [109.5]) $^+$; 517.5 (squalene [410] $+$ Ag [107.5]) $^+$; 519.5 (squalene [410] $+$ Ag [109.5]) $^+$.

Modification of the Slides

Application of the Squalene Coupling Agent to the Surface: Q-Sq

The quartz slides were thoroughly cleaned before use. After initially soaking in a EtOH/KOH/H$_2$O bath (5:1:1 wt ratio) for 1 day, they were transferred to a 5 M hydrochloric acid solution for at least 2 days. A thorough rinse with distilled water and acetone was followed by a 20-min cleaning period using an argon plasma, just before grafting to the surface. The slides were then removed from the plasma cleaning system, the contact angles were recorded, and they were removed to a clean glass container and transferred to an oven where they were heated for 30 min at 110°C, before being transferred to the modification apparatus. Contact angles measured for the clean slides were in the range of 2−3°.

The modification apparatus was built from a Pyrex tube that was specially designed to fit the slide, above the cell floor, with a magnetic stirrer bar below to permit stirring during the modification process (Figure 1). The tube, which contains the quartz slide, was attached to a condenser and a solution of the coupling agent **3** in acetone (≈ 2 wt%)
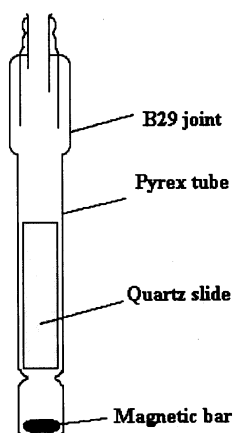
FIGURE 1 Slide modification apparatus.

with the slide was refluxed at 56°C for 5 min The slide was then removed slowly and vertically out of the solution at approximately 1 cm/sec, then put into the oven at 110°C for 6 h before it was subjected to Soxhlet extraction using cyclohexane for 24 h to give **Q-Sq**.

Application of a PDMS Elastomer to the Surface: Q-PDMS

The modification of quartz by a silicone elastomer was used to permit a comparison of the surface properties of a polysiloxane film with the other surfaces prepared in the course of this project (see below). After cleaning the slide as previously described, the quartz slides were first refluxed in a ≈ 4 wt% solution of vinyltriethoxysilane (VTES) in acetone for 24 h at 56°C followed by rinsing in acetone. They were then incubated in an oven at 110°C for 3 h. The slides were washed by a Soxhlet extraction procedure for 24 h. In the second step, the surface-bound double bond was hydrosilylated (Scheme 3) in the apparatus described above with 4 wt% of hydrogen-terminated polydimethylsiloxane silicone (n $\approx$ 230, cSt. 500) and 1−2 drops of Karstedt's catalyst in either hexane or pentane, previously dried over anhydrous $MgSO_4$. The solution was stirred overnight under nitrogen, then the slides were rinsed with hexane and cleaned by Soxhlet extraction using dried cyclohexane for 24 h.

Reactions on Grafted Quartz Slides with Squalene Coupling Agent

Epoxidation and Hydroxylation: Q-Sq-Epox and Hydrolysis: Q-Sq-PAA-H₂O

The slide **Q-Sq** was placed in a tube equipped with a magnetic stirrer bar and containing a mixture of peracetic acid (10 ml of a 32 wt% solution in acetic acid, 47.5 mmol and acetonitrile (50 ml).

= silicone
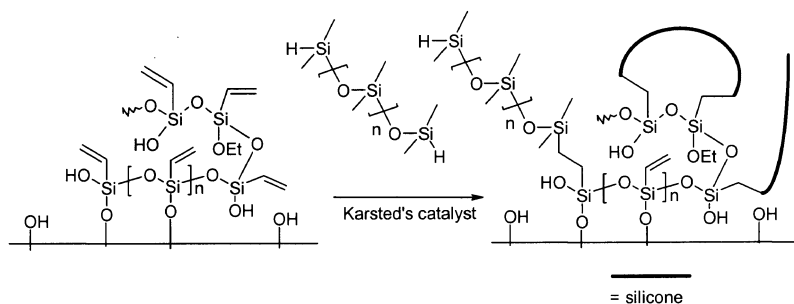
SCHEME 3

The reaction was stirred for 40 min before the slide was removed, rinsed with water and acetone, and dried in the oven at 110°C for ≈ 30 min. The slide was transferred to another tube (equipped with a condenser and drying tube charged with $CaCl_2$) that contained acetone (65 ml analytical grade, dried previously over $MgSO_4$) and refluxed at 56°C. $BF_3 \cdot Et_2O$ solution (1.5 ml 11.84 mmol) was added to the tube and the reaction mixture was refluxed for 40 min [5]. The slide was then removed and washed briefly by acetone, and then it was put in another tube equipped with condenser and containing MeOH (≈ 60 ml) and water (2.0 ml). Concentrated HCl (7−8 drops) was added to the solution. The mixture was refluxed for 45 min after which the slide was removed, rinsed with water and acetone and set aside to dry. XPS and contact angle measurements were recorded (see Table 2, Figure 2).

Oxidation by KMnO$_4$: Q-Sq-KMnO$_4$

Q-Sq was placed in the modification vessel containing a solution of $KMnO_4$ (1 g in 60 ml milliQ water, 0.11 M) equipped with magnetic stirr bar [6, 7]. The reaction was left for 1 h before the slide was removed, rinsed with MeOH, soaked in HCl solution in water (6 M), and finally washed thoroughly with water followed by acetone. Contact angles and XPS analysis were undertaken (Table 2, Figure 2).

Ozonization: Q-Sq-O$_3$

Q-Sq was put in the vessel used for its preparation and ozone gas was applied through a hollow glass tube that entered the lower portion of the tube. The reaction was left for 3 h. UV measurements showed an increase in the transmittance at 254 nm from $\approx 81\%$ to 88%.

Ozonization Followed by Oxidation Using H$_2$O$_2$: Q-Sq-O$_3$-H$_2$O$_2$

Q-Sq was put in the reaction vessel and submerged in methanol (≈ 65 ml); ozone gas was bubbled through a hollow glass tube injected into the lower portion of the solvent column for 1.5 h. The slide was

TABLE 2 Contact Angle Recorded for the Modified Slides with Time

Modification	Initial average°	time (hour)	Final average (°)
Q-PDMS	97 ± 1	24	90.5 ± 0.5
Q-Sq	99 ± 0.6	20	86.3 ± 0.6
Q-Sq-PAA-H$_2$O	69.4 ± 1	−	−
Q-Sq-O$_3$-H$_2$O$_2$	98.9 ± 2	−	−
Q-Sq-KMnO$_4$	91.6 ± 1.8	18	73 ± 1
Q-Sq-O$_3$-redu	90.4 ± 4.1	20	80 ± 1
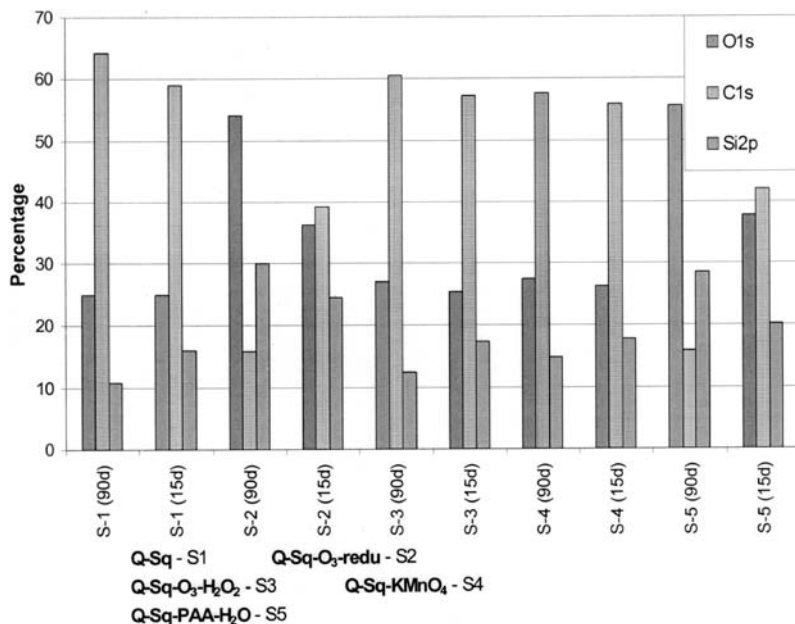
FIGURE 2 XPS analysis for the modified slides (90d and 15d refer to 90° and 15° takeoff angles, respectively).

removed, washed with water and acetone, and then placed in another tube containing 30% H_2O_2 (≈ 65 ml, with 4–6 drops of acetic acid) [8, 9]. The reaction was left stirring for 3 h before the slide was removed and rinsed with water followed by acetone. Contact angles and XPS analysis were undertaken (see Table 2, Figure 2).

Ozonolysis Followed by Reduction with Zn/AcOH: Q-Sq-O₃-redu

Zinc metal was activated by washing the metal powder briefly with 10% hydrochloric acid solution in distilled water, filtered, then washed with methanol. The metal was then subjected to vacuum pumping for ca. 18 h and was then stored under nitrogen.

In the same reaction vessel used for surface modification, glacial acetic acid (30 ml) was added to dichloromethane (30 ml) and zinc metal (1.5 g, 22.9 mmol), and the mixture was stirred for 5 min before the ozonide-containing slide **Q-Sq-O₃** was added to the tube [10]. The reaction was left at room temperature for 15 min before the slide was removed, rinsed thoroughly with water and acetone, and then set

aside to dry. Contact angles and XPS analysis were performed (see Table 2, Figure 2).

Coupling with DNPH: Q-Sq-O₃-redu-DNPH

The ozonized, reduced slide **Q-Sq-O₃-redu** was directly transferred to another vessel containing dinitrophenylhydrazine (DNPH) solution (ethanol 50 ml water 11 ml conc. sulfuric acid 5 ml, DNPH 1.4 g, 7.07 mmol) [11]. The reaction was left for 30 min with stirring before the slide was removed, rinsed with ethanol and acetone, and then Soxhlet extracted with acetone for 2 days. The UV spectrum showed a decrease of transmittance at 365 nm (56%), and the typical DNP-hydrazone absorbance (Figure 3).

X-ray Photoelectron Spectroscopy (XPS) of the Modified Surfaces

Modified surfaces were characterized by XPS (Leybold MAX 200 XPS, Figure 2). Slides were broken/cut into pieces of approximately 1 cm^2. Unmonochromatized Al K$_\alpha$ (15 kV and 25 mA) X-ray radiation was used as the excitation source. Features in the resultant low resolution spectra due to excitation from the weaker X-ray satellite lines, which are also present in the nonmonochromatic source, were subtracted by use of an algorithm supplied with the instrument [12]. Atomic percentages of the elements present were derived from spectra run in a low-resolution mode (pass energy = 192 eV), which were normalized to unit transmission of the electron spectrometer by means
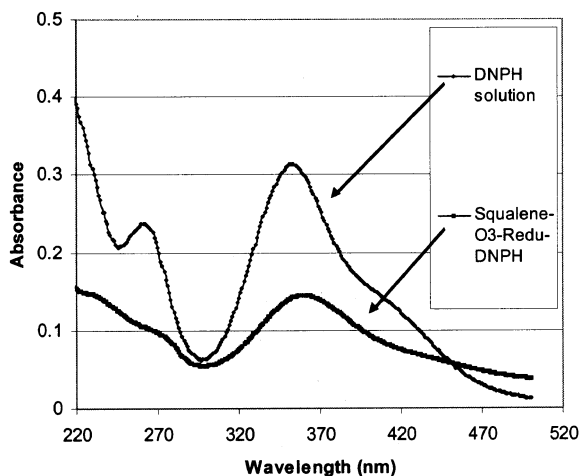

FIGURE 3 UV spectra of dinitrophenylhydrazine and squalene after ozonization/reduction by Zn/HOAc and dinitrophenylhydrazine.

of a routine provided by the manufacturer [13]. The sensitivity factors used (O 1 s = 0.78, C 1 s = 0.34, Si 2p = 0.40) were empirically derived by Leybold for the normalized spectra. Binding energies and peak areas were obtained by the use of the standard provided with the spectrometer. The energy scale of the spectrometer was calibrated to the Cu $2p_{3/2}$ (932.7 eV) and Cu 3p (75.1 eV) peaks, respectively, and the binding energy scale was then shifted to place the C 1 s feature present at 285.0 eV [14]. Large-area analysis (2×4 mm or 4×7 mm) was performed so that exposure of the samples to the X-ray would be minimized while sufficient signal-to-noise ratios could be obtained for the spectral features. Data were recorded with electron take-off angle adjusted to $90°$ and then $15°$ for each sample.

RESULTS

Classical coupling agents usually graft to siliceous surfaces by means of a substitution at chlorosilane or, more frequently, alkoxysilane groups. This precedent, which we also chose to utilize, required the modification of squalene. Normally, internal alkenes only undergo hydrosilylation with difficulty. However, because it is so simple to perform, the efficiency of hydrosilylation with squalene, which contains six internal bonds, was examined.

The hydrosilylation of squalene by $HSiMe_2OSiMe_3$ worked remarkably well. The preparation of adducts ranging from $1:1 \rightarrow 1:5$ (squalene:silane) was readily effected using Karstedt's catalyst. However, the analogous reaction between squalene and $HSi(OEt)_3$ did not occur: the alkoxysilane groups would be necessary for subsequent binding to the quartz surface. Therefore, a new coupling agent combining the characteristics of both triethoxysilane and a disiloxane was prepared by the hydrosilylation of vinyltriethoxysilane with tetramethyldisiloxane. In addition to the normally favored addition (ca. 75%) of the silyl group to the terminal position **1** [15], significant quantities (ca. 25%) of the internal regioisomer **2** were obtained (Scheme 2).

The mixture of isomers was used directly to hydrosilylate squalene, leading, on average, to the incorporation of one silyl group onto the squalene chain **3** (Scheme 4). GC-MS was utilized in the analysis of the crude product. The results indicated the formation of 63%, 16%, and 1% of the mono-, di-, and trihydrosilylated squalenes, respectively, and 20% of the recovered squalene starting material. The ^{1}H NMR data are consistent with hydrosilylation with the regiochemistry shown. Doublets of integration 3H accompanied the hydrosilylation ($RH(R'_3Si)C$-CHMe) rather than the alternative methyl singlets,
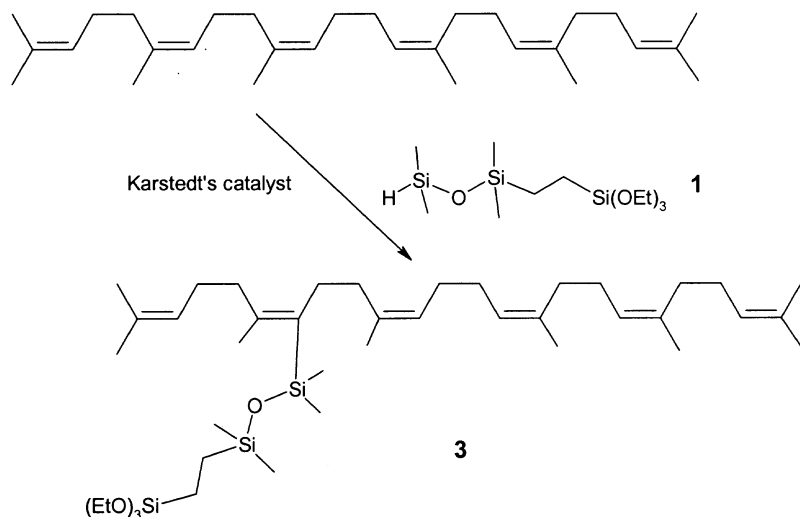
SCHEME 4

which would be expected in the other regioisomer $(RH_2C-C(SiR'_3)Me)$. With forcing conditions, on average up to two silyl groups could be incorporated on squalene using hydrosilylation. Attempts to incorporate more than two groups by use of elevated temperatures, or by increasing the concentration of selected reagents, were unsuccessful.

It should be noted that side reactions could not be avoided during this hydrosilylation. Double bond migration, one of the common problems in such systems [14], manifested itself through the formation of dienes. These conjugated systems were readily observed in the UV spectrum.

Squalene coupling agent **3** was grafted to quartz slides by classical procedures to give **Q-Sq** (see Experimental section above). The contact angle shifted from $2°$ for unmodified quartz to $\approx 99°$, while the UV transmittance at 254 nm dropped from $\approx 90\%$ to $\approx 81\%$, indicating successful grafting of squalene to the surface. X-ray photoelectron spectroscopic studies similarly showed the deposition of the coupling agent on the surface (see below). Several attempts were made to modify the method used for curing the coupling agent to the surface. In particular, a reduction of heating times and temperatures, in order to reduce the magnitude of squalene autoxidation (see below), were examined. However, it was shown that incomplete grafting accompanied the use of these less vigorous conditions.

Surface Modification

There are many known methods for double bond oxidation, including epoxidation (using peracetic acid or *m*-chloroperbenzoic acid [3]) or direct oxidation (using oxidative reagents such as $KMnO_4$ or ozone), all of which will change the polarity of the organic group and thus of the squalene-modified surface **Q-Sq** [7, 8, 16]. Several of the oxidation methods were examined, and the subsequent characteristics of the resulting slides established by contact angle goniometry and X-ray electron spectroscopy.

Epoxidation of the slide using peracetic acid to give **Q-Sq-epox** led to increases in the UV transmittance of the surface as a result of loss of the alkene and diene residues. Hydrolysis to the diol **Q-Sq-PAA-H₂O** (Scheme 5) using acid catalysis ($BF_3 \cdot Et_2O$) was expected to increase the hydrophilicity of the surface, as discussed further below.

Ozonization of the surface **Q-Sq**, either by simply passing the ozone gas inside the tube or bubbling ozone into methanol in which the slide was submerged, readily occurred to cause the oxidation of the alkenes to the ozonide **Q-Sq-O₃**, as shown by the improved UV transmittance of the ozonized slide. Contrary to ozonides of ordinary alkenes, ozonides from alkenes proximal to a silicon atom are relatively stable [17].

Oxidative work-up of the ozonide using hydrogen peroxide was utilized to obtain surface-bound ketones and carboxylic acids **Q-Sq-O₃-H₂O₂** (Scheme 5). Alternatively, the squalene surface could be directly oxidized to carboxylic acids with aqueous potassium permanganate solution, resulting in an improvement of the UV transmittance **Q-Sq-KMnO₄** (data not shown).

Reductive work-up of the bound ozonide **Q-Sq-O₃** using Zn/acetic acid as a reducing agent [10, 18] caused an increase in UV transmittance during the conversion of the ozonide into a mixture of ketones and aldehydes **Q-Sq-O₃-redu** [19]. These could easily be trapped by dinitrophenylhydrazine to form highly colored hydrazones **Q-Sq-O₃-redu-DNPH**, which facilitated detection: comparison of the UV spectra of dinitrophenylhydrazine and the surface hydrazones resulting from the oxidation of the oxidized squalene surface shows the characteristic red shift (λ_{max} increase from 353 nm to 361 nm; see Scheme 5, Figure 3).

The surfaces of the squalene-modified and subsequently oxidized slides were characterized by contact angle goniometry (Table 2) and by X-ray photoelectron spectroscopy (Figure 2). Initially, contact angles for the oxidized squalene slides indicated a hydrophobic surface (ca. $90-100°$), with the exception of the polyol surface **Q-Sq-PAA-H₂O**, which had a much lower starting contact angle of about $70°$. However,

SCHEME 5

the contact angle exhibited a temporal dependence over the first several hours after the water droplet was placed on the surface, after which no further change was noted (Table 2). A slide grafted with a silicone elastomer (PDMS) was used as a reference for the contact

angle variation experiment, as it represented a nonfunctional poly-siloxane whose surface behavior did not change with time.

DISCUSSION

The efficient hydrosilylation of the internal bonds of squalene by **1** and **2** was somewhat unexpected, although it should be noted that fairly vigorous conditions were used for the hydrosilylation (up to about 75°C). It was not clear which of the double bonds reacted most efficiently, although, as noted, the addition to the double bond was regioselective. In addition to hydrosilylation, it is apparent that double bond migration was simultaneously occurring, as shown by the presence of a new, red-shifted absorbance at 240 nm in the UV spectrum of **3**, consistent with diene fragments (Figure 4).

The alkoxysilane groups so introduced to squalene remain surface active. It was possible, using standard conditions, to graft the coupling agent **3** to the surface of quartz. After grafting, the coupling agent could not be removed from the surface by exhaustive extraction, and its presence on the surface was confirmed by contact angle, both reductions in the transmittance through the slide, UV spectroscopy, and changes in the spectral distribution.

It was anticipated that, once on the surface, the squalene could be readily oxidized to provide a series of functional surfaces. This premise was examined by measuring the X-ray photoelectron spectra
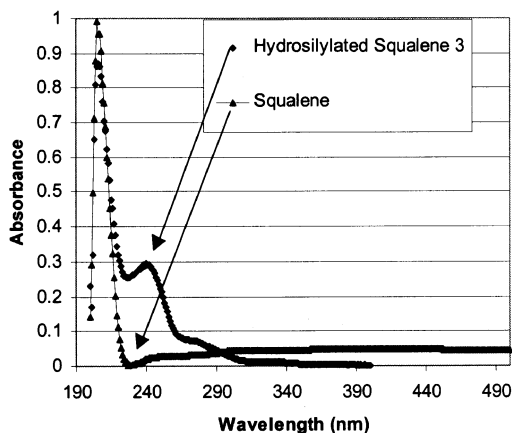
FIGURE 4 UV spectra of squalene and hydrosilylated squalene 3 showing presence of diene fragments in the latter material.

(XPS) of the oxidized surfaces at two different exit angles and comparing the results with that of the squalene-modified slide **Q-Sq** (Figure 2).

Initially, it was somewhat surprising to see the amount of oxygen in the **Q-Sq** slide. Once the contribution from underlying silica is taken into account, significant amounts of oxygen remained (ca. 6 atom%). This is likely due to the autoxidation of squalene. It is believed that partial autoxidation of squalene can take place even at $55°C$, where alkenes are converted to the diperoxide; such antioxidant behavior is believed to play a major rule in olive oil stability [20]. Many attempts were made to optimize the grafting process of **3** in order to avoid the relatively harsh conditions, especially the incubation at $110°C$ in the oven, that might facilitate autoxidation process. However, milder grafting conditions led to poorly adhering films of the coupling agent. Thus, self-oxidation is a penalty that must be paid with this coupling agent.

Q-Sq-O$_3$-redu and **Q-Sq-PAA-H$_2$O** were shown by the XPS to form very thin films on the surface as indicated by low carbon content. The data at the $90°$ take-off angle, which can probe into surfaces approximately $80-90\text{Å}$, shows mostly the presence of SiO_2 (atom% Si/O of about 2; note, however, that the coupling agents themselves possess considerable quantities of Si and O, which are constituents of the observed Si and O atom%). Thus, the films are clearly much thinner than that. The data taken at the low, $15°$ take-off angle clearly show significant quantities of carbon from the modified coupling agents (Figure 3). The former was reduced using Zn/AcOH, while the latter was epoxidized with peracetic acid and then treated with $BF_3 \cdot Et_2O$ and acidified aqueous methanol. In both cases, therefore, acidic conditions were present that can catalyze not only the surface cleavage via the trifunctional silyl group (Scheme 6A), but also at the silicone linkages via redistribution; the latter groups are more sensitive to acid (Scheme 6B) [21, 22]. The relatively high loss of the material grafted on the surface can thus be explained in these cases [21, 22]. Depending on the application, the ability to prepare thin films (see next section) could be advantageous.

Examination of the XPS of different take-off angles of these two films demonstrated that Si atom% was higher at the film/quartz interface than at the air/film interface. This is consistent with classical pictures of surface modification in which the silicon in the coupling agent's silyl groups acts primarily to immobilize the coupling agent on the siliceous surface.

For slides **Q-Sq**, **Q-Sq-O$_3$-H$_2$O$_2$**, and **Q-Sq-KMnO$_4$**, it was found that the Si atom% was higher at the air/film interface than within the film thickness or at the film/quartz interface, opposite to the films just
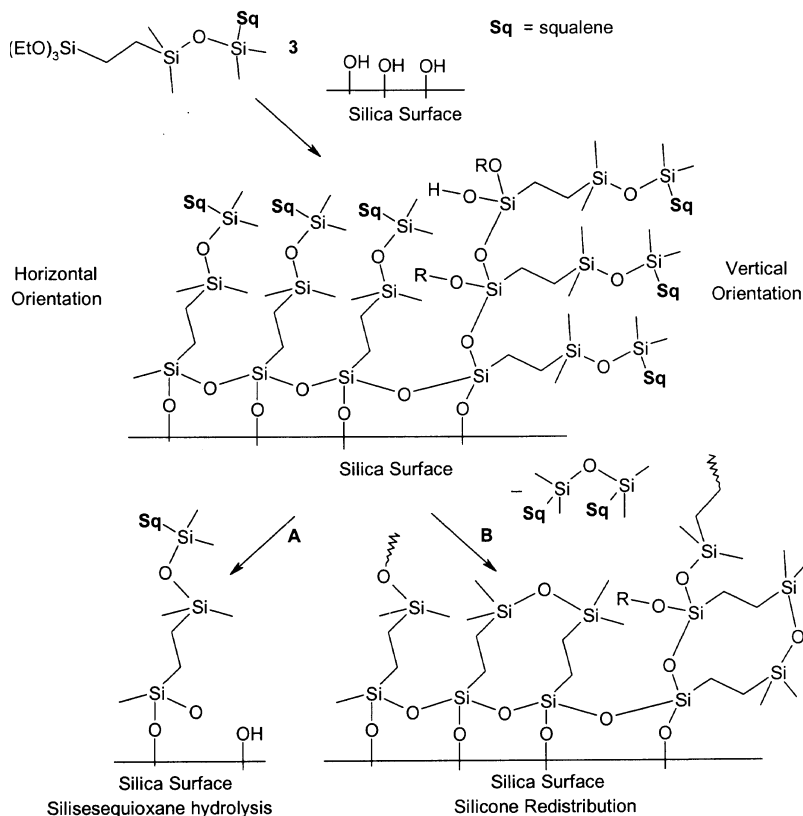
SCHEME 6

discussed. The unexpectedly high Si content at the air interface can be explained if a significant fraction of the siloxane linker arms are located there. In other words, these data suggest that in these thicker siloxane films not all the siloxane arms are directly bound to the quartz interface; a vertical MT[1] network structure permits both siloxane groups and carboxylic acid groups to orient themselves at the external air interface. The tendency for silicones to orient at air interfaces is one of their most exploited properties [23]. This behavior would similarly explain the high initial contact angle measurements

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[1]MT describes a mono/trifunctional silicone resin, using the normal silicone nomenclature. M refers to Me3SiO, D to Me2SiO2/2, and T to MeSiO3/2. See Brook, M. A. Silicon in Organic, Organometallic, and Polymer Chemistry (Wiley: New York, 2000), Chap. 1.

(silicone/air interface, Table 2) and, additionally, the reduction of the contact angle over time as carboxylic acid groups orient into the water droplet. Thus, depending on the reaction conditions, both types of silane chemistry are exhibited with coupling agent **3**. Here the migratory aptitude of the siloxane behavior is seen, whereas in slides **Q-Sq-O$_3$-redu** and **Q-Sq-PAA-H$_2$O** the coupling agent layer is too thin for such rearrangements to be important, and the silsesquioxane structure is manifested.

Even with careful comparison of the high-resolution XPS (data not shown) of **Q-Sq**, **Q-Sq-O$_3$-H$_2$O$_2$**, and **Q-Sq-KMnO$_4$**, it was difficult to observe clearly the different levels of oxidation of the samples (i.e., OH, CHO, COOH). Clearly, there is less carbon in the latter two slides and more oxygen, but the carbonyl substitution is a perturbation of a hydrocarbon matrix rather than a significant component. Similarly, while nitrogen could be observed in sample **Q-Sq-O$_3$-redu-DNPH**, attempts to characterize the surface further using high-resolution XPS were unsuccessful.

The objective of this research was to establish if the oxidation, which, as just described, was not always as efficient as desired, could change the surface energy on demand. Initial analyses of contact angles were not encouraging; most surfaces exhibited an initial contact angle of >90°. However, this angle was temporally dependent. Depending on the surface, the contact angle dropped over about 20 hs by between 7−30° as a function of the nature of the oxidation. Here the chemical groups manifest themselves clearly. The most hydrophobic and least mobile group, the crosslinked silicone **Q-PDMS**, showed the smallest variation (7°). The squalene surface, **Q-Sq**, which, as noted, had partly undergone autoxidation, showed more polarity (14°). The aldehyde/ketone surface **Q-Sq-O$_3$-redu** dropped by 10° and the acid surface **Q-Sq-KMnO$_4$** by 19°. Note that these changes were completely reversible.

In all cases, the changes in polarity may be ascribed to a flexible surface film. Normally, the hydrophobic silicone residues in the thick films are found at the air interface and exhibit a high contact angle. Once in contact with the water droplet, the hydrophilic groups can diffuse to the polymer/water interface and reduce the observed contact angle, as has been observed in other amphiphilic polymer films [24, 25, 26].

The oxidized functional groups in the squalene films remain chemically available. Exposure of **Q-Sq** to dinitrophenylhydrazine led to no significant change in absorption; as the chemical was washed off. By contrast, **Q-Sq-O$_3$-H$_2$O$_2$** and particularly **Q-Sq-O$_3$-redu** reacted irreversibly to form the dinitrophenylhydrazone.

CONCLUSIONS

These studies show that squalene, a natural oxygen-sensitive moiety hexaene, can be converted to a coupling agent by hydrosilylating the internal double bonds. Once grafted to the surface, polar groups can be introduced by various types of oxidation that increase the surface energy of the initially hydrophobic surface. The resulting films are sufficiently flexible that, in the absence of a polar external environment, hydrophobic domains reside at the air interface. Regardless, the functional groups remain chemically accessible to allow grafting to the carbonyl groups formed. Thus, this approach allows control of both surface energy and polarity. Future work will examine routes to more highly oxidized surfaces and the use of the oxidized surfaces to graft to external polymers.

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