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Solvent Effects on Bonding Organo-silane to Silica Surfaces

T. M. CHEN and G. M. BRAUER

Food and Drug Administration, Washington, DC, and Dental and Medical Materials, Polymer Science and Standards Division, National Bureau of Standards, Washington, DC 20234

*Interfacial bonding and stability of γ -methacryloxypropyltrimethoxysilane with silica surfaces have been studied by means of infrared spectroscopy. The addition of *n*-propylamine enhances silanization of γ -methacryloxypropyltrimethoxysilane to silica surfaces in normal aliphatic hydrocarbons, and cyclohexane yields a more water-resistant silica-silane bond, and improves the diametral tensile strength of the composite.*

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Introduction.

The service life of dental composites is assumed to be strongly dependent on the bonding between the resin matrix and reinforcing filler.¹ This bonding is greatly improved by addition of a coupling agent, which is usually applied at the surface of the filler.

Many silanization conditions have been published in the literature.¹⁻⁸ Among them, the most promising procedure was first described by Kaas and coworkers.¹ They found that *n*-propylamine dissolved in acetone promotes the silanization of γ -methacryloxypropyltrimethoxysilane. Various polar or non-polar solvents, e.g., water,^{2,3} ethanol,^{4,5} propanol,³ acetic acid,⁶ toluene,⁷ cyclohexane,³ methyl ethyl ketone,³ trichlorotrifluoroethane, and methylene chloride,⁸ have also been employed. However, studies of silanization in these different solvents and stability of the interface have not been conducted systematically.

It would have been simplest to employ glass as a filler to study the interfacial bonding between glass and silane. Unfortunately, its opacity to infrared radiation and generally large particle size ($\sim 25\mu\text{m}$) render this material insensitive to measurement of its infrared absorption. Colloidal fumed silica was used in the present study, because of its high purity, fine particle size ($\sim 12\mu\text{m}$), and the ease with which silica pellets, suitable for infrared measurements, can be molded under pressure. Furthermore, silica represents approximately 60% of the ingredients of most glasses.

The objective of this study was to determine: (1) the nature and extent of interaction between the filler and resin achieved by the silane coupling agent; (2) the solvent system or mode of application of the coupling agent producing optimum bond formation; (3) the effect of the addition of various amines to the reaction mixture on the strength and stability of the silane bond in water; and (4) the extent to which properties of composites could be improved by optimizing interfacial bonding.

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Materials and methods.

All chemicals and solvents used were reagent grade. A very pure, high-surface-area silica (99.8% SiO_2 , BET surface area - $150\text{ m}^2/\text{g}$) was employed.* Silica wafers, approximately 0.2 mm thick, 12 mm long, and 6 mm wide, were prepared by pressing silica powder between discs of aluminum foil at room temperature and a pressure of approximately 82 MPa for ten min. The aluminum foil was stripped from the fragile silica wafers which were then silanized in various solvents.

The silane studied, γ -methacryloxypropyltrimethoxysilane,[†] was used without further purification. Unless otherwise specified, silanization solutions were prepared by mixing 2% by volume A-174 in various solvents in the absence or the presence of 2% by volume of *n*-propylamine. In the typical treatment, the silica wafers were reacted with a silanization solution for two h at room temperature. This was followed by washing with reagent grade acetone for ten min and air-drying prior to the infrared measurements. For assessing the hydrogen bonding effect on interfacial bonding, a part of the silanized silica wafers was treated with NH_4OH solution (pH=9) for ten min at 24°C prior to the acetone washing and infrared measurements.

The infrared spectra were determined with a Perkin-Elmer Model 337 infrared spectrophotometer.[‡] The stability of silane-silica bonding was assessed by immersing silane-treated silica wafers in water for 280 h at 68°C and then observing changes in the infrared spectra.

Two paste-paste composites containing 22.47% silanized fumed silica filler were prepared: one with silica silanized in the presence, and the other in the absence of *n*-propylamine. The diametral tensile strengths were measured according to American Dental Association Specification No. 27.⁹

Attempts to polymerize methyl methacrylate on silanized silica were investigated with a Cary-14[§] near-infrared spectrophotometer. The fumed silica wafer, silanized with A-174 in the presence of *n*-propylamine, was immersed in 5 ml benzoyl peroxide solution (2.6 g benzoyl peroxide/50 ml methyl methacrylate), followed by addition of 5 ml *N,N*-dimethyl-*p*-toluidine solution (1 ml *N,N*-dimethyl-*p*-toluidine/50 ml methyl methacrylate). The reaction was conducted at room temperature for one h. The treated silica wafer was extracted with boiling acetone to remove homopolymer prior to the infrared measurement.

The sources for the ingredients of the experimental composite are given in Table 4.

Results.

The surface silanol groups (SiOH) on fine silica are principally of two types (Fig., curve 1): free silanols which have a sharp infrared absorption band at 3740 cm^{-1} in good agreement with the literature,^{1,10} and adjacent silanols which hydrogen-bond to each other and/or absorb water having a broad region centered around 3600 cm^{-1} .

*Cab-O-Sil M-5, Godfrey L. Cabot, Inc., Boston, MA

†A-174, Union Carbide, New York, NY

‡Perkin-Elmer Corp., Norwalk, CT

§Varian Associates, Palo Alto, CA

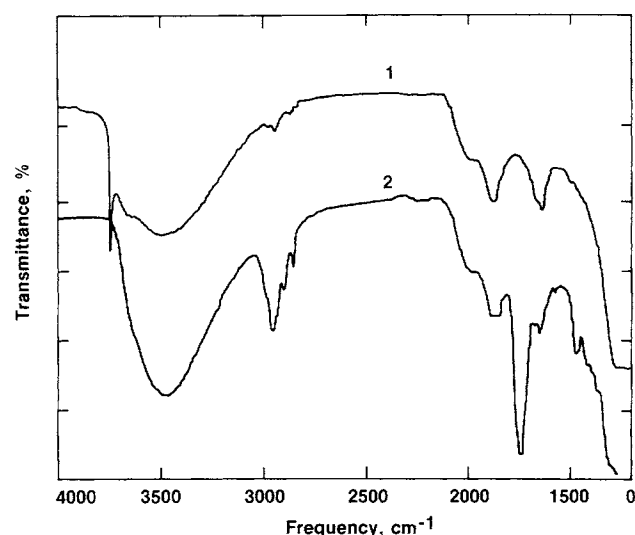


Fig. — Infrared absorption curves: (1) high surface area silica; and (2) high surface area silica silanized with γ -methacryloxypropyltrimethoxysilane in the presence of *n*-propylamine.

The complete spectrum of the silica wafer also shows two other bands. A band at 1870 cm^{-1} is attributed to the siloxane linkages in the bulk of the silica¹¹ and is unaffected by the surface treatment; therefore, it can be employed as an internal standard, and the ratio of the absorbances of the peaks at 3740 cm^{-1} and 1870 cm^{-1} can be used to determine the effectiveness of silanization. Likewise, a band in the region 1630 cm^{-1} is believed to be due to the structure of the bulk silica.¹¹ In a preliminary study, the intensity ratio of infrared absorption peaks at 3740 cm^{-1} and 1870 cm^{-1} was found to be relatively constant for nine fumed silica wafers (1.36 with a standard deviation = 0.06). Thus, the relative standard deviation, mainly resulting from instrument error, is 4.4%. When a sample is silanized with A-174 in the presence or absence of *n*-propylamine, the peak at 3740 cm^{-1} loses its intensity or disappears, and peaks at 1720 cm^{-1} — due to the carbonyl group — and at 1470 cm^{-1} — due to a double bond — appear (Fig., curve 2). The intensities of these peaks do not change after immersion of the specimen in NH_4OH solution ($\text{pH}=9$), indicating that the hydrogen-bonding has little effect on interfacial bonding of dried silanized silica wafers. Formation of chemical bonds between the silica and the silane is, therefore, detected by the change in the intensity ratio of infrared absorption peaks at 3740 cm^{-1} and 1870 cm^{-1} when compared to the untreated material.

The effects of solvents used in the silanization of silica with A-174 on the chemical bonding of silane to the silica are given in Table 1. Addition of 2% *n*-propylamine to the solvent significantly increased the coupling effectiveness of the silane. Complete elimination of the free silanol band occurred when acetone, *n*-pentane, *n*-hexane, *n*-heptane, xylene, or cyclohexane were used as solvents in the presence of *n*-propylamine. Initial reduction of the free silanol absorption was also large with the addition of dimethyl sulfoxide (DMSO) or dimethylformamide (DMF). However, after the specimens were allowed to stand, the free silanol band reappeared or increased again. This behavior was also observed from infrared spectroscopic data when unsilanized silica was exposed to these solvents and, therefore, appears to be caused by silica-solvent interaction. None of the other

TABLE 1
EFFECTS OF SOLVENT AND *n*-PROPYLAMINE ON
CHEMICAL BONDING OF SILANES TO SILICA SURFACES

Silane Solvent	Bonding, %‡	
	No Catalyst	2% <i>n</i> -propylamine
0.05 Vol % Acetic Acid ($\text{pH} = 3.6$)¶	32	•
0.05 Vol % Acetic Acid ($\text{pH} = 3.6$)†	32	•
20% Ethanol-80% H_2O ($\text{pH} = 3.6$)	2	•
50% Ethanol-50% H_2O ($\text{pH} = 3.6$)	53	•
95% Ethanol	13	70
50% Acetone-50% H_2O	31	•
90% Acetone-10% H_2O	23	100
Acetone§	0	100
Dimethyl sulfoxide	89 (48)∞	42
Dimethylformamide	48	78
<i>n</i> -pentane	34	100
<i>n</i> -hexane	26	100
<i>n</i> -heptane	40	100
Cyclohexane	26	100
Toluene	4	70
Xylene	11	100

Silane: 2 vol % solution of A-174 (γ -methacryloxypropyltrimethoxysilane).

Reaction time: two hours at room temperature.

‡Calculated from relative intensity ratio of infrared absorption peak at 3740 cm^{-1} (free OH band) and around 1870 cm^{-1} (siloxane linkage in the bulk of the silica). Samples were washed with acetone for ten min and air-dried prior to infrared measurements. Based on the precision for the untreated silica, a relative standard deviation of approximately 5% should be expected.

•Solution became cloudy on addition of *n*-propylamine.

¶Silane was hydrolyzed in 0.05 vol % acetic acid for seven d prior to reaction with silica.

†Silane was hydrolyzed in 0.05 vol % acetic acid for one h prior to reaction with silica.

§Solution decomposes on standing.

∞Numbers in parentheses indicate change in chemical bonding of wafer after one h.

solvents studied formed intermolecular hydrogen bonds with silanol groups.

The stability of the silica-silane bond was studied by aging specimens in water at 68°C for 280 h (Table 2), and most of the interfacial bonding was observed to undergo considerable degradation. Reduced hydrolytic deterioration was observed for silanized silica treated in the presence of *n*-propylamine with *n*-pentane, *n*-hexane, *n*-heptane, or cyclohexane as solvent. Specimens silanized in aromatic solvents, e.g., xylene or toluene with *n*-propylamine, despite their initial high degree of bonding, showed, on aging in 68°C water for 280 h, a drastic drop in this parameter.

The influence of the type of amine added on the effectiveness of the silanization is shown in Table 3. Aliphatic, especially primary, amines are excellent promoters for this reaction, whereas an aromatic amine, probably because of the lower basicity, produces a low degree of bond formation. The effects of different silanization conditions on the diametral tensile strengths of composites are demonstrated in Table 4. The diametral tensile strength of the *n*-propylamine-treated silica composite is much higher than that of the untreated one, but the tensile strength for both materials drops substantially on thermocycling between 5° and 55°C for one wk. The strength of the composite containing the propylamine-treated silica decreased only slightly on further thermocycling in water, whereas the composite with conventionally silanized silica filler continued to decrease in strength during the three-week observation period.

TABLE 2
STABILITY OF SILICA-SILANE BOND

Silane Solvent	% <i>n</i> -Propylamine in Solvent	Bonding, %**	
		Before Storage	After H ₂ O Storage
95% Ethanol	—	9	0
95% Ethanol	2	70	14
50% Ethanol (pH = 3.6)	—	12	0
20% Ethanol (pH = 3.6)	—	2	0
Acetone	2	100	26
90% Acetone-10% H ₂ O	—	23	20
90% Acetone-10% H ₂ O	2	100	41
Dimethyl sulfoxide	—	75 ^π	0
Dimethyl sulfoxide	2	100 ^π	26
Dimethylformamide	—	18 ^π	18
Pentane	—	34	34
Pentane	2	100	72
<i>n</i> -hexane	—	33	9
<i>n</i> -hexane	2	100	74
<i>n</i> -heptane	—	40	16
<i>n</i> -heptane	2	100	64
Cyclohexane	—	26	0
Cyclohexane	2	100	80
Xylene	—	11	8
Xylene	2	100	10
Toluene	—	4	0
Toluene	2	70	38

After silane treatment, silica wafer was stored in water at 68°C for 280 h.

**Calculated from relative intensity ratio of IR peaks at 3740 cm⁻¹ and 1870 cm⁻¹. Based on the precision for the untreated silica, a relative standard deviation of approximately 5% should be expected.

^πBonding decreased on standing.

TABLE 3
THE EFFECTS OF AMINES ON THE SILANIZATION OF
SILICA SURFACES

Amines	Dissociation Constant, pK _a [¶] 16	Bonding, % ⁺⁺
<i>Aliphatic</i>		
Primary amines		
<i>n</i> -propylamine	10.72	100
<i>sec</i> -butylamine	—	100
<i>tert</i> -butylamine	10.68	100
Secondary amines		
diethylamine	10.98	100
di- <i>n</i> -propylamine	11.00	100
di- <i>n</i> -hexylamine	11.01	100
di-isopropylamine	11.13 ²¹	73
di-isobutylamine	10.91 ²¹	58
Tertiary amines		
triethylamine	10.67	66
tri- <i>n</i> -butylamine	9.93	68
<i>N,N</i> -dimethylbenzylamine	8.91	53
quinuclidine	10.65 ²²	75
<i>Aromatic</i>		
<i>N,N</i> -dimethylaniline	5.07	5

Fumed silica pellets were treated with A-174 and a respective amine (molar ratio=1/0.0042) in cyclohexane for 1/2 hr, washed with acetone for ten min, and then air-dried.

[¶] Acid dissociation constant of the protonated base at 25°C unless temperature of measurement is given in superscript.

⁺⁺ Calculated from relative intensity ratio of IR peaks of 3740 cm⁻¹ (free OH bond) and 1870 cm⁻¹ (siloxane bond in the silica).

The near-infrared spectra of untreated fumed silica showed two absorption peaks at 4608 cm⁻¹ and 4484 cm⁻¹. Silica wafers silanized with A-174 in cyclohexane with *n*-propylamine as a promoter, in agreement with results reported in the literature,¹² gave an additional absorption peak at 4630 cm⁻¹, because of the C=C bond of the methacrylate groups present on the surface. This peak disappeared after the silanized silica was polymerized with methyl methacrylate, indicating that few, if any, unsaturated carbon-to-carbon double bonds remained after this procedure.

Discussion.

Application of coupling agents to fillers used in reinforced composites resulted in improved composite properties. This improvement was most notable in the ability of the composite to retain its strength after long exposure to water kept at elevated temperatures.

No completely satisfactory mechanism has been offered for the action of coupling agents, but the following theory has proved a useful working hypothesis for the application of silanes to improve bonding. It assumes that the coupling agent forms a chemical bond with the surface of the filler involving methoxyl and silanol groups, whereas another functional group, e.g., a methacryl group in A-174, chemically bonds to the resin. Adhesion of the resin to filler is therefore strengthened through a bridge of chemical bonds connecting the two phases.

Schrader¹³ utilized radioisotopic techniques to study bonding of γ -aminopropyltriethoxysilane (A-1100) at the glass interface and found that most (98%) of A-1100 exists as loosely adsorbed layers. Maximum joint lifetime was obtained with maximum amounts of chemisorbed A-1100. Too large an excess of physically adsorbed A-1100 caused deterioration of the bond. The A-174 silane should

TABLE 4
THE EFFECT OF THERMOCYCLING TIME ON TENSILE STRENGTH OF SILICA-CONTAINING COMPOSITES^{‡‡}

		Tensile Strength, MPa		
	0	1 wk	2 wk	3 wk
Composite containing fumed silica treated with A-174 ^{••} + <i>n</i> -propylamine	18.1 ± 1.0	10.9 ± 0.6	9.3 ± 0.7	9.5 ± 0.9
Composite containing fumed silica treated with A-174	9.4 ± 0.5	7.1 ± 0.4	6.3 ± 0.5	5.4 ± 0.1
Thermocycling at 5°C – 55°C (540 cycles per d)				
‡‡ <i>Composition of the composite:</i> § §				
Benzoyl peroxide paste,	% by weight		Amine paste,	% by weight
BIS-GMA	53.62		BIS-GMA	53.88
TEGDMA	22.99		TEGDMA	23.11
BHT	0.154		BHT	0.154
Benzoyl peroxide	0.766		Dimethyl- <i>p</i> -toluidine	0.386
Filler	22.47		Filler	22.47

^{••}γ-methacryloxypropyltrimethoxysilane

§ § The ingredients for the experimental composite were obtained from the following sources: BIS-GMA, Freeman Chemical Co., Milwaukee, WI; triethyleneglycol dimethacrylate (TEGDMA), Esschem Co., Essington, PA; butylated hydroxytoluene (BHT), Eastman Chemical Co., Inc., Kingsport, TN; dimethyl-*p*-toluidine, Aldrich Chemical Co., Inc., Milwaukee, WI.

show a similar behavior. Acetone washing should remove most of the loosely adsorbed silane. The remaining A-174 on the silica surface represents chemisorbed A-174. This belief is supported by our infrared study in which the free silanol absorption peak at 3740 cm⁻¹ disappears on silanization or loses its intensity, and peaks at 1470 cm⁻¹ and 1720 cm⁻¹, attributable to C=C and C=O absorptions, appear. The extent of chemical bonding depends on the silanization system used. In the absence of promoter, the silanization reaction is very inefficient, especially in aromatic solvents. Addition of *n*-propylamine to the solvent greatly increases the chemical bonding of A-174.

The stability of silane-containing solutions of *n*-pentane, *n*-hexane, *n*-heptane, cyclohexane, and xylene in the presence of *n*-propylamine was found to be very high; however, in acetone, the storage life of the solution decreased with standing, presumably involving the formation of a charge transfer complex having an ultraviolet absorption peak at 338 nm.¹⁴

The role of the promoter on the silanization was assessed for various amines. An aromatic amine was a poor promoter because of its low basicity ($K_B=10^{-9}$ or $PK_A=5$) compared to aliphatic amines ($K_B=10^{-3}$ to 10^{-4} or $PK_A=11$ to 10). Primary amines, especially *n*-propylamine, were most efficient in the silanization reaction, probably because of the absence of steric hindrance. Thus, di-isopropylamine and di-isobutylamine containing bulky side groups attached to the nitrogen atom were much less efficient than was diethyl or di-*n*-propylamine. The latter two compounds have about the same basicity constants. Silanization in the presence of tertiary amines may undergo a different reaction mechanism, and the percentage of bond formation appears to be unrelated to the basicity of the amine.

The silicon-oxygen bond was calculated to be 50% ionic;¹⁵ therefore, it was essential to evaluate the stability of the interfacial bonds in an aqueous environment. This was done by the accelerated aging test: namely, immersing the silanized silica in 68°C water for 280 h. Silica silanized in aliphatic hydrocarbon solvents or cyclohexane to which had been added a few percent *n*-propylamine yielded the most stable interfacial silicon-silane bonds. On the other

hand, in the presence of some of the more polar or aromatic solvents, a high formation of bonds initially took place, but substantial debonding occurred after immersion of the specimens in water.

The stable, highly silanized silica should enhance the performance of dental composites. This is confirmed by results obtained with a composite formulation containing 22.47% fumed silica filler. The diametral tensile strength of the *n*-propylamine-treated silica composite is much higher than that of the untreated one. However, tensile strengths of both types of specimens drop substantially after one wk of thermocycling. This may be attributed to an incomplete copolymerization of the methacrylate groups on the silica surface and/or those of bis-GMA or the diluent monomer (Table 4) under the curing conditions employed. Although we have obtained some infrared evidence that silanized silica does indeed co-polymerize with methyl methacrylate under slow-reaction conditions, it is not certain to what extent this copolymerization would take place using fast-curing conditions and with semi-paste reactants.

For hydrolysis to occur in dental composites, water must be able to penetrate the network structure of the polysiloxane interface. Therefore, for developing a water-resistant dental composite, a more hydrophobic polymer matrix would be preferable, along with improved silanization, as indicated in this study.

Conclusions.

Primary amines, especially *n*-propylamine dissolved in normal, aliphatic hydrocarbons or cyclohexane, enhanced the silanization of γ-methacryloxypropyltrimethoxysilane (A-174) to silica and yielded greater and more stable silica-silane bonding.

Silica-reinforced filler treated by this procedure, when incorporated into composites, improved the tensile strength and water-resistance of these materials.

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