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Characterization of adsorbed silane on fillers used in dental composite restoratives and its effect on composite properties

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Abstract The purpose was to study the effect of silane treatment of fillers on viscosity, flexural strength, and hydrolytic degradation of experimental dental composite resins fabricated with these fillers. The fillers consisted of a mixture of barium glass and amorphous silica. The resin was mainly based on ethoxylated bisphenol A dimethacrylate and polycarbonate dimethacrylate. The adsorption of silane on the filler surface was characterized by FTIR. There was significant correlation between the adsorbed silane on filler surface and the silane concentration in silane/methanol solution used for filler treatment. The silane concentration varied from 0.75 to 14% by weight. An increase in silane concentration led to a decrease in viscosities of the corresponding composite resins. The flexural strengths of composites with silanated fillers were greater than that of composites with unsilanated fillers: however, no significant difference was found between the flexural strengths of various silanated groups. The resistance to hydrolytic degradation of different composites increased when the fillers were treated with silane and was the highest at 1.1% silane.

Introduction

Composite resins are extensively used in restorative dentistry. They possess adequate physical and mechanical properties, and exhibit satisfactory clinical performance [1]. In these materials, two major phases, a resin matrix and siliceous fillers, are bonded together by an interfacial coupling agent. The most common dental resins are based on acrylate or methacrylate type monomers, and the fillers are silica, silicate glasses or a mixture of the two. The use of silane such as γ-methacryloxypropyl trimethoxy silane (γ-MPS) as a coupling agent is universal. The silane treatment of fillers not only improves the physical properties of the resultant composites but also their resistance to hydrolytic degradation [2]. To be effective, the amount of silane adsorbed on the filler surface must be optimal. Incomplete silane coverage of the filler surface leads to inadequate bonding with the resin contributing to non-uniform filler dispersion, increased viscosity, and inferior mechanical properties of the resultant composites [3]. Silane in excess of optimal amount can also lead to deterioration in mechanical properties [4].

Selection of the optimal amount of silane for dental composite resins is generally based on a consideration of their physical properties with little or no attention to their hydrolytic stability—a property crucial for the longevity of composite resin restorations. The amount of silane that is optimal for mechanical properties may not be beneficial from the standpoint of their resistance to hydrolysis in the aqueous oral environment.

The main objective of this study was to evaluate the effect of different concentrations of silane on the filler

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surface on the hydrolytic degradation of experimental composite resins. Selected other properties, namely, flexural strengths and viscosities of these composites were also evaluated to determine whether what is optimal silane content for hydrolytic stability is also optimal for the other two properties as well.

Materials and methods

Materials

Three different fillers, barium glass (Pentron, CT), Aerosil 50 and 200 (both from Degussa, Germany) were blended together at weight ratio of about 17:2:1. Relevant characteristics of these materials are shown in Table 1. Both Aerosil 50 and 200 were amorphous silica with average agglomerate size of 40 and 12 nm, respectively. The glass was based on barium alumina borosilicate composition with an average particle size of 700 nm. The silane used was γ-methacryloxypropyltrimethoxysilane, γ-MPS (OSI Specialties, NY). The resin matrix was 70/30 (by weight) blend of ethoxylated bisphenol A dimethacrylate (Esstech, PA) and polycarbonate dimethacrylate (Pentron, CT). 0.5% of 2,4,6 trimethylbenzoyl phosphine oxide (BASF, NC) and 0.2% of 2-diethylaminoethyl methacrylate (Aldrich Chemical) were added as photo initiator and accelerator respectively, based on the total amount of resin.

Table 1 Individual filler properties and the content in the filler blend

Filler type	Avg. particle size (nm)	Surface area (m^2/g)	Content (wt.%)
Aerosil 50	40	45[a]	11.5
Aerosil 200	12	175[a]	5.0
Barium glass (55% SiO_2, 25% BaO, 10% B_2O_3, 10% Al_2O_3)	700	3[b]	83.5

[a] BET surface are provided by the manufacturer

[b] Calculated from the average particle size

Filler treatment

Seven different batches of filler blends were treated by a wet process in solution of methanol and silane. The concentration of silane in the methanol/silane solution was 0.75, 1.5, 2.0, 3.0, 6.0, 8.0 and 14.0% by weight, respectively (Table 2). The fillers were added to the solution at ratio of 2:3 v/v. This ratio is based on our prior experience. It ensures uniform dispersion of fillers into the solution during mixing. The fillers contained about 0.5% (by weight) moisture and no extra water was added to the system. After mechanically mixing of fillers into the solution for about 6 h, the slurry was drained using filter press and dried at 120 °C for 45 min. The fillers were then washed with excessive methanol for three times and air dried for 30 min to remove any loosely attached silane molecules from the filler surface.

Characterization of adsorbed Silane

The amount of silane adsorbed on filler surfaces was determined by two different techniques: (a) conventional ashing, and (b) FTIR Avatar 360 (Thermo Nicolet, Madison, WI). In ashing technique, the fillers were dried in an oven at 100 °C for 1 h and desiccated for 30 min and weighed. They were then heated up to 500 °C for 4 h in a furnace, cooled to room temperature; oven dried (100 °C, 1 h) and desiccated (30 min), and then weighed again. Untreated filler blends were also heat treated under the same condition to determine their weight loss. When calculating the final silane content of treated blends, these values were used to correct for the weight loss from untreated fillers alone. FTIR was used in a diffuse reflectance mode with the resolution and number of sample scans of 4 and 64, respectively. Each FTIR sample comprised of a mixture of .03 g of filler and .27 g of KBr that was blended with a small mortar and a pestle. The reaction of silane with the filler surface hydroxyl groups was monitored by determining the integrated intensities of the peak assigned to carbonyl (–C = O) group of

Table 2 Silane content in solution, on filler surface and respective integrated intensity

Silane concentration in solution (wt.%)	Silane on filler surface (wt.%)	Integrated intensity		
		1700 cm^{-1}	1720 cm^{-1}	Combined
0.75	0.3	0.0012	0	0.0012
1.50	0.37	0.0015	0	0.0015
2.00	0.6	0.0018	0.0015	0.0033
3.00	1.1	0.002	0.002	0.004
6.00	2.17	0.0022	0.0057	0.0079
8.00	3.27	0.0032	0.0082	0.0114
14.00	4.3	0.0041	0.0103	0.0144

silane. This technique has been found to be very useful in determining the end point of surface monomolecular coverage [5].

Composite preparation

Four batches of composite pastes were prepared by blending the fillers with resin in a planetary mixer followed by roll milling to minimize the agglomeration of filler. They were hand-pressed into sheets of about 2–3 mm thickness, and subjected to vacuum under pressure to remove any air trapped into the pastes during processing. The filler and silane contents of different composite pastes are shown in Table 3. The amount of filler content in each batch was varied to maintain almost the same handling characteristics for all pastes. The handling characteristic of each batch was subjectively evaluated by at least two dental technicians. The technique, though qualitative, is customary in the field and the only method available in the dental office to evaluate the handling characteristics of dental composites.

Viscosity measurement

The rheological behavior of the composites was characterized by a viscometer, SR5 (Rheometrics Scientific, NJ, USA), measuring viscosity as a function of stress at room temperature. The experiment was conducted at dynamic stress sweep mode with constant frequency of 1.0 rad/s using 25 mm parallel plate and a gap of about 2 mm.

Flexural test

The flexure strength was evaluated by a three-point bend test as per ISO 10477. Specimens, 2 mm × 2 mm × 25 mm, were prepared by curing in a metal mold with visible light curing unit (Cure-Light Plus, Pentron, CT, USA) for 5 min. They were then stored in distilled water for 24 h at 37 °C. The bend test was conducted with a support span of 20 mm and at a cross head speed of 0.5 mm/min at room temperature, using ATS testing machine (Model 1105C, Buttler, PA, USA).

Table 3 Different composite formulations

Group	Silane content (weight%)	Silane treated filler content (weight%)	Actual filler content (weight%)
A	0	68	68
B	0.6	71	70.4
C	1.1	74	72.9
D	4.3	79.5	75.2

Hydrolytic degradation test

The hydrolytic stability of different composites was measured in terms of their respective depth of degradation in an aqueous NaOH solution at elevated temperature of 60 °C. The methodology used is described elsewhere [6]. The essential features of the test protocol were as follows. Disc specimens, 6 mm × 3 mm, of different composite resins cured under the same conditions as the flexure test specimens were stored in 0.1N NaOH solution at 60 °C for 4 weeks. To stop continuing reaction of residual NaOH absorbed within the materials, they were immersed in 2% HCl solution for 24 h followed by another 24 h' immersion in distilled water. The pH of the 2% HCl solution is 1.08. Microscopic studies in our laboratory indicated that at pH level of 1.08, the composite resins remained virtually unattacked by the acid. This observation is consistent with the reported behavior of dental composite resins in acidic medium [7, 8]. The discs were sectioned diagonally. The sectioned halves were mounted in epoxy resin (EPON 815/EPI-Cure, 3234 System from Miller-Stephenson Chem Co., CA, USA) with the cut surface exposed, and then final ground with 600 grit SiC paper under water flow and air-dried. The depth of hydrolytic degradation corrosion was measured by optical microscopic (Olympus BX 41M, Japan) examination of the ground sample surfaces.

Results

Silane adsorption

The concentration of silane in silane/methanol solution, the adsorbed silane content on filler surface and the respective integrated intensities are listed in Table 2. Representative FTIR spectra obtained from selected fillers are illustrated in Fig. 1. The unsilanated filler, as expected, did not show any carbonyl peak. The spectrum with 0.37% silane represents the filler groups where only one silane peak was observed at 1700 cm^{-1} due to the reaction of carbonyl group with the filler surface. On the other hand, the spectrum with 0.6% silane represents the filler groups where an additional silane peak at around 1720 cm^{-1} was observed indicating unreacted carbonyl group. The integrated intensities of the two peaks separately and their combined values versus the silane content of respective fillers determined by ashing technique are plotted in Fig. 2. Regression analysis indicated an excellent linear correlation ($R^2 \approx 0.99$) between the combined intensities

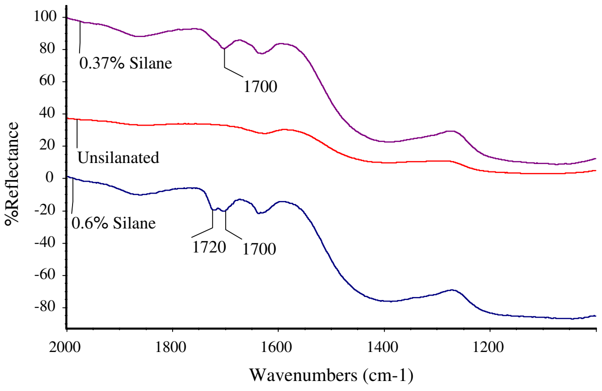

Fig. 1 FTIR spectra of unsilanated and silanated fillers

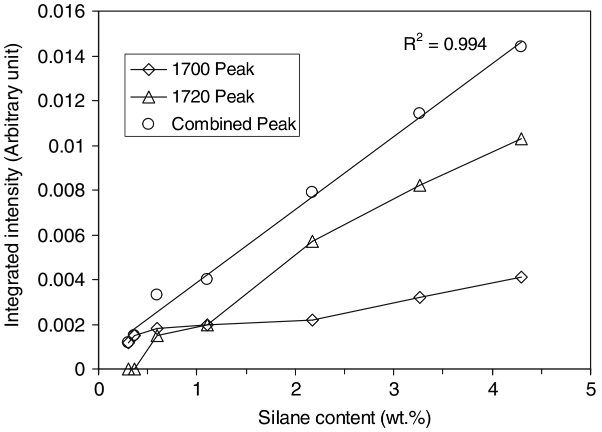

Fig. 2 Integrated FTIR intensity versus silane content on filler surface

and the silane content. In Fig. 3, the adsorbed silane content on filler surface was plotted against the silane concentration in solution. The data fitted well to the polynomial (2nd order) regression curve ($R^2 \approx 0.99$).

Viscosity

The viscosities of selected composite pastes as a function of applied stress are shown in Fig. 4. The viscosities of pastes with fillers containing 0.37% and no silane were similar but higher than the other two pastes. The viscosities of the pastes with higher silane contents (1.1 and 4.3%) showed a significant drop at stress level of about 30,000 dynes/cm^2.

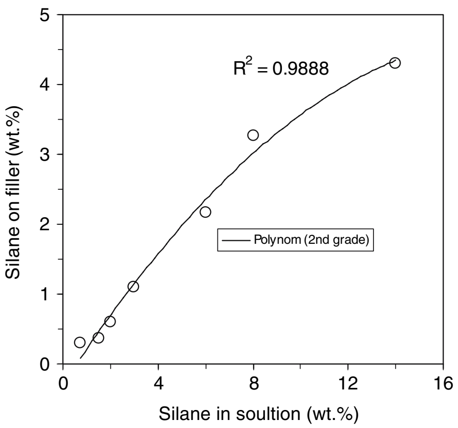

Fig. 3 Silane content on filler surface versus silane concentration in solution

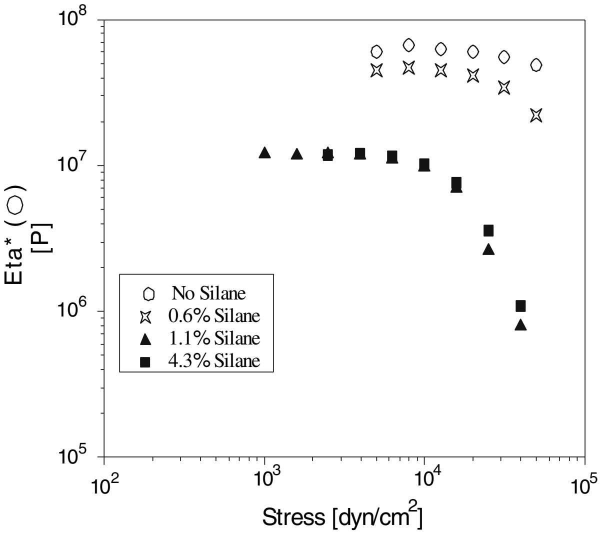

Fig. 4 Viscosity versus stress of different composite formulations

Flexural strength

Average flexural strengths, with standard error bars, of the different composite pastes are presented in Fig. 5. The flexural strength (49.4 ± 6.6 MPa) of the unsilanated filler group was only about 50% of that of any silane treated filler group. The flexural strengths of group B, C and D were 112.6 ± 10.3, 117.0 ± 8.9 and 123.4 ± 11.8 MPa respectively. One-way analysis of variance (ANOVA) with Tukey's pair-wise comparison showed no significant ($P < 0.001$, 95% confidence interval) difference in the flexural strengths among the groups with silanated fillers.

Hydrolytic degradation

Figure 6 illustrates the partial view of polished cross section of a composite sample treated with NaOH solution. The whitish band between two arrows represents the degraded layer caused by NaOH treatment. A total of 20 measurements were taken from all 4 sides of each

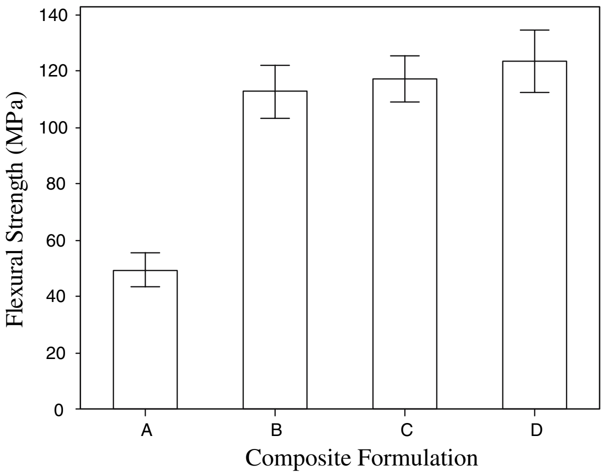

Fig. 5 Flexural strength of different composite formulations (Silane: *A* = 0%, *B* = 0.6%, *C* = 1.1%, *D* = 4.3%)

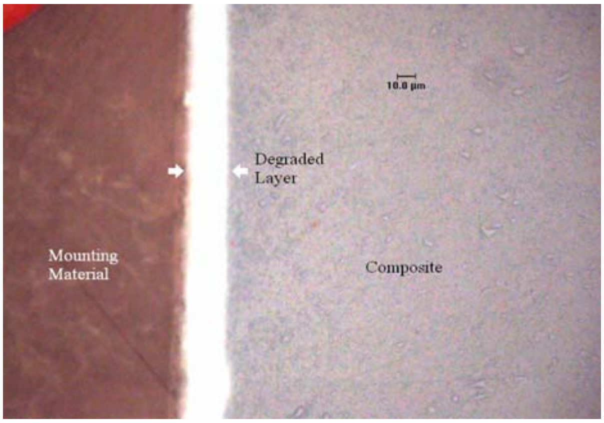

Fig. 6 Partial view of polished sample surface showing degraded region after treatment in 0.1N NaOH solution

specimen per batch and the average values with standard error bars are shown in Fig. 7. The group C (1.1% silane) showed the lowest degradation depth with 53 ± 11 and 192 ± 15 µm after 1 and 4 weeks of treatment time, respectively. The highest degradation depth occurred for group A with 511 ± 21 and 1049 ± 54 µm after 1 and 4 weeks of treatment time, respectively. Two-way analysis of variance (ANOVA) showed significant ($P < 0.001$) evidence of main effects of both silane and treatment time and their interaction effect.

Discussion

Silane adsorption

At deposited silane levels of 0.3 and 0.37% on filler surface, no peak for free carbonyl group (1720 cm^{-1}) was detected, indicating the occurrence of reaction between carbonyl and filler surface hydroxyl groups. On the other hand, the appearance of 1720 cm^{-1} peak at 0.6% silane indicates the possibilities of the occurrence of reactions: (1) between silanols and filler surface hydroxyl groups, and (2) between residual silanols of already reacted silane and silanols of fresh unreacted silane molecules. Free $-C=O$ groups are present in both cases and detected by FTIR. Furthermore, the curves for free and reacted carbonyl groups (Fig. 2) intersect each other at 1.1% silane level. It is of interest to note that this is the same level of silane that is present in the composite that exhibits the highest resistance to hydrolytic degradation (Fig. 7). The above observation strongly suggests that the optimal silane level on filler surface is 1.1%. The filler surface area covered per silane molecule was calculated using the following equation:

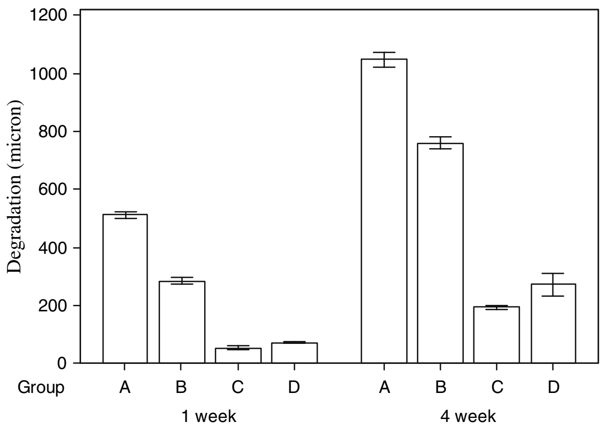

Fig. 7 Degradation of different composite formulations (Silane: *A* = 0%, *B* = 0.6%, *C* = 1.1%, *D* = 4.3%)

$$\text{Coverage} = \frac{\text{surface area of 1 g filler} \times \text{silane molecular weight}}{\text{silane content in 1 g filler} \times N_L}$$

where $N_L = 6.023 \times 10^{23}$ (Avogadro's number), molecular weight of γ-MPS = 248.3 and the surface area of the filler blends = 16.43 m^2/g. The calculated surface area covered per molecule at 1.1% silane amounted to be 0.62 nm^2/g. This value is within the range reported in other studies [5, 9] for monomolecular coverage.

Viscosity

As mentioned before, all pastes used in this study had similar handling characteristics, when evaluated subjectively. However, as apparent from Fig. 4 they exhibit different viscosities when measured by rheometry. This discrepancy may have been due to the difference in the amount of stress exerted during the two procedures. The stress during subjective measurement was not measured. The viscosities of the pastes appear to be dependent on their respective silane contents. The composites with less than 1.1% silane, shear thinning of the respective pastes, A and B, begins at about 30,000 dyn/cm^2 which is significantly higher than, about 6,000 dyn/cm^2, for higher silane containing pastes. The adsorbed silane film imparts lubricity and enhances the flow characteristics of the paste. This role of silane is fully realized only when there is an optimum amount of silane for complete coverage of filler surfaces. The viscosity data suggests that this optimum amount is about 1.1% that is consistent with the conclusion drawn above from FTIR measurement.

Flexure strength

The Fig. 5 however provides a different picture in that no significant difference was found to exist between strength values of composite resins with different silane contents. This observation was not anticipated as interfacial silane coupling between matrix and filler in general is known to improve the strength characteristics of composite resins. Further investigation is needed to elucidate the true role of filler/matrix interface under flexure mode.

Hydrolytic degradation

The results in Fig. 7 indicate that hydrolytic degradation is drastically reduced with the addition of silane, reaches a minimum at 1.1% silane, and then increases slightly. Hydrolytic degradation in composites is associated with the hydrolysis of silane coupling agent [2, 10, 11]. With time, the absorbed water hydrolyzes the interface silane and opens up an extra pathway for water diffusion. The debonded interface is the fastest path for water migration into the interior layer of composite resins. It is not surprising therefore that in the composite resin with no silane, hydrolytic corrosion is the most severe resulting in the deepest degradation depth. When the fillers are silanated, the adsorbed silane film before undergoing hydrolysis resists water diffusion. The degree to which such protection is attained depends on whether the silane coverage of the filler surface is complete. It appears from the results in Fig. 7 that the complete coverage is obtained at 1.1% silane. This observation is in agreement with the FTIR and viscosity data. It is hypothesized that the deteriorating effect of silane at above 1.1% is due to the presence of free silane that is prone to hydrolysis and accelerates the hydrolytic degradation.

Conclusion

FTIR was found to be an important tool in characterizing the adsorbed silane on the filler surface. A complete and optimal coverage of filler surface appeared to be achieved at silane level of 1.1% where peaks for both reacted and free carbonyl groups were detected by FTIR. The optimized silane content of 1.1% provided composites with lower viscosity and the highest resistance against hydrolytic degradation. The silane treatment of filler in general improved the flexural strength of the composites against unsilanated filler. However, the degree of strength enhancement with silane was found to be independent of silane concentration.

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