

# Effect of mixed silanes on the hydrolytic stability of composites

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**SUMMARY** A filler for a urethanedimethacrylate composite was silanated with mixtures of fluoroalkyl-, aminoalkyl-, phenyl-, vinyl-, bis silyl ethane- and 3-methacryloxypropyltrimethoxysilane (MAOP) in an attempt to increase the hydrophobicity of the coupling agent layer. Diametral tensile strength was used to evaluate composites stored for (1) 24 h in 23°C (RT) air; (2) 24 h in RT air plus 24 h in 100°C air; (3) 24 h in RT air plus 24 h in 100°C water; and (4) 24 h in RT air plus 24 h in 100°C air plus 24 h in 100°C water. Water sorption and solubility of composites was also determined on samples stored for 24 h in RT air. Heating composites for 24 h in 100°C air increased the tensile strength in eight of 13 silane treatments, while heating in 100°C water for 24 h caused decreases for

five silane treatments, no change for six and increases in tensile strength for two silane treatments. When composites that had been stored for 24 h at RT plus heated for 24 h in 100°C air were then heated for 24 h in 100°C water, only one silane treatment, the vinyltriethoxysilane at 25% (25% V), showed no significant decrease in tensile strength. Also, the composite silanated with 25% V had the highest value for tensile strength after storing for 24 h at RT air plus 24 h in 100°C air plus 24 h in 100°C water. These data indicate that the use of vinyltriethoxysilane increases the hydrolytic stability of the composite. Water sorption and solubility of the silanated composites were not satisfactory tests for evaluating hydrolytic stability of composites.

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## Introduction

The hydrolytic stability of composites has been shown by Söderholm *et al.* (1984) to be an important factor in their service life. Earlier, Schrader, Lerner & D'Oria (1967) had used radiotagged silanes to demonstrate that coupling agents in reinforced plastics formed covalent bonds to silica, a hydrogen bonded layer, and the molecules were condensed by cohesive forces. Later, Nishiyama, Katsuki & Horie (1987) measured the adsorption of 3-methacryloxypropyltrimethoxysilane (MAOP), on colloidal silica, and demonstrated that both monolayer and multilayer adsorption occurred. Söderholm & Shang (1993) studied the molecular orientation of MAOP on colloidal silica and proposed that the amount of silane needed for surface treatment depended on the number of isolated hydroxy groups

available on the surface of the filler. Chen & Brauer (1982) found that the presence of 2% n-propylamine with MAOP increased the silanization on silica and yielded a more stable silane bond as shown by increases in tensile strength and water resistance of composites containing these treated fillers. Nishiyama *et al.* (1986) studied the effect of functional groups of silanes on the adhesion of composite to silanated glass. Of those silanes which gave reasonable tensile adhesion the methacryoxypropyl group gave the highest value followed by vinyl- and mercaptopropyl-. They also measured contact angles of Bis-GMA on silanated glass and found the highest contact angle of 42° for glass treated with vinyltriethoxysilane. Kurata & Yamazaki (1988) used 3-methacryloxypropyltriisocyanatosilane to treat silica surfaces and found higher adhesive strength of poly(methyl methacrylate) to the treated glass than

when treated by MAOP; this result was explained by the higher reactivity of the isocyanato group compared to the ethoxy group. The authors claimed better water resistance resulted because of this reactivity and a higher crosslinking in the siloxane phase. Umemoto *et al.* (1990) mixed 3-mercaptopropyltrimethoxysilane with MAOP and used the mixture as a primer for adhesion of poly(methyl methacrylate) to stainless steel and glass and found the mixed silanes were highly adhesive with tensile values after 3 days in 37°C water of 23 and 17 MPa, respectively. Rosenstiel *et al.* (1993) studied the use of fluoroalkylethylsilane as a coating for a moisture barrier for dental ceramics and found it reduced the stress corrosion in glass and feldspathic porcelain.

Thus, it appears that increasing the hydrophobicity of the silane should increase the hydrolytic stability of the coupling layer and the service life of a composite. Fluorinated silanes would seem to be a logical choice, but unfortunately they are not available with reactive double bonds to react with the monomers and oligomers of the composite during setting. An alternative approach would be to use mixtures of saturated fluoroalkyl-trialkoxysilanes and MAOP. Mixtures of other silanes having hydrophobic groups such as phenyl- or vinyl- could improve the hydrolytic stability of composites. Since *n*-propylamine has been shown to improve silanization of MAOP, addition of aminopropyl-trimethoxysilane might be useful. Finally, the addition of bis functional silanes such as 1,2-bis(trimethoxysilyl)-ethane might improve the stability of the coupling agent layer by improving the crosslinking of the silane. It was the purpose of this study to evaluate the above types of mixtures of silanes on the hydrolytic stability of composites by determining their diametral tensile strength after accelerated ageing in water and by measuring the water sorption and solubility of the composites.

## Materials and methods

Silanes used plus their codes are listed in Table 1. The silanes were obtained from Hüls America, Inc., Piscataway, NJ, U.S.A. Zirconia-silica, having an average particle diameter of 1.6 µm, was silanated at three times the amount needed to obtain a minimum uniform surface coverage. This amount of silane was calculated according to the formula described by Mohsen & Craig (1995). Silanation, except when using BTMSE or BTCSE, was undertaken using 25%

or 50% TDF, TFP, AP, P and V with the balance being MAOP. The bis-ethanes were used at 10% with the balance being 25% TFP and 65% MAOP. Silanation was done from ethanol solutions of the silanes as described by Mohsen & Craig (1995) using a tumbling time of 90 min in a sealed polyethylene round bottle.

The polymer was a urethanedimethylacrylate containing 10% 1,6-hexanedioldimethacrylate\*. Composite pastes were formulated by hand with 19.75 wt.% of the above with 80 wt.% of the silanated filler, 0.152 wt.% dl-camphoroquinone, and 0.9 wt.% of N,N-dimethylaminoethylmethacrylate.

The pastes were placed in stainless steel moulds 6 mm in diameter and 3 mm high for diametral tensile strength specimens and 50 mm diameter and 1 mm high for water sorption and solubility specimens. The top of the moulds were covered with a glass slide and initial polymerization was accomplished with blue light<sup>†</sup>. The end of the light wand completely covered the end of the diametral tensile specimen and a 90 s exposure was used; the specimen was unmoulded and was cured for an additional hour in an Astron XL light unit<sup>‡</sup>. Initial curing of the water sorption and solubility specimens was carried out for 4 min with the light wand scanned over the wide surface; the specimens were unmoulded and further cured for 1 h in the Astron XL light unit.

The diametral tensile strength (DTS) of the specimens was determined after four storage conditions: (1) after 24 h storage in air at 23°C (RT); (2) after 24 h in RT air followed by 24 h in air at 100°C; (3) after 24 h in RT air followed by 24 h in distilled water at 100°C; and (4) after 24 h in RT air followed by 24 h in air at 100°C and then 24 h in distilled water at 100°C. Diametral tensile strengths were determined at RT in an Instron<sup>§</sup> at a crosshead speed of 0.5 mm/min. The ends of the specimens were cushioned by a piece of file cardboard 0.3 mm thick. Five specimens were tested for each silane and each storage condition.

Water sorption and solubility tests were conducted according to A.D.A. specification no. 12 for denture base polymers (1975). Three specimens were tested for each silane treatment.

\*Esschem Co., Essington, PA, U.S.A.

<sup>†</sup>Marathon unit by Den Mat Corporation, Santa Maria, CA, U.S.A.

<sup>‡</sup>Astron Dental Corporation, Wheeling, IL, U.S.A.

<sup>§</sup>Canton, MA, U.S.A.

Silane	Code
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2=\text{C}-\text{C}-\text{OCH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_3)_3 \end{array}$	
3-methacryloxypropyltrimethoxysilane	MAOP
$\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_2\text{CH}_3)_3$	
tridecafluoro-1,1,2,2-tetrahydroocetyl-1-triethoxysilane	TDF
$\text{CF}_3\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_3)_3$	
(3,3,3-trifluoropropyl)trimethoxysilane	TFP
$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_3)_3$	
3-aminopropyltrimethoxysilane	AP
$\text{C}_6\text{H}_5-\text{Si}(\text{OCH}_2\text{CH}_3)_3$	
phenyltriethoxysilane	P
$\text{CH}_2=\text{CHSi}(\text{OCH}_2\text{CH}_3)_3$	
vinyltriethoxysilane	V
$(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	
1,2-bis(trimethoxysilyl)ethane	BTMSE
$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3$	
1,2-bis(trichlorosilyl)ethane	BTCSE

**Table 1.** Silanes used for silanation and their codes

## Results

The diametral tensile strengths of the composites with various silanated fillers are reported in Table 2 along with their standard deviations in parentheses. Table 3 indicates whether there was a statistical difference at the 95% confidence level between the value for the 24 h in RT air specimen (control) and the values for the other three conditions. A statistical comparison was also made between samples stored for 24 h at RT followed by 24 h at 100°C in air and samples stored for 24 h at RT followed by 24 h in 100°C air and then 24 h in 100°C H<sub>2</sub>O. The results show that heating in air for 24 h at 100°C increased the tensile strength in eight of the silane treatments; caused no significant change in four of the treatments; and resulted in a significant decrease with only one silane treatment (50% P). However, heating in water for 24 h at 100°C resulted in five significant decreases; six no significant changes; and two significant increases in tensile strength compared to the 24 h in RT air control. When specimens were heated in air at 100°C for 24 h followed by heating in water at 100°C for 24 h, only two silane treatments

resulted in no significant change in tensile strength and only one treatment (25% V) having a significant increase compared to the control. When specimens that had been stored in RT air for 24 h followed by storage in 100°C air for 24 h, were then stored in H<sub>2</sub>O for 24 h all but those silanated with 25% V showed a statistically significant decrease in tensile strength.

A statistical comparison of the magnitudes of the diametral tensile strengths of the various composites first heated in air at 100°C followed by heating in water at 100°C for 24 h each showed that silanation with 25% V resulted in significantly higher tensile strength values than any other treatment and there was considerable overlap in the ranking of the other treatments. Composites with fillers silanated with 25% TDF + 10% BTMSE, 25% AP, 100% MAOP, 25% TDF, and 25% TPF had tensile strengths that were not statistically different at the 95% confidence level. Also, 25% AP, 100% MAOP, 25% TDF, 25% TFP and 25% P had tensile strengths that were not statistically different.

Water sorption and solubility values are listed in Table 4. The water sorption of composites with fillers

**Table 2.** Diametral tensile strengths of composites with various silanated fillers, kg/cm<sup>2</sup>

Silane treatment*	After 24 h	After 24 h + 24 h in 100°C air	After 24 h + 24 h in 100°C H <sub>2</sub> O	After 24 h + 24 h in 100°C air + 24 h in 100°C H <sub>2</sub> O
100% MAOP	501(34)	554(91)	379(45)	319(35) <sup>#†</sup>
25% TDF	336(25)	428(43)	433(29)	315(19) <sup>#†</sup>
50% TDF	285(36)	372(25)	321(71)	—
25% TFP	435(31)	596(82)	501(66)	298(27) <sup>#†</sup>
50% TFP	397(71)	433(32)	489(41)	—
25% AP	459(39)	545(56)	459(41)	342(48) <sup>#†</sup>
50% AP	459(40)	560(66)	357(48)	—
25% P	435(40)	472(93)	444(41)	311(46) <sup>†</sup>
50% P	449(40)	308(17)	312(47)	—
25% V	389(47)	545(88)	348(41)	508(26)
50% V	440(44)	524(36)	309(47)	—
25% TDF + 10% BTMSE	402(70)	551(68)	382(38)	390(63) <sup>#</sup>
25% TDF + 10% BTCSE	347(31)	381(41)	159(25)	—

\*Balance of silane used in treatment was MAOP; <sup>#</sup>values not statistically different at 95%; <sup>†</sup>values not statistically different at 95%.

**Table 3.** Comparison of storage in air and/or water at 100°C with storage for 24 h at RT (control), or with storage in RT air plus 100°C in air versus 24 h at RT followed by 100°C air and 100°C water\*

Silane treatment	24 h in 100°C air vs. control	24 h in 100°C H <sub>2</sub> O vs. control	24 h in 100°C air + 24 h in 100°C H <sub>2</sub> O vs. control	24 h in RT air + 24 h in 100°C air vs. 24 h in RT air + 24 h in 100°C air + 24 h in 100°C H <sub>2</sub> O
100% MAOP	N.S.	↓	↓	↓
25% TDF	↑	↑	N.S.	↓
50% TDF	↑	N.S.	—	—
25% TFP	↑	N.S.	↓	↓
50% TFP	N.S.	↑	—	—
25% AP	↑	N.S.	↓	↓
50% AP	↑	↓	—	—
25% P	N.S.	N.S.	↓	↓
50% P	↓	↓	—	—
25% V	↑	N.S.	↑	N.S.
50% V	↑	↓	—	—
25% TDF + 10% BTMSE	↑	N.S.	N.S.	↓
25% TDF + 10% BTCSE	N.S.	↓	—	—

\*↑ = condition was significantly higher than control; ↓ = condition was significantly lower than control; N.S. = no significant difference between condition and control.

silanated with 50% AP and 50% V were the only ones statistically different at the 95% confidence level from 100% MAOP. Although the means of the water solubility for composites silanated with V were less than for the standard MAOP, statistical analysis indicated they were not different at the 95% level of confidence, based on a sample size of three and their standard deviations.

## Discussion

Since the hydrolytic resistance of composites has been shown to be important in their service life (Söderholm *et al.*, 1984), increasing the stability of the silanated interfacial layer between the organic matrix and the filler should improve the clinical quality of composites. Therefore, increasing the hydrophobicity of this interfacial layer would be a reasonable approach. The

**Table 4.** Water sorption and solubility of composites with various silanated filters (%)

Silane treatment*	Sorption	Solubility
100% MAOP	1.58 (0.39)	0.33 (0.17) <sup>#</sup>
25% TDF	1.44 (0.13)	0.32 (0.04) <sup>#</sup>
50% TDF	1.39 (0.08)	1.12 (0.01)
25% TFP	1.39 (0.06)	0.43 (0.04) <sup>#</sup>
50% TFP	1.29 (0.07)	0.36 (0.02) <sup>#</sup>
25% AP	1.36 (0.21)	0.60 (0.14) <sup>#</sup>
50% AP	0.73 (0.06)	0.13 (0.07) <sup>#</sup>
25% P	1.27 (0.03)	0.61 (0.06) <sup>#</sup>
50% P	1.25 (0.17)	0.66 (0.11) <sup>#</sup>
25% V	1.19 (0.12)	0.16 (0.05) <sup>#</sup>
50% V	0.88 (0.04)	0.12 (0.04) <sup>#</sup>
25% TDF + 10% BTMSE	1.24 (0.05)	0.27 (0.05) <sup>#</sup>

\*Balance of silane used in treatment was MAOP; <sup>#</sup>values not statistically different at 95%.

substitution of fluorinated silanes for 3-methacryloxypropyltrimethoxysilane (MAOP), which contains the polar oxygen atoms, appears logical. Unfortunately, fluoroalkyltrialkoxysilanes with reactive carbon double bonds to react with the monomers to form the polymer matrix are not available. However, there are several alternative choices of silanes to increase the hydrophobicity of the interfacial layer. First, hydrophobicity of the silane layer could be increased and reaction with the organic matrix maintained by silanating with mixtures of saturated fluoroalkyltrialkoxysilanes and MAOP. Second, mixtures of aminoalkyltrialkoxysilanes and MAOP could improve silanation as shown by Chen & Brauer (1982). Third, increasing hydrophobicity by silanating with mixtures of aromatic silanes, such as phenyltriethoxysilane, and MAOP. Fourth, increasing hydrophobicity and maintaining reaction with the matrix by using mixtures of unsaturated aliphatic silanes, such as vinyltriethoxysilane and MAOP. Fifth, increasing hydrolytic stability of the silanated layer by using mixtures of bis-functinal alkoxy- or chloro-silanes and fluoroalkyltrialkoxysilanes with MAOP to increase crosslinking of the silane layer.

Diametral tensile strength at 24 h was used to evaluate the effectiveness of the silanation, since it has been shown by Suh, Ferber & Baez (1990) that this property was a good indicator. The tensile strength after an additional 24 h in 100°C air was to evaluate whether there was additional polymerization of the

urethanedimethacrylate matrix or further condensation of the silanes. The tensile strengths after 24 h in 100°C H<sub>2</sub>O gave an indication of the hydrolytic stability, especially when compared to those samples stored in air for 24 h at 100°C. Finally, the tensile strengths of samples stored for 24 h at RT followed by 24 h in 100°C air and then 24 h at 100°C in water, indicated the hydrolytic stability of composites that were post-cured and then subjected to strongly hydrolytic conditions. Also, storing in 100°C water for various times followed by mechanical testing for strength is an accepted method for evaluating the hydrolytic stability of the silane bond (Plueddemann, 1982).

Since most of the composites treated with the various silanes showed an increase in DTS after heating in air at 100°C compared to the control, the decreases in DTS after boiling in water at a 100°C compared to the control are conservative estimates of their hydrolytic stability, since the values would be a balance between the increase in strength from the temperature effect and the decrease in strength from the hydrolytic attack. Thus, even those samples which showed no significant decrease after 24 h in 100°C water compared to the control actually suffered some hydrolytic degradation.

As a result, samples first heated to 100°C in air for 24 h followed by storing in water at 100°C for 24 h give a clearer estimate of the hydrolytic stability. Only samples silanated with 25% V and 75% MAOP showed an increase in DTS compared to the control. Furthermore, samples silanated with 25% V were the only ones that did not show a decrease in tensile strength when samples stored for 24 h at RT plus 24 h in 100°C air were then stored in 100°C water for 24 h. The results may be the effect of using the hydrophobic vinyltriethoxysilane which also has the opportunity to react with the matrix through the carbon double bond. Samples silanated with 25% TDF (315 MPa) and 25% TDF plus 10% BTMSE (390 MPa) after the above testing showed no significant change in DTS, the latter being higher but not statistically different. These data suggest that the highly hydrophobic fluorinated silane increases hydrolytic stability even though it does not contain a carbon double bond to react with the organic matrix and that used in combination with a bis-trimethoxysilyl ethane further increases hydrolytic stability probably as a result of crosslinking the silane.

Water sorption and solubility values were less satisfactory than DTS in estimating hydrolytic stability. This result may be due to the polymer matrix being the

same for the composites containing the same filler silanated with various silanes. Thus, the silane coupling layer had no major impact on water sorption and solubility. The low solubility of composites silanated with vinyltriethoxysilane and 3-aminopropyltrimethoxysilane, although not statistically different from the other silanated composites, lends additional support to the use of the former in improving the hydrolytic stability of composites. For whatever reason the low solubility of the aminosilane is not coupled with high DTS after storage in 100°C water for 24 h.

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