Hydrolytic stability of silanated zirconia-silica-urethane dimethacrylate composites

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SUMMARY The effect of the method of silanation of zirconia-silica by 3-methacryloxypropyltrimethoxysilane (MAPM) and 3-acryloxypropyltrimethoxysilane (APM) on the diametral tensile and transverse strength of composites made from these silanated fillers and a urethane dimethacrylate was determined after 0–108 h of boiling in water. The water sorption of these composites was also measured at times up to 108 h. Silanation with either silane significantly increased the tensile and transverse strengths and decreased water sorption relative to comparable unsilanated controls. Silanation with MAPM from ethanol solution at three times the minimum uniform coverage gave the best overall results, and the tensile strength tests appeared to be most predictive of effectiveness of the silane treatments.

Introduction

The presence of silane coupling agents at the polymer-filler interface has been shown by Bowen (1963) to dramatically influence the mechanical properties of the dental composites. It has also been demonstrated by Nishiyama *et al.* (1991) that the properties are strongly influenced by the amount and adsorption of silane at the interface. The dispersability of quartz and zirconia-silica by bisphenol-A diglycidyl dimethacrylate (bis-GMA) and urethane dimethacrylate (UDMA) monomer systems were shown by Craig & Mohsen (1992) to be affected by the specific silane and the method of silanation.

Several mechanisms have been proposed by Plueddemann (1982) to explain the function of the silane at the interface. Chemical bonding of silane to the organic and inorganic phases has been proposed, where an organic-functional group on the silane reacts covalently with the polymer matrix while hydrolysable groups on the silane are hydrolysed to silanol groups by moisture on the inorganic phase which then bond to the inorganic phase. The silanol groups on adjacent silanes can also condense with each other forming a polymer film on the surface. The deposition of silane is multilayered, and the outermost layers, which account for 98% of the amount deposited, is physically adsorbed silane that can be removed by rinsing in cold water. The inner layer of silane is chemisorbed to the surface and is more hydrolytically stable, and can only be removed by prolonged immersion in boiling water. The layer adjacent to the filler is the most stable as a result of multiple bonding to an inorganic phase. Based on this information, the stability of the silane bond has been evaluated by measuring the decrease in mechanical properties of composites after boiling them for a given period in water.

The retention of the mechanical properties of dental composites in a wet environment is essential, and the effect of silanation of the filler on the maintenance of the interfacial bond is highly important. In this study, the hydrolytic stability of the silanated layer is evaluated by measuring the change in diametral tensile and transverse strength of composites after accelerated ageing in boiling water. In addition, the amount of water sorption by the composites was determined after the boiling test.

Materials and methods

The monomer system used was urethane dimethacrylate (UDMA), which was diluted with 10 wt% 1,6 hexane diol dimethacrylate (HDDMA)* to control the viscosity ($12·5$ N.s./m²). Zirconia-silica with a surface area of $1·33$ m²/g and an average diameter of $1·6$ μm† was used as the filler. The filler was silanated with either 3-methacryloxypropyltrimethoxysilane (MAPM) or 3-acryloxypropyltrimethoxysilane (APM)‡. MAPM was selected because it has been shown by Craig & Mohsen (1992) to be one of the most effective silanating agents on increasing the dispersion and wetting behaviour of the filler particles by the monomer and has a carbon double bond to react with the monomer. APM was selected because it also has a carbon double bond and the functional group is slightly less bulky than the one in MAPM, silane. $-$H vs. $-$CH₃.

Silanation was carried out from ethanol solutions of the silanes (method A), direct addition of silane to zirconia-silica at room temperature (24°C) (method B), and at the boiling points of the silanes (method C); the methods were described by Craig & Mohsen (1992). The amount of silane coupling agent (X) used for the filler treatment was based on the following relationship reported by Arkles (1987):

$$X = \frac{A}{\omega} f \qquad (1)$$

where X = the amount of coupling agent in grams needed to obtain minimum uniform coverage; f = amount of filler (g); A = surface area of the filler (m²/g); ω = wetting surface of silane (m²/g)§.

Three times (3X) the calculated amount of silane for minimum uniform coverage was used for methods A, B and C. In addition, silanation by method A was also carried out at the minimum amount (1X).

Composites were formulated from UDMA and MAPM or APM-silanated zirconia-silica, using *dl*-camphoroquinone catalyst and 2-(dimethylamino)-ethylmethacrylate acceleterator in concentrations described by Douglas, Craig & Chen (1979). The optimum monomer-zirconia-silicate ratio was determined for various silanated fillers by a consistency test described

by Craig & Mohsen (1992). The mixed composite paste was packed into disks ($6·0$ mm diameter × $3·5$ mm thick) or rectangular ($20 × 4·5 × 2·5$ mm) Teflon moulds for the preparation of diametral tensile and three-point transverse strength specimens. The composite paste was placed in two layers and each layer cured in a TRIAD II oven¶ for 80s at room temperature (24°C). The specimens were then removed from the moulds and post-cured for 1 h in the same oven at room temperature. Dimensions and weights of specimens were determined for strength and water sorption tests and were then placed in boiling water for either 0, 24, 48, 72 or 108 h. The specimens were wiped dry, weighed, and strength measurements made using an Instron at crosshead rate of $0·05$ cm/min. Furthermore, the diametral tensile strengths for specimens cured at 98°C in air for 108 h were also tested for composites with the silanes prepared by method A at 3X. Five replications for each experimental condition were made as well as for unsilanated control samples. An analysis of variance using a two-way factorial design with $P < 0·01$ was used to determine the effect of silanation of the filler and the effect of each experimental condition on the tensile and transverse strengths and water sorption of composites. A one-way analysis of variance for a fixed effect model at $P < 0·01$ was also used to determine the effect of immersion in boiling water and the effect of thermal curing in air on the tensile strength of composites.

Results

The optimum weight percentages of the silanated zirconia-silica in the composite samples are listed in Table 1. Flow point values previously reported by Craig & Mohsen (1992) are also in Table 1 for comparison. All silanated treatments resulted in substantial increases in the weight percentage of filler that could be added to the monomer system to reach the same consistency as the unsilanated control.

Diametral tensile strengths of composites containing filler silanated with MAPM or APM after the various times of boiling in water are presented in Figs 1 and 2, respectively. Control values for composites with unsilanated fillers are shown in comparison. The strength values of composites with MAPM and APM that were thermally cured at 98°C in air for 108 h are also shown in both figures.

Table 1. Weight per cent of silanated filler* in UDMA at constant consistency and flow point values

| Silane | Method of silanation | | | | | | | |
| | A at 1X | | A at 3X | | B at 3X | | C at 3X | |
	Wt %	Flow point (mL)	Wt %	Flow point (mL)	Wt %	Flow point (mL)	Wt %	Flow point (mL)
MAPM	81·0	1·40 (0·07)	82·5	1·65 (0·07)	85·0	1·95 (0·07)	84·5	2·40 (0·07)
APM	77·0	1·98 (0·11)	82·0	1·68 (0·04)	82·5	2·28 (0·04)	82·5	2·93 (0·25)

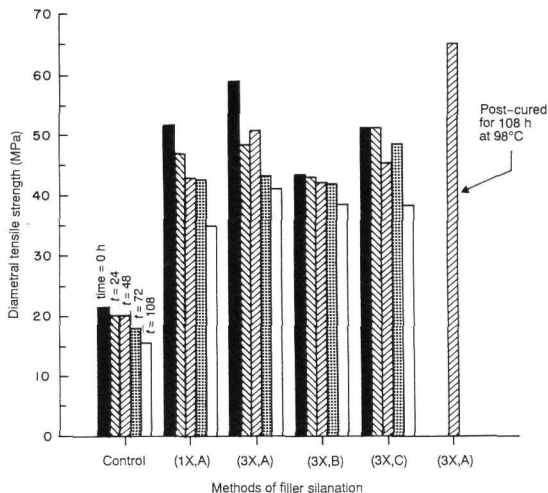* 72·0 wt% of filler needed with unsilanated control.

Fig. 1. Diametral tensile strength of composites containing filler silanated with MAPM after boiling in water for 0–108 h.

The transverse strength of MAPM and APM silanated zirconia-silica-containing composites, along with unsilanated composites, are shown in Figs 3 and 4, respectively, after boiling in water from 0–108 h. In general, the decrease in transverse strength was greatest after 24 h of boiling in water. Silanation using method A at 3X gave highest initial transverse strengths with MAPM (100 MPa) while method B at 3X gave the highest with APM (113 MPa), however, after boiling in water for 108 h, the transverse strength value with MAPM was 75 MPa and for APM as 65 MPa.

The water sorption of silanated and unsilanated control composites are shown in Figs 5 and 6 for samples silanated with MAPM and APM. The control values for composites with unsilanated fillers are also shown.

Discussion

Silanation of the filler by MAPM and APM showed substantial increases in filler incorporation in composites, regardless of the method used to treat the filler particles. Silanation of the filler with either of the silanes using method A at 3X gave lower flow point values than the control, which causes more filler incorporation than 72 wt%. This result is caused by better dispersion of the filler and wetting of the filler by the resin in the presence of the silane. Silanation of the filler using method C at 3X gave high flow point values compared to silanation by method A at 3X, and thus silanation by method C resulted in a higher degree of filler incorporation to reach constant consistency.
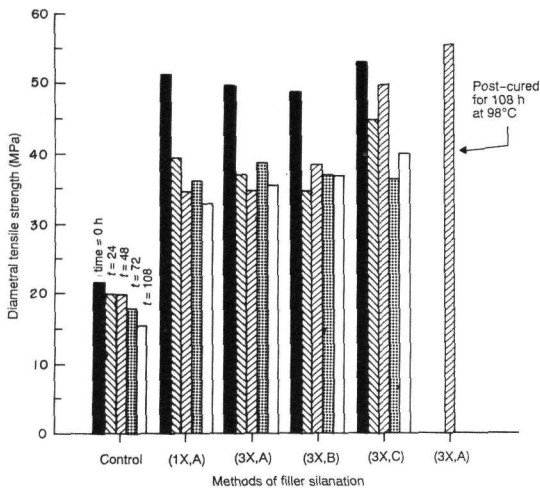
Fig. 2. Diametral tensile strength of composites containing filler silanated with APM after boiling in water for 0−108 h.
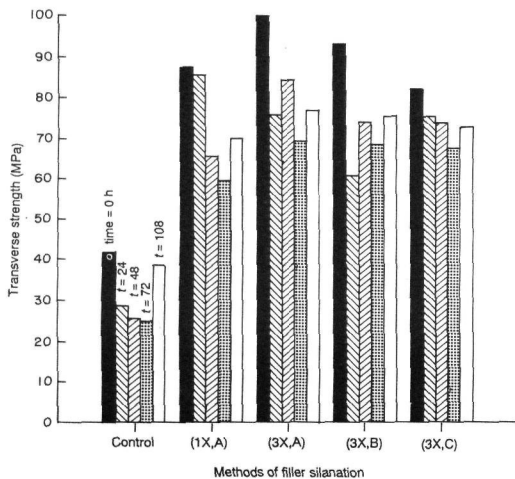

Fig. 3. Transverse strength of composites containing filler silanated with MAPM after boiling in water for 0−108 h.
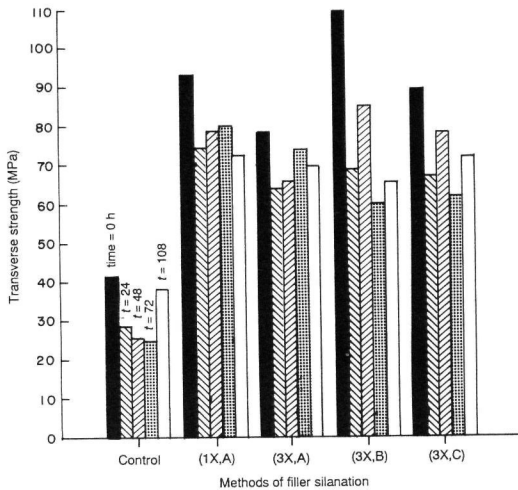
Fig. 4. Transverse strength of composites containing filler silanated with APM after boiling in water for 0–108 h.
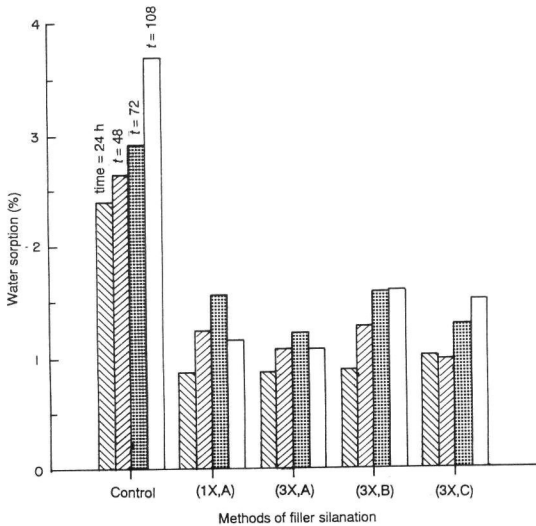

Fig. 5. Water sorption of composites containing MAPM silanated zirconia-silica after storage in water for 24–108 h.
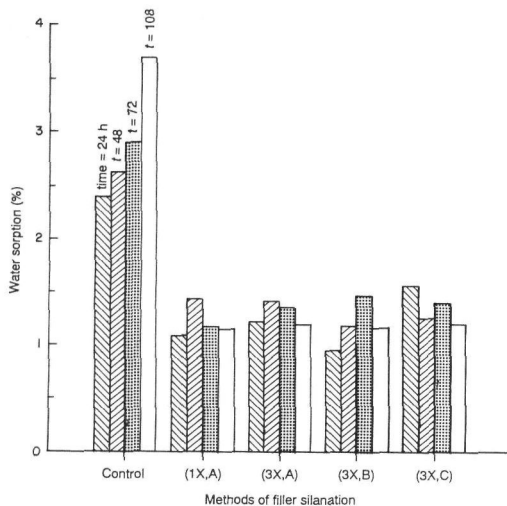
Fig. 6. Water sorption of composites containing APM silanated zirconia-silica after storage in water for 24–108 h.

Silanation of zirconia-silica-filled UDMA composites with either MAPM or APM resulted in statistically significant increases in diametral tensile and transverse strengths, and statistically significant decreases in water sorption compared with unsilanated controls. The analysis of variance using a two-way factorial design with $P < 0.01$ showed that the tensile and transverse strengths of silanated composites were significantly higher than unsilanated composites. The analysis also showed that composites with silanated fillers had significantly lower water sorption at all boiling times compared with unsilanated controls. The increase in strength is a result of the attachment of the silane to the inorganic filler and the organic matrix which improves the transfer of stress from one strong filler particle to another across the weaker organic matrix. The significant decrease in water sorption may result from either the bonds of silane to the filler being not readily hydrolysed by moisture, or the silane may provide some degree of protection to both the resin and the filler against hydrolytic deterioration. The hydrolytic deterioration according to Plueddemann (1982) is a result of either the breaking of chemical bonds in the resin or softening through the plasticizing action of water.

Although curing of the resin at 98°C in air for 108 h increased the tensile strengths 10 and 11%, respectively, for composites with MAPM and APM, immersion in boiling water for the same length of time resulted in statistically significant lower values of tensile strength for the composites silanated with either silanes using method A at 3X. The one-way analysis of variance for the fixed effect model at $P < 0.01$ showed that the strength values of the composites immersed in boiling water were statistically different from the strength values of the composites that were cured thermally in air. Also, the analysis of variance using the two-way factorial design with $P < 0.01$ showed that immersion in boiling water had a significant effect, decreasing the tensile strengths of controls and composites silanated with either MAPM or APM. This trend of decreasing the tensile strength of the control and the silanated samples could be caused by a plasticization effect by water. However, the decrease of the tensile strength with immersion time was more gradual for the composites silanated with MAPM, while it was more abrupt for the composites silanated with APM. The per cent retention of tensile strength for composites silanated with MAPM using method A at 3X were 82·0, 86·1, 72·9 and 69·5%, and for composites silanated with APM they were

74·0, 69·5, 77·5 and 71·2% for 24, 48, 72 and 108 h of immersion time. This result is an indication that the hydrolytic stability at the interface is different for the two silanes.

The method of silanation had a more significant effect on the tensile strengths of composites silanated with MAPM than APM. This observation was substantiated by two-way analysis of variance at $P < 0.01$. Silanation with MAPM from alcohol solution at 3X coverage gave the best initial tensile strength of 58 MPa, however, boiling in water for 108 h caused the value to decrease to 42 MPa. This latter value was still higher than any comparable composites silanated with APM of $32 - 39$ MPa. In general, the tensile strengths of composites silanated with MAPM degraded more slowly with boiling time in water than those silanated with APM, suggesting that the silane bond with MAPM was more stable by hydrolytic degradation. This suggestion is supported by lower water sorption for composites silanated with MAPM at 3X using method A compared to those silanated with APM.

The method of silanation using APM had less effect on the tensile strength of composites than those using MAPM. The greater variation in the tensile strengths of composites with MAPM using various methods may have resulted from poorer packing of the silanes at the surface using method A at 1X and the lower room temperature vapour pressure of MAPM using method B at 3X.

Silanation of the filler with either MAPM or APM resulted in highly statistically significant increases in transverse strength regardless of the time in boiling water, compared with the unsilanated controls. The initial transverse strength values for composites silanated by various methods with MAPM were in a different order than for the diametral tensile strengths. Method B at 3X gave the second highest initial transverse strength rather than method A at 3X for the highest initial diametral tensile strength. Samples silanated by method B at 3X, however, had large decreases in transverse strength after 24 h in boiling water. Also, only minor changes in transverse strength occurred, considering the variance among samples, after the first 24 h in boiling water, this effect was true regardless of the method of silanation.

Similar trends were observed for the transverse strength of samples silanated with APM. The method of silanation witn APM resulted in differences in transverse strength whereas much less effect of the method was observed for the diametral tensile strengths. Method B at 3X gave the highest initial transverse strength, and it had the largest decrease in strength after 24, 72 and 108 h. The rather small changes in transverse strength after the 24 h boiling period may result from a combination of the increased degree of conversion and extraction of low molecular weight fragments so that the degradation of silane bond may be obscured. If this observation is true, then the transverse test is a less critical predictor of degradation.

In general, silanation with MAPM produced composites that had gradual decreases in tensile and transverse strengths and gradual increases in water sorption with boiling time. Silanation of filler with MAPM using method A at 3X gave composites with the highest tensile and transverse strengths and the lowest water sorption. Silanation at 1X showed the same trends, but lower composite strengths and higher water sorption. Silanation of filler using method C appeared to be better than method B at 3X, because it gave higher tensile strength for composites and lower water sorption, although the higher transverse strength greatly decreased within 24 h of boiling time. Silanation with APM resulted in composites with abrupt decreases in tensile and transverse strengths and abrupt increases in water sorption. Silanation of filler using method C gave composites with the highest tensile strengths, while silanation using method B gave the composites the highest initial transverse strength that substantially decreased at 24 h of boiling time. The water sorption test had even less discrimination than the transverse strength test in assessing the methods of silanation. The increase in water sorption of the controls and the samples is a result of an increase of resin conversion and resulting polymerization shrinkage in boiling at 100°C, which could open more voids. The increase of the water sorption of the controls is evidence of such reaction taking place. The water sorption tests did, however, demonstrate the value of silanating fillers for composites. Statistically significant lower water sorption of composites with silanated fillers at all boiling times compared with unsilanated controls were found at $P < 0.01$. The lower water sorption of silanated composites most likely assists in maximizing their hydrolytic stability since less water will be at the inorganic-organic interface. One weakness of the water sorption test is that it assumes that the weight gain in the samples represents the water gain, when in reality it is the difference between the gain in water and the dissolution of low molecular

weight organics. Thus, the true water sorption values would be somewhat higher than those reported. However, a reliable comparison can be made between the water sorption values and the silanated samples since approximately the same amount of extractable material would be removed, except for the small differences in the oligomer content for the various treatments. Nevertheless, the water sorption value does indicate whether good silanation of the filler has occurred since the water sorption of the control continued to increase while the silanated samples had stable water sorption with increased time of boiling.

Acknowledgment

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