Effects of Silane Coupling Agent Amount on Mechanical Properties and Hydrolytic Durability of Composite Resin After Hot Water Storage

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The purpose of this study was to evaluate the effects of the silane coupling agent amount on the flexural properties and hydrolytic durability on an experimental composite resin for understanding the optimum amount of silanation. A spherical filler was silanated with 7 different amounts of  $\gamma$ -MPTS, 0, 0.17, 0.34, 0.66, 1.36, 2.72 and 5.45 mass%. Photopolymerized experimental composite resins were made from a 70/30 mass% of UDMA/TEGDMA and a 65 mass% of different silanated amounts of filler. Bar-shaped specimens were prepared for a 3-point bending test in 37°C water after 1-day water storage at 37°C and after an additional 1, 7, and 28 days hot water storage in Soxhlet's extractor. The flexural strength and flexural modulus of unsilanated filler dramatically decreased after 28 days hot water storage while those of silanated filler showed a slight change. These results suggested that the silanated amount on the silica filler is not sensitive for flexural properties and hydrolytic stability of composite resin.

Key words: y-MPTS, Flexural properties, Hydrolytic durability

### INTRODUCTION

Modern dental composite resins demonstrated improved mechanical properties and were widely used in many applications but the durability of composite resins is still ambiguous. The degradation of composite resin in the oral environment is considered to occur from resin matrix $^{1-3)}$ , the degradation of filler particles<sup>1,4,5)</sup> and hydrolytic instability of silane coupling agent at the polymer-silica interface layer $^{6,7)}$ . With respect to hydrolytic stability of the coupling agent, there are several approaches to improve coupling ability using novel silane coupling agents and/or the suitable silanation processes such as amount of silane coupling agent, heat application during silanation and pH of the silanation vehicle. More hydrolytic durable coupling agents were achieved by newly synthesized polyfunctional silanes  $^{8-10)}$ . However, the conventional coupling agent, gammamethacryloxypropyltrimethoxysilane,  $\gamma$ -MPTS, is still popular in silanating fillers.

The silane coupling agent adsorbed on the fillers creates bi-layer, chemisorbed and physisorbed silane layers. The chemisorbed silane is absorbed on the surface via covalent bond. The physisorbed layer is a loosely bound layer over the chemisorbed layer by hydrogen bond and van der Waals force among silane coupling molecules. Recently, Wang and Jones<sup>11)</sup> confirmed the deposited structure of  $\gamma$ aminopropyltriethoxysilane ( $\gamma$ -APS) on glass surface. Three layers from the glass surface are advocated: two types of the chemisorbed layer, a high hydrolytic resistance grafted "interfacial" layer and a removable chemisorbed layer, and the outer physisorbed layer. The physical and mechanical properties of this network depend on the nature of the silane deposited on the filler; *i.e.* amount of coupling agent, pH, rate of hydrolysis and condensation, and the drying condition used in silanation.

The silane coupling agent amount on the filler is important because the silane coupling agent creates a suitable filler morphology or thickness of silane to protect filler from hydrolytic degradation. Such an interface/interphase region plays some roles in determining mechanical properties and provides durability of the composite materials. Therefore, this study will focus on the amount of silane coupling agent absorbed on the silica surface. To date, there is no consensus on the amount of silane coupling agent, covering silica in providing optimal mechanical properties and durability of composite resin in moist environments such as in the oral environment. Most studies utilized the mass percentage of the filler to calculate the amount of silane coupling agent used. The common empirical amounts were 10 mass $\%^{12-14)}$ and 4 mass  $\%^{15)}$ . Mohson and Craig<sup>16)</sup> advocated three times of the recommended coverage amount based on surface area of silica and surface coverage of the silane coupling agent suggested by Akles<sup>17)</sup>. The existence of the excess amount over the uniform

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coverage is hypothesized responsible for the modulus of elasticity and to provide a more hydrolytic durability property to the composite resin.

Therefore, the purpose of the present study was to find the optimum amount of silane coupling agent based on the surface area and the number of functional groups of the silane coupling agent required to cover the silica filler, that provided both better mechanical properties and durability.

# MATERIALS AND METHODS

# Silanation of filler

The filler used in the present study was sphericalshaped silica filler (SS15, Osaka Chemical, Osaka, Japan),  $1.5 \,\mu$  m in diameter, surface area of 2.06  $m^2/g$ , and density of 2.2 g/cm<sup>3</sup>. Gamma-MPTS (KBM 503, Shin-Etsu Chemical, Tokyo, Japan) was used in silanating the filler. Seven concentrations in mass percentage of  $\gamma$ -MPTS, calculated based on surface area of filler and coverage surface area of  $\gamma$ -MPTS, used in silanation were 0, 0.17, 0.34, 0.66, 1.36, 2.72, and 5.45 mass%. The amount of coupling agent used in this study was based on the wetting surface area of silane and surface area of filler. The relationship of the amount of coupling agent required to obtain a minimum uniform coverage is the equation suggested by Arkles<sup>17)</sup>. The surface area of the filler used in the present study was 2.06 m<sup>2</sup>/g and  $\gamma$ -MPTS can cover the silica on  $314 \text{ m}^2/\text{g}$ . Therefore, one gram of the filler theoretically requires 0.0066 g of  $\gamma$ -MPTS (0.66%) for monolayer coverage. The proposed amount was 7.7 molecules/1  $nm^2$  of the filler surface area. Then, the amounts of the silane coupling agent, 0.17, 0.34, 0.66, 1.36, 2.72 and 5.45 mass%, were 2, 4, 7.7, 16, 32, 64 molecules/1 nm<sup>2</sup>, respectively.

The filler was silanated using 70 mass% ethanol aqueous solution at room temperature. After silanation, the filler was left dry at 25°C for 14 days prior to mixing with the resin matrix.

# Characteristics of silanated filler

Silanated filler of each concentration was investigated to understand its characteristics by an organic element analysis. Silanated filler before and after organic solvent cleaning were examined to confirm amounts of adherent silane coupling agents on the filler surface using an organic element analyzer (CHS Corder MT3, Yanaco, Tokvo. Japan). Silanated filler from each group was dispersed in tetrahydrofurane, THF, (Wako Pure Chemical, Osaka, Japan) and stirred. After stirring, the suspension was centrifuged discarded and the silica residue was rinsed with THF again. This procedure was repeated until the UV peak at 225 nm due to  $\gamma$ -MPTS was not observed in the supernatant solution. The filler was then dried at room temperature.

Percentage amounts of ash, carbon of fillers were analyzed. Four to 10 mg of fillers were heated at 950 °C for burning, 850°C for oxidization and 550°C for reducing with air and oxygen purging at 200 and 20 ml/min, respectively. The measurements were performed twice. The amounts of  $\gamma$ -MPTS were computed from the detected carbon weight based on the mass composition of carbon in the  $\gamma$ -MPTS molecule. This carbon ratio was assumed to be 40.7 mass%. The molecular ratio of  $\gamma$ -MPTS on the filler was calculated using the specific surface area of the filler, 2.06 m<sup>2</sup>/g.

Composite resin specimens for mechanical evaluation The resin matrix of all experimental composite was 70/30 mass% of urethane dimethacrylate (UDMA; Art resin SH-500B, Negami Chemical, Ishikawa, Japan) triethyleneglycol and dimethacrylate (TEGDMA; 3G, Shin Nakamura, Wakayama, Japan). Zero point five mass% of camphorquinone (Aldrich Chemical, Milwaukee, Wis) and 1.0 mass% of dimethylaminoethylmethacrylate (DMAEMA; Wako Pure Chemical, Osaka, Japan) were used as the photoinitiator and reducing agent, respectively. All materials were used as received without any further purification. The  $2 \times 2 \times 25$  mm rectangular specimen was fabricated as suggested in ISO  $4049:2000^{18}$ . The filler loading in all experimental composite resins was kept constant at 65 mass%. One hundred and sixty-eight specimens, 24 from each composite, were fabricated from seven experimental composite resins. The specimen was irradiated using a laboratory light-polymerizing unit (Labolight II, GC, Tokyo, Japan) for 3 minutes on each side. The specimen was later kept in the 37℃ water. After 24 hours storage in the incubator at 37°C, six specimens were randomly selected from each group and tested for baseline value on day 0. The remaining specimens were then placed in the Soxhlet's extractor and subjected to a boiling water condition for an additional 1, 7, and 28 days. At the end of each time, six specimens were again randomly selected and tested. All specimens were subjected to a 3-point bending test in the  $37^{\circ}$  water using a micro material test machine (MMT-250N, Shimadzu, Kyoto, Japan). Flexural strength and flexural modulus were obtained from each test using analyzing software (Trapezium II, Shimadzu, Kyoto, Japan). The data were analyzed using 2-way ANOVA and Tukey HSD. The statistic significance was considered at p < 0.05.

### SEM observation

Fracture surfaces of specimens after the flexural test were gold sputter coated and examined by secondary electron imaging using a scanning electron microscope (Hitachi S-4500, Tokyo, Japan).

# RESULTS

#### Organic elemental analysis

Figure 1 showed the detected amount of  $\gamma$ -MPTS molecules before and after THF cleaning. Before THF cleaning, the  $\gamma$ -MPTS amount increased with the increasing silanated amount of  $\gamma$ -MPTS. Organic elemental analysis could not detect the carbon content in the 0.17% group due to the small amount



Fig. 1 Detected amount of  $\gamma$ -MPTS molecules from various silanated amounts before and after THF cleaning.

of  $\gamma$ -MPTS, which was less than the detectable limit of the apparatus. Therefore the exact amounts of silanated coupling agents of all fillers could not be calculated. While the detected amount of  $\gamma$ -MPTS molecule after THF cleaning did not change regardless of the increase in the silanated amount of  $\gamma$ -MPTS. The amount of silane chemisorbed on the silica increased with the increase of the silane amount in the treated solution. When the silane concentration was above 0.66%, the chemisorbed amount of silane leveled off. This implied that the saturated amount of silane chemisorbed on the 1 nm<sup>2</sup> of silica surface was approximately 8 molecules. The silane molecules, which could not be chemisorbed on the silica surfaces, existed on the chemisorbed silane layer as a physisorbed silane.

### Flexural strength and flexural modulus

The flexural strength, flexural modulus and their standard deviations are shown in Table 1. The flexural strengths of the unsilanated group, 32.4 to 47.8 MPa, were smaller than those of silanated groups, 96.6 to 119.0 MPa. The flexural strengths slightly increased at 1 or 7 days storage. The flexural moduli at 0 day, 3.1 to 3.6 GPa, were fairly similar regardless of silane amounts. The flexural moduli of silanated groups slightly increased at 1 or 7 days storage, while those of the unsilanated group decreased with longer storage periods. Because the

Table 1 Flexural strengths (MPa) and flexural moduli (GPa) after hot water storage

	Amount of coupling agent (mass%)								
Storage period (day) -	0	0.17	0.34	0.66	1.36	2.72	5.45		
Flexural strength						·			
0	$43.8 \pm 5.4$	$96.6 \pm 5.2$	$103.1 \pm 8.7$	$111.3 \pm 7.7$	$112.8 \pm 9.4$	$105.0 \pm 6.8$	$102.2 \pm 12.8$		
1	$47.8 \pm 4.3$	$113.4 \pm 8.3$	$113.1 \pm 8.2$	$112.7 \pm 10.1$	$117.4 \pm 13.8$	$117.6 \pm 7.3$	$108.8 \pm 11.8$		
7	$41.5 \pm 3.8$	$110.1 \pm 10.0$	$115.4 \pm 6.5$	$115.7 \pm 13.8$	$118.0 \pm 19.2$	$116.9 \pm 9.6$	$109.2 \pm 12.2$		
28	$32.4 \pm 1.7$	$99.7 \pm 2.6$	$109.7 \pm 6.5$	$119.0 \pm 12.8$	$110.4 \pm 12.0$	$114.2 \pm 17.7$	$113.7 \pm 11.7$		
Flexural modulus									
0	$3.5\pm0.6$	$3.2 \pm 0.4$	$3.6\pm0.5$	$3.6\pm0.3$	$3.6\pm0.4$	$3.4 \pm 0.1$	$3.1 \pm 0.3$		
1	$3.1\pm0.4$	$3.9\pm0.4$	$3.9\pm0.5$	$3.7 \pm 0.2$	$3.8 \pm 0.6$	$3.9\pm0.4$	$3.2 \pm 0.5$		
7	$1.8 \pm 0.2$	$3.8 \pm 0.3$	$4.1 \pm 0.3$	$3.5\pm0.3$	$3.9\pm0.3$	$3.9 \pm 0.3$	$3.8 \pm 0.3$		
28	$1.2 {\pm} 0.1$	$3.4\pm0.9$	$3.7\pm0.5$	$3.9\pm0.3$	$3.8\pm0.5$	$3.7\pm0.4$	$3.6\pm0.3$		
							$\pm$ s.d, n=6		

Table 2 Result of 2-way ANOVA regarding flexural strengths

Table 3	Result	of	2-way	ANOVA	regarding	flexural
	moduli					

Strengths					
Factors	Df	SS	MS	F Ratio	Probability
A: amount of coupling agent	5	1833	366.6	2.84	0.019
B: immersed period	3	1887	629.0	4.87	0.003
A×B	15	1269	84.6	0.65	0.824
Error	120	15516	129.3		
Total	143	20505			

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Factors	Df	SS	MS	F Ratio	Probability
A: amount of coupling agent	5	23391	4678	2.92	0.016
B: immersed period	3	30778	10259	6.41	0.001
A×B	15	27996	1866	1.17	0.308
Error	120	192174	1601		
Total	143	274339			

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Fig. 2 Effects of amount of silane coupling agent and immersion period on flexural strength. Bars with the same superscript were not significantly different (p>0.05).



Fig. 3 Effects of amount of silane coupling agent and immersion period on flexural modulus. Bars with the same superscript were not significantly different (p>0.05).





b





Fig. 4 Typical SEM images of the fracture surfaces after 28-day hot water immersion. a: unsilanated, b: 0.17 mass%, c: 0.66 mass%, d: 5.45 mass%.

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data between unsilanated and silanated groups were so greatly different therefore the unsilanated group was excluded from statistic analysis. For both flexural strength and flexural modulus of silanated groups, 2-way ANOVA revealed the significance of two main factors, amounts of silane coupling agent and immersion periods, but not their interaction (Table 2 and 3). Regarding amounts of silane coupling agent, flexural strengths of the 0.66% and 1.36% groups were significantly greater than the 0.17% group (Fig.2). The flexural moduli of the 0.34% group were significantly greater than the 5.45% group. Regarding the effect of immersion period, flexural strengths after 1 and 7 days boiling water storage were significantly greater than that of 0 day boiling water storage (Fig. 3). The flexural modulus of 0 day was significantly smaller than those of the others.

### $S\!E\!M$ observation

Figure 4 shows a typical different SEM image of the fracture surfaces between unsilanated and silanated groups. The unsilanated group obviously showed filler surface without resin matrix coverage. Therefore, the fracture of the unsilanated group was considered to occur at the interface between the fillers and matrix resin. On the contrary, the silanated group exhibited coverage of matrix resin on the filler surface. This finding suggested good bonding between fillers and matrix resin when fillers were silanated. There were no obvious differences at the fracture surfaces among the silanated groups.

# DISCUSSION

The result of organic elemental analysis suggested that at least two types of silane layers were absorbed on the silica surface. One layer, the chemisorbed layer, could not be removed through rinsing filler by THF. The second layer, the physisorbed layer, could be easily removed by THF. The amount of chemisorbed silane increased with the increased amount of silane coupling agent in the silane solution until saturation. The amount over 0.66% then became physisorbed silane as demonstrated in Fig. 1. This finding was not in agreement with that of Nishiyama *et al.*<sup>19)</sup>, whose study was based on colloidal silica. They found that the saturated chemisorbed amount of  $\gamma$ -MPTS occupied 1 nm<sup>2</sup> of silica surface was 2 molecules. This amount was found to be a specific property of  $\gamma$ -MPTS regardless of substrate as demonstrated by Miller and Ishida<sup>20)</sup> on clay and lead oxide. The difference in this characteristic of absorption may be due to the effect of filler size, as both studies used a very small particle size. The greater in the amounts of silane than the previous reports were attributed to the adsorption of the silane oligomer. The condensation reaction of

the silane molecules on the silica surface simultaneously occurs along with condensation among the silane molecules with a slower rate. Therefore, the higher molecular weight molecules such as tetramer, trimer or dimer would be chemisorbed on the silica surface. SEM images showed the interfacial fracture only in the unsilanated group. The unsilanated group was degraded upon it being subjected to moist heat in the Soxhlet's extractor. This indicated that the Soxhlet's extractor could accelerate degradation of the composite resins. Accelerated aging using the Soxhlet's extractor was intended to promote hydrolysis of the silane layer. But only a slight decrease in the flexural strength and flexural modulus of the silanated composite was observed over time. This may be due to the reversible bonding characteristic between physisorbed and chemisorbed layers.

The present study showed that the filler silanated with slightly under or over the amount of silane coupling agent calculated by the equation of Arkles was adequate enough to provide the composite with strength and hydrolytic durability. The effect of silane coupling agent amount on the filler was similar to that in a report by Wang and Jones<sup>21)</sup>.

The initial flexural modulus decreased as the amount of physisorbed silane increased. If the silane molecule dispersed in the resin matrix, the modulus would decrease due to the plasticizer effect of silane molecules<sup>22)</sup>. The flexural moduli of silanated groups increased after 1 day boiling water storage, which can be explained by the effect of heating from the Soxhlet's extractor causing the postpolymerization of matrix resin. The result shows that the amount of silane has a slight effect on the flexural strength and hydrolytic durability of composite resin.

The silane coupling agent forms a bi-layer consisting of the chemisorbed and the physisorbed silane species on the filler surface. The interface is maintained at the equilibrium, which allows for effective stress transfer between the matrix and filler resulting in a composite with high strength, high modulus and hydrolytic durabiliy. Therefore, manufacturers can tailor the composite resin properties by varying the amount of silanation. The effect of the silanated amount is not sensitive in flexural properties and durability as shown in the present study. Specifically, the physisorbed silane species does not affect the hydrolytic stability of the composite resin.

### CONCLUSION

The effects of the amount of silane coupling agent on the flexural properties and hydrolytic durability on an experimental composite resin were evaluated to understand the optimum amount of silanation. Within the limitation of the present study, even the small amount of silane coupling agent could provide the composite with good flexural properties and

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durability after 28 days in hot water storage.

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