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EFFECT OF SPHERICAL SILICA FILLER ADDITION ON IMPROVING THE CHARACTERISTICS OF RESIN-MODIFIED GLASS IONOMER CEMENT

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ABSTRACT

This study investigated the effects of spherical silica fillers on the physical and mechanical properties of resin-modified glass-ionomer cement (RMGIC), the material itself and its behavior in tooth cavities. Specimens were fabricated by mixing untreated (UF) or silanized (SF) spherical silica filler into the powder of a commercially prepared RMGIC. In correlation with marginal gap formation in the tooth cavity, these influencing factors were also examined: marginal gap and setting shrinkage of cement in the Teflon mold, as well as the shear bond strength to tooth substrate. The original RMGIC and a preparation containing 20wt% spherical silica filler were also examined with regard to their fractured surface and fluoride release. The fillers increased the compressive strength remarkably: up to 17% in the case of SF and 9% in the case of UF. Both UF and SF increased the flexural strength by up to 17%. The addition of SF increased the DTS up to 38%, but UF decreased the DTS. The addition of SF improved the workability and the mechanical properties of the RMGIC. When compared with the control (*i.e.* original RMGIC), the addition of SF significantly decreased immediate marginal gap in tooth cavities and setting shrinkage in Teflon mold up to 63% and 66% respectively. Fluoride release was significantly reduced too. Apart from these results, this study showed that addition of 5wt% SF increased the shear bond strength to human enamel and dentin.

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Contents:

CHAPTER 1

INTRODUCTION

Until the 1990s amalgam was the worldwide, all-round material of choice especially for posterior restorations in primary and permanent teeth. However, changes have occurred for several reasons. The development of alternative tooth-colored restorative materials as well as the controversy over the possible, potential side effects of amalgam has had an influence on the selection of restorative materials. The dramatic reduction in caries during the last decades, together with the increased welfare in the industrialized world, calls for treatment with materials other than amalgam[1)]. Moreover, in some countries, environmental and health authorities have placed increasing pressure on dentists to reduce the use of dental amalgam with the intention of protecting the environment and, hence, the population from exposure to mercury[1-5)]. Therefore, alternative restorative materials to amalgam were in progressively developed. One of the alternative materials is glass-ionomer cement (GIC).

The first glass-ionomer materials were developed in the Laboratory of the Government Chemist in England during the late 1960s as a result of a systematic attempt to develop an adhesive material for dental use[6,7)]. The original GIC consisted of an aqueous solution of poly (acrylic acid) at a concentration of about 45%, which was reacted with a powder of ion leachable glasses that based on SiO_2-Al_2O_3-CaF_2-$AlPO_4$-Na_3AlF_6 composition[8-10)]. The Al_2O_3/SiO_2 ratio is required to be 1:2 or more and the F content can be up to 23%. Later glasses in commercial materials contained more sodium and less fluoride. One of typical compositions of the glass in %mass is SiO_2 (41.9%) – Al_2O_3 (28.6%) – CaF_2 (15.7%) –

NaF (9.3%) – $AlPO_4$ (3.8%) – AlF_3 (1.6%). More recently glasses containing Sr, Ba and Zn have been used in commercial material[9]. The liquid component of the original GIC was aqueous polyacrylic acid. Since a low molecular weight was required to achieve a high concentration without gelation, an acrylic acid-itaconic acid copolymer has been used. The principal additional copolymer materials in practical use appear to have been acrylic acid – maleic acid, and acrylic acid–3–butene–1,2,3–tricarboxylic acid. The introduction of dicarboxylic or tricarboxylic acid into the polymer chain not only prevents gelation of liquid, but also provides greater reactivity because of the increasing number of carboxyl groups per chain unit and the higher acidity. The setting reaction of GIC is complex and may vary with composition. In general, it has been represented[8,9] as an acid-base reaction between the polyacid liquid and the glass in which Ca and Al ions are released by attack on the surface of the glass particles and ultimately cross-linking of the polyacid chains into a network. This ion release is facilitated by tartaric acid that readily forms complexes with these ions, which form a molecular structure with the polyacrylate chains[11]. Initial setting (gelation) is now regarded as due to chain entanglement as well as weak ionic cross-linking which corresponds with the viscoelastic behavior of the freshly set material[9]. The final set structure has been presented as a complex composite of the original glass particles sheathed by a siliceous hydrogel and bonded together by a matrix phase consisting of hydrated fluoridated calcium and aluminum polyacrylates[8,9].

When GIC was introduced into dental use, the original intention was to develop a material for several different applications, such as restoration of anterior teeth, filling of erosion cavities, general cementation purposes, fissure sealant, cavity lining and root-end

filling material[6,7,12-14]. All these original aims have been realized, and even further applications have been developed, since GICs possess certain properties that make them useful as filling materials for restorations, including release of fluoride ions, reduced enamel demineralization due to reduction in the level of *S. mutans*, chemical bonding and a similar coefficient of thermal expansion to teeth[14-23]. GICs are, however, brittle and exhibit limited mechanical strength and low wear-resistance[24].

Newer versions of light-cured glass-ionomers are known as resin-modified glass-ionomer cements (RMGICs). The main composition of RMGIC is fluoroaluminosilicate glass and pigments in the powder, while the liquid contains copolymer of polyacrylic acid, maleic acid, distilled water and HEMA[25-28], or a powder that contains of calcium-aluminum-fluorosilicate, freeze-dried tartaric acid, freeze dried poly(acrylic acid) and a liquid of distilled water[13]. RMGICs combine the favorable properties of GICs with those of resin composites. These include the inherent adhesion and cariostatic properties of the former and the command setting behavior, good mechanical properties, and wear resistance of the latter[22,29-31]. Compared with conventional analogs, RMGICs have been characterized as having a longer working time, a rapid set, improved appearance and translucency, in addition to a higher early strength along with higher bond strength to enamel and dentin[25,32-37]. The weak organic-salt matrix of GIC is strengthened by modification of the resin as in methacrylate modified systems. As a result, RMGICs also have less microleakage than conventional GICs[34-36,38]. However, RMGICs still need surface protection to reduce margin microleakage[28,39,40], and they also show less fluoride release and caries resistance than GICs[32].

To improve cement strength and wear-resistance, McLean, Gasser and Simmons added metals to the powder component of GIC[22,41]. Kobayashi *et al.* and Kawano *et al.* added glass short fibers ($CaO-P_2O_5-SiO_2-Al_2O_3$) to GIC[33,42], while Yap *et al.* and Arita *et al.* added hydroxyapatite particles to improve the mechanical properties and microstructural properties of GIC[43,44]. However, the use of spherical silica filler in RMGIC has not been reported in spite of its great potential to increase the flowability of GICs. Besides, the success of the spherical silica filler addition would have a greater value if it could reduce the marginal gap or microleakage and possess other advantages in correlation with the tooth substrate.

Therefore, in this study, the first hypothesis to be tested was that the addition of spherical silica filler would significantly increase the workability and mechanical properties of RMGIC, and there was a correlation among the filler content, consistency and compressive strength. The second hypothesis was that the addition of spherical silica filler would decrease the water uptake of RMGIC. The third hypothesis was that the addition of spherical silica filler would reduce the fluoride release of RMGIC. The fourth hypothesis was that the addition of SF to RMGIC would reduce the immediate and 24-hour marginal gaps in tooth cavities. The final hypothesis was that the marginal gap and rate of setting shrinkage in Teflon mold, and the shear bond strength of RMGIC would influence marginal gap formation in tooth cavities. Since it is reported in a one year *in vitro* study that long-term water storage did not decrease the values of compressive strength, compressive modulus or diametral tensile strength[25], and the weight increased very quickly

in the first day of immersion in water following Fick's law[45], in this study the immediate and or the 24-hour properties were observed.

In chapter 2, the preparation of silanized spherical silica filler was discussed. Then, the effect of spherical silica filler addition to the consistency and compressive strength of RMGICs was evaluated and discussed.

In chapter 3, the measurement of various mechanical properties and water uptake of RMGICs based on the maximum workability were evaluated and discussed.

In view of the fact that the using of GIC is still continuous because of its fluoride release, in chapter 4 the fluoride release from RMGICs were analyzed and discussed.

Since the addition of spherical silica filler to the RMGICs may influence their capability in bonding with the tooth substrates, and for resin contained restorative materials the bond strength to dentin is different with that to enamel[46]; the shear bond strengths to dentin and enamel were observed. The results of shear bond strength and marginal gap of RMGICs were analyzed and discussed at the last part, in chapter 5.

CHAPTER 2

SILANIZATION, CONSISTENCY AND COMPRESSIVE STRENGTH MEASUREMENT

2.1. INTRODUCTION

Silane coupling agents are used to reinforce the adhesion of filler to matrix polymer and also to increase hydrolitic stability[47,48]. The organofunctional silane γ-methacryloxy propyl trimethoxysilane (γ-MPTS) is the filler-matrix coupling agent most commonly utilized for dental resin-based composite materials to chemically bond to the filler surface and co-polymerize with the methacrylic polymer[49,50]. Therefore, in this chapter the effects of original unsilanized filler and silanized filler on the consistency and compressive strength of RMGIC were observed.

In addition to mixing procedure[51], the powder/liquid ratio (P/L) is important to be considered in mechanical strength test of material, which consists of powder and liquid, since it has already been known that increasing the P/L leads to a decrease in consistency.

Therefore, the hypothesis was that the addition of spherical silica filler would significantly increase the workability and compressive strength of RMGIC, and there was a correlation among the filler content, consistency and compressive strength of the RMGIC.

2.2.MATERIALS AND METHODS

2.2.1. *Materials*

The RMGIC material used in this study was Fuji II LC EM (powder Lot #0205211, liquid Lot #0204301, GC Corp., Tokyo, Japan) with a recommended P/L of 3.0. The detailed composition of the material has not been released. But according to

manufacturer's information, it was given that the powder is fluoro–alumino–silicate glass, and the liquid is composed of methacrylic acid ester, polyacrylic acid and water.

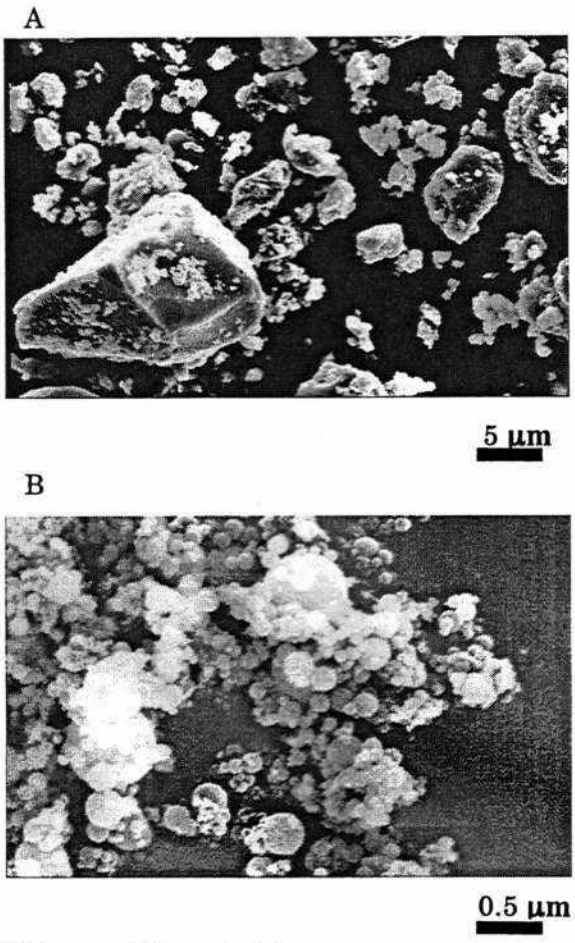


Fig.2.1 SEM images of the materials.

A. Powder of the original RMGIC.

B. Spherical silica filler has an average particle diameter of 0.3 μm.

The spherical silica filler (GC, Tokyo, Japan) has an average particle diameter of 0.3 μm (Fig.2.1). γ- MPTS (KBM 503, Shin-Etsu Chemical Co., Tokyo, Japan) was used to silanize the untreated filler. Spherical silica filler particles (15 g) were immersed in γ-MPTS solution [0.30 g of γ-MPTS, 0.15 g of CH_3COOH (Nakarai Chemical Ltd. Kyoto, Japan), 15 g of ethanol (Wako Chemical, Osaka, Japan) and 15 g of H_20] at room

temperature for 10 minutes. The slurries were stirred and heated at 95°C for 1 hour, then tray dried at 65°C for 24 hours.

The RMGIC powder was modified by initially mixing it with either the untreated spherical silica filler (UF) or silanized spherical silica filler (SF) at different weight percentages (5%, 10% and 20%), before mixing it with Fuji II LC EM liquid. The mixing method was to shake 5.000 ± 0.050 g of mixture in a 50-ml bottle by hand with a frequency of 120 cycle/min and an amplitude of 20 cm. The prepared cement powders are noted as UF5, UF10, UF20, SF5, SF10, and SF20 — hence indicating the type of filler added and its filler content in weight percentage.

A visible-light curing unit (New Light VL-II, GC, Tokyo, Japan, irradiated diameter: 10 mm) was used for activating the specimens, and close contact was ensured between exit window of the lamp and glass plate. The light intensity was checked and maintained at 450 mW/cm^2 before each application of restorative material using a radiometer (Demetron/Kerr, Danbury, CT, USA).

2.2.2. *Determination of the surface of silica after silanization*

In order to evaluate the silane coupling agent adsorbed on the surface of the silica, trifluoropropyl trimethoxysilane (FPTS) (KBM 7103, Shin-Etsu Chemical Co., Tokyo, Japan) containing fluoride was used as a tagged coupling agent. Silica plates (Lot #SK-4303, Sumikinsekiei, Tokyo, Japan) were used since they allowed for a more standardized and detailed quantification of the silane coupling agent attached to the surface of the silica.

The three following groups were chemically analyzed using X-ray photoelectron spectroscopy (XPS).

(1) Silica plates were immersed in FPTS solution (0.30 g of FPTS, 0.15 g of CH_3COOH,

15 g of ethanol and 15 g of H_20) at room temperature for 10 minutes, heated at 95°C for 1 hour, and dried at 65°C for 24 hours.

(2) Silica plates were silanized as mentioned above, immersed in distilled water at room temperature for 2 hours and air-dried.

(3) Silica plates were silanized as mentioned above, immersed in the Fuji II LC EM liquid at room temperature for 2 hours, rinsed off with distilled water, rinsed again with acetone and air-dried.

All silica plates were analyzed *in vacuo* of less than 10^{-7} Pa using an AXIS-HS spectrometer (Kratos Analytical, Manchester, UK). Al-Kα monochromatic X-rays with a power source of 150 W were utilized. Wide and arrow scans were measured at a pass energy of 80 and 40 eV, respectively. Quantitative data were obtained from peak areas[50].

2.2.3. *Consistency measurements*

The RMGIC was mixed with a P/L of 2.8 to 4.8 (g/g). Since hand mixing produced a significantly greater compressive strength and Vickers hardness, and less roughness after abrasion[51,52], mixing procedure was taken by hand. Both the mixing time and preparation time were 30 seconds each. Then, 0.05 cc of mixed glass-ionomer cement was placed on a glass plate. Within 2 minutes of the start of mixing, a force of 127 N was applied to the top of the plate and left for 1 minute. The maximum and minimum diameters of material were measured using a vernier caliper (U39818, Mitutoyo, Kawasaki, Japan) and the mean result was recorded to the nearest 0.05 mm.

2.2.4. *Compressive strength measurements*

For the preparation of compressive strength samples, a cylindrical Teflon split mold with a depth of 6.0 mm and diameter of 3.0 mm was used to minimize the stress exerted on

the specimens during their retrieval.

All specimens were mixed in 30 seconds using a plastic spatula on a mixing pad, loaded into a Teflon split mold using a syringe tip (Centrix C-R Syringe System; Centrix, Shelton, CT, USA), covered with a glass plate and clamped. Taking into consideration the thickness of the glass plate and the specimens, the specimens were light cured for 60 seconds on each side. Then, they were removed from the mold, varnished and immersed in distilled water. After storage for 24 hours in a 37°C incubator, the compressive strength was measured using a universal testing machine (Autograph DCS-2000, Shimadzu, Kyoto, Japan) with a cross-head speed of 0.5 mm min^{-1} outlined in ISO 7489-1986[53], with a maximal external force of 200 kgf (1960 N). Then the compressive strength were calculated using the following formula:

$$\sigma = 4F/\pi d^2$$

where σ is the compressive strength, F is the maximum applied load (in Newton) at the point of the fracture and d is the measured mean diameter of the specimen (in mm).

Six specimens were prepared for each of the material and conditions. All dimensions were measured using a digital micrometer (293-421-20, Mitutoyo, Kawasaki, Japan). All procedures, except for mechanical testing, were performed in a thermo-hygrostatic room kept at 23 $\pm$ 0.5°C and 50 $\pm$ 2%.

2.2.5. *Statistical analysis*

The results of measurements were analyzed using an ANOVA and Tukey test, with the level of significance set at 0.05[54]. The difference among the regression lines of the data was compared with a *t*-test[55].

2.3. RESULTS

2.3.1. *Determination of the surface of silica after silanization*

Fig.2.2 shows the XPS wide-scan spectra of silanized silica plates. Fluoride peaks were detected on the surfaces of treated silica plates, indicating that the silane coupling agent presents on the surfaces. It was found that the fluoride peaks area of samples 1, 2 and 3 did not differ significantly.

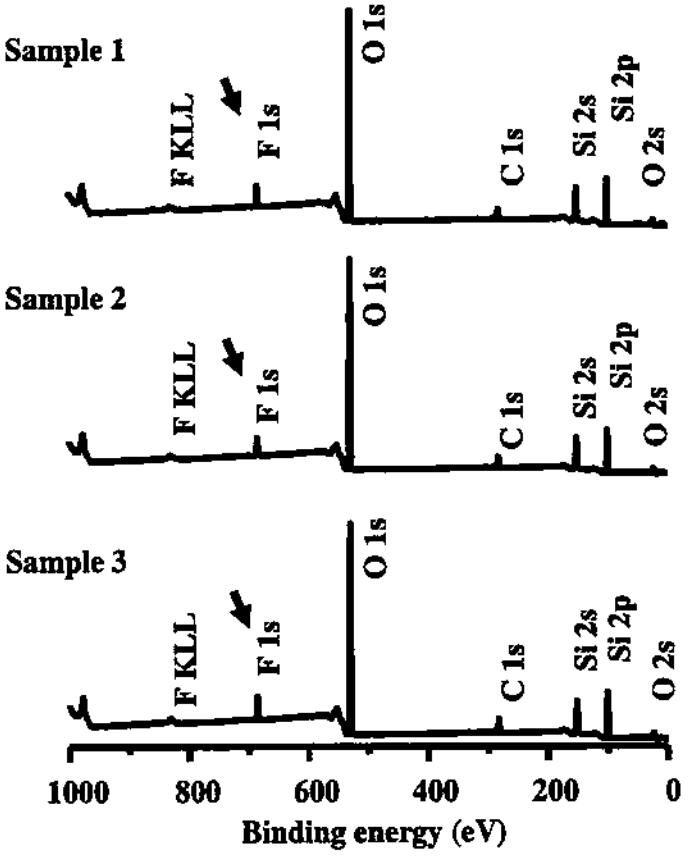


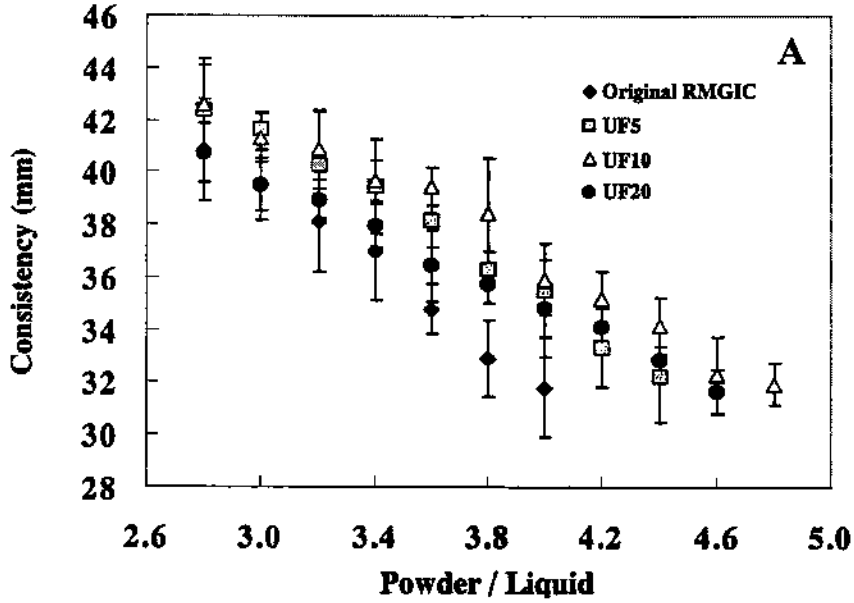
Fig.2.2 XPS images of silanized silica plates.
Arrows indicate the fluoride peaks of the spectra.

2.3.2. *Consistency*

Fig. 2.3 presents the results of consistency tests. The original RMGIC can be mixed at a P/L of up to 4.0. The addition of 5wt% SF or UF made it possible to use a P/L of up to 4.4, while the addition of 10wt% SF or 20wt% UF made it possible to use a P/L up to 4.6. The addition of 10wt% UF or 20wt% SF allowed the RMGIC to be mixed with a P/L of up to 4.8.

At a P/L of 3.0, the value recommended by the manufacturer, the consistency of the RMGIC was 39.52 $\pm$ 1.00 mm. Increasing the P/L to 4.0 (max.) caused the consistency to decrease to 31.79 $\pm$ 1.86 mm. For the UF5, UF10 and UF20, consistency values at P/L 3.0 were 41.68 $\pm$ 0.59 mm, 41.31 $\pm$ 0.95 mm and 39.48 $\pm$ 1.34 mm, respectively. At the P/L maximum, the consistency decreased to 32.23 $\pm$ 1.76 mm, 31.93 $\pm$ 0.79 mm and 31.66 $\pm$ 0.84 mm. For the SF5, SF10 and SF20, consistency values at P/L 3.0 were 41.04 $\pm$ 1.54 mm, 41.33 $\pm$ 1.10 mm and 36.92 $\pm$ 0.97 mm, respectively. At the P/L maximum, these values decreased to 31.77 $\pm$ 2.33 mm, 32.13 $\pm$ 0.68 mm and 31.03 $\pm$ 0.35 mm.

The regression analysis of the correlation between P/L and consistency gave linear results with $r = -0.99$ and $p < 0.001$. The gradient for the original RMGIC is –7.81, while the gradients for the SF5, SF10 and SF20 were –6.26, -5.56 and –3.39, and those for the UF5, UF10 and UF20 were –6.53, -5.56 and –4.92, respectively. The comparison of the regression analysis of the correlation between P/L and consistency is presented in Table 2.1. There are significant differences among the materials ($p < 0.01$ or less). However, there was no significant difference between the regression lines of the SF5 and SF10, the UF10 and UF20 or the SF5 and UF5.



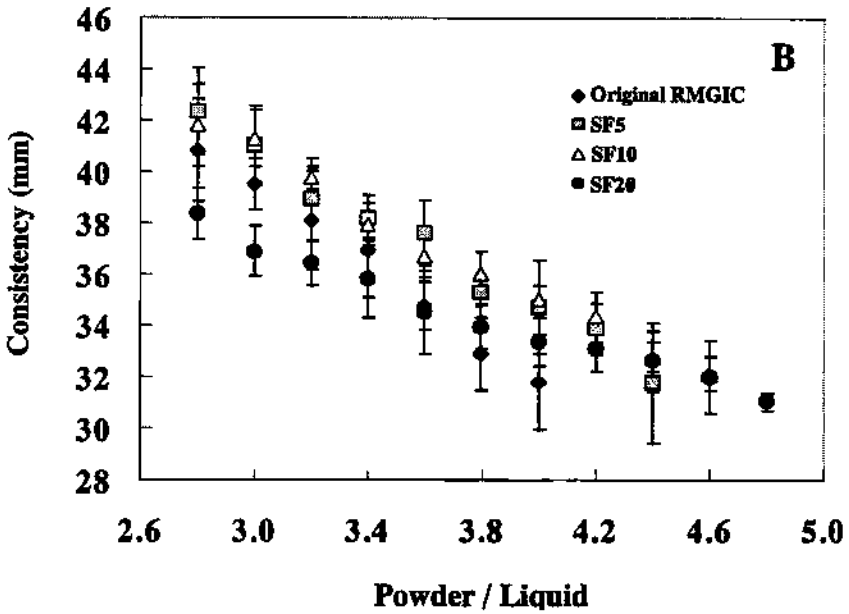


Fig.2.3 Powder / liquid vs. consistency of spherical silica filler-added RMGIC; n = 6.

A. The correlation in UF-added RMGIC.

Original RMGIC	y = 7.81 x + 62.96	r = 0.99	p < 0.001
UF5	y = 6.53 x + 61.22	r = 0.99	p < 0.001
UF10	y = 5.56 x + 58.55	r = 0.99	p < 0.01
UF20	y = 4.92 x + 54.48	r = 0.99	p < 0.001

B. The correlation in SF-added RMGIC.

Original RMGIC	y = 7.81 x + 62.96	r = 0.99	p < 0.001
SF5	y = 6.26 x + 59.64	r = 0.99	p < 0.001
SF10	y = 5.56 x + 57.37	r = 0.99	p < 0.001
SF20	y = 3.39 x + 47.25	r = 0.99	p < 0.001

Table 2.1 Differences in P/L vs. consistency regression analysis of the original RMGIC and spherical silica filler-added RMGIC

Comparison			Significance*
Original RMGIC	vs.	UF5	$p < 0.001$
		UF10	$p < 0.001$
		UF20	$p < 0.001$
UF5	vs.	UF10	$p < 0.01$
		UF20	$p < 0.001$
UF10	vs.	UF20	$p > 0.05$ (NS)
Original RMGIC	vs.	SF5	$p < 0.001$
		SF10	$p < 0.001$
		SF20	$p < 0.001$
SF5	vs.	SF10	$p > 0.05$ (NS)
		SF20	$p < 0.001$
SF10	vs.	SF20	$p < 0.001$
UF5	vs.	SF5	$p > 0.05$ (NS)
UF10	vs.	SF10	$p < 0.001$
UF20	vs.	SF20	$p < 0.001$

* : Analyzed using the t-test[54]

2.3.3. *Compressive strength*

The effect of the spherical silica fillers on the compressive strength of the materials is summarized in Fig.2.4. At P/L 3.0, the compressive strength of RMGIC is 153 ± 4 MPa. Increasing the P/L to 4.0 (max.) increased the compressive strength to 170 ± 6 MPa. For the UF5, UF10 and UF20, the compressive strength values at P/L 3.0 were 160 ± 5 MPa, 139 ± 6 MPa and 121 ± 6 MPa, respectively. At the P/L maximum, the compressive strength was 185 ± 6 MPa, 168 ± 16 MPa and 158 ± 7 MPa. For the SF5, SF10 and SF20, the compressive strength values at P/L 3.0 were 153 ± 6 MPa, 160 ± 5 MPa and 149 ± 4 MPa, respectively. At the P/L maximum, these values increased to 193 ± 5 MPa, 196 ± 6

MPa and 199 ± 8 MPa.

The regression analysis of the correlation between P/L and compressive strength gave linear results ($r = 0.86$ or more and $p < 0.05$ or $p < 0.001$). The gradient for the original RMGIC is 17.27. The gradients for the SF5, SF10 and SF20 were 28.32, 27.60 and 25.81, while those for the UF5, UF10 and UF20 were 18.15, 17.32 and 19.80, respectively. The comparisons of these regression analyses are presented in Table 2.2. There was no significant difference among the regression lines of the SF5, SF10 and SF20, between the regression lines of the original RMGIC and SF20, also between the regression lines of the original RMGIC and UF5.

Table 2.2 Differences in P/L vs. compressive strength regression analysis of the original RMGIC and spherical silica filler-added RMGIC

Comparison			Significance*
Original RMGIC	vs.	UF5	$p > 0.05$ (NS)
		UF10	$p < 0.01$
		UF20	$p < 0.001$
UF5	vs.	UF10	$p < 0.001$
		UF20	$p < 0.001$
UF10	vs.	UF20	$p < 0.001$
Original RMGIC	vs.	SF5	$p < 0.001$
		SF10	$p < 0.05$
		SF20	$p > 0.05$ (NS)
SF5	vs.	SF10	$p > 0.05$ (NS)
		SF20	$p > 0.05$ (NS)
SF10	vs.	SF20	$p > 0.05$ (NS)
UF5	vs.	SF5	$p < 0.001$
UF10	vs.	SF10	$p < 0.001$
UF20	vs.	SF20	$p < 0.001$

* : Analyzed using the t-test[54)]

The correlation between consistency and compressive strength is presented in Fig.2.5. The regression analysis of the correlation gave linear results ($r = -0.81$ or more and $p < 0.05$ or less). The gradient of the original RMGIC was –2.08. The gradient of the SF5, SF10 and SF20 were –4.50, -4.88 and –7.79, while those of UF5, UF10 and UF20 were –2.71, -2.94 and –4.00, respectively. The comparison of the regression analysis of the correlation between consistency and compressive strength is shown in Table 2.3. With the exception of RMGIC and UF10 ($p > 0.05$), the regression analysis of the correlation between consistency and compressive strength showed significant differences among the materials ($p < 0.05$ or less).

Table 2.3 Differences in consistency vs. compressive strength regression analysis of the original RMGIC and spherical silica filler-added RMGIC

Comparison			Significance*
Original RMGIC	vs.	UF5	$p < 0.001$
		UF10	$p > 0.05$ (NS)
		UF20	$p < 0.001$
UF5	vs.	UF10	$p < 0.001$
		UF20	$p < 0.001$
UF10	vs.	UF20	$p < 0.001$
Original RMGIC	vs.	SF5	$p < 0.001$
		SF10	$p < 0.001$
		SF20	$p < 0.001$
SF5	vs.	SF10	$p < 0.05$
		SF20	$p < 0.001$
SF10	vs.	SF20	$p < 0.001$
UF5	vs.	SF5	$p < 0.01$
UF10	vs.	SF10	$p < 0.001$
UF20	vs.	SF20	$p < 0.001$

*: Analyzed using the t-test[54)]

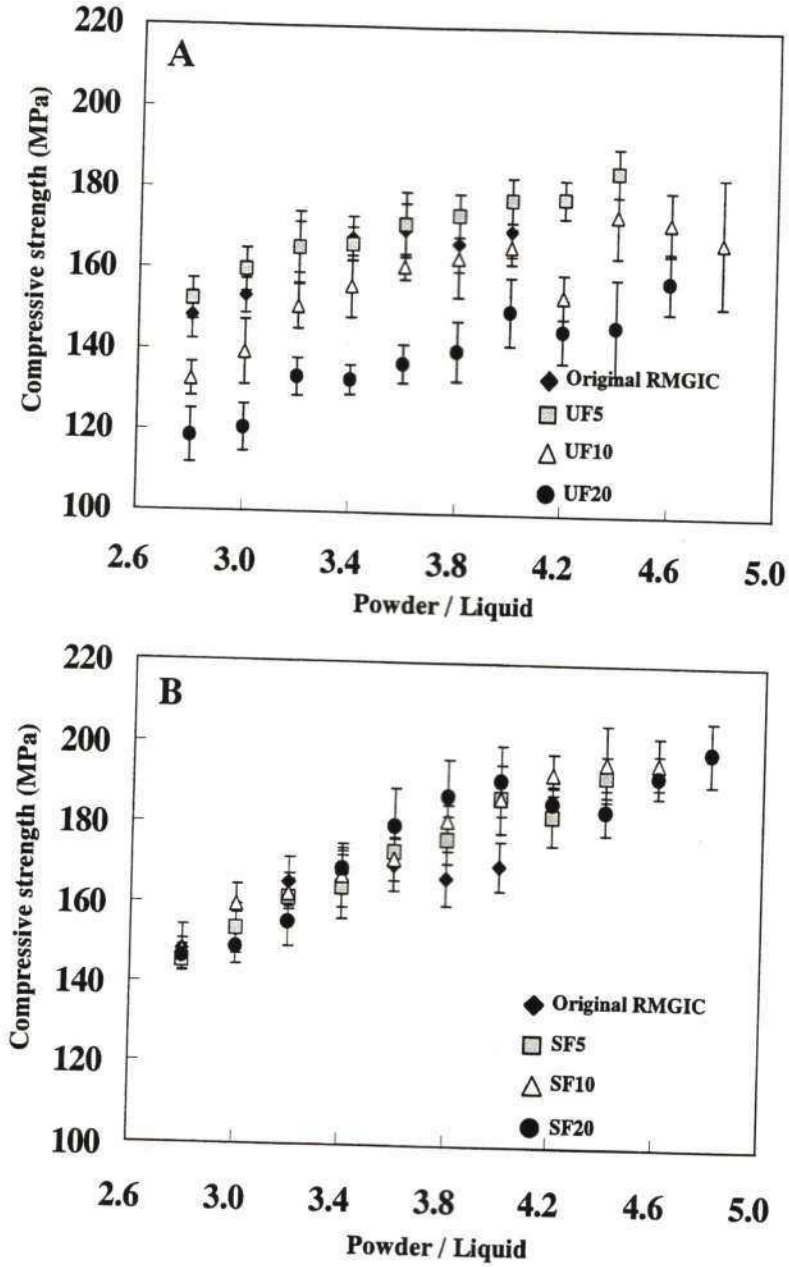


Fig.2.4 Powder / liquid vs. compressive strength of spherical silica filler-added RMGIC; n = 6.

A. The correlation in UF-added RMGIC.

Original RMGIC	y = 17.27 x + 104.36	r = 0.86	p < 0.05
UF5	y = 18.15 x + 104.65	r = 0.98	p < 0.001
UF10	y = 17.32 x + 19.16	r = 0.87	p < 0.01
UF20	y = 19.80 x + 65.06	r = 0.96	p < 0.001

B. The correlation in SF-added RMGIC.

Original RMGIC	y = 17.27 x + 104.36	r = 0.86	p < 0.05
SF5	y = 28.32 x + 68.78	r = 0.98	p < 0.001
SF10	y = 27.60 x + 74.01	r = 0.99	p < 0.001
SF20	y = 25.81 x + 78.24	r = 0.93	p < 0.001

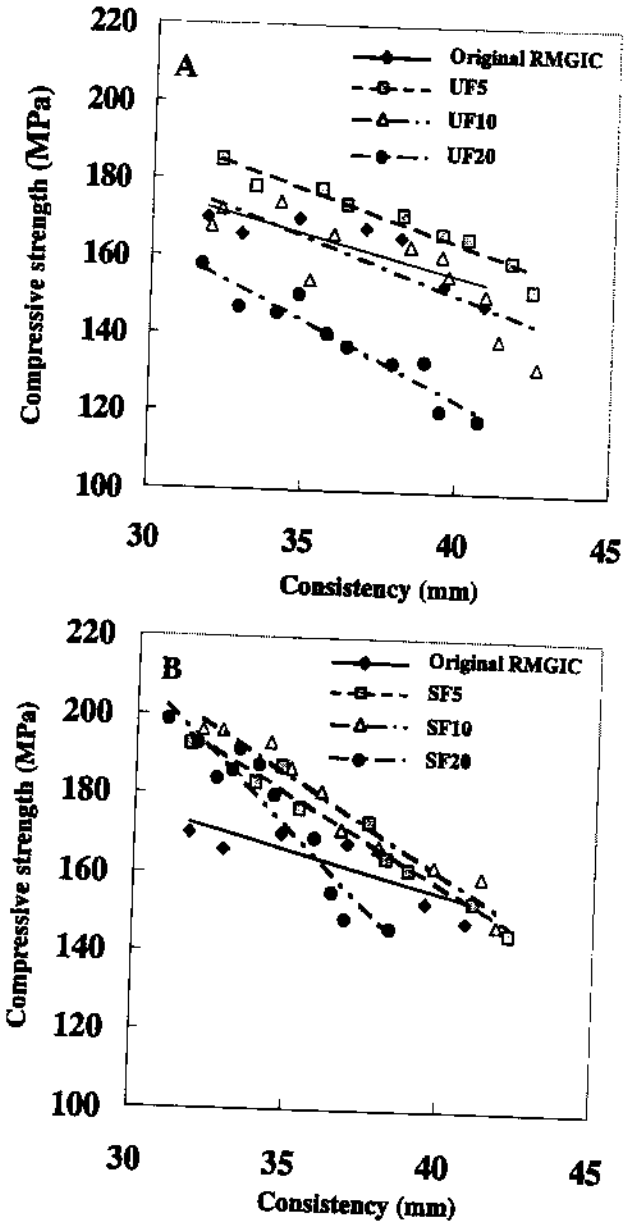


Fig.2.5 Consistency vs. compressive strength of spherical silica filler-added RMGIC, n = 6.

A. The correlation in UF-added RMGICs.

Original RMGIC	$y = 2.08x + 238.56$	$r = 0.81$	$p < 0.05$
UF5	$y = 2.71x + 272.23$	$r = 0.97$	$p < 0.001$
UF10	$y = 2.94x + 267.95$	$r = 0.83$	$p < 0.01$
UF20	$y = 4.00x + 283.29$	$r = 0.95$	$p < 0.001$

B. The correlation in SF-added RMGICs.

Original RMGIC	$y = 2.08x + 238.56$	$r = 0.81$	$p < 0.05$
SF5	$y = 4.50x + 337.65$	$r = 0.98$	$p < 0.001$
SF10	$y = 4.88x + 355.66$	$r = 0.98$	$p < 0.001$
SF20	$y = 7.79x + 444.08$	$r = 0.96$	$p < 0.001$

2.4. DISCUSSION

The enhanced stability of composites compounded with filler treated with γ-MPTS or with another silane coupling agent is attributed, in part, to the formation of a siloxane bond between the filler and the coupling agent[47,56]. Consequently, the interaction between the resin component of the matrix RMGIC and spherical silica filler in this study was considered to be reinforced by the silane coupling agent, and not to be affected by the liquid of the RMGIC as presented in the XPS image.

In the XPS analysis, the peaks for the presence of fluoride tags of the silane coupling agent on the surface of the silica plates were detected based on binding energy. The area of fluoride peaks that present the fluoride tags of the silane coupling agent on the surface of the silica plate did not differ significantly (Fig.2.2). Therefore, it is suggested that immersion in distilled water and in the liquid of the RMGIC, which contained polyacrylic acid, for 2 hours did not affect the attachment of the silane coupling agent to the treated silica surface.

As mentioned, the light-curing process polymerizes the monomers in the liquid of the RMGIC. However, the polymerization is seldom complete and residual or unpolymerized free monomer molecules can leach out and cause an allergy or have harmful effects[56,57]. Increasing the P/L will reduce the amount of liquid used and so reduce the release of free monomers from the filling materials.

It was reported that increasing the P/L leads to a decrease in consistency and an increase in the spatulation force required to adequately mixing the cementitious mass[58,59]. This condition was also observed in the present experiment. The addition of 10wt% UF or 20wt% SF raised the consistency of RMGIC, making it possible to use a P/L of up to 4.8. This gave a mixture with about the same consistency as the original RMGIC. Specifically,

the addition of silica filler to RMGIC powder will extend the workability of the material. The addition of UF or SF influenced the correlation of P/L with consistency, as marked by a shift in the gradient of the regression line (Fig.2.3). The gradient of SF-added RMGIC and that of UF-added RMGIC was less than the gradient of original RMGIC, which means that the rate of decrease in consistency caused by the increase in P/L, was less in the cements containing SF and UF. However, the difference was not significant between the RMGICs with SF5 and SF10, UF10 and UF20, or with SF5 and UF5. Since the amount of hydrophobic SF was small and the filler was scattered throughout the matrix powder, it is assumed that the difference between 5 and 10wt% is too small to significantly influence the consistency of the RMGIC. It can also be assumed that at 5wt%, the hydrophilic or hydrophobic characteristics of the filler do not play a distinct role. This might explain the lower level of significance in the correlation between consistency and compressive strength. In contrast, it is assumed that at more than 10wt%, UF would act as an impurity and not influence the rate of decrease in consistency caused by the increase in P/L.

The addition of UF or SF also influenced the correlation between P/L and compressive strength (Fig.2.4). The gradient of SF-added RMGIC was 1.49 – 1.64 times, and that of UF-added RMGIC almost the same as (1.00 – 1.15 times) the gradient of original RMGIC. It is showed that the rate of increase in compressive strength caused by the increase of P/L was greater in the cement containing SF than in the original or UF-added RMGIC. Yet, silanization of the filler had a marked effect, as shown by the significant difference between the addition of SF and UF at the same amount of filler ($p < 0.001$).

The decrease in consistency that follows the increase in P/L also leads to a change in mechanical properties. Fig.5 and Table 3 show that the addition of UF or SF significantly influences the correlation between consistency and compressive strength, as marked by a shift in the gradient of the regression line. The gradients for SF-added RMGIC were 2.25

– 3.75 times greater than that of the cement without filler, while the gradient of UF-added RMGIC was increased 1.30 – 1.92 fold. It is suggested that the decrease in consistency and increase in compressive strength occurred more rapidly in the preparation with SF than in the UF-added or original RMGIC.

The gradients of the correlation between consistency and compressive strength in the RMGICs (Fig.2.5) were also interrelated with the addition of the filler, as shown in Fig.2.6. Yet, the correlation for UF-added RMGIC ($r = -0.99$, $p < 0.01$) is a little more distinctive than that for SF-added RMGIC ($r = -0.98$, $p < 0.05$) and there is significant difference between the two values ($p < 0.05$). The gradient of the correlation in SF-added RMGIC has a larger negative value than that in UF-added RMGIC, indicating that due to silane pretreatment, which changes the characteristics of the spherical silica fillers; the addition of SF influenced the RMGIC more than the addition of UF.

Hard filler particles in the resin matrix would reduce the wear rate in case of the applied stress less than a critical value. However the mean distance between neighboring particles for bigger particles was bigger than for the smaller particles[60,61]. Therefore, spherical silica particles with an assortment of particle size were used in this study. With the incorporation of spherical silica particles into the resin matrix, the propagation of cracks into the matrix was hindered to a certain degree by the particles on or near the surface layer[60]. Therefore, Fig.2.5 showed that the addition of UF at up to 5wt% and SF at up to 20wt% increased the compressive strength remarkably at a similar low consistency. Consequently, in order to examine more characteristics of cement to which spherical silica filler was added, the maximum P/L that could be mixed in the dental clinic was chosen for further experiments.

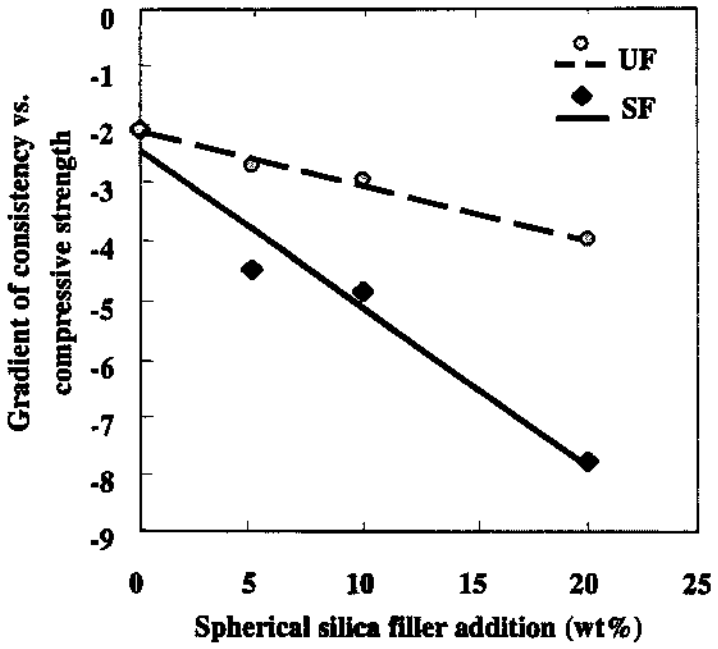


Fig.2.6 The amount of spherical silica filler vs. gradient of correlation between consistency and compressive strength of spherical silica filler-added RMGICs.
UF: $y = -9.29x - 2.12$, $r = -0.99$, $p < 0.01$
SF: $y = -26.82x - 2.47$, $r = -0.98$, $p < 0.05$

It seems that the compressive strength value of the GIC in this study is higher than previous data, since it is stated that the compressive strength of light cured GIC is between 90-110 MPa and the modulus of elasticity is 20 GPa[62]. Still it is lower than the compressive strength value of enamel (384 MPa), dentin (297 MPa) or composite resin (277 MPa)[62]. However this data depend on the geometry of the specimens.

2.5. CONCLUSION

The addition of spherical silica fillers to RMGIC powder improves the workability and compressive strength of the material. At up to 20wt% spherical silica filler, there is a significant linear correlation among the filler amount, consistency and compressive strength of the RMGIC.

CHAPTER 3

MECHANICAL PROPERTIES AT THE MAXIMUM CONSISTENCY AND WATER UPTAKE MEASUREMENT

3.1. INTRODUCTION

In previous chapter it was shown that the addition of spherical silica filler would increase the workability and compressive strength of RMGIC. Since RMGIC contains resin in its composition, to confirm the result of compressive strength test, the flexural strength test is one of recommended alternative, since the flexural strength measurement is a collective measurement of tensile, compressive and shear stresses simultaneously used to evaluate the fracture resistance and the elasticity of the materials[56,63]. Therefore, in this chapter the first hypothesis to be tested was that the addition of spherical silica filler would also significantly increase the diametral tensile strength and flexural strength. The second hypothesis was that the addition of spherical silica filler would decrease the water uptake of RMGIC.

3.2. MATERIALS AND METHODS

3.2.1. *Materials*

As being explained in chapter 2, the RMGIC material used in this study was Fuji II LC EM (powder Lot #0205211, liquid Lot #0204301) with a recommended P/L of 3.0.

The silanization process of spherical silica filler, which has an average particle diameter of 0.3 μm with γ-MPTS and the modification of the RMGIC powder was taken as previously described in chapter 2.

The same visible-light curing unit was used for activating the specimens, and close contact was ensured between the exit window of the lamp and the glass plate. The light

intensity was also checked and maintained at 450 mW/cm^2 before each application of restorative material using a radiometer.

3.2.2. *Compressive strength measurements*

For the preparation of compressive strength samples, a cylindrical Teflon split mold with a depth of 6.0 mm and diameter of 3.0 mm was used to minimize the stress exerted on the specimens during their retrieval.

The maximum P/L was chosen to mix the material. All specimens were mixed in 30 seconds using a plastic spatula on a mixing pad, syringe-loaded into a Teflon split mold, covered with a glass plate and clamped. Taking into consideration the thickness of the glass plate and the specimens, the specimens were light cured for 60 seconds on each side. Then, they were removed from the mold, varnished and immersed in distilled water. After storage for 24 hours in a 37°C incubator, the compressive strength was measured using a universal testing machine with a cross-head speed of 0.5 mm min^{-1} as being described in chapter 2.

3.2.3. *Diametral tensile strength (DTS) measurements*

One of the subsequent experiments performed was the measurement of DTS. The maximum P/L was chosen to mix the material. Sample preparation in the cylindrical Teflon split mold (h = 3.0 mm, d = 6.0 mm), light curing and the testing procedure were the same as described for the compressive strength measurements.

The formulation used to calculate the DTS is:

$$DTS = (2P)/(\pi Dt)$$

where DTS is the diametral tensile strength strength, P the maximum load at the point of the fracture, D the diameter of the specimen and t the thickness of the specimen[56].

3.2.4. *Flexural strength measurements*

As in the DTS measurements, the maximum P/L was chosen to mix the material. The procedure used to measure flexural strength was similar to that used to measure compressive strength except that the internal dimensions of the Teflon split mold were 25.0 mm × 2.0 mm × 2.0 mm and the light curing was for 60 seconds at 3 overlapping sites. The flexural strength was measured using the 3-point bending method with a 20-mm span. A universal testing machine was used with a cross-head speed of 0.5 mm min^{-1} and a maximal external force of 10 kgf (98 N) was applied to the midpoint of the test beam, then the flexural strength of each material were calculated using the following formula:

$$\sigma = (3PL)/(2bd^2)$$

In this equation σ is the flexural strength, P the maximum load at the point of the fracture, L the distance between supports, b the width of the specimen and d the thickness of the specimen[56,63-66].

3.2.5. *Water uptake measurements*

Before being immersed in distilled water, the specimens to be used for the 24-hour diametral tensile strength measurements were weighed with an electric balance (AJ 100, Mettler, Greifensee, Switzerland). After being immersed in distilled water for 24 hours in a 37°C incubator and dried for 1 minute on the Kim Wiper, the specimens were weighed again. The degree of water uptake was calculated from the changes in the specimen's weight and was expressed as a percentage.

Six specimens were prepared for each of the material and conditions. All dimensions were measured using a digital micrometer. All procedures, except for mechanical testing, were performed in a thermo-hygrostatic room kept at 23 ± 0.5°C and 50 ± 2% relative

humidity.

3.2.6. *Statistical analysis*

The results of measurements were analyzed using an ANOVA and Tukey test, with the level of significance set at 0.05[54]. The difference among the regression lines of the data was compared with a *t*-test[55].

3.2.7. *Fractured surface analysis*

After the flexural strength measurements, the modes of fracture were analyzed with a field emission scanning electron microscope (FE-SEM) (DS-720, Topcon, Tokyo, Japan).

3.3. RESULTS

3.3.1. *Compressive strength*

The effect of the spherical silica fillers on the compressive strength of the materials has been summarized in Fig.2.4, while the results of the compressive strength at maximum P/L, analyzed statistically, are summarized in Table 3.1. At P/L 3.0, the compressive strength of RMGIC is 153 $\pm$ 4 MPa. Increasing the P/L to 4.0 (max.) increased the compressive strength to 170 $\pm$ 6 MPa. For the UF5, UF10 and UF20, the compressive strength values at P/L 3.0 were 160 $\pm$ 5 MPa, 139 $\pm$ 6 MPa and 121 $\pm$ 6 MPa, respectively. At the P/L maximum, the compressive strength was 185 $\pm$ 6 MPa, 168 $\pm$ 16 MPa and 158 $\pm$ 7 MPa. For the SF5, SF10 and SF20, the compressive strength values at P/L 3.0 were 153 $\pm$ 6 MPa, 160 $\pm$ 5 MPa and 149 $\pm$ 4 MPa, respectively.

In the compressive strength measurements, there was a significant difference between the SF-added RMGIC and the original RMGIC ($p < 0.05$). There was no significant

difference among the original RMGIC and UF10 or UF20, or among UF5 and SF5 or SF10. The addition of SF increased the compressive strength significantly up to 17%, while the addition of UF only increased the strength up to 9%.

Table 3.1 Compressive strength and diametral tensile strength of the original and spherical silica filler-added RMGIC at the maximum workability

Materials	P/L	Compressive strength* (MPa)			Diametrical tensile strength* (MPa)		
Original RMGIC	4.0	170 ± 6		c, d	21.1 ± 0.7		k
UF5	4.4	185 ± 6	(9%)	b, c	20.0 ± 1.3	(-5%)	k, l
UF10	4.8	168 ± 16	(-1%)	c, d	18.0 ± 1.5	(-15%)	l, m
UF20	4.6	158 ± 7	(-7%)	d	15.5 ± 0.7	(-27%)	m
SF5	4.4	193 ± 5	(14%)	a, b	25.3 ± 1.0	(20%)	n
SF10	4.6	196 ± 6	(15%)	a, b	29.2 ± 2.0	(38%)	p
SF20	4.8	199 ± 8	(17%)	a	25.1 ± 2.1	(19%)	n

( ) = increasing rate, compared to original RMGIC

UF = untreated filler, SF = silanized filler

*: Same letters show no significant difference analyzed using the Tukey test[54], $p > 0.05$, $n = 6$.

3.3.2. *Diametral tensile strength*

In the DTS measurements, there was a significant difference between the original RMGIC and SF-added RMGIC ($p < 0.05$) (Table 3.1). The addition of 10wt% SF increased the DTS significantly up to 38%, from 21.1 ± 0.7 MPa to 29.2 ± 2.0 MPa. However, the addition of UF decreased the DTS. There was no significant difference between the original RMGIC and UF5 (20.0 ± 1.3 MPa), between the UF5 and UF10 (18.0 ± 1.5 MPa) or between the UF10 and UF20 (15.5 ± 0.7 MPa).

3.3.3. *Flexural strength*

Except with UF20, there was no significant difference among the materials in the flexural strength measurements (Table 3.2). The addition of SF or UF increased the flexural strength up to 17%. The flexural strength of the original RMGIC was 53.8 ± 8.3 MPa, while the greatest gain in flexural strength was obtained in SF20 (63.2 ± 5.8 MPa) and UF10 (63.1 ± 3.8 MPa).

Table 3.2 Flexural strength of the original and spherical silica filler-added RMGIC at the maximum workability

Materials	P/L	Flexural strength* (MPa)		
Original RMGIC	4.0	53.8 ± 8.3		a
UF5	4.4	56.8 ± 6.0	(5%)	a
UF10	4.8	63.1 ± 3.8	(17%)	a
UF20	4.6	30.7 ± 4.3	(-43%)	b
SF5	4.4	56.7 ± 4.6	(5%)	a
SF10	4.6	60.1 ± 4.9	(12%)	a
SF20	4.8	63.2 ± 5.8	(17%)	a

( ) = increasing rate, compared to original RMGIC

UF = untreated filler, SF = silanized filler

* : Same letters show no significant difference analyzed using the Tukey test[54], $p > 0.05$, $n = 6$.

3.3.4. *Water uptake*

The water uptake measurements are also listed in Table 3.3. The addition of UF reduced the water uptake of RMGIC, though not significantly, up to 9%: from 3.11 ± 0.27 % to 2.82 ± 0.21 % at 10wt%. However, the water uptake of SF20 was 2.09 ± 0.16 %, a decrease of 33% ($p < 0.05$).

Table 3.3 Water sorption of the original and spherical silica filler-added RMGIC at the maximum workability

Materials	Water uptake*(%)		
Original RMGIC	3.11 ± 0.27		x
UF5	2.85 ± 0.10	(-8%)	x, y
UF10	2.82 ± 0.21	(-9%)	x, y
UF20	3.11 ± 0.13	(0%)	x
SF5	2.72 ± 0.29	(-13%)	y
SF10	2.21 ± 0.11	(-29%)	z
SF20	2.09 ± 0.16	(-33%)	z

( ) = increasing rate, compared to original RMGIC

UF = untreated filler, SF = silanized filler

* : Same letters show no significant difference analyzed using the Tukey test[54], $p > 0.05$, $n = 6$.

3.3.5. *Fractured surface analysis*

Fig.3.1 shows the modes of fracture of RMGIC with spherical silica filler analyzed by SEM. The original RMGIC shows an irregular fractured surface (Fig.3.1 A). Debonded spherical silica fillers are observed at the fractured surface of the UF-added RMGIC (Fig.3.1 B). In contrast, at the fractured surface of the SF-added RMGIC (Fig.3.1 C), spherical silica fillers are clearly visible, however they are bonded with the matrix of RMGIC.

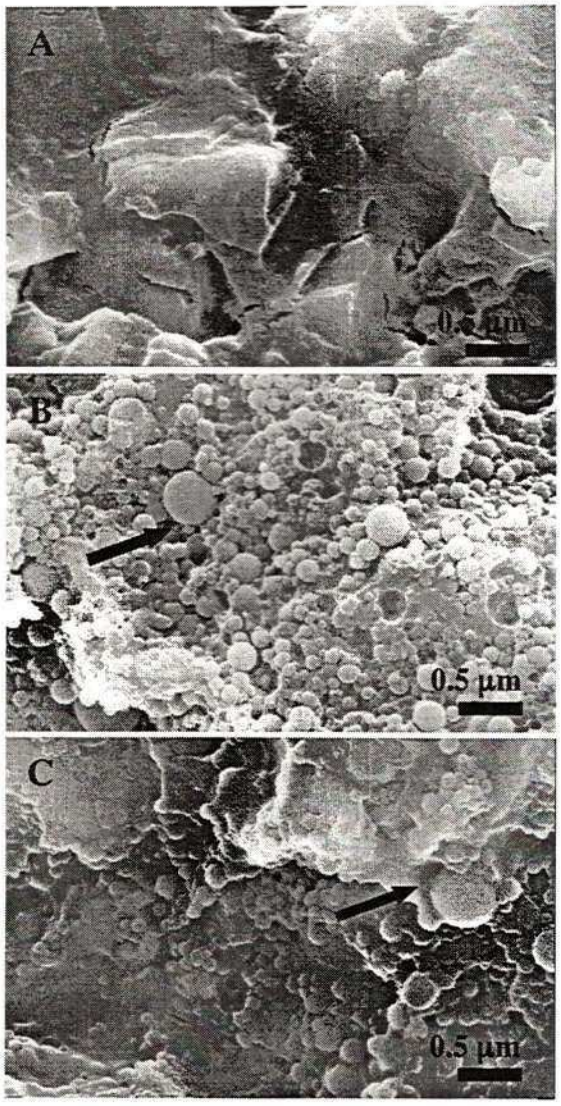


Fig.3.1 The modes of fracture of RMGICs analyzed with SEM.

Arrows indicate the interfacial bonding between fillers and matrix of RMGIC.

A. Fractured surface of the original RMGIC.
B. Fractured surface of UF20. Fillers were separated from the matrix due to mechanical bonding failure at the interface between filler and the matrix of RMGIC.
C. Fractured surface of SF20. Silanized fillers were bonded by chemical bonding at the interface between filler and the matrix of RMGIC.

3.4. DISCUSSION

As mentioned, the light-curing process polymerizes the monomers in the liquid of the RMGIC. However, the polymerization is seldom complete and residual or unpolymerized free monomer molecules can leach out and cause an allergy or have harmful effects[56,57]. Increasing the P/L will reduce the amount of liquid used and so reduce the release of free monomers from the filling materials.

Hard filler particles in the resin matrix would reduce the wear rate in case of the applied stress less than a critical value. However the mean distance between neighboring particles for bigger particles was bigger than for the smaller particles[60]. Therefore, spherical silica particles with an assortment of particle size were used in this study. With the incorporation of spherical silica particles into the resin matrix, the propagation of cracks into the matrix was hindered to a certain degree by the particles on or near the surface layer[60]. Therefore, Fig.2.5 showed that the addition of UF at up to 5wt% and SF at up to 20wt% increased the compressive strength remarkably at a similar low consistency. Consequently, in order to examine more characteristics of cement to which spherical silica filler was added, the maximum P/L that could be mixed in the dental clinic was chosen for DTS and flexural strength measurements. This maximum P/L also gave a similar consistency to the original RMGIC mixed at P/L 4.0. The addition of UF to 5wt% increased the compressive and flexural strength. However, at more than 5wt%, UF addition reduced the cement's strength, because the filler became an impurity that did not bond to the matrix of the RMGIC. The opposite effect was observed with the addition of SF. Since the fillers were silane-treated, their ability to bond to the matrix was improved and the addition of SF at up to 20wt% increased the compressive strength and DTS significantly, as well as increased the flexural strength. More significant evidence is

provided by the SEM observations of the fractured surface of the specimens (Fig.3.1). It was found that the interfacial bonding between UF and the matrix of RMGIC was due to mechanical bonding, while that between SF and the matrix was due to chemical bonding as a result of silanization.

It was reported that flexural strength was more sensitive to changes in material substructure than compressive strength[43,59,67]. However, in this experiment, the DTS test was more sensitive for distinguishing the effect of UF and SF. The DTS values also showed that the increase in strength is more dependent on the chemical reaction than the morphology of the fillers.

As the compressive strength increased, the flexural strength and DTS also tended to increase, although the results of the regression analysis of the correlation were not significant. This correlation should be examined more closely.

Another factor that may influence mechanical properties is the uptake of water. UF did not reduce the water uptake of RMGIC significantly, while SF did (up to 33%). The hydrophobic characteristic of SF might influence surface and grain boundary diffusion[68], then increase the resistance of the cement to water uptake.

3.5. CONCLUSION

The silanized spherical silica fillers increased the compressive strength, diametral tensile strength and flexural strength, and reduced the water uptake of the RMGIC. The silanized spherical silica filler also improved the mechanical properties of the cement more than the untreated spherical silica filler.

CHAPTER 4

FLUORIDE RELEASE MEASUREMENTS

4.1. INTRODUCTION

It is quite clear that fluoride is the most effective agent in caries prevention. For that reason, one point that makes GIC one of the favorite restorative materials is its capability to release fluoride[20,21,23]. Consequently, the addition of spherical silica fillers will give no meaning if they eliminate the fluoride release from the GIC. It is reported that RMGICs show less fluoride release and caries resistance than GICs[32]. However, another studies showed that RMGICs not only could be used in the case where a strong initial fluoride effect is desired, but also in the long term condition since they released fluoride in the same amount or more than the conventional GICs did[23,69]. In chapter 3, it was shown that the addition of SF reduced the water uptake of RMGIC significantly. In view of the fact that the material must absorb water to initiate any attack on fluoride glass[70], in this chapter the hypothesis to be tested was that the addition of SF would reduce the fluoride release of RMGIC

4.2. MATERIALS AND METHODS

4.2.1. *Materials*

The RMGIC material used was Fuji II LC EM (powder Lot #0205211, liquid Lot #0204301) as was explained in chapter 2.

The silanization process of spherical silica filler, which has an average particle diameter of 0.3 μm with γ-MPTS and the modification of the RMGIC powder was taken as previously described in chapter 2.

The RMGIC powder was modified by initially mixing it with either the SF or UF at 20 weight percentages before mixing it with Fuji II LC EM liquid. The prepared cement powders are described as SF20 and UF20, which show the type of filler added and its filler content in weight percentage. The mixing time and preparation time is 30 seconds for each. Since a conventional hand mixed system GIC produced a significantly less fluoride release than a capsulated system[71], in this study hand-mixing material and procedure was taken. The P/L was chosen for the maximum P/L value of each material in the chapter 2 and as reported in previous study[72]. The Fuji II LC EM was mixed with P/L = 4.0 (FLCEM) as the maximum P/L value of the original RMGIC. SF20 was mixed with P/L of 4.8, while UF20 was mixed with P/L of 4.6, respectively.

The same visible-light curing unit was used for activating the specimens, and close contact was ensured between the exit window of the lamp and the matrix. The light intensity was also checked and maintained at 450 mW/cm^2 before each application of restorative material using a radiometer.

All procedures, except for cavity preparation and mechanical testing, were performed in a thermo-hygrostatic room maintained at 23 ± 0.5°C and 50 ± 2% relative humidity. The results were analyzed statistically using ANOVA, the t-test, and Mann-Whitney U-test[52,73].

4.2.2. Fluoride release measurements

The release of fluoride from SF20, UF20, and FLCEM was measured. All specimens were mixed for 30 seconds using a plastic spatula on a mixing pad, syringe-loaded into a cylindrical Teflon split mold (d = 20.0 mm, h = 0.5 mm), covered with a glass plate and clamped. After being light-cured for 20 seconds at five overlapping sites, the samples were removed from the mold, placed in polyethylene vials with 25 ml of distilled water, and stored in an incubator at 37°C for 1 day, 2 days, 3 days, 1 week, and 2 weeks. For

each material and each time period, three samples were prepared. After each specified period, the samples were removed from the medium, and 10 ml of the medium was transferred to another vial and mixed with 1 ml of TISAB III solution (Thermo Orion, Beverly, USA). The amount of fluoride ions released from the RMGIC sample in this solution was measured using a pH/ion meter (F23-S937, Horiba, Kyoto, Japan). Then, using a SigmaPlot 8.0 program (SPSS, Chicago, Illinois, USA) by placing the cumulative fluoride release ($[F]_c$, mg/L) as a function of time (t, day), the data were fitted to a single rectangular II, 3-parameter equation as follows:

$$[F]_c = [F]_1 t/(t_{1/2}+t) + \alpha t$$

where $[F]_1$ was the total amount of fluoride to be released, $t_{1/2}$ the time needed to release half of this total amount, and α the kinetic parameter[70].

4.3. RESULTS

Fig. 4.1 shows the effects of spherical silica fillers on fluoride release from RMGIC. SF or UF reduced the release of fluoride. During two weeks' immersion in distilled water, the fluoride release of SF20 (which fulfilled the equation $F = 4.80t/(0.01 + t) + 0.79t$) was 49.4%-57.7% of FLCEM's ($F = 12.79t/(0.46 + t) + 1.10t$). For the same period, the value for UF20 ($F = 15.71t/(1.12 + t) + 0.68t$) was 84.6%-99.8% of FLCEM's. In two weeks, the cumulative fluoride release value of SF20 was 15.88 $\pm$ 1.89 mg/L, while those of FLCEM and UF20 were 27.87 $\pm$ 0.64 mg/L and 23.83 $\pm$ 0.64 mg/L respectively.

Analyses using ANOVA revealed that both the addition of spherical silica fillers and the period of immersion in distilled water significantly ($p < 0.001$) influenced fluoride release from RMGIC.

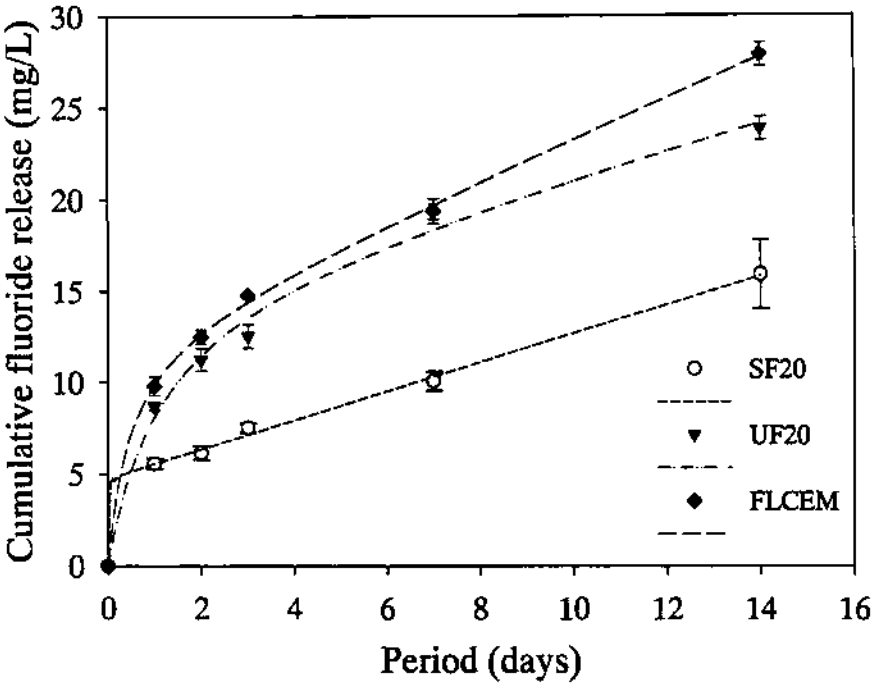


Fig.4.1 Cumulative fluoride release of SF20, UF20 and FLCEM in 14 days, n = 3.

Points indicate the observed values and the lines indicate the fitted curves fulfilling the equation of $[F]_t = [F]_i t/(t_{1/2}+t) + \alpha t$, with r = 0.99 and p < 0.01.

4.4. DISCUSSION

The hydrophobic characteristic of SF may influence both surface diffusion and grain boundary diffusion[68], and increase the resistance of cement to water uptake[72]. Since the material must first absorb water to initiate any attack on fluoride glass and the dissociation of acid groups[70], it was not surprising that the addition of SF would reduce fluoride release (Fig. 4.1). A previous study reported that fluoride has a low rate of diffusion through an organic cross-linked matrix because of strong interaction with aluminum and calcium ions linked to the polyalkenoate chains[74]. The strong interaction between SF and the RMGIC matrix also affected the diffusion rate of fluoride, but fluoride release was not eliminated. This effect should be taken into consideration, because the presence of saliva *in vivo* may retard the release of fluoride from glass-ionomer filling materials[15,75]. Although

observations were limited to a period of just 14 days in this study, the equation for fluoride release in glass-ionomer cement $[F]_t = [F]_i t/(t_{1/2}+t) + \alpha t$, as previously described[70], adequately approximated the release of fluoride from RMGIC with or without a spherical silica filler ($r = 0.99$, $p < 0.01$). A similar pattern of release was also obtained, and the release was much greater in the first 24 hours than subsequently. The small but significant initial release was undoubtedly the result of fluoride leaching from glass particles in the surface layer[70]. A previous study showed that γ-MPTS treatment was useful for the regulation of NaF release from bis-GMA/TEGDMA resin. There was evidence that a large amount of fluoride was released from the resin containing NaF powder without γ-MPTS treatment in the initial stage, and the release of fluoride ceased in a relatively shorter time. However, smaller amounts of fluoride were released from the resin containing NaF treated with higher concentrations of γ-MPTS, and the release lasted for longer periods[76]. GICs release and take up fluoride ions[77,78]. Therefore, the shortcoming due to SF addition may, however, be overcome by fluoride "recharging" using topical fluoride[69]. As such, the fluoride release and fluoride recharge capabilities of spherical silica filler-added RMGICs should be examined for a longer period in a further study.

4.5. CONCLUSION

The addition of spherical silica fillers decreased but did not eliminate fluoride release from RMGIC.

CHAPTER 5

MARGINAL GAP AND SHEAR BOND STRENGTH ANALYSIS

5.1. INTRODUCTION

The bond strength of restorative material to tooth substrate, especially dentin depends not only on the materials but also on enormous clinical factors such as dentin depth[79,80], calcium concentration[81], age[82,83], surface wetness[84], relative humidity[85-87], saliva and blood contamination[88-92], caries-affected dentin[93-97], sclerotic cervical erosion[97-102] or polymerization stress related to cavity configuration[103-104]. To obtain a successful adhesive restoration, focus on such clinical factors and control on clinical situation is very important.

In this study, the bond strength of the RMGICs was evaluated by shear bond strength measurement. It was supposed that shear bond strength and marginal gap in tooth cavity affect each other, and these characteristics might be influenced the setting shrinkage[34]. Therefore, to study the setting shrinkage, the marginal gaps in the Teflon mold were also observed.

In order to study marginal gap formation of GIC and RMGIC in the tooth cavity, an *in vitro* preliminary study was taken[27]. Class V cavity preparations were made on the facial surface of premolars and filled with Fuji II or Fuji II LC. As a result, it was shown that RMGIC (Fuji II LC) still showed marginal gap, as was also shown by the conventional GIC (Fuji II). And it was also suggested to delay polishing after 1 days of filling procedure, since the gap width reduced after 24-hour water storage.

Consequently, the following hypothesis was thought, that the addition of spherical silica filler would reduce the immediate and 24-hour marginal gaps created by RMGIC filling material in tooth cavities. The other hypothesis was that the marginal gap and rate of

setting shrinkage in Teflon mold and the shear bond strength of RMGIC would influence marginal gap formation in tooth cavities.

5.2. MATERIALS AND METHODS

5.2.1. *Materials*

As being explained in chapter 2, the RMGIC material used in this study was Fuji II LC EM (powder Lot #0205211, liquid Lot #0204301) with a recommended P/L of 3.0.

The silanization process of spherical silica filler, which has an average particle diameter of 0.3 μm with γ-MPTS and the modification of the RMGIC powder was taken as previously described in chapter 2.

The RMGIC powder was modified by initially mixing it with either the SF or UF at different weight percentages (5%, 10%, and 20%) before mixing it with Fuji II LC EM liquid. The prepared cement powders are described as SF5, SF10, SF20, UF5, UF10, and UF20 — hence indicating the type of filler added and filler content in weight percentage. Both the mixing time and preparation time were 30 seconds each. As for the P/L, each one was chosen according to the maximum compressive strength value of each cement in chapter 2, as also reported in the previous study[72]. Fuji II LC EM was mixed with P/L = 3.0 as the control and with P/L = 3.6 (FLCEM) as the maximum compressive strength of the original RMGIC. SF5, SF10, and SF20 were mixed with P/L of 4.0, 4.4, and 4.0; while UF5, UF10, and UF20 were mixed with P/L of 4.4, 4.4, and 4.0, respectively.

The same visible-light curing unit was used for activating the specimens, and close contact was ensured between the exit window of the lamp and the matrix. The light intensity was also checked and maintained at 450 mW/cm^2 before each application of restorative material using a radiometer.

Although much information has been generated on the use of bovine teeth, the use of human teeth is a preferred option[105]. A total of 320 human premolars, extracted for orthodontic reasons, were used to measure the marginal gap in tooth cavities and the shear bond strength to tooth tissues in this study. After extraction, the teeth were stored immediately in distilled water at about 4°C within 3 months before use. Since occlusal dentin tends to give lower bond strengths than proximal or buccal dentin[106,107], and that dentin tubule orientation and location significantly influence the results of mechanical strength tests [108-110], proximal flat enamel or dentin surfaces were used in this study.

All procedures, except for cavity preparation and mechanical testing, were performed in a thermo-hygrostatic room maintained at 23 ± 0.5°C and 50 ± 2% relative humidity. The results were analyzed statistically using ANOVA, the t-test, and Mann-Whitney U-test[54,73].

5.2.2. *Marginal gap in tooth cavities*

Human premolars (N = 10 for each material and condition) were embedded in a slow-setting epoxy resin (Epofix Resin, Struers, Copenhagen, Denmark). Flat enamel surfaces on the proximal area of the teeth were obtained by grinding with wet silicon carbide paper (#800). The cylindrical cavity on the coronal region of each tooth was prepared to a depth of approximately 1.5 mm with a diameter of 3.5 mm with a tungsten carbide bur (200,000 rpm) and a fissure bur (8,000 rpm) using water spray. The dimensions of the cavity were measured using a vernier caliper. Each cavity was treated with a Cavity Conditioner (Lot #0205101, GC Corp., Tokyo, Japan) for 10 seconds according to manufacturer's instructions, rinsed thoroughly with distilled water, air-sprayed, and filled with the material using a syringe tip. Covered with a plastic strip, the material was light-cured for 20 seconds. Surfaces were polished immediately after light activation or after storage in distilled water at 37°C for 24 hours. Excess filling material was

removed by wet grinding with a wet silicon carbide paper (#1000), followed by polishing using an aqueous slurry of 0.3 μm aluminum oxide (Alfa Micropolish, Buehler Ltd., Lake Bluff, IL, USA) and thorough rinsing with distilled water. Each restoration margin was inspected under a traveling microscope (400×, Measurescope, MM-11, Nikon, Tokyo, Japan)[33,111,112]. The maximum gap width and opposing width (if any) between the cement and cavity wall were measured, and the sum of these two values was expressed as the marginal gap in that tooth cavity. As some specimens had zero marginal gaps, especially after 24-hour water storage, the overall sum of 10 specimens examined per material was calculated as the total marginal gap for the group[112].

5.2.3. *Setting shrinkage in Teflon mold*

Teflon does not react with the filled material. Therefore Teflon molds of the same diameter and depth were prepared to measure the degrees of setting shrinkage (immediately after set) and hygroscopic expansion (after 24-hour water storage), as well as to compare the marginal gap width in the tooth cavity. The Teflon mold was placed on a silicon oil-coated glass plate and a matrix strip that would not react with or bind to the filling material. Each mold was filled with the material using a syringe tip, then covered with a plastic strip and light-cured for 20 seconds. Immediately after setting or after 24-hour storage in distilled water at 37°C, any excess material was removed. The maximum gap width and opposing width between the cement and the Teflon cavity were measured, and the sum of these two values was expressed as the marginal gap in the Teflon cavity. The degree of setting shrinkage was determined using the formula below:

$$S = (G/d) \times 100\%$$

where S was the setting shrinkage, G the marginal gap, and d the diameter of the Teflon mold[111]. Ten specimens were prepared for each material and their conditions investigated.

5.2.4. *Shear bond strength to enamel and dentin*

The shear bond strength to enamel and dentin, which comprise the cavity wall, was measured to evaluate the bonding effect between the filling material and the cavity. Bond strength to flat enamel and dentin surfaces was determined both immediately after light activation and after 24-hour distilled water storage at 37°C. Specimens (N = 10 for each material and condition) were obtained from human premolars embedded in the slow-setting epoxy resin. Proximal flat enamel or dentin surfaces were obtained by grinding with a wet silicon carbide paper (#1000) followed by treatment with the Cavity Conditioner for 10 seconds. To prepare the shear bond strength samples, a cylindrical Teflon split mold (3.6-mm diameter × 2.0-mm height) was used to minimize the stress exerted on the specimens during their retrieval. Each material was placed into the Teflon mold set on the enamel or dentinal surface using a syringe tip, then hardened by light-curing. The specimens thus obtained were mounted on a universal testing machine and shear stress was applied at 0.5 mm/min, with a maximum external force of 50 kgf (490 N). After shear bond strength measurements were taken, the fractured surfaces were analyzed using a light microscope (4×, SMZ-10, Nikon, Tokyo, Japan) to ascertain the nature of fractures[34,111,112].

5.3. RESULTS

5.3.1. *Marginal gap in tooth cavities*

Table 5.1 lists the effects of spherical silica fillers on the marginal gap in tooth cavities. The marginal gaps of all SF-added RMGICs were 67% of the control's or less. The marginal gap of SF10 was 63% of the control's or 83% of FLCEM's, while that of UF10 was 62% of the control's or 81% of FLCEM's. Comparing the sums of the immediate gap width using a non-parametric t-test[54,73], all materials with fillers showed significant differences among SF5, SF10, and UF10; or among SF5, SF10, and UF20; or between SF20 and UF5.

Table 5.1 Marginal gap in the tooth cavity

Material	P/L	The sum of marginal gaps for all specimens (μm) [1]								α value [2]
		Immediately				After 24-hours				
SF5	4.0	74	[0]	(4-10)	a, b	6	[4]	(0-1)	g	$p < 0.05$
SF10	4.4	73	[0]	(5-11)	b	6	[4]	(0-1)	g	$p < 0.05$
SF20	4.0	77	[0]	(2-11)	c	6	[4]	(0-1)	g	$p < 0.05$
UF5	4.4	82	[0]	(5-13)	c	6	[4]	(0-1)	g	$p < 0.05$
UF10	4.4	71	[0]	(2-11)	a, b	6	[4]	(0-1)	g	$p < 0.05$
UF20	4.0	77	[0]	(5-12)	a	7	[3]	(0-1)	h	$p < 0.05$
FLCEM	3.6	88	[0]	(4-14)	d	7	[3]	(0-1)	h	$p < 0.05$
Control	3.0	115	[0]	(7-17)	f	7	[3]	(0-1)	h	$p < 0.05$

SF = Silanized spherical silica filler, UF = Untreated spherical silica filler

FLCEM = Fuji II LC EM mixed with P/L 3.6, Control = Fuji II LC EM mixed with P/L 3.0, n = 10

[ ]= Number of specimen with no gaps, ( ) = Range of values

[1] : Identical letters indicate no significant difference among the materials analyzed using the t-test ($p > 0.05$, non parametric)[54,73]

[2] : Significant difference, analyzed using the Mann-Whitney U-test between two sums[54]

After 24-hour storage in distilled water, there were no significant differences among the control, FLCEM, and UF20, as well as among all other spherical filler-added RMGICs. The Mann–Whitney U-test showed a significant difference ($\alpha < 0.05$) between the immediate and 24-hour values for each material. Compared with the control, the immediate gap width mean values of all spherical filler-added RMGICs showed a significant difference (Fig. 5.1).

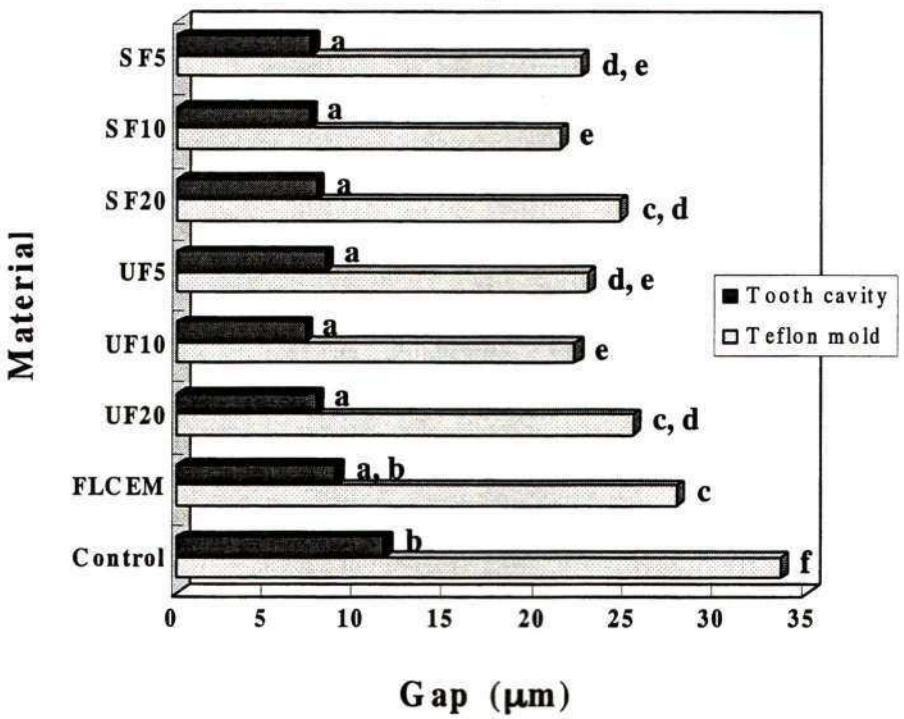


Fig.5.1 Comparison of immediate marginal gap mean values of the RMGICs in the Teflon mold and the tooth cavity, n = 10.

Identical letters indicate no significant difference among the materials analyzed using the t-test for differences among several means ($p > 0.05$)[54].

5.3.2. *Setting shrinkage in Teflon mold*

Table 5.2 lists the effects of spherical silica fillers on the setting shrinkage of RMGIC in the Teflon mold. At the immediate time point, there were no significant differences among FLCEM, UF5, UF20, and SF20. All materials, except FLCEM, showed a significant difference ($p < 0.05$) in comparison with the control.

Table 5.2 Setting shrinkage in Teflon mold

Materials	P/L	Immediately (%) [1]	After 24-hours (%) [1]	α value [2]
SF5	4.0	0.64 ± 0.10 [a]	0.15 ± 0.04 [d]	$p < 0.05$
SF10	4.4	0.62 ± 0.08 [a]	0.14 ± 0.04 [d]	$p < 0.05$
SF20	4.0	0.69 ± 0.11 [a, b]	0.16 ± 0.04 [d]	$p < 0.05$
UF5	4.4	0.65 ± 0.09 [a, b]	0.14 ± 0.05 [d]	$p < 0.05$
UF10	4.4	0.63 ± 0.07 [a]	0.15 ± 0.06 [d]	$p < 0.05$
UF20	4.0	0.71 ± 0.08 [a, b]	0.15 ± 0.05 [d]	$p < 0.05$
FLCEM	3.6	0.80 ± 0.08 [b, c]	0.16 ± 0.03 [d]	$p < 0.05$
Control	3.0	0.94 ± 0.10 [c]	0.17 ± 0.05 [d]	$p < 0.05$

SF = Silanized spherical silica filler; UF = Untreated spherical silica filler

FLCEM = Fuji II LC EM mixed with P/L 3.6; Control = Fuji II LC EM mixed with P/L 3.0; n = 10

Identical letters indicate no significant difference among the materials analyzed using the t-test for differences among several means ($p > 0.05$)[54]

[1] : percentage to the diameter of the Teflon mold (inner diameter : 3.5 mm)

[2] : significant difference, analyzed using the t-test between two values.

The immediate setting shrinkage of all SF-added RMGICs was 73% of the control's or less. SF10 had a setting shrinkage of $0.62 \pm 0.08\%$, of which its value was 66% of the control's or 78% of FLCEM's. However, there were no significant differences among the 24-hour setting shrinkage values in the Teflon mold. There was a significant difference ($p < 0.05$) though, between the immediate and 24-hour values for each material. Compared with the control, the immediate gap width mean values of all spherical filler-added

RMGICs showed a significant difference (Fig.5.1). There was also a significant difference between the immediate marginal gaps in the tooth cavity and in the Teflon mold ($p < 0.05$).

5.3.3. *Shear bond strength to enamel and dentin*

Table 5.3 lists the effects of spherical silica fillers on the shear bond strength of RMGIC to enamel. Examining the immediate shear bond strengths to enamel, there was a significant difference between SF5 with the control and with UF20 ($p < 0.05$). After 24-hour storage, there was a significant increase ($p < 0.05$) in shear bond strength to enamel, and SF5 showed the highest shear bond strength value.

Table 5.3 Shear bond strength of RMGIC to enamel surface

Materials	P/L	Immediate (MPa)			24-hour (MPa)			α value [1]
SF5	4.0	7.85 ± 1.57	(8)	a	27.47 ± 5.12	(10)	f	$p < 0.05$
SF10	4.4	7.34 ± 2.02	(10)	a, b, c	22.47 ± 5.31	(10)	g, h	$p < 0.05$
SF20	4.0	6.94 ± 1.43	(10)	a, b, c	19.74 ± 4.94	(10)	h, i	$p < 0.05$
UF5	4.4	7.03 ± 1.39	(9)	a, b, c	21.17 ± 4.69	(10)	g, h, i	$p < 0.05$
UF10	4.4	6.42 ± 2.15	(9)	a, b, c	18.01 ± 4.86	(10)	i	$p < 0.05$
UF20	4.0	6.02 ± 1.02	(6)	c	12.13 ± 3.86	(10)	k	$p < 0.05$
FLCEM	3.6	7.61 ± 1.65	(9)	a, b	24.78 ± 3.75	(10)	f, g	$p < 0.05$
Control	3.0	6.35 ± 1.72	(8)	b, c	23.93 ± 3.41	(10)	f, g	$p < 0.05$

SF = Silanized spherical silica filler, UF = Untreated spherical silica filler

FLCEM = Fuji II LC EM mixed with P/L 3.6, Control = Fuji II LC EM mixed with P/L 3.0, n = 10

Identical letters indicate no significant difference among the materials analyzed using the t-test for differences among several means ($p > 0.05$)[54]

( ): cohesive failure, among 10 specimens

[1] : significant difference, analyzed using the t-test between two values.

Table 5.4 lists the effects of spherical silica fillers on the shear bond strength of RMGIC to dentin. There were no significant differences among the immediate shear bond strengths to dentin. However, after 24-hour storage, SF5 and FLCEM showed a significant difference in comparison with SF10, SF20, UF10, and UF20. There was also a significant increase ($p < 0.05$) in shear bond strength to dentin after 24-hour water storage. However, the increase was not significant in SF20 and UF20.

During the course of shear bond strength tests, the majority of failures occurred in RMGIC itself rather than at the RMGIC/tooth interface, which is defined as a cohesive failure[113,114].

Table 5.4 Shear bond strength of RMGIC to dentin surface

Materials	P/L	Immediate (MPa)			24-hour (MPa)			α value [1]
SF5	4.0	7.60 ± 2.16	(10)	a	13.54 + 3.60	(10)	d	$p < 0.05$
SF10	4.4	7.42 ± 1.49	(10)	a	10.28 ± 3.60	(10)	e, f	$p < 0.05$
SF20	4.0	7.89 ± 3.68	(10)	a	10.29 ± 3.64	(10)	e, f	NS
UF5	4.4	7.67 ± 1.57	(10)	a	11.54 ± 3.32	(10)	d, e	$p < 0.05$
UF10	4.4	7.45 ± 2.62	(10)	a	10.03 ± 2.54	(10)	e, f	$p < 0.05$
UF20	4.0	7.30 ± 2.40	(10)	a	8.16 ± 2.44	(10)	f	NS
FLCEM	3.6	6.47 ± 2.39	(10)	a	13.48 ± 3.77	(10)	d	$p < 0.05$
Control	3.0	6.44 ± 2.31	(10)	a	10.74 ± 3.27	(10)	d, e, f	$p < 0.05$

SF = Silanized spherical silica filler; UF = Untreated spherical silica filler

FLCEM = Fuji II LC EM mixed with P/L 3.6;Control = Fuji II LC EM mixed with P/L 3.0; n = 10

Identical letters indicate no significant difference among the materials analyzed using the t-test for differences among several means ($p > 0.05$)[54]

( ): cohesive failure, among 10 specimens

[1] : significant difference, analyzed using the t-test between two values

5.4. DISCUSSION

Many factors challenge the marginal integrity of GIC restorations. These factors include cavity preparation method[115], cavity pretreatment, curing shrinkage[116-118], and hygroscopic expansion[111,112,116] of the material. For RMGICs, stress development due to cement setting starts immediately after light irradiation is commenced[119], and curing shrinkage can create marginal gaps that may contribute to restoration failure[116,117]. Therefore water exposure was recommended to control stress development[120,121], and it was suggested to delay polishing by at least one day to prevent gap formation at the cement-tooth cavity interface by anticipating the hygroscopic expansion of the restorative material[111,112,119]. This effect was reported as uptake of water by the RMGIC matrix to form a poly-HEMA complex[91].

In previous chapter, it was reported that the 24-hour water uptake of SF-added RMGICs was less than that of UF-added RMGICs or the original RMGIC. However, after 24-hour storage there were no significant differences between the marginal gap widths of SF-added RMGICs and those of UF-added RMGICs, except for UF20. Nonetheless, RMGIC's added with either filler type showed significant differences in comparison with the control and FLCEM (Table 5.1). Although the hygroscopic expansion did not entirely compensate the setting shrinkage in the Teflon mold (Table 5.2) after 24-hour water storage, the marginal gaps in tooth cavities were remarkably eliminated.

At the immediate time point, the marginal gaps in the Teflon mold were about three-fold of those in the tooth cavity (Fig. 5.1). Smaller marginal gaps observed in the tooth cavity than in the Teflon mold clearly demonstrated that adhesion between the cement and cavity walls was an important factor influencing marginal gaps[118]. For this reason, direct studying of marginal gaps in tooth cavities was a useful simulation of clinical

conditions[112]. However, by examining the setting shrinkage in the Teflon mold, the marginal gap in the tooth cavity could be predicted since there was a linear correlation between the values [118] (Fig. 5.2).

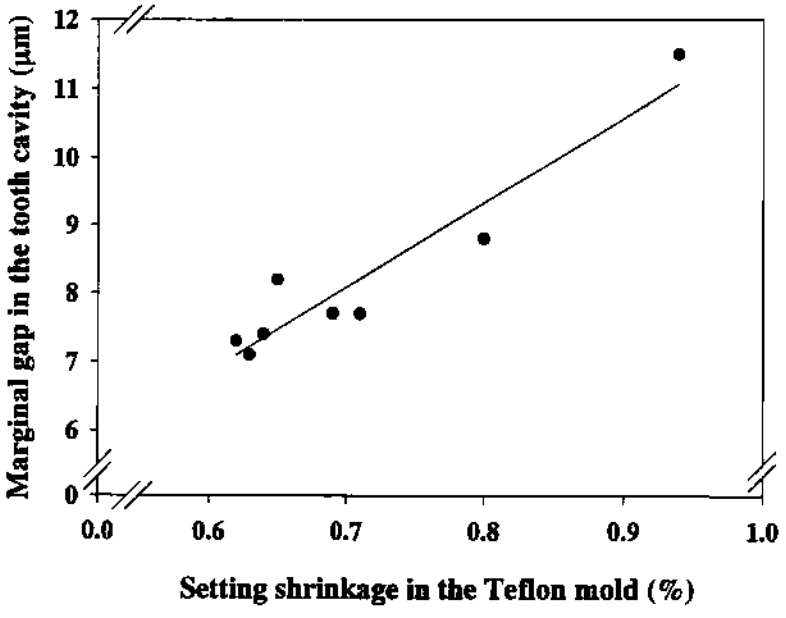


Fig.5.2 Correlation of immediate setting shrinkage in the Teflon mold vs. immediate marginal gap in the tooth cavity.
The correlation fulfilled the equation of $y = 12.42x - 0.60$ ($r = 0.95$ and $p < 0.001$)[54].

It was reported that resin infiltration into the expanded decalcified layer would prevent microleakage and nanoleakage[122]. Furthermore, marginal integrity is of primary importance in maintaining the long-term function of resin-based restorations[123]. At the immediate time point, when compared with the control, the SF- and UF-added RMGICs had significantly less marginal gaps in the tooth cavity and setting shrinkage in the Teflon mold. This occurred due to one or both of the following reasons. First, the SF- or UF-added RMGIC was mixed with higher P/L. The higher the P/L, the smaller the

marginal gap[119] and the greater mechanical strength of the GIC[43,72,119]. Second, the spherical form of silica fillers increased the flowability of RMGIC[71], leading to better penetration into the decalcified layer and reducing the immediate marginal gap.

Following post-set water uptake, the acidic monomers of RMGIC ionize then react with the glass filler to initiate an acid-base reaction, producing ionic cross-linking[124]. In these dual setting systems, resin-reinforcement produces higher bond strengths to dental tissues as well as enhanced mechanical strength[34,117]. Van Meerbeek *et al.*[124] found a gradual transition of resin concentration in the decalcified superficial dentin. Resin concentration was highest at the top of the hybrid layer, and lowest near the base. If resin did not penetrate through the full depth of the decalcified zone, the non-infiltrated weak collagen layer at the bottom of the zone would perhaps be susceptible to long-term hydrolitic degradation[125]. Since the majority of shear bond failures were cohesive failures, the interfacial bond formed between the RMGIC and the solid substrate was stronger than the cohesive bond within the material itself[33]. However, at the immediate time point, UF20 showed apparently less cohesive failure than other materials. It was thought to stem from poor bonding of UF to the RMGIC matrix[72]. As a result, the reaction was delayed, hence affecting the penetration of RMGIC to the decalcified layer. This condition should be studied further.

There was a tendency for the shear bond strength to enamel and dentin to decrease when a large amount of fillers was added. This was clearly shown with the addition of 20 wt% filler, especially in UF20. As shown in chapter 3, since UF did not bond with the RMGIC matrix, a large amount of UF may act as an impurity that hinders the reaction in RMGIC. In contrast, SF5 showed higher shear bond strength to enamel and dentin than those of the control and FLCEM. In addition, up to 10wt% SF, the RMGICs showed no significant differences in shear bond strength to enamel compared with those of the control

and FLCEM. This result is in agreement with previous study[126], although the form of filler particles was not explained, and the peak was at 10 wt % filler addition. It was thought that an increase in mechanical strength would lead to an increase in bonding ability[119]. Although the 24-hour shear bond strength to dentin did not show a significant difference, supported by the results of mechanical properties in previous chapter, the SF-added RMGICs showed better mechanical and bond strengths than the UF. These results obviously showed that silanization, which creates siloxane bridges (Si–O–Si) — between the silica surface and the silane molecules — facilitate better interaction between the RMGIC matrix and the filler[50,72,127].

It seemed that the shear bond strength value of the GIC in this study was much lower than the shear strength of the dentin (138 MPa) or enamel (90 MPa)[62]. However, the shear strength data of dentin or enamel was taken through the punch method, which was different with the procedure in this study. Previous data of the bond strength of GIC to dentin was 4 MPa, while to enamel was 5 MPa[62], but the procedure was not stated. Therefore, it was not appropriate to compare the data.

It has been reported that decrease in marginal gap due to increase in P/L would result in increased shear bond strength of the GIC[119]. However, in this study, there was no significant relationship between marginal gap width and shear bond bond strength, since the filler content of the materials varied. Nonetheless, the shear bond strength results made a great contribution since the SF-added RMGICs were mixed with higher P/L. As mentioned, increasing the P/L will reduce the amount of liquid used and consequently reduce allergies or harmful effects caused by the release of non-polymerized free monomers from the filling materials[56,57].

5.5. CONCLUSION

The addition of spherical silica fillers to RMGIC significantly decreased the marginal gap and the setting shrinkage in the Teflon cavity. This condition led to a significant decrease in immediate marginal gaps in the tooth cavity. This study also revealed that shear bond strength was not in correlation with marginal gap width and setting shrinkage rate. Nonetheless, if up to 5% of silanized spherical silica fillers were added to RMGIC powder, the shear bond strength of RMGIC to enamel and dentin surfaces would increase.

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Effect of Adding Spherical Silica Filler on Physico-mechanical Properties of Resin Modified Glass-ionomer Cement

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This study investigated the effects of spherical silica fillers on the physical and mechanical properties of resin-modified glass-ionomer cement (RMGIC). Specimens were fabricated by mixing untreated (UF) or silanized (SF) spherical silica filler into the powder of a commercially prepared RMGIC. The original RMGIC and a preparation containing 20 wt% spherical silica filler were also examined with regard to their fractured surface and fluoride release. The fillers increased the compressive strength remarkably: up to 17% in the case of SF and 9% in the case of UF. Both UF and SF increased the flexural strength by up to 17%. The addition of SF increased the DTS up to 38%, but UF decreased the DTS. The addition of SF improved the workability and the mechanical properties of the RMGIC.

Key words: Resin-modified glass-ionomer cement, Spherical silica fillers, Silanization

INTRODUCTION

Glass-ionomer cements (GICs) possess certain properties that make them useful as filling materials for restorations. These properties include fluoride release, chemical bonding and a similar coefficient of thermal expansion to teeth. GICs are, however, brittle and exhibit limited mechanical strength and low wear-resistance[1]. To improve the strength of conventional GICs, resin-modified glass-ionomer cements (RMGICs) have been developed[2]. The mechanical properties of RMGIC (containing compomer) are superior to those of conventional GIC[3,4]. The weak organic-salt matrix of GIC is strengthened by modification of the resin as in methacrylate modified systems. However, such resin-modified cements have decreased fluoride release and caries resistance[5]. To improve cement strength and wear-resistance, McLean, Gasser and Simmons added metals to the powder component of GIC[1,6]. Kobayashi *et al.* added glass short fibers (CaO-P_2O_5-SiO_2-Al_2O_3) to GIC[7], while Yap *et al.* and Arita *et al.* added hydroxyapatite particles to improve the mechanical properties and microstructural properties of GIC[8,9]. However, the use of spherical silica filler in RMGIC has not been reported in spite of its great potential to increase the flowability of GICs. Therefore, in this study, the effect of spherical silica fillers on the properties of RMGIC was evaluated. The hypothesis to be tested was that the addition of spherical silica filler would significantly increase the workability, physical properties and mechanical properties of RMGIC.

MATERIALS AND METHODS

Materials

The RMGIC material used in this study was Fuji II LC EM (powder Lot #0205211, liquid Lot #0204301, GC, Tokyo, Japan) with a recommended powder/liquid ratio (P/L) of 3.0. Although the detailed composition of the material is not published, it is reported that the powder was fluoro-alumino-silicate glass; the liquid was composed of methacrylic acid ester, polyacrylic acid and water.

The spherical silica filler (GC, Tokyo, Japan) had an average particle diameter of 0.3 μm (Fig. 1). γ-methacryloxypropyl trimethoxysilane (γ-MPTS) (KBM 503, Shin-Etsu Chemical Co., Tokyo, Japan), the filler-matrix coupling agent most commonly utilized by dental composite manufacturers to chemically bond to the filler surface and co-polymerize with the methacrylic polymer matrix[10], was used to silanize the untreated filler. Spherical silica filler particles (15 g) were immersed in γ-MPTS solution {0.30 g of γ-MPTS, 0.15 g of CH_3COOH (Nakarai Chemical Ltd. Kyoto, Japan), 15 g of ethanol (Wako Chemical, Osaka, Japan) and 15 g of H_2O} at room temperature for 10 minutes. The slurries were stirred and heated at 95℃ for 1 hour, then tray dried at 65 ℃ for 24 hours.

The RMGIC powder was modified by initially mixing it with either the untreated spherical silica filler (UF) or the silanized spherical silica filler (SF) at different weight percentages (5%, 10% and 20%), before mixing with Fuji II LC EM liquid. The mixing method was to shake 5.000±0.050 g of mixture in a 50-ml bottle by hand with a frequency of 120 cycle/min and an amplitude of 20 cm. The prepared

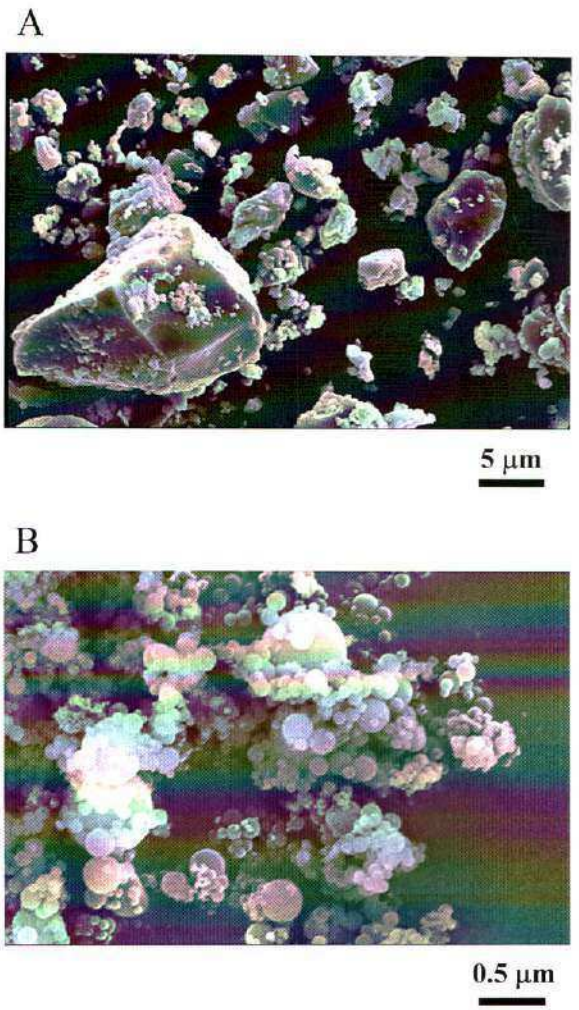

Fig. 1 SEM images of materials.
A. Powder of the original RMGIC.
B. Spherical silica fillers had an average particle diameter of 0.3 μm.

cement powders are noted as UF5, UF10, UF20, SF5, SF10 and SF20, which show the type of filler added and its filler content in weight percentage.

A visible-light curing unit (New Light VL-Ⅱ, GC, Tokyo, Japan, irradiated diameter: 10 mm) was used for activating the specimens, and close contact was ensured between the exit window of the lamp and the glass plate. The light intensity was checked and maintained at 450 mW/cm^2 before each application of restorative material using a radiometer (Demetron/Kerr, Danbury, CT, USA).

Determination of the surface of silica after silanization

In order to evaluate the silane coupling agent adsorbed on the surface of the silica, trifluoropropyl trimethoxysilane (FPTS) (KBM 7103, Shin-Etsu Chemical Co., Tokyo, Japan) containing fluoride was used as a tagged coupling agent. Silica plates (Lot #SK-4303, Sumikinsekiei, Tokyo, Japan) were used since they allowed for a more standardized and detailed quantification of the silane coupling agent attached to the surface of the silica.

The three following groups were chemically analyzed using X-ray photoelectron spectroscopy (XPS).

(1) Silica plates were immersed in FPTS solution (0.30 g of FPTS, 0.15 g of CH_3COOH, 15 g of ethanol and 15 g of H_20 at room temperature for 10 minutes, heated at 95℃ for 1 hour, and dried at 65℃ for 24 hours.

(2) Silica plates were silanized as mentioned above, immersed in distilled water at room temperature for 2 hours and air-dried.

(3) Silica plates were silanized as mentioned above, immersed in the Fuji II LC EM liquid at room temperature for 2 hours, rinsed off with distilled water, rinsed again with acetone and air-dried.

All silica plates were analyzed *in vacuo* of less than 10^{-7} Pa using an AXIS-HS spectrometer (Kratos Analytical, Manchester, UK). Al-Kα monochromatic X-rays with a power source of 150 W were utilized. Wide and arrow scans were measured at a pass energy of 80 and 40 eV, respectively. Quantitative data were obtained from peak areas[11].

Consistency measurements

The RMGIC was mixed with a P/L of 2.8 to 4.8 (g/g). The mixing time was 30 seconds and the preparation time was 30 seconds. Then, 0.05 cc of mixed glass-ionomer cement was placed on a glass plate. Within 2 minutes of the start of mixing, a force of 127 N was applied to the top of the plate and left for 1 minute. The maximum and minimum diameters of material were measured using vernier calipers (U39818, Mitutoyo, Kawasaki, Japan) and the mean result was recorded to the nearest 0.05 mm.

Compressive strength measurements

For the preparation of compressive strength samples, a cylindrical Teflon split mold with a depth of 6.0 mm and diameter of 3.0 mm was used to minimize the stress exerted on the specimens during their retrieval.

All specimens were mixed in 30 seconds using a plastic spatula on a mixing pad, syringe-loaded into a Teflon split mold, covered with a glass plate and clamped. Taking into consideration the thickness of the glass plate and the specimens, the specimens were light cured for 60 seconds on each side. Then, they were removed from the mold, varnished and immersed in distilled water. After storage for 24 hours in a 37℃ incubator, the compressive strength was measured using a universal testing machine (Autograph DCS-2000, Shimadzu, Kyoto, Japan) with a cross-head speed of 0.5 mm min^{-1} outlined in ISO 7489-1986, with a maximal external force of 200 kgf (1960 N).

Diametral tensile strength (DTS) measurements
The maximal P/L was chosen based on the compressive strength value. One of the subsequent experiments performed was the measurement of DTS. Sample preparation in the cylindrical Teflon split mold (h=3.0 mm, d=6.0 mm), light curing and the testing procedure were the same as described for the compressive strength measurements.

Flexural strength measurements
The procedure used to measure flexural strength was similar to that used to measure compressive strength except that the internal dimensions of the Teflon split mold were 25.0 mm×2.0 mm×2.0 mm and the light curing was for 60 seconds at 3 overlapping sites. The flexural strength was measured using the 3-point bending method with a 20-mm span. A universal testing machine was used with a cross-head speed of 0.5 mm min^{-1} and a maximal external force of 10 kgf (98 N) was applied to the midpoint of the test beam.

Water uptake measurements
Before being immersed in distilled water, the specimens to be used for the 24-hour diametral tensile strength measurements were weighed with an electric balance (AJ 100, Mettler, Greifensee, Switzerland). After being immersed in distilled water for 24 hours in a 37℃ incubator and dried for 1 minute on the Kim Wiper, the specimens were weighed again. The degree of water uptake was calculated from the changes in the specimen's weight and was expressed as a percentage.

Six specimens were prepared for each of the material and conditions. All dimensions were measured using a digital micrometer (293-421-20, Mitutoyo, Kawasaki, Japan). All procedures, except for mechanical testing, were performed in a thermohygrostatic room kept at 23±0.5℃ and 50±2% relative humidity.

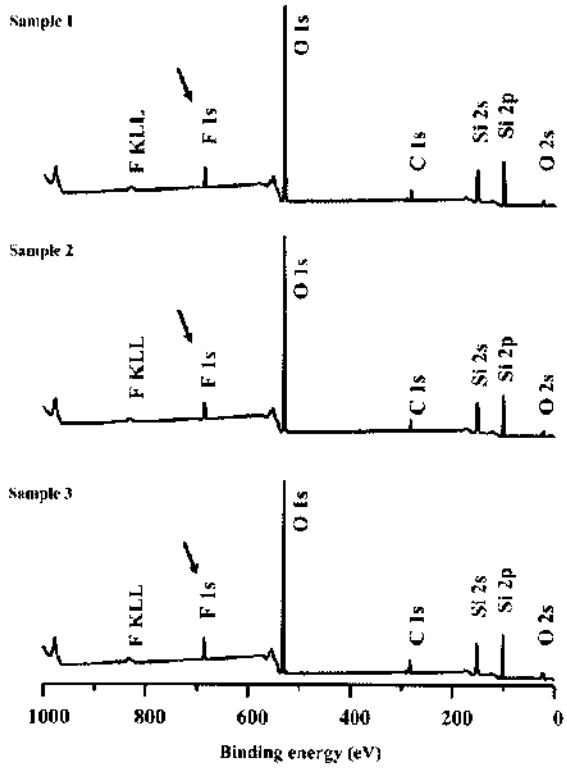

Fig. 2 XPS images of silanized silica plates. Arrows indicate the Fluoride peaks of the spectra.

Statistical analysis
The results of measurements were analyzed using an ANOVA and Tukey test, with the level of significance set at 0.05[12]. The difference among the regression lines of the data was compared with a *t*-test[13].

Fractured surface analysis
After the flexural strength measurements, the fracture surfaces of the samples were analyzed with a field emission scanning electron microscope (FE-SEM) (DS-720, Topcon, Tokyo, Japan).

RESULTS

Determination of the surface of silica after silanization
Fig. 2 shows the XPS wide-scan spectra of silanized silica plates. Fluoride peaks were detected on the treated silica plates surfaces, indicating that the silane coupling agent presents on the surface of the silica plates. It was found that the fluoride peaks area of samples 1, 2 and 3 did not differ significantly.

Consistency
Fig. 3 presents the results of consistency tests. The original RMGIC can be mixed at a P/L of up to 4.0. The addition of 5 wt% SF or UF made it possible to use a P/L of up to 4.4, while the addition of 10 wt% SF or 20 wt% UF made it possible to use a P/L up to 4.6. The addition of 10 wt% UF or 20 wt% SF allowed the RMGIC to be mixed with a P/L of up to 4.8.

At a P/L of 3.0, the value recommended by the manufacturer, the consistency of the RMGIC was 39.52±1.00 mm. Increasing the P/L to 4.0 (max.) caused the consistency to decrease to 31.79±1.86 mm. For the UF5, UF10 and UF20, consistency values at P/L 3.0 were 41.68±0.59 mm, 41.31±0.95 mm and 39.48±1.34 mm, respectively. At the P/L maximum, the consistency decreased to 32.23±1.76 mm, 31.93±0.79 mm and 31.66±0.84 mm. For the SF5, SF10 and SF20, consistency values at P/L 3.0 were 41.04±1.54 mm, 41.33±1.10 mm and 36.92±0.97 mm,

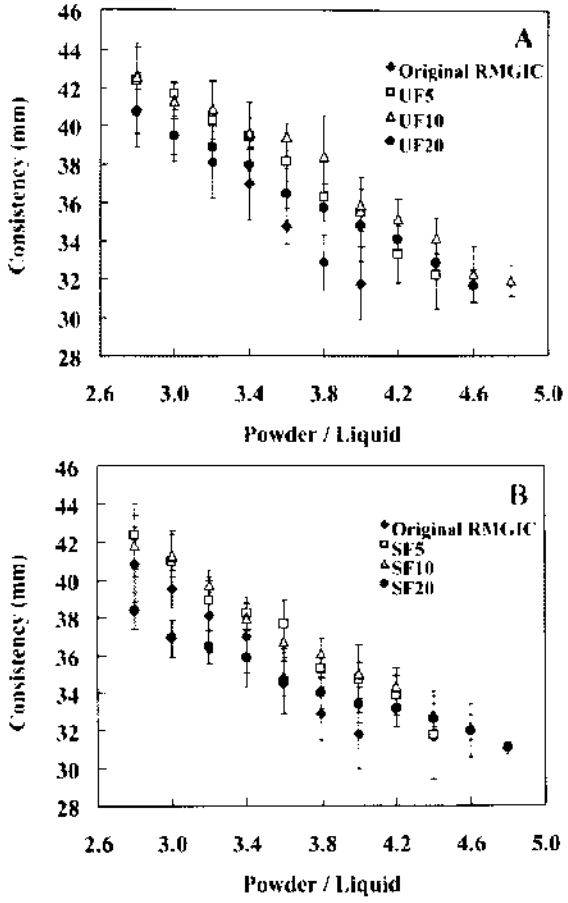

Fig. 3 Powder/liquid vs. consistency of spherical silica filler-added RMGIC, n=6.
A. The correlation in UF-added RMGIC.
Original RMGIC: y=−7.81x+62.96, r=−0.996, p<0.001.
UF5: y=−6.53x+61.22, r=−0.99, p<0.001.
UF10: y=−5.56x+58.55, r=−0.99, p<0.01.
UF20: y=−4.92x+54.479, r=−0.998, p<0.001.
B. The correlation in SF-added RMGIC.
Original RMGIC: y=−7.81x+62.96, r=−0.996, p<0.001.
SF5: y=−6.26x+59.64, r=−0.99, p<0.001.
SF10: y=−5.56x+57.37, r=−0.99, p<0.001.
SF20: y=−3.39x+47.25, r=−0.99, p<0.001.

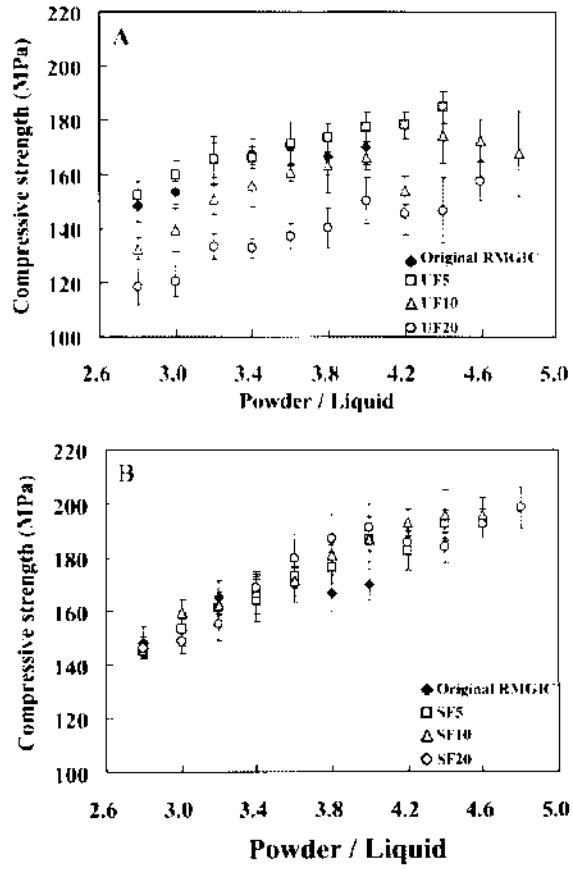

Fig. 4 Powder/liquid vs. compressive strength of spherical silica filler-added RMGIC, n=6.
A. The correlation in UF-added RMGIC.
Original RMGIC: y=17.27x+104.36, r=0.86, p<0.05.
UF5: y=18.15x+104.65, r=0.98, p<0.001.
UF10: y=17.32x+119.16, r=0.87, p<0.01.
UF20: y=19.80x+65.06, r=0.96, p<0.001.
B. The correlation in SF-added RMGIC.
Original RMGIC: y=17.27x+104.36, r=0.86, p<0.05.
SF5: y=28.32x+68.78, r=0.98, p<0.001.
SF10: y=27.60x+74.01, r=0.99, p<0.001.
SF20: y=25.81x+78.24, r=0.93, p<0.001.

respectively. At the P/L maximum, these values decreased to 31.77±2.33 mm, 32.13±0.68 mm and 31.03±0.35 mm.

The regression analysis of the correlation between P/L and consistency gave linear results with r=−0.99 and p<0.001. The gradient for the original RMGIC is −7.81, while the gradients for the SF5, SF10 and SF20 were −6.26, −5.56 and −3.39, and those for the UF5, UF10 and UF20 were −6.53, −5.56 and −4.92, respectively. The comparison of the regression analysis of the correlation between P/L and consistency is presented in Table 1. There are significant differences among the materials (p<0.01 or less). However, there was no significant difference between the regression lines of the SF5 and SF10, the UF10 and UF20 or the SF5 and UF5.

Compressive strength measurements

The effect of the spherical silica fillers on the compressive strength of the materials is summarized in Fig. 4. At P/L 3.0, the compressive strength of RMGIC is 153±4 MPa. Increasing the P/L to 4.0 (max.) increased the compressive strength to 170±6 MPa. For the UF5, UF10 and UF20, the compressive

Table 1 Differences in P/L vs. consistency regression analysis of the original RMGIC and spherical silica filler-added RMGIC

Comparison			Significance*
Original RMGIC	vs.	UF5	$p<0.001$
		UF10	$p<0.001$
		UF20	$p<0.001$
UF5	vs.	UF10	$p<0.01$
		UF20	$p<0.001$
UF10	vs.	UF20	$p>0.05$ (NS)
Original RMGIC	vs.	SF5	$p<0.001$
		SF10	$p<0.001$
		SF20	$p<0.001$
SF5	vs.	SF10	$p>0.05$ (NS)
		SF20	$p<0.001$
SF10	vs.	SF20	$p<0.001$
UF5	vs.	SF5	$p>0.05$ (NS)
UF10	vs.	SF10	$p<0.001$
UF20	vs.	SF20	$p<0.001$

*: Analyzed using the t-test

Table 2 Differences in P/L vs. compressive strength regression analysis of the original RMGIC and spherical silica filler-added RMGIC

Comparison			Significance*
Original RMGIC	vs.	UF5	$p>0.05$ (NS)
		UF10	$p<0.01$
		UF20	$p<0.001$
UF5	vs.	UF10	$p<0.001$
		UF20	$p<0.001$
UF10	vs.	UF20	$p<0.001$
Original RMGIC	vs.	SF5	$p<0.001$
		SF10	$p<0.05$
		SF20	$p>0.05$ (NS)
SF5	vs.	SF10	$p>0.05$ (NS)
		SF20	$p>0.05$ (NS)
SF10	vs.	SF20	$p>0.05$ (NS)
UF5	vs.	SF5	$p<0.001$
UF10	vs.	SF10	$p<0.001$
UF20	vs.	SF20	$p<0.001$

*: Analyzed using the t-test

strength values at P/L 3.0 were 160±5 MPa, 139±6 MPa and 121±6 MPa, respectively. At the P/L maximum, the compressive strength was 185±6 MPa, 168±16 MPa and 158±7 MPa. For the SF5, SF10 and SF20, the compressive strength values at P/L 3.0 were 153±6 MPa, 160±5 MPa and 149±4 MPa, respectively. At the P/L maximum, these values increased to 193±5 MPa, 196±6 MPa and 199±8 MPa.

The regression analysis of the correlation between P/L and compressive strength gave linear

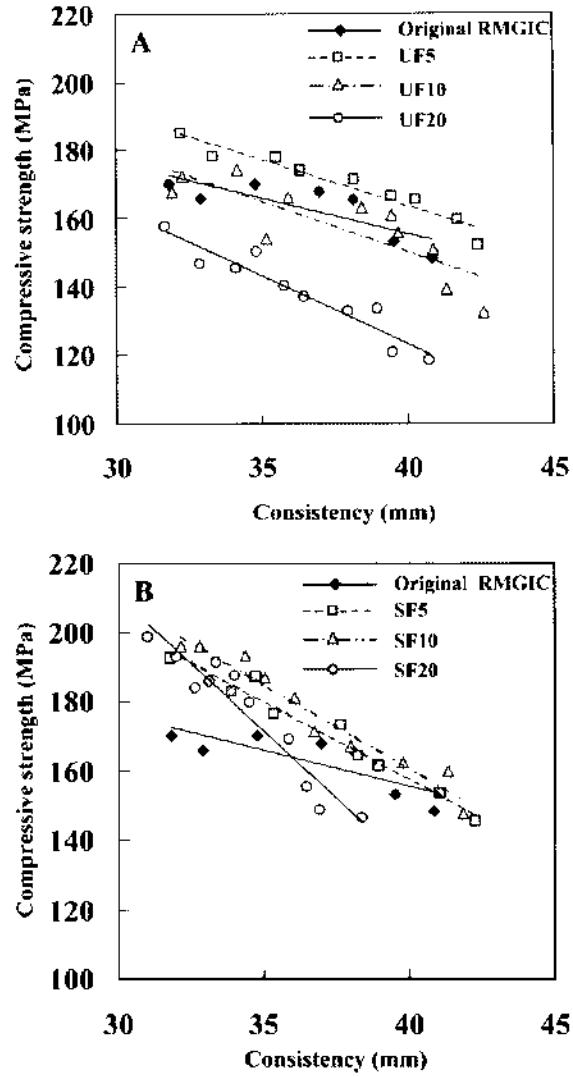

Fig. 5 Consistency vs. compressive strength of spherical silica filler-added RMGIC, n=6.
A. The correlation in UF-added RMGICs.
Original RMGIC: $y=-2.08x+238.56$, $r=-0.81$, $p<0.05$.
UF5: $y=-2.71x+272.23$, $r=-0.97$, $p<0.001$.
UF10: $y=-2.94x+267.95$, $r=-0.83$, $p<0.01$.
UF20: $y=-4.00x+283.29$, $r=-0.95$, $p<0.001$.
B. The correlation in SF-added RMGICs.
Original RMGIC: $y=-2.08x+238.56$, $r=-0.81$, $p<0.05$.
SF5: $y=4.50x+337.65$, $r=-0.98$, $p<0.001$.
SF10: $y=-4.88x+355.66$, $r=-0.98$, $p<0.001$.
SF20: $y=-7.79x+444.08$, $r=-0.96$, $p<0.001$.

results ($r=0.86$ or more and $p<0.05$ or $p<0.001$). The gradient for the original RMGIC is 17.27. The gradients for the SF5, SF10 and SF20 were 28.32, 27.60 and 25.81, while those for the UF5, UF10 and UF20 were 18.15, 17.32 and 19.80, respectively. The comparisons of these regression analyses are presented in Table 2. There was no significant

difference among the regression lines of the SF5, SF10 and SF20, between the regression lines of the original RMGIC and SF20, also between the regression lines of the original RMGIC and UF5.

The correlation between consistency and compressive strength is presented in Fig. 5. The regression analysis of the correlation gave linear results ($r=0.81$ or more and $p<0.05$ or less). The gradient of the original RMGIC was −2.08. The gradient of the SF5, SF10 and SF20 were −4.50, −4.88 and −7.79, while those of UF5, UF10 and UF20 were −2.71, −2.94 and −4.00, respectively. The comparison of the regression analysis of the correlation between consistency and compressive strength is shown in Table 3. With the exception of RMGIC and UF10 ($p>0.05$), the regression analysis of the correlation between consistency and compressive strength showed significant differences among the materials ($p<0.05$ or less).

Table 3 Differences in consistency vs. compressive strength regression analysis of the original RMGIC and spherical silica filler-added RMGIC

Comparison			Significance*
Original RMGIC	vs.	UF5	$p<0.001$
		UF10	$p>0.05$ (NS)
		UF20	$p<0.001$
UF5	vs.	UF10	$p<0.001$
		UF20	$p<0.001$
UF10	vs.	UF20	$p<0.001$
Original RMGIC	vs.	SF5	$p<0.001$
		SF10	$p<0.001$
		SF20	$p<0.001$
SF5	vs.	SF10	$p<0.05$
		SF20	$p<0.001$
SF10	vs.	SF20	$p<0.001$
UF5	vs.	SF5	$p<0.01$
UF10	vs.	SF10	$p<0.001$
UF20	vs.	SF20	$p<0.001$

*: Analyzed using the t-test

The results of the mechanical properties at maximum P/L, which were analyzed statistically, are summarized in Table 4. In the compressive strength measurements, there was a significant difference between the SF-added RMGIC and the original RMGIC ($p<0.05$). There was no significant difference among the original RMGIC, and UF10 or UF20, or among UF5 and SF5 or SF10. The addition of SF increased the compressive strength significantly up to 17%, while the addition of UF only increased the strength up to 9%.

DTS measurements

In the DTS measurements, there was a significant difference between the original RMGIC and SF-added RMGIC ($p<0.05$) (Table 4). The addition of 10 wt% SF increased the DTS significantly up to 38%, from 21.1±0.7 MPa to 29.2±2.0 MPa. However, the addition of UF decreased the DTS. There was no significant difference between the original RMGIC and UF5 (20.0±1.3 MPa), between the UF5 and UF10 (18.0±1.5 MPa) or between the UF10 and UF20 (15.5±0.7 MPa).

Flexural strength measurements

Except with UF20, there was no significant difference among the materials in the flexural strength measurements (Table 4). The addition of SF or UF increased the flexural strength up to 17%. The flexural strength of the original RMGIC was 53.8±8.3 MPa, while the greatest gain in flexural strength was obtained in SF20 (63.2±5.8 MPa) and UF10 (63.1±3.8 MPa).

Water uptake

The water uptake measurements are also listed in Table 4. The addition of UF reduced the water uptake of RMGIC, though not significantly, up to 9%.

Table 4 Physical and mechanical properties of the original and spherical silica filler-added RMGIC at the maximum workability

Materials	P/L	Compressive strength* (MPa)		Diametrical tensile strength* (MPa)		Flexural strength* (MPa)		Water uptake* (%)	
Original RMGIC	4.0	170±6	c, d	21.1±0.7	k	53.8±8.3	q	3.11±0.27	x
UF5	4.4	185±6 (9%)	b, c	20.0±1.3 (−5%)	k, l	56.8±6.0 (5%)	q	2.85±0.10 (−8%)	x, y
UF10	4.8	168±16 (−1%)	c, d	18.0±1.5 (−15%)	l, m	63.1±3.8 (17%)	q	2.82±0.21 (−9%)	x, y
UF20	4.6	158±7 (−7%)	d	15.5±0.7 (−27%)	m	30.7±4.3 (−43%)	r	3.11±0.13 (0%)	x
SF5	4.4	193±5 (14%)	a, b	25.3±1.0 (20%)	n	56.7±4.6 (5%)	q	2.72±0.29 (−13%)	y
SF10	4.6	196±6 (15%)	a, b	29.2±2.0 (38%)	p	60.1±4.9 (12%)	q	2.21±0.11 (−29%)	z
SF20	4.8	199±8 (17%)	a	25.1±2.1 (19%)	n	63.2±5.8 (17%)	q	2.09±0.16 (−33%)	z

( ) increasing rate, compared to original RMGIC

UF: untreated filler, SF: silanized filler

*: Same letters show no significant difference analyzed using the Tukey test, $p>0.05$, $n=6$.

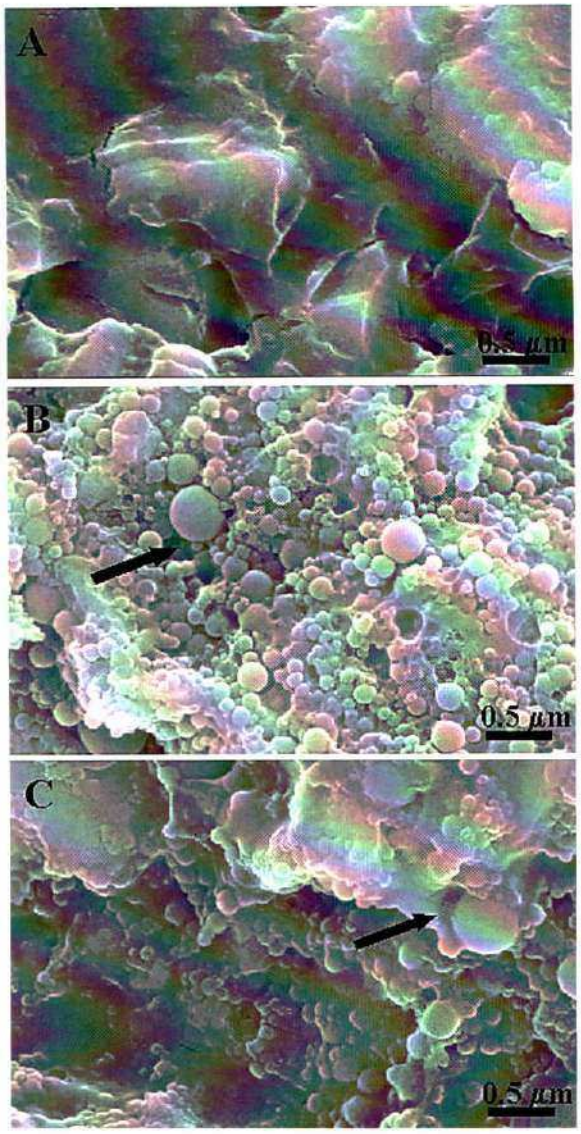

Fig. 6 SEM images of the flexural strength fractured surface of RMGICs.
Arrows indicate the interfacial bonding between fillers and matrix of RMGIC.
A. Fractured surface of the original RMGIC.
B. Fractured surface of UF20. Fillers were separated from the matrix due to mechanical bonding failure at the interface between filler and the matrix of RMGIC.
C. Fractured surface of SF20. Silanized fillers were bonded by chemical bonding at the interface between filler and the matrix of RMGIC.

from 3.11±0.27% to 2.82±0.21% at 10 wt%. However, the water uptake of SF20 was 2.09±0.16%, a decrease of 33% ($p<0.05$).

Fractured surface analysis

Fig. 6 shows the fractured surface of RMGIC with spherical silica filler analyzed by SEM. The original

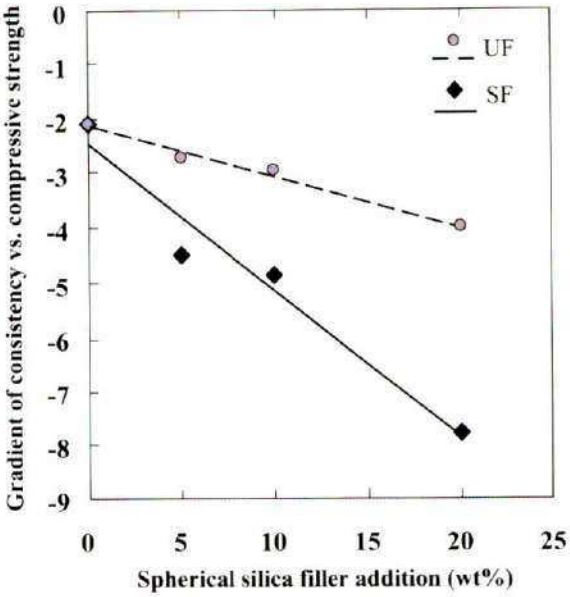

Fig. 7 The amount of spherical silica filler vs. gradient of correlation between consistency and compressive strength of spherical silica filler-added RMGICs.
UF: $y=-9.29x-2.12$, $r=-0.99$, $p<0.01$
SF: $y=-26.82x-2.47$, $r=-0.98$, $p<0.05$

RMGIC shows an irregular fracture surface (Fig. 6A). Debonded spherical silica fillers are observed at the fracture surface of the UF-added RMGIC (Fig. 6B). In contrast, at the fractured surface of the SF-added RMGIC (Fig. 6C), spherical silica fillers are clearly visible, however they are bonded with the matrix of RMGIC.

DISCUSSION

Silane coupling agents are used to reinforce the adhesion of the filler to the matrix polymer and also to increase hydrolitic stability[14,15]. The organofunctional silane γ-MPTS has been used extensively in dental resin-based composite materials[10,11]. The enhanced stability of composites compounded with filler treated with γ-MPTS or with another silane coupling agent is attributed, in part, to the formation of a siloxane bond between the filler and the coupling agent[14,16]. Consequently, the interaction between the resin component of the matrix RMGIC and spherical silica filler in this study was considered to be reinforced by the silane coupling agent, and not to be affected by the liquid of the RMGIC as presented in the XPS image.

In the XPS analysis, the peaks for the presence of fluoride tags of the silane coupling agent on the surface of the silica plates were detected based on binding energy. The area of fluoride peaks that present the fluoride tags of the silane coupling agent on

the surface of the silica plate did not differ significantly (Fig. 2). Therefore, it is suggested that immersion in distilled water and in the liquid of the RMGIC, which contained polyacrylic acid, for 2 hours did not affect the attachment of the silane coupling agent to the treated silica surface.

As mentioned, the light curing process polymerizes the monomers in the liquid of the RMGIC. However, the polymerization is seldom complete and residual or unpolymerized free monomer molecules can leach out and cause an allergy or have harmful effects[6,17]. Increasing the P/L will reduce the amount of liquid used and so reduce the release of free monomers from the filling materials.

It was reported that increasing the P/L leads to a decrease in consistency and an increase in the spatulation force required to adequately mixing the cementitious mass[18,19]. This condition was also observed in the present experiment. The addition of 10 wt% UF or 20 wt% SF raised the consistency of RMGIC, making it possible to use a P/L of up to 4.8. This gave a mixture with about the same consistency as the original RMGIC. Specifically, the addition of silica filler to RMGIC powder will extend the workability of the material. The addition of UF or SF influenced the correlation of P/L with consistency, as marked by a shift in the gradient of the regression line (Fig. 3). The gradient of SF-added RMGIC and that of UF-added RMGIC was less than the gradient of original RMGIC, which means that the rate of decrease in consistency caused by the increase in P/L was less in the cements containing SF and UF. However, the difference was not significant between the RMGIC's with SF5 and SF10, UF10 and UF20, or with SF5 and UF5. Since the amount of hydrophobic SF was small and the filler was scattered throughout the matrix powder, it is assumed that the difference between 5 and 10 wt% is too small to significantly influence the consistency of the RMGIC. It can also be assumed that at 5 wt%, the hydrophilic-hydrophobic characteristics of the filler do not play a distinct role. This might explain the lower level of significance in the correlation between consistency and compressive strength. In contrast, it is assumed that at more than 10 wt%, UF would act as an impurity and not influence the rate of decrease in consistency caused by the increase in P/L.

The addition of UF or SF also influenced the correlation between P/L and compressive strength (Fig. 4). The gradient of SF-added RMGIC was 1.49-1.64 times, and that of UF-added RMGIC almost the same as (1.00-1.15 times) the gradient of original RMGIC. It is showed that the rate of increase in compressive strength caused by the increase of P/L was greater in the cement containing SF than in the original or UF-added RMGIC. Yet, silanization of the filler had a marked effect, as shown by the significant difference between the addition of SF and UF at the same amount of filler ($p<0.001$).

The decrease in consistency that follows the increase in P/L also leads to a change in mechanical properties. Fig. 5 and Table 3 show that the addition of UF or SF significantly influences the correlation between consistency and compressive strength, as marked by a shift in the gradient of the regression line. The gradients for SF-added RMGIC were 2.25-3.75 times greater than that of the cement without filler, while the gradient of UF-added RMGIC was increased 1.30-1.92 fold. It is suggested that the decrease in consistency and increase in compressive strength occurred more rapidly in the preparation with SF than in the UF-added or original RMGIC.

The gradients of the correlation between consistency and compressive strength in the RMGICs (Fig. 5) were also interrelated with the addition of the filler, as shown in Fig. 7. Yet, the correlation for UF-added RMGIC ($r=-0.99$, $p<0.01$) is a little more distinctive than that for SF-added RMGIC ($r=-0.98$, $p<0.05$) and there is significant difference between the two values ($p<0.05$). The gradient of the correlation in SF-added RMGIC has a larger negative value than that in UF-added RMGIC, indicating that due to silane pretreatment, which changes the characteristics of the spherical silica fillers, the addition of SF influenced the RMGIC more than the addition of UF.

Fig. 5 showed that the addition of UF at up to 5 wt% and SF at up to 20 wt% increased the compressive strength remarkably at a similar low consistency. Consequently, in order to examine more characteristics of cement to which spherical silica filler was added, the maximum P/L that could be mixed in the dental clinic was chosen for DTS and flexural strength measurements. This maximum P/L also gave a similar consistency to the original RMGIC mixed at P/L 4.0. The addition of UF to 5 wt% increased the compressive and flexural strength. However, at more than 5 wt%, UF addition reduced the cement's strength, because the filler became an impurity that did not bond to the matrix of the RMGIC. The opposite effect was observed with the addition of SF. Since the fillers were silane-treated, their ability to bond to the matrix was improved and the addition of SF at up to 20 wt% increased the compressive strength and DTS significantly, as well as increased the flexural strength. More significant evidence is provided by the SEM observations of the fractured surface of the specimens (Fig. 6). It was found that the interfacial bonding between UF and the matrix of RMGIC was due to mechanical bonding, while that between SF and the matrix was due to chemical bonding as a result of silanization.

It was reported that flexural strength was more sensitive to changes in material substructure than compressive strength[9,10,20]. However, in this experiment, the DTS test was more sensitive for

distinguishing the effect of UF and SF. The DTS values also showed that the increase in strength is more dependent on the chemical reaction than the morphology of the fillers.

As the compressive strength increased, the flexural strength and DTS also tended to increase, although the results of the regression analysis of the correlation were not significant. This correlation should be examined more closely.

Another factor that may influence mechanical properties is the uptake of water. UF did not reduce the water uptake of RMGIC significantly, while SF did (up to 33%). The hydrophobic characteristic of SF might influence surface and grain boundary diffusion[20], then increase the resistance of the cement to water uptake.

In the next study, it is necessary to investigate the ability to bond tooth tissue, the setting shrinkage and more characteristics of RMGIC containing spherical silica filler.

CONCLUSION

The addition of spherical silica fillers to RMGIC powder improves the workability of the material. At up to 20 wt% spherical silica filler, there is a significant linear correlation among the filler amount, consistency and compressive strength of the RMGIC.

The silanized spherical silica fillers increased the compressive strength, diametral tensile strength and flexural strength, and reduced the water uptake of the RMGIC. The silanized spherical silica filler also improved the mechanical properties of the cement more than the untreated spherical silica filler.

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7.2. Marginal gap formation and fluoride release of resin-modified glass-ionomer cement: Effect of silanized spherical silica filler addition

Marginal Gap Formation and Fluoride Release of Resin-Modified Glass-Ionomer Cement: Effect of Silanized Spherical Silica Filler Addition

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Marginal Gap Formation and Fluoride Release of Resin-Modified Glass-Ionomer Cement: Effect of Silanized Spherical Silica Filler Addition

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The purpose of this study was to investigate the effects of silanized spherical silica fillers (SF) on the immediate and 24-hour marginal gaps of resin-modified glass-ionomer cement (RMGIC) in tooth cavities. In correlation with marginal gap formation in the tooth cavity, these influencing factors were also examined: marginal gap and setting shrinkage of cement in the Teflon mold, as well as the shear bond strength to tooth substrate. Moreover in correlation with caries prevention, fluoride release was examined too.

In this investigation, the fillers were mixed into the RMGIC powder (Fuji II LC EM). Untreated spherical silica filler (UF)-added RMGIC was used as a comparison. When compared with the control (*i.e.*, original RMGIC), the addition of SF significantly decreased immediate marginal gap in tooth cavities and setting shrinkage in Teflon mold up to 63% and 66% respectively. Fluoride release was significantly reduced too. Apart from these results, this study showed that addition of 5 wt% SF increased the shear bond strength to human enamel and dentin.

Key words: Resin-modified glass-ionomer cement, Silanized spherical silica fillers, Marginal gap

INTRODUCTION

Glass-ionomer cements (GICs) possess several beneficial properties, including physicochemical adhesion to tooth structures and release of fluoride ions. Newer versions of light-cured glass-ionomer, which are known as resin-modified glass-ionomer cements (RMGICs), combine the favorable properties of GICs with those of resin composites. These include the inherent adhesion and cariostatic properties of the former and the command setting behavior, good mechanical properties, and wear resistance of the latter[1-4]. Compared with conventional analogs, RMGICs have been characterized as having a longer working time, a rapid set, improved appearance and translucency, in addition to a higher early strength along with higher bond strength to enamel and dentin[2,4-9]. As a result, RMGICs also have less microleakage than conventional GICs[6-8,10,11]. However, RMGICs still need surface protection to reduce margin microleakage[12], and they also show less fluoride release and caries resistance than GICs[13].

In a previous study[14], we reported that the addition of spherical silica fillers to a RMGIC powder improved the workability of the cement. The addition of silanized spherical silica fillers (SF) increased the compressive strength, diametral tensile strength and flexural strength, and reduced the water uptake of RMGIC. It was shown through the previous study that SF improved the mechanical properties of the cement more than untreated spherical silica fillers (UF)[14]. Indeed, the success of SF addition would have had a greater value if it could reduce marginal gap or microleakage and possess other advantages in correlation with the tooth substrate.

Therefore, in this study, the first hypothesis was that the addition of SF to RMGIC would reduce the immediate and 24-hour marginal gaps in tooth cavities. The second hypothesis was that the marginal gap and rate of setting shrinkage in Teflon mold and the shear bond strength of RMGIC would influence marginal gap formation in tooth cavities. The final hypothesis was that the addition of SF would reduce the fluoride release of RMGIC.

MATERIALS AND METHODS

Materials

The RMGIC material used in this study was Fuji II LC EM (powder lot #0205211, liquid lot #0204301, GC Corp., Tokyo, Japan) with a recommended powder/liquid ratio (P/L) of 3.0. The detailed composition of the material has not been released. But according to manufacturer's information, it was given that the powder is fluoro-alumino-silicate glass, and the liquid is composed of methacrylic acid ester, polyacrylic acid, and water.

The silanized spherical silica filler (GC Corp., Tokyo, Japan), which has an average particle diameter of 0.3 μm with γ-methacryloxypropyl trimethoxysilane (γ-MPTS) (KBM 503, Shin-Etsu Chemical Co., Tokyo, Japan), was prepared as previously described[14].

The RMGIC powder was modified by initially

mixing it with either the SF or UF at different weight percentages (5%, 10%, and 20%) before mixing it with Fuji II LC EM liquid. The prepared cement powders are described as SF5, SF10, SF20, UF5, UF10, and UF20 — hence indicating the type of filler added and filler content in weight percentage. Both the mixing time and preparation time were 30 seconds each. As for the P/L, each one was chosen according to the maximum compressive strength value of each cement in the previous study[14]. Fuji II LC EM was mixed with P/L=3.0 as the control and with P/L=3.6 as the maximum compressive strength of the original RMGIC (FLCEM). SF5, SF10, and SF20 were mixed with P/L of 4.0, 4.4, and 4.0; while UF5, UF10, and UF20 were mixed with P/L of 4.4, 4.4, and 4.0, respectively.

A visible-light curing unit (New Light VL-II, GC Corp., Tokyo, Japan, irradiated diameter: 10 mm) was used for activating the specimens, and close contact was ensured between exit window of the lamp and matrix. The light intensity was checked and maintained at 450 mW/cm^2 using a radiometer (Demetron/Kerr, Danbury, CT, USA).

Although much information has been generated on the use of bovine teeth, the use of human teeth is a preferred option[15]. A total of 320 human premolars, extracted for orthodontic reasons, were used to measure the marginal gap in tooth cavities and the shear bond strength to tooth tissues in this study. After extraction, the teeth were stored immediately in distilled water at about 4℃ within 3 months before use. Since occlusal dentin tends to give lower bond strengths than proximal or buccal dentin[16,17], and that dentin tubule orientation and location significantly influence the results of mechanical strength tests[18,19], proximal flat enamel or dentin surfaces were used in this study.

All procedures, except for cavity preparation and mechanical testing, were performed in a thermohygrostatic room maintained at 23±0.5℃ and 50±2 % relative humidity. The results were analyzed statistically using ANOVA, the t-test, and Mann-Whitney U-test[20,21].

Marginal gap in tooth cavities

Human premolars (N=10 for each material and condition) were embedded in a slow-setting epoxy resin (Epofix Resin, Struers, Copenhagen, Denmark). Flat enamel surfaces on the proximal area of the teeth were obtained by grinding with wet silicon carbide paper (#800). The cylindrical cavity on the coronal region of each tooth was prepared to a depth of approximately 1.5 mm with a diameter of 3.5 mm with a tungsten carbide bur (200,000 rpm) and a fissure bur (8,000 rpm) using water spray. The dimensions of the cavity were measured using a vernier caliper (U39818, Mitutoyo, Kawasaki, Japan). Each cavity was treated with a Cavity Conditioner (Lot #0205101, GC Corp., Tokyo, Japan) for 10 seconds according to manufacturer's instructions, rinsed thoroughly with distilled water, air-sprayed, and filled with the material using a syringe tip (Centrix C-R Syringe System; Centrix, Shelton, CT, USA). Covered with a plastic strip, the material was light-cured for 20 seconds. Surfaces were polished immediately after light activation or after storage in distilled water at 37℃ for 24 hours. Excess filling material was removed by wet grinding with a wet silicon carbide paper (#1000), followed by polishing using an aqueous slurry of 0.3 μm aluminum oxide (Alfa Micropolish, Buehler Ltd., Lake Bluff, IL, USA) and thorough rinsing with distilled water. Each restoration margin was inspected under a traveling microscope (400×, Measurescope, MM-11, Nikon, Tokyo, Japan)[6,22,23]. The maximum gap width and opposing width (if any) between the cement and cavity wall were measured, and the sum of these two values was expressed as the marginal gap in that tooth cavity. As some specimens had zero marginal gaps, especially after 24-hour water storage, the overall sum of 10 specimens examined per material was calculated as the total marginal gap for the group[23].

Setting shrinkage in Teflon mold

Teflon does not react with the filled material. Therefore Teflon molds of the same diameter and depth were prepared to measure the degrees of setting shrinkage (immediately after set) and hygroscopic expansion (after 24-hour water storage), as well as to compare the marginal gap width in the tooth cavity. The Teflon mold was placed on a silicon oil-coated glass plate and a matrix strip that would not react with or bind to the filling material. Each mold was filled with the material using a syringe tip, then covered with a plastic strip and light-cured for 20 seconds. Immediately after setting or after 24-hour storage in distilled water at 37℃, any excess material was removed. The maximum gap width and opposing width between the cement and the Teflon cavity were measured, and the sum of these two values was expressed as the marginal gap in the Teflon cavity. The degree of setting shrinkage was determined using the formula below:

$$S=(G/d)\times 100\%$$

where S was the setting shrinkage, G the marginal gap, and d the diameter of the Teflon mold[22]. Ten specimens were prepared for each material and their conditions investigated.

Shear bond strength to enamel and dentin

The shear bond strength to enamel and dentin, which comprise the cavity wall, was measured to evaluate the bonding effect between the filling material and the cavity. Bond strength to flat enamel and dentin

surfaces was determined both immediately after light activation and after 24-hour distilled water storage at 37℃. Specimens (N=10 for each material and condition) were obtained from human premolars embedded in the slow-setting epoxy resin. Proximal flat enamel or dentin surfaces were obtained by grinding with a wet silicon carbide paper (#1000) followed by treatment with the Cavity Conditioner for 10 seconds. To prepare the shear bond strength samples, a cylindrical Teflon split mold (3.6-mm diameter × 2.0-mm height) was used to minimize the stress exerted on the specimens during their retrieval. Each material was placed into the Teflon mold set on the enamel or dentinal surface using a syringe tip, then hardened by light-curing. The specimens thus obtained were mounted on a universal testing machine (Autograph DCS-2000, Shimadzu, Kyoto, Japan) and shear stress was applied at 0.5 mm/min, with a maximum external force of 50 kgf (490 N). After shear bond strength measurements were taken, the fractured surfaces were analyzed using a light microscope (4×, SMZ-10, Nikon, Tokyo, Japan) to ascertain the nature of fractures[6,22,23].

Fluoride release measurement

The release of fluoride from SF20, UF20, and FLCEM was measured. All specimens were mixed for 30 seconds using a plastic spatula on a mixing pad, syringe-loaded into a cylindrical Teflon split mold (d=20.0 mm, h=0.5 mm), and covered with a glass plate and clamped. After being light-cured for 20 seconds at five overlapping sites, the samples were removed from the mold, placed in polyethylene vials with 25 ml of distilled water, and stored in an incubator at 37℃ for 1 day, 2 days, 3 days, 1 week, and 2 weeks. For each material and each time period, three samples were prepared. After each specified period, the samples were removed from the medium, and 10 ml of the medium was transferred to another vial and mixed with 1 ml of TISAB III solution (Thermo Orion, Beverly, USA). The amount of fluoride ions released from the RMGIC sample in this solution was measured using a pH/ion meter (F23-S937, Horiba, Kyoto, Japan). Then, using a SigmaPlot 8.0 program (SPSS, Chicago, Illinois, USA) by placing the cumulative fluoride release ($[F]_r$, mg/L) as a function of time (t, day), the data were fitted to a single rectangular II, 3-parameter equation as follows:

$$[F]_r = [F]_t t/(t_{1/2}+t) + \alpha t$$

where $[F]_t$ was the total amount of fluoride to be released, $t_{1/2}$ the time needed to release half of this total amount, and α the kinetic parameter[24].

RESULTS

Marginal gap in tooth cavities

Table 1 lists the effects of spherical silica fillers on the marginal gap in tooth cavities. The marginal gaps of all SF-added RMGICs were 67% of the control's or less. The marginal gap of SF10 was 63% of the control's or 83% of FLCEM's, while that of UF10 was 62% of the control's or 81% of FLCEM's. Comparing the sums of the immediate gap width using a non-parametric t-test[20,21], all materials with fillers showed significant differences from the control and FLCEM ($p<0.05$). However, there were no significant differences among SF5, SF10, and UF10; or among SF5, SF10, and UF20; or between SF20 and UF5. After 24-hour storage in distilled water, there were no significant differences among the control, FLCEM, and UF20, as well as

Table 1 Marginal gap in the tooth cavity

Material	P/L	The sum of marginal gaps for all 10 specimens (μm)[1]		α value[2]
		Immediately	After 24 hours	
SF5	4.0	74 [0] (4−10)[a,b]	6 [4] (0−1)[g]	p<0.05
SF10	4.4	73 [0] (5−11)[b]	6 [4] (0−1)[g]	p<0.05
SF20	4.0	77 [0] (2−11)[c]	6 [4] (0−1)[g]	p<0.05
UF5	4.4	82 [0] (5−13)[c]	6 [4] (0−1)[g]	p<0.05
UF10	4.4	71 [0] (2−11)[a,b]	6 [4] (0−1)[g]	p<0.05
UF20	4.0	77 [0] (5−12)[a]	7 [3] (0−1)[h]	p<0.05
FLCEM	3.6	88 [0] (4−14)[d]	7 [3] (0−1)[h]	p<0.05
Control	3.0	115 [0] (7−17)[f]	7 [3] (0−1)[h]	p<0.05

SF=Silanized spherical silica filler; UF=Untreated spherical silica filler

FLCEM=Fuji II LC EM mixed with P/L 3.6; Control=Fuji II LC EM mixed with P/L 3.0, n=10

[ ]=Number of specimens with no gaps

( )=Range of values

1: Identical letters indicate no significant differences among the materials analyzed using the t-test ($p>0.05$, non parametric)[20,21]

2: Significant difference, analyzed using the Mann-Whitney U-test between two sums

among all other spherical filler-added RMGICs. The Mann-Whitney U-test showed a significant difference ($\alpha < 0.05$) between the immediate and 24-hour values for each material. Compared with the control, the immediate gap width mean values of all spherical filler-added RMGICs showed a significant difference (Fig. 1).

Setting shrinkage in Teflon mold

Table 2 lists the effects of spherical silica fillers on the setting shrinkage of RMGIC in the Teflon mold. At the immediate time point, there were no significant differences among FLCEM, UF5, UF20, and SF20. All materials, except FLCEM, showed a significant difference ($p<0.05$) in comparison with the control. The immediate setting shrinkage of all SF-added RMGICs was 73% of the control's or less. SF10 had a setting shrinkage of $0.62 \pm 0.08\%$, of which its value was 66% of the control's or 78% of FLCEM's. However, there were no significant differences among the 24-hour setting shrinkage values in the Teflon mold. There was a significant difference ($p<0.05$) though, between the immediate and 24-hour values for each material. Compared with the control, the immediate gap width mean values of all spherical filler-added RMGICs showed a significant difference (Fig. 1). There was also a significant difference between the immediate marginal gaps in the tooth cavity and in the Teflon mold ($p<0.05$).

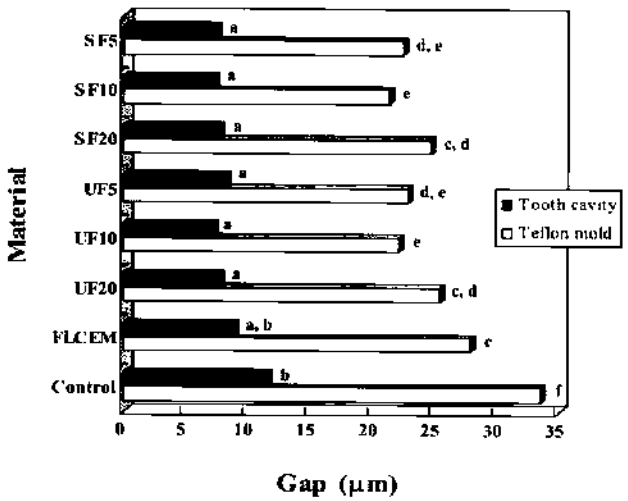

Fig. 1 Comparison of immediate marginal gap mean values of RMGICs in the Teflon mold and in the tooth cavity, n = 10.
Identical letters indicate no significant difference among the materials analyzed using the t-test for differences among several means ($p>0.05$).

Shear bond strength to enamel and dentin

Table 3 lists the effects of spherical silica fillers on the shear bond strength of RMGIC to enamel. Examining the immediate shear bond strengths to enamel, there was a significant difference between SF5 with the control and with UF20 ($p<0.05$). After 24-hour storage, there was a significant increase ($p<0.05$) in shear bond strength to enamel, and SF5 showed the highest shear bond strength value.

Table 4 lists the effects of spherical silica fillers on the shear bond strength of RMGIC to dentin. There were no significant differences among the immediate shear bond strengths to dentin. However, after 24-hour storage, SF5 and FLCEM showed a significant difference in comparison with SF10, SF20, UF10, and UF20. There was also a significant increase ($p<0.05$) in shear bond strength to dentin after 24-hour water storage. However, the increase was not significant in SF20 and UF20.

During the course of shear bond strength tests, the majority of failures occurred in RMGIC itself rather than at the RMGIC/tooth interface, which is defined as a cohesive failure[25,26].

Table 2 Setting shrinkage in Teflon mold

Material	P/L	Immediately (%)[1]	After 24 hours (%)[1]	α value[2]
SF5	4.0	0.64 ± 0.10^{b}	0.15 ± 0.04^{a}	$p<0.05$
SF10	4.4	0.62 ± 0.08^{a}	0.14 ± 0.04^{a}	$p<0.05$
SF20	4.0	$0.69 \pm 0.11^{a,b}$	0.16 ± 0.04^{a}	$p<0.05$
UF5	4.4	$0.65 \pm 0.09^{a,b}$	0.14 ± 0.05^{a}	$p<0.05$
UF10	4.4	0.63 ± 0.07^{a}	0.15 ± 0.06^{a}	$p<0.05$
UF20	4.0	$0.71 \pm 0.08^{a,b}$	0.15 ± 0.05^{a}	$p<0.05$
FLCEM	3.6	$0.80 \pm 0.08^{b,c}$	0.16 ± 0.03^{a}	$p<0.05$
Control	3.0	0.94 ± 0.10^{c}	0.17 ± 0.05^{a}	$p<0.05$

SF=Silanized spherical silica filler; UF=Untreated spherical silica filler
FLCEM=Fuji II LC EM mixed with P/L 3.6; Control=Fuji II LC EM mixed with P/L 3.0, n=10
Identical letters indicate no significant differences among the materials analyzed using the t-test for differences among several means ($p>0.05$)[20]
1: Percentage to the diameter of the Teflon mold (inner diameter: 3.5 mm)
2: Significant difference, analyzed using the t-test between two values

Table 3 Shear bond strength of RMGIC to enamel surface

Material	P/L	Immediately (MPa)	After 24 hours (MPa)	α value[1]
SF5	4.0	7.85±1.57 (8)[a]	27.47±5.12 (10)[f]	p<0.05
SF10	4.4	7.34±2.02 (10)[a,b]	22.47±5.31 (10)[g,h]	p<0.05
SF20	4.0	6.94±1.43 (10)[a,b]	19.74±4.94 (10)[h,i]	p<0.05
UF5	4.4	7.03±1.39 (9)[a,b]	21.17±4.69 (10)[g,h,i]	p<0.05
UF10	4.4	6.42±2.15 (9)[a,b]	18.01±4.86 (10)[i]	p<0.05
UF20	4.0	6.02±1.02 (6)[b]	12.13±3.86 (10)[k]	p<0.05
FLCEM	3.6	7.61±1.65 (9)[a,b]	24.78±3.75 (10)[f,g]	p<0.05
Control	3.0	6.35±1.72 (8)[a,b]	23.93±3.41 (10)[f,g]	p<0.05

SF=Silanized spherical silica filler; UF=Untreated spherical silica filler
FLCEM=Fuji II LC EM mixed with P/L 3.6; Control=Fuji II LC EM mixed with P/L 3.0, n=10
Identical letters indicate no significant differences among the materials analyzed using the t-test for differences among several means ($p>0.05$)[20]
( ): Cohesive failure, among 10 specimens
1: Significant difference, analyzed using the t-test between two values

Table 4 Shear bond strength of RMGIC to dentin surface

Material	P/L	Immediately (MPa)	After 24 hours (MPa)	α value[1]
SF5	4.0	7.60±2.16 (10)[a]	13.54±3.60 (10)[d]	p<0.05
SF10	4.4	7.42±1.49 (10)[a]	10.28±3.60 (10)[e,f]	p<0.05
SF20	4.0	7.89±3.68 (10)[a]	10.29±3.64 (10)[e,f]	NS
UF5	4.4	7.67±1.57 (10)[a]	11.54±3.32 (10)[d,e]	p<0.05
UF10	4.4	7.45±2.62 (10)[a]	10.03±2.54 (10)[e,f]	p<0.05
UF20	4.0	7.30±2.49 (10)[a]	8.16±2.44 (10)[f]	NS
FLCEM	3.6	6.47±2.39 (10)[a]	13.48±3.77 (10)[d]	p<0.05
Control	3.0	6.44±2.31 (10)[a]	10.74±3.27 (10)[d,e,f]	p<0.05

SF=Silanized spherical silica filler; UF=Untreated spherical silica filler
FLCEM=Fuji II LC EM mixed with P/L 3.6; Control=Fuji II LC EM mixed with P/L 3.0, n=10
Identical letters indicate no significant differences among the materials analyzed using the t-test for differences among several means ($p>0.05$)[20]
( ): Cohesive failure, among 10 specimens
1: Significant difference, analyzed using the t-test between two values

Fluoride release

Fig. 2 shows the effects of spherical silica fillers on fluoride release from RMGIC. SF or UF reduced the release of fluoride. During two weeks' immersion in distilled water, the fluoride release of SF20 (which fulfilled the equation $F=4.80t/(0.01+t)+0.79t$) was 49.4% − 57.7% of FLCEM's ($F=12.79t/(0.46+t)+1.10t$). For the same period, the value for UF20 ($F=15.71t/(1.12+t)+0.68t$) was 84.6% − 99.8% of F LCEM's. In two weeks, the cumulative fluoride release value of SF20 was 15.88 ± 1.89 mg/L, while those of FLCEM and UF20 were 27.87 ± 0.64 mg/L and 23.83±0.64 mg/L respectively.

Analyses using ANOVA revealed that both the addition of spherical silica fillers and the period of immersion in distilled water significantly ($p<0.001$) influenced fluoride release from RMGIC.

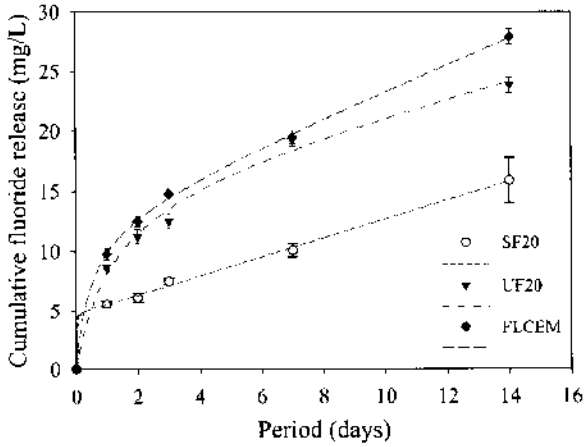

Fig. 2 Cumulative fluoride release of SF20, UF20 and FLCEM in 14 days, n=3.
Points indicate the observed values and lines indicate the fitted curves fulfilling the equation of $[F]_t=[F]_1 t/(t_{1/2}+t)+\alpha t$, with r=0.99 and $p<0.01$.

DISCUSSION

Many factors challenge the marginal integrity of GIC restorations. These factors include cavity preparation method[27], cavity pretreatment, curing shrinkage[28-30], and hygroscopic expansion[22,23,28] of the material. For RMGICs, stress development due to cement setting starts immediately after light irradiation is commenced[31], and curing shrinkage can create marginal gaps that may contribute to restoration failure[28,29]. Therefore water exposure was recommended to control stress development[32,33], and it was suggested to delay polishing by at least one day to prevent gap formation at the cement-tooth cavity interface by anticipating the hygroscopic expansion of the restorative material[22,23,31]. This effect was reported as uptake of water by the RMGIC matrix to form a poly-HEMA complex[34].

It was reported that the 24-hour water uptake of SF-added RMGICs was less than that of UF-added RMGICs or the original RMGIC[14]. However, after 24-hour storage there were no significant differences between the marginal gap widths of SF-added RMGICs and those of UF-added RMGICs, except for UF20. Nonetheless, RMGICs added with either filler type showed significant differences in comparison with the control and FLCEM (Table 1). Although the hygroscopic expansion did not entirely compensate the setting shrinkage in the Teflon mold (Table 2) after 24-hour water storage, the marginal gaps in tooth cavities were remarkably eliminated.

At the immediate time point, the marginal gaps in the Teflon mold were about three-fold of those in the tooth cavity (Fig. 1). Smaller marginal gaps observed in the tooth cavity than in the Teflon mold clearly demonstrated that adhesion between the cement and cavity walls was an important factor influencing marginal gaps[30]. For this reason, direct studying of marginal gaps in tooth cavities was a useful simulation of clinical conditions[23]. However, by examining the setting shrinkage in the Teflon mold, the marginal gap in the tooth cavity could be predicted since there was a linear correlation between the values[30] (Fig. 3).

It was reported that resin infiltration into the expanded decalcified layer would prevent microleakage and nanoleakage[34]. Furthermore, marginal integrity is of primary importance in maintaining the long-term function of resin-based restorations[35]. At the immediate time point, when compared with the control, the SF- and UF-added RMGICs had significantly less marginal gaps in the tooth cavity and setting shrinkage in the Teflon mold. This occurred due to one or both of the following reasons. First, the SF- or UF-added RMGIC was mixed with higher P/L. The higher the P/L, the smaller the marginal gap[31] and the greater mechanical strength of the GIC[14,31,36]. Second, the spherical form of silica fillers

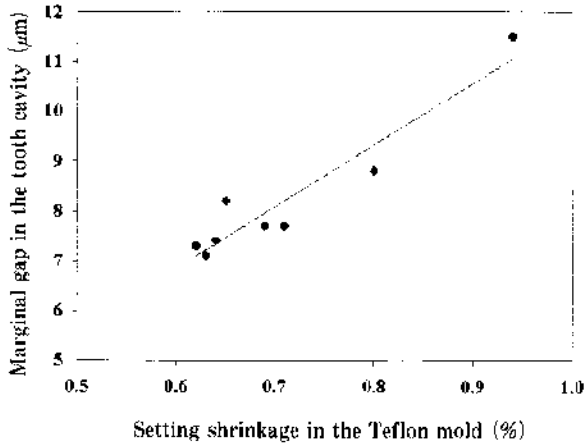

Fig. 3 Correlation of immediate setting shrinkage in the Teflon mold vs. immediate marginal gap in the tooth cavity.
The correlation fulfilled the equation of $y=12.42\times-0.60$, with $r=0.95$ and $p<0.001$.

increased the flowability of RMGIC[14], leading to better penetration into the decalcified layer and reducing the immediate marginal gap.

Following post-set water uptake, the acidic monomers of RMGIC ionize then react with the glass filler to initiate an acid-base reaction, producing ionic cross-linking[37]. In these dual setting systems, resin-reinforcement produces higher bond strengths to dental tissues as well as enhanced mechanical strength[7,29]. Van Meerbeek *et al.*[37] found a gradual transition of resin concentration in the decalcified superficial dentin. Resin concentration was highest at the top of the hybrid layer, and lowest near the base. If resin did not penetrate through the full depth of the decalcified zone, the non-infiltrated weak collagen layer at the bottom of the zone would perhaps be susceptible to long-term hydrolitic degradation[38]. Since the majority of shear bond failures were cohesive failures, the interfacial bond formed between the RMGIC and the solid substrate was stronger than the cohesive bond within the material itself[7]. However, at the immediate time point, UF20 showed apparently less cohesive failure than other materials. It was thought to stem from poor bonding of UF to the RMGIC matrix[14]. As a result, the reaction was delayed, hence affecting the penetration of RMGIC to the decalcified layer. This condition should be studied further.

There was a tendency for the shear bond strength to enamel and dentin to decrease when a large amount of fillers was added. This was clearly shown with the addition of 20 wt% filler, especially in UF20. As mentioned previously, since UF did not bond with the RMGIC matrix[14], a large amount of UF may act as an impurity that hinders the reaction in RMGIC. In contrast, SF5 showed higher shear

bond strength to enamel and dentin than those of the control and FLCEM. In addition, up to 10 wt% SF, the RMGICs showed no significant differences in shear bond strength to enamel compared with those of the control and FLCEM. It was thought that an increase in mechanical strength[14] would lead to an increase in bonding ability[31]. Although the 24-hour shear bond strength to dentin did not show a significant difference, supported by the results of mechanical properties in previous study[14], the SF-added RMGICs showed better mechanical and bond strengths than the UF. These results obviously showed that silanization, which creates siloxane bridges (Si-O-Si) — between the silica surface and the silane molecules[39,40] — facilitate better interaction between the RMGIC matrix and the filler[14].

It has been reported that decrease in marginal gap due to increase in P/L would result in increased shear bond strength of the GIC[31]. However, in this study, there was no significant relationship between marginal gap width and shear bond strength, since the filler content of the materials varied. Nonetheless, the shear bond strength results made a great contribution since the SF-added RMGICs were mixed with higher P/L. As mentioned, increasing the P/L will reduce the amount of liquid used and consequently reduce allergies or harmful effects caused by the release of non-polymerized free monomers from the filling materials[41,42].

The hydrophobic characteristic of SF may influence both surface diffusion and grain boundary diffusion[43], and increase the resistance of cement to water uptake[14]. Since the material must first absorb water to initiate any attack on fluoride glass and the dissociation of acid groups[24], it was not surprising that the addition of SF would reduce fluoride release (Fig. 2). A previous study reported that fluoride has a low rate of diffusion through an organic cross-linked matrix because of strong interaction with aluminum and calcium ions linked to the polyalkenoate chains[44]. The strong interaction between SF and the RMGIC matrix also affected the diffusion rate of fluoride, but fluoride release was not eliminated. This effect should be taken into consideration, because the presence of saliva *in vivo* may retard the release of fluoride from glass-ionomer filling materials[45,46]. Although observations were limited to a period of just 14 days in this study, the equation for fluoride release in glass-ionomer cement $[F]_c = [F]_i t / (t_{1/2} + t) + \alpha t$, as previously described[24], adequately approximated the release of fluoride from RMGIC with or without a spherical silica filler ($r = 0.99$, $p < 0.01$). A similar pattern of release was also obtained, and the release was much greater in the first 24 hours than subsequently. The small but significant initial release was undoubtedly the result of fluoride leaching from glass particles in the surface layer[24]. A previous study showed that γ-MPTS treatment was useful for the regulation of NaF release from bis-GMA/TEGDMA resin. There was evidence that a large amount of fluoride was released from the resin containing NaF powder without γ-MPTS treatment in the initial stage, and the release of fluoride ceased in a relatively shorter time. However, smaller amounts of fluoride were released from the resin containing NaF treated with higher concentrations of γ-MPTS, and the release lasted for longer periods[47]. GICs release and take up fluoride ions[48,49]. As such, the fluoride release and fluoride recharge capabilities of spherical silica filler-added RMGICs should be examined for a longer period in a further study.

CONCLUSION

The addition of spherical silica fillers to RMGIC significantly decreased the marginal gap and the setting shrinkage in the Teflon cavity. This condition led to a significant decrease in immediate marginal gaps in the tooth cavity. This study also revealed that shear bond strength was not in correlation with marginal gap width and setting shrinkage rate. Nonetheless, if up to 5% of silanized spherical silica fillers were added to RMGIC powder, the shear bond strength of RMGIC to enamel and dentin surfaces would increase. Finally, the addition of spherical silica fillers decreased but did not eliminate fluoride release from RMGIC.

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Phosphate-bonded $ZrSiO_4$ Investments Added with ZrC and ZrN for Casting Titanium

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In this study, new investments for titanium were developed by adding ZrC or ZrN as chemical additive for thermal expansion to a phosphate-bonded zircon ($ZrSiO_4$) investment. The following effects were then examined: setting expansion, residual thermal expansion, and compressive strength of these experimental investments; surface roughness of cast plate; and casting accuracy of titanium crown. For residual thermal expansion, it occurred even while investments were cooled to room temperature after firing in air atmosphere. This was due to the additives' oxidation to ZrO_2, suggesting that residual thermal expansion increased with increased amount of these additives. As for casting accuracy of full-crown cast into molds at room temperature, it correlated with the ZrN content. Hence by adding the right amount of ZrN, cast titanium crowns with low surface roughness and good adaptability could be obtained.

Key words: Investment, Thermal expansion, Titanium

INTRODUCTION

Recently, many new concepts on dental investments have evolved: ammonia-free phosphate-bonded investments[1], investments preventing blackening of noble alloys[2,3], rapid heating investments[4,5], and a resin-bonded calcia investment[6]. Though new, all these recently-evolved concepts adopt a common, established principle: that is, to make use of the setting and thermal expansions of investment materials to compensate the casting shrinkage of dental alloy. However, when patterns exist, large setting expansion is known to be heterogeneous, thus leading to distortion of patterns in casting investments[7-13]. This is a problem that remains to be solved, especially when investing hard resin patterns for superstructures on implant bodies.

It is necessary to develop an investment which compensates the casting shrinkage of titanium (about 1.8%) by thermal expansion only. To date, the thermal expansion of investment materials for titanium has been supported by various methods. They are namely, α - β transformation of silica (cristobalite and quartz), transformation of spinel (such as $MgO + Al_2O_3 \rightarrow MgAl_2O_4$)[14], and oxidization of metallic zirconium (Zr) powder[15] and titanium (Ti) powder[16]. Silica has high reactivity with molten titanium, thus causing titanium to deteriorate due to formation of oxide and silicide. Though this reaction can be suppressed by low mold temperature, thermal expansion decreases due to the reversible α - β transformation of silica. Since transformation of spinel is irreversible, it seems like the reaction between mold and molten titanium can be circumvented by casting titanium into mold at a lower temperature. However, spinel transformation requires a special furnace that is able to heat above 1,000℃. Like spinel transformation, thermal expansion due to oxidization of zirconium is also irreversible. However, metallic zirconium powder is too expensive.

In a previous study[17] we developed thermal expansion-type investments by adding ZrC and ZrN powders to a magnesia (MgO) cement. Like metallic zirconium, ZrC and ZrN are able to oxidize and expand by heating in the atmosphere. Commercial magnesia cement had been selected as a base investment, since it has low thermal expansion and magnesia (MgO) has lower reactivity with molten titanium than silica (SiO_2)[18-21]. However, MgO cement as a base investment has two glaring disadvantages: high cost and a long setting time of about two hours.

The purpose of the present study was to develop a cheap, easy-to-operate, and precise casting investment for titanium. Therefore, we selected phosphate as a binder material (which is established in commercial investments for casting of high melting point metals) and zircon ($ZrSiO_4$) as a refractory material (which has intermediate reactivity between ZrO_2 and SiO_2 with molten titanium). Next, the characteristics of phosphate-bonded $ZrSiO_4$ investments with varying contents of ZrC and ZrN were examined, as well as the casting accuracy of titanium crown.

MATERIALS AND METHODS

Two kinds of $ZrSiO_4$ powder were selected as

inspected points in the axial region, 4-11.

Table 8 summarizes the findings of the gap formation for the Composite (Silux Plus) observed in the Class V restorations with various storage periods. When the six storage time procedures were compared, the immediate procedure was 64, the 30-minute was 48, the 3-hour was 53 and the 12-hour was 51. No significant differences were observed among the four sum numbers of gaps in the cavity-restoration interfaces. At the severest points, 1 and 14, half showed a gap in this condition. However, when the specimen was polished and inspected after storing in water for 24 hours or 1 week, 28 and 25 gaps were observed around the restorative cavities, respectively. Significant differences were observed between the 12-hour and 24-hour condition. However, not only the dentin margin but also the enamel margin, namely, the entire margin, showed several gaps in the six conditions.

Table 7: *Effect of Delayed Polishing Period on Interfacial Gap Formation Around Class V Restoration: GIC (Fuji II)*

	Number of Specimens Showing Gaps														
Delayed Polishing Period	**Coronal**					**Axial**							**Cervical**		**Sum**
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Immediately	10	5	7	6	8	8	9	8	10	9	10	8	9	10	117 (A)
30 minutes	10	0	0	1	0	0	0	0	0	2	4	0	0	9	26 (B)
3 hours	2	0	0	0	0		0	0	0	0	4	0	0	3	9 (B)
12 hours	1	0	0	0	0	0	0	0	0	0	2	0	0	3	6 (B)
24 hours	0	0	0	1	1	0	0	0	0	1	3	0	0	1	7 (B)
1 week	2	0	0	0	0	0	0	0	0	0	2	0	0	1	5 (B)

N=10 (total measuring points, 1~14=140)
Values with the same letters were not significantly different by Tukey Test (Conover & Iman, 1981) (p<0.05).

Table 8: *Effect of Delayed Polishing Period on Interfacial Gap Formation Around Class V Restoration: Composite (Silux Plus)*

	Number of Specimens Showing Gaps														
Delayed Polishing Period	**Coronal**					**Axial**							**Cervical**		**Sum**
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Immediately	8	4	3	8	6	4	4	3	2	4	8	2	3	5	64(A)
30 minutes	5	2	0	1	4	5	4	3	2	3	6	1	4	8	48 (A, B)
3 hours	5	1	1	3	7	6	5	4	6	4	6	0	1	4	53 (A, B)
12 hours	4	1	0	0	3	5	6	7	6	4	7	2	2	4	51 (A, B)
24 hours	3	0	0	0	2	4	5	3	2	3	4	0	1	1	28 (B)
1 week	5	0	0	5	1	2	3	4	3	1	0	0	0	1	25 (B)

N=10 (total measuring points, 1~14=140)
Values with the same letters were not significantly different by Tukey Test (Conover & Iman, 1981) (p<0.05).

DISCUSSION

This study clearly demonstrated that polishing three RMGICs and one CGIC (Fuji II LC, Vitremer, Photac-Fil and Fuji II) should not be performed immediately after the filling and setting procedure. Polishing should be delayed between 3 and 12 hours to prevent gap formation at the material-tooth cavity interface. In contrast to the presence of approximately 100-140 of 140 (total measurement points) gaps at the material-tooth cavity interface in the Class V cavity of specimens polished immediately after setting, the gap was near zero or only a few when the specimen was polished after storage in water for 3 or 12 hours. RMGIC or CGIC shrinks during the setting reaction. Gaps form as the adhesion between the tooth cavity and glass ionomer does not resist the stress formed by cement shrinkage (Feilzer, de Gee & Davidson, 1988; Sidhu, 1994; Feilzer & others, 1995). One reason for the gap being dependent on the storage period may be the hygroscopic expansion of the glass ionomer. As soon as adhesion of a restoration is disturbed by shrinkage stress during setting, subsequent swelling by water sorption will never lead to closure. A mismatch between the surface of the cavity wall and the opposing surface of the restoration, due to dimensional changes of the various restorations, almost prevent this. After 12 hours of water storage, curing contraction stresses of the materials are effectively compensated for or even converted into expansion stress due to water uptake and swelling (Feilzer & others, 1995). This effect is reported for the uptake of water by the matrix of resin-modified glass ionomers forming a poly-HEMA complex (Wilson, 1990). In addition, CGIC forms a hydrogel of calcium and aluminum polyacrylates by its uptake of water (Wilson & McLean, 1988). Water absorption of RMGICs and CGICs reportedly affects cavity adaptation and reduces microleakage (Fritz & others, 1996b; Irie & Suzuki, 2000). Although hygroscopic expansion may not be enough to compensate for setting shrinkage, it plays an important role in reducing shrinkage caused by the cement setting reaction and thus improves the marginal seal (Sidhu & others, 1997; Irie & Suzuki, 2000).

The cement is expected to show higher bond and mechanical strengths when fully set rather than during setting reaction. It is suggested that the bonding ability to tooth substrate increases with the development of glass ionomer/tooth substrate interaction during stor-

Table 5: *Effect of Delayed Polishing Period on Interfacial Gap Formation Around Class V Restoration: RMGIC (Photac-Fil)*

	Number of Specimens Showing Gaps														
Delayed Polishing Period	**Coronal**					**Axial**					**Cervical**				**Sum**
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Immediately	10	10	9	10	10	10	10	10	10	10	10	9	10	10	138 (A)
30 minutes	10	9	8	10	10	10	10	10	10	10	10	10	10	10	137 (A)
3 hours	9	7	5	1	0	2	6	6	6	4	10	7	9	10	82 (B)
12 hours	6	2	0	0	0	0	2	2	4	3	6	3	0	4	32 (C)
24 hours	7	0	0	0	1	1	1	0	0	4	8	0	0	10	32 (C)
1 week	9	0	0	1	1	1	0	0	0	1	8	3	2	9	35 (C)

N=10 (total measuring points, 1~14=140)
Values with the same letters were not significantly different by Tukey Test (Conover & Iman, 1981) (p<0.05).

Table 6: *Effect of Delayed Polishing Period on Interfacial Gap Formation Around Class V Restoration: Compomer (Dyract)*

	Number of Specimens Showing Gaps														
Delayed Polishing Period	**Coronal**					**Axial**					**Cervical**				**Sum**
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Immediately	9	6	3	1	2	1	0	0	0	0	1	0	6	9	38 (A)
30 minutes	10	10	4	2	0	0	0	0	0	0	4	1	1	10	42 (A)
3 hours	10	10	5	4	0	0	0	0	0	0	0	2	2	10	43 (A)
12 hours	10	5	1	4	2	1	0	0	0	0	4	0	2	10	39 (A)
24 hours	9	4	3	2	3	2	0	0	0	0	0	0	3	9	35 (A)
1 week	9	7	6	2	1	1	0	0	0	0	2	0	0	7	35 (A)

N=10 (total measuring points, 1~14=140)
Values with the same letters were not significantly different by Tukey Test (Conover & Iman, 1981) (p<0.05).

regions showed a few gaps in the same conditions. However, at polished points, 1 and 14 (enamel substrate), all showed gaps in the restorative cavities.

Table 5 summarizes the findings for gap formation of RMGIC (Photac-Fil) observed in Class V restorations with various storage periods. With the two storage periods (immediately and after 30 minutes), the authors observed 138 and 137 gaps, respectively, around the restorative cavities. At the severest points, 1 and 14, all showed gaps in the two conditions. The coronal, axial and cervical areas also mostly showed gaps. However, when the specimen was cut and inspected after storing in water for three hours, 82 gaps were observed around the restorative cavities. Significant differences were observed between the two storage periods (immediately and after 30 minutes) and after the three-hours storage time. Next, when the specimen was cut and inspected after storing in water for 12 hours, the authors observed 32 gaps around the restorative cavities. Significant differences were observed between the 3- and 12-hour storage times. No significant differences were observed among the sum of gaps for the three different storage period restorations (12 hours, 24 hours and 1 week). The axial regions showed a few gaps in the same conditions. However, polished points 1 and 14 (enamel substrate) mostly showed gaps in the restorative cavities.

Table 6 summarizes the findings for gap formation of the Compomer (Dyract) observed in the Class V restorations with various storage periods. When the six storage period procedures were compared, the immediate procedure was 38, the 30-minute period was 42, the 3-hour period was 43, the 12-hour period was 35, the 24-hour period was 35 and the 1-week period was 35, respectively. No significant differences were observed among the six-period sum number of gaps in the cavity-restoration interfaces. For Dyract, there was no effect in delaying the polishing for 12 hours, 24 hours or 1 week. When the restoration surface was polished, 1 and 14 (enamel substrate) showed the most gaps after the polishing procedures for all six conditions. The authors observed several gaps at a closer point, 2 (enamel substrate). Namely, there was no significant difference among the storage period procedures. However, the dentin margin showed no or few gaps in the six conditions.

Table 7 summarizes the findings of the gap formation of CGIC (Fuji II) observed in the Class V restorations with various storage periods. With immediate inspection after setting, the authors observed 117 gaps around the restorative cavities. At the severest points, 1 and 14, most showed gaps in this condition. At the cervical corner area, 9-11, most also showed gaps. At the axial regions, most showed gaps in the same condition. However, when the specimen was polished and inspected after storing in water for only 30 minutes, 26 gaps were observed around the restorative cavities. Significant differences were observed between the two conditions. No significant differences were observed among the sum of gaps for the five different storage period restorations. When the specimens were polished and inspected after storing in water for more than three hours, only a few gaps were observed around the restorative cavity. However, at polished points 1 and 14 (enamel substrate), a few gaps appeared in the restorative cavities. The cervical corner, 11, also showed many gaps. The presence of gaps was almost zero at all

hardened. Fuji II LC, Vitremer, Photac-Fil, Dyract and Silux Plus were exposed to a visible light source with irradiation times of 20 seconds, 40 seconds, 20 seconds, 40 seconds and 40 seconds, respectively. Fuji II was stored in an incubator at 37°C and 100% relative humidity for four minutes after mixing to allow for chemical-curing to occur and was coated with a varnish (Fuji Varnish, Tokyo, Japan).

Inspection Procedure

Immediately after light curing, setting or after storage in distilled water at 37°C, and at 30 minutes, 3 hours, 12 hours, 24 hours and 1 week, the restorations were polished with abrasive points (Silicone Mide, Shofu, Kyoto, Japan) in wet condition to avoid desiccation and breakdown. Each tooth was sectioned in a buccolingual direction through the center of the restoration with a low-speed diamond saw (Isomet, Buehler Ltd, Lake Bluff, IL, USA). Thus, the presence or absence of marginal gaps was measured at 14 points (each 0.5-mm apart) along the cavity restoration interface (n=10; total points measured=140). This was performed using a traveling microscope (x1,000, Measurescope, MM-11, Nikon, Tokyo, Japan) positioned parallel with the cavity wall and bottom on each half of the sample (Figure 1). The number of gaps in each sample was totaled and expressed as the sum of each sample (Irie & Suzuki, 2002).

The results were analyzed statistically using Tukey Test (Non-parametric) (Conover & Iman, 1981; Irie & Suzuki, 2002).

RESULTS

Table 3 summarizes the findings for the gap formation of RMGIC (Fuji II LC) observed in the Class V restorations with various storage periods. With immediate inspection conducted after setting, the authors observed 101 gaps at the restoration interfaces. The severest points, 1 and 14, showed all gaps in this condition. At the cervical corner area, 10-11, most also showed gaps. The axial regions, 5-9, showed more than half the number of gaps in the same condition. However, when the specimen was cut and inspected after storing in water for only 30 minutes, 34 gaps were observed around the restorative cavities. Significant differences were observed between the two conditions. No significant differences were found among the sum of gaps for five different storage period restorations (30 minutes—1 week). However, polished points, 1 and 14 (enamel substrate), showed half the number of gaps in the restorative cavities. The cervical corner, 11, also showed many gaps.

Table 4 summarizes the findings for the gap formation of RMGIC (Vitremer) observed in the Class V restorations with various storage periods. With the three storage periods (immediately, after 30 minutes and after three hours), the authors observed 128, 119 and 95 gaps, respectively, around the restorative cavities. At the severest points, 1 and 14, all showed gaps in the three conditions. The coronal and cervical areas also mostly showed gaps. The axial regions showed more than half the number of gaps in the same condition. However, when the specimen was cut and inspected after storing in water for 12 hours, the authors observed 37 gaps around the restorative cavities. Significant differences were observed among the three storage periods (immediately, after 30 minutes and after three hours) and after the 12 hour-storage period. No significant differences were observed among the sum of gaps of the three different storage period restorations. The axial

Table 3: *Effect of Delayed Polishing Period on Interfacial Gap Formation Around Class V Restoration: RMGIC (Fuji II LC)*

	Number of Specimens Showing Gaps														
Delayed Polishing Period	**Coronal**						**Axial**						**Cervical**		**Sum**
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Immediately	10	7	6	6	7	7	6	8	9	10	10	0	5	10	101 (A)
30 minutes	6	3	1	2	2	2	1	0	0	1	3	2	1	10	34 (B)
3 hours	3	0	0	0	1	2	1	2	0	0	2	0	0	6	17 (B)
12 hours	3	0	0	1	0	1	0	0	1	0	3	0	0	4	14 (B)
24 hours	1	0	0	1	1	2	0	0	2	1	4	0	0	5	17 (B)
1 week	5	0	1	0	0	1	1	0	1	0	0	0	1	7	17 (B)

N=10 (total measuring points, 1-14: 140)
Values with the same letters were not significantly different by Tukey Test (Conover & Iman, 1981) ($p<0.05$)

Table 4: *Effect of Delayed Polishing Period on Interfacial Gap Formation Around Class V Restoration: RMGIC (Vitremer)*

	Number of Specimens Showing Gaps														
Delayed Polishing Period	**Coronal**						**Axial**						**Cervical**		**Sum**
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Immediately	10	10	10	10	9	10	8	8	8	7	10	8	10	10	128 (A)
30 minutes	10	10	10	10	6	7	7	8	8	8	8	8	9	10	119 (A)
3 hours	10	9	8	5	5	4	2	5	4	7	9	9	8	10	95 (A)
12 hours	10	2	0	1	1	2	2	1	1	1	2	2	2	10	37 (B)
24 hours	9	1	0	2	0	0	0	1	2	1	3	0	0	10	29 (B)
1 week	10	1	0	0	0	0	0	0	3	1	5	3	0	10	33 (B)

N=10 (total measuring points, 1-14: 140)
Values with the same letters were not significantly different by Tukey Test (Conover & Iman, 1981) ($p<0.05$)

speed mixer (Silamat, Vivadent, Schaan, Liechtenstein) for 15 seconds. For light activation of the priming or sealing agents and of the restorative materials, a curing unit (New Light VL-II, GC, Tokyo, Japan; irradiated diameter: 8 mm) was used. The curing distance from tip to material surfaces was as near as possible. The light intensity was checked immediately before each application of the adhesive resin and restorative material using a radiometer (Demetron/Kerr, Danbury, CT, USA). During the experiment, the light intensity was maintained at 450 mW/cm². For each material and storage period, 10 specimens were made. All procedures, except for cavity preparation, were performed in a thermo-hygrostatic room kept at 23±0.5C° and 50±2% relative humidity.

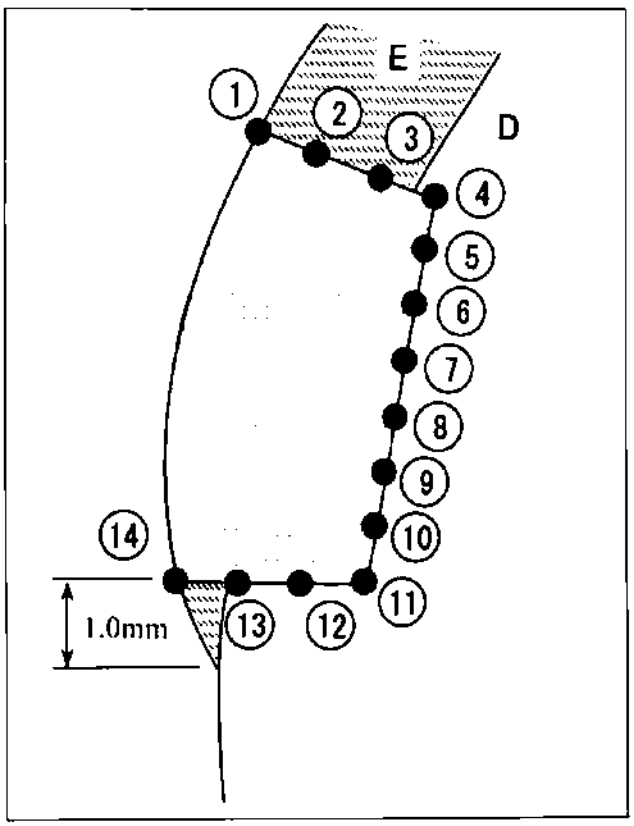

Figure 1. *Class V restoration and each measured point in the Class V restorations. E: Enamel substrate. D: Dentin substrate.*

Class V Restoration

Cavity preparations were made in the premolars on the facial surface. A cylindrical cavity was prepared with a tungsten carbide bur (200,000-rpm) and a fissure bur (8,000-rpm) under wet conditions to a depth of 1.5 mm with a diameter of 3.5 mm. A cavity preparation was placed parallel to the cementoenamel junction (CEJ) with the preparation extended 1.0 mm above the CEJ (Figure 1). Cavosurface walls were finished to a butt joint. One cavity was prepared in each tooth. In total, cavities were prepared in 360 teeth (6 materials X 6 polishing times X 10 repeats).

The prepared cavity surface was treated with the conditioner/primer according to each manufacturer's instructions. Dentin Conditioner and Ketac Conditioner were applied for 20 and 10 seconds, respectively, and rinsed with water. Vitremer Primer was applied for 30 seconds, air dried and light cured for 20 seconds. An ample amount of Dyract-PSA was applied and left undisturbed for 30 seconds. Excess solvent was removed by compressed air. The light curing time was 10 seconds. A second layer of Dyract-PSA was applied with a brush. Etchant was applied for 15 seconds, rinsed and air dried. Primer was applied and air dried following Adhesive that was photocured for 10 seconds.

The cavity was filled with mixed materials using a syringe tip (Centrix C-R Syringe System, Shelton, CT, USA) and covered with a plastic strip and

Table 2: *Conditioner/Primer Agents Investigated*

Material	Manufacturer	Batch #	Components and Surface Treatment
Dentin Conditioner	GC Corp Tokyo, Japan	151021	Polyacrylic acid, water Apply with brush 20 seconds → rinse 15 seconds → gently dry five seconds
Vitremer Primer	3M Dental Products St Paul, MN, USA	35	HEMA, maleic acid in aqueous solution ethyl alcohol Apply with brush 30 seconds → gently dry five seconds → light cure 20 seconds
Ketac-Conditioner	3MESPE GmbH Seefeld, Germany	0002	Polyacrylic acid, water Apply with brush 10 seconds → rinse 15 seconds → gently dry five seconds
Dyract-PSA	DeTrey/Dentsply Konstanz, Germany	931020	PENTA, TEGDMA, acetone Apply 30 seconds → gently dry five seconds → light cure 10 seconds
Scotchbond Multi-Purpose	3M Dental Products St Paul, MN, USA	Etchant(2AC) Primer(2AC) Adhesive(2AB)	10% maleic acid, water HEMA, polyalkenoic acid, coplymer, water Etch 15 seconds → rinse 15 seconds → gently dry five seconds→ Apply with brush (Primer) gently dry five seconds → Apply with brush (Adhesive) → light cure 20 seconds

Key: HEMA, 2-hydroxtethyl methacrylate; PENTA, dipentaerythritolpenta-acrylatemonophosphate; TEGDMA, triethylene glycol dimethacrylate; Bis-GMA, bisphenol A-glycidyl methacrylate

types of combination materials, RMGIC and compomer, have been developed. RMGIC is unlike a light-cured resin composite or a CGIC; it has a dual setting reaction consisting of an acid-base reaction and a photochemical polymerization process. The final set materials have been described as having a complex structure in which glass particles are sheathed in a matrix consisting of two networks—one derived from the glass ionomer, the other from the resin (Wilson, 1990; Mitra, 1991). In these dual-setting systems, the resin reinforcement provides higher mechanical strength (Uno, Finger & Fritz, 1996; Irie & Suzuki, 1999; Irie & Suzuki, 2000; Yap & others, 2001) and higher bond strength to tooth surfaces compared with CGICs. RMGIC claimed to have an improved marginal seal and gap formation of restoration by hygroscopic expansion (Sidhu, Sherriff & Watson, 1997; Irie & Suzuki, 2000) and improved bonding ability after storage in water (Fritz, Finger & Uno, 1996a,b; Irie & Suzuki, 1999; Irie & Suzuki, 2000; Irie & Suzuki, 2002).

A compomer may be a single- or two-component material containing one or both of the essential components of a glass ionomer. However, the components do not react as part of the setting process (McLean, Nicholson & Wilson, 1994). It consists of a resin matrix and a fluoroaluminosilicate glass filler. However, it undergoes no dimensional change by hygroscopic expansion (Irie & Suzuki, 2000). Therefore, it may not improve the marginal seal and gap formation of a restoration (Irie & Suzuki, 2002). The monomer in resin matrix ionizes following water uptake during storage after light activation. The released hydrogen ions then react with the glass filler to initiate an acid-base reaction. Ionic cross-linking also occurs and fluoride is released (Hammesfahr, 1994). Therefore, it may improve the marginal seal and gap formation of restorations by enhancing the bond ability.

The polishing periods serve as other factors that may influence the seal ability around a cervical restoration. Polishing after storage in water for one day resulted in improved gap formation for three positioned cervical restorations of one RMGIC and one CGIC. However, delayed polishing did not improve gap formation for a compomer (Irie & Suzuki, 2002). Due to the structure of glass ionomers and their hydrophilic nature, water sorption and subsequent swelling may lead to partial compensation of the shrinkage. The preservation of sealing around a restoration would benefit most if water sorption and setting shrinkage could occur simultaneously. However, water sorption occurs only at a later stage compared with setting shrinkage (Feilzer & others, 1995). Currently, no information is available regarding the gap formation behavior around Class V of a CGIC, RMGIC and a compomer.

In this study, the effects of the polishing period on the gap formation around Class V restorations using RMGICs and a compomer were evaluated *in vitro*. The hypothesis tested was that the difference in polishing times would result in gap formation for the tested materials.

METHODS AND MATERIALS

Human premolars, extracted for orthodontic reasons, were used for the experiment. After extraction, each tooth was immediately stored in cold distilled water at 4°C for one to two months before testing. The basic properties of three RMGICs, one compomer, one CGIC and one microfilled composite are summarized in Tables 1 and 2. All processing of the materials was carried out according to the manufacturer's instructions. Capsules of Photac-Fil were triturated using a high-

Table 1: *Restorative Materials Investigated*

Material	Manufacturer	Batch #	Type (Powder/Liquid)/Components
Fuji II LC	GC Corp Tokyo, Japan	P: 030921 L: 250721	Resin-modified GIC (3.0g/1.0g) P: fluoroaluminosilicate glass L: copolymer of acrylic and maleic acid, HEMA, water
Vitremer	3M Dental Products St Paul, MN, USA	19930203	Resin-modified GIC (2.5g/1.0g) P: fluoroaluminosilicate glass L: polyalkenoate copolymer, HEMA, water
Photac-Fil	3MESPE GmbH Seefeld, Germany	X033	Resin-modified GIC (Precapsulated) P: fluoroaluminosilicate glass L: copolymer of maleic acid and acrylic acids monomers oligomers, water
Dyract	DeTrey/Dentsply Konstanz, Germany	B 930776	Compomer fluoroaluminosilicate, polyacrylic acid, UDMA
Fuji II	GC Corp Tokyo, Japan	P: 300802 L: 120901	Conventional GIC (2.7g/1.0g) P: fluoroaluminosilicate glass L: copolymer of acrylic and maleic acids, polybase carboxylic acid, water
Silux Plus	3M Dental Products St Paul, MN, USA	1DW1	Microfilled resin composite colloidal silica (38 vol%), Bis-GMA, TEGDMA

Key: GIC, Glass ionomer cement; HEMA, 2-Hydroxiethyl methacrylate; UDMA, urethane dimethacrylate; Bis-GMA, bisphenol A-glycidyl methacrylate, TEGDMA, triethylene glycol dimethacrylate.

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Effect of Delayed Polishing Periods on Interfacial Gap Formation of Class V Restorations

M Irie • R Tjandrawinata • K Suzuki

Clinical Relevance

Delaying polishing for one day resulted in improved gap formation for Class V restorations of conventional and resin-modified glass ionomers and a microfilled composite. Delaying polishing was not necessary for a compomer.

SUMMARY

This *in vitro* study evaluated the effect of the initial polishing period through 30 minutes, 3 hours, 12 hours, 24 hours and 1 week after setting on the gap formation around Class V restorations. Three resin-modified glass ionomers, one compomer, one conventional glass ionomer and one microfilled composite were used as controls.

When specimens of the two types of glass ionomers and a microfilled composite were polished immediately after the setting procedure, this study showed 100-140 gaps around the X-section of the restorations. In contrast, only 10-40 gaps around the Class V restoration were observed when the specimens were polished after 12 hours of storage. Significant differences were observed between polishing immediately and polishing after 12 hours of storage in the two glass ionomer restorative materials. The compomer did not show this pattern. No significant differences were observed among the six polishing periods of the sum number of gaps at the cavity-restoration interfaces. The tendency of Silux Plus was similar to the two types of glass ionomer materials; namely, when the specimen was polished and inspected after storage in water for 24 hours or one week, the authors observed almost 30 gaps around the restorative cavities.

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INTRODUCTION

Class V restorations are an indication of a conventional glass ionomer cement (CGIC), a resin-modified glass ionomer cement (RMGIC) and a polyacid-modified resin composite (compomer) (Ferrari & others, 1998; Gladys & others, 1998; Tyas, 2000; Folwaczny & others, 2000a,b; Di Lenarda & others, 2000; Brackett & others, 2001; Brackett & others, 2002). CGIC has several beneficial properties, such as physicochemical bonding to the tooth substrate, fluoride release and uptake and tooth color. However, it also demonstrates brittle fracture, erosion and wear in the oral environment (Wilson & McLean, 1988). To improve these deficiencies, two

7.3. Effect of delayed polishing periods on interfacial gap formation of Class V restorations

age in water, and the cohesive strength of the cement itself improves with the setting process (Irie & Suzuki, 2000). The pH, an index of the degree of hardening reaction of set glass ionomer, is reported to be lower at the initial stage (until 30 minutes) regardless of the type of cement, whether CGIC or RMGIC. Although there was no significant difference among 3-, 12- and 24-hour conditions, all of which prevent gap formation at the material-tooth cavity interface, the pH value of the set cement gradually increases for 24 hours (Tosaki & Hirota, 1994; Anusavice, 1996). Therefore, it can be presumed that completing the setting reaction of an RMGIC or CGIC requires 24 hours. Thus, RMGIC or CGIC requires 24 hours for adequate mechanical strength, which has a close relationship with bond strength (Irie & Suzuki, 2000). RMGIC has a dual setting reaction: one is the light-initiated cross-linking of methacrylate groups similar to the setting of light-cured resin composites; the other is an acid-base reaction similar to that of a CGIC (Wilson, 1990; Mitra, 1991).

The cervical corner of Class V cavity restorations showed more gaps than the coronal corner in RMGICs and CGICs. This was expected because bond strength to coronal dentin is usually higher than bond strength to cervical dentin, because cervical dentin is a less favorable bonding substrate (Heymann & Bayne, 1993; Irie & Suzuki, 2002).

Not one of the samples prevented gaps at the two polished points for Vitremer (1 and 14; enamel substrate). The reason is that Vitremer shows a low bond value to enamel after one day. A failure site after debonding showed a mixed failure of Vitremer bonded to enamel (Fritz & others, 1996a; Irie & Suzuki, 2000).

Photac-Fil showed no effect in preventing gaps around Class V restorations during the initial stage. Fracturing of the debonded area in the material-tooth cavity interface showed very weak bonding during the early phase and probably produced very low bond value to dentin (Irie & Suzuki, 2000). It is possible that exposure of Photac-Fil surface to water immediately after light activation may have a similar adverse effect on setting, as commonly found with CGICs after early water exposure. Other investigations have also reported the poor bonding capacity of Photac-Fil with Ketac Conditioner (Sidhu & Watson, 1995; Fritz & others, 1996a,b).

This study demonstrated that delaying polishing of a compomer for one day does not prevent gap formation in the material-tooth cavity interface. Therefore, it did not prevent bonding to the tooth structure and the hygroscopic expansion of compomer, itself (Irie & Suzuki, 2000). The marginal gaps observed even after the specimen was stored in water for one day indicated that hygroscopic expansion does not fully compensate for shrinkage caused by setting reaction. The degree of hygroscopic expansion of the compomer was smaller than RMGICs, because the composition of the compomer is similar to the resin composite system (Hammesfahr, 1994; Irie & Suzuki, 2000). The values of the bond strengths to enamel and dentin measured after one-day storage were not significantly higher than those measured immediately for the compomer (Irie & Suzuki, 2000). Since no micro-mechanical interlocking with conditioned enamel was available when Dyract-PSA was used, a low shear bond strength to enamel was shown even after storage for one day (Fritz & others, 1996a).

This study demonstrated that the polishing period of the compomer showed no effect in preventing gaps around Class V restorations, especially at the enamel margin. The gap width of the enamel margin was found to result from polishing procedures because the enamel margin had no gaps without the polishing procedure (Irie & Suzuki, 2002). The manufacturer suggests that tooth etching with Dyract is unnecessary for most restorative procedures. Although the recommended primer is considered adequate to condition tooth-hard tissues, it has been demonstrated that compomer restorations lack marginal adaptation (Ferrari & others, 1998; Tyas, 2000; Di Lenarda & others, 2000; Brackett & others, 2001). A modified formulation of Dyract is now available (Dyract AP, Dentsply/DeTrey, Konstanz, Germany). However, the manufacturer still considers etching unnecessary even for this material. To improve the enamel/compomer interface, the manufacturer's protocol should be modified, introducing enamel etching to achieve the compomer restorations' clinical success.

Silux Plus demonstrated that preventing gap formation to enamel substrate was poor immediately following setting, and for dentin substrate, it was not significantly better compared with RMGICs and CGICs in all conditions. It is suggested that bonding at the material-tooth cavity interface was insufficient. A previous study showed that not only the value of the bond strength to enamel substrate of Silux Plus immediately following setting was low (only 6.83 MPa), but also that the value of the bond strength to dentin substrate after one-day storage of Silux Plus was significantly lower (immediately: 5.97 MPa; after one-day storage: 8.63 MPa) than RMGICs and CGICs (Irie & Suzuki, 2000). It may be suggested that the enamel cavosurface margin is not a bevel but a butt joint.

The restorative materials tested in this study should not be polished at the placement appointment except for the compomer, based on gap formation at the material-tooth cavity interface and completion of the setting reaction. Instead, the prepared cavity should be filled at the placement appointment and polished at a subsequent appointment (Irie & Suzuki, 2000; 2002).

CONCLUSIONS

All materials except compomer showed a significant reduction in interfacial gap formation by 24 hours after insertion. Although compomer did not exhibit a change in gap formation, the number of gaps at any time interval was similar to the other materials at their lowest gap conditions. Of the materials undergoing changes in gap formation, CGICs showed the most improvement and microfilled composite showed the least improvement.

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岡 山 大 学 長　殿

学　位　申　請　書

岡山大学学位規程第７条の規定に基づき，学位論文，学位論文の要旨，論文目録及び履歴書を添えて博士（歯学）の学位の授与を申請いたします。

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論文題名

Effects of spherical silica filler addition on improving the characteristics of resin-modified glass-ionomer cement

(球状シリカフィラー添加によるレジンモディファイドグラスアイオノマーセメントの物性改良について)

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2. Marginal gap formation and fluoride release of resin-modified glass-ionomer cement: Effect of silanized spherical silica filler addition. Dental Materials Journal 2004; 23(3): 305-313.
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