Hydroxyapatite particle characteristics influence the enhancement of the mechanical and chemical properties of conventional restorative glass ionomer cement

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The aims of this study were to improve the mechanical and chemical properties of conventional restorative glass ionomer cement (GIC) by adding hydroxyapatite (HAp) preparations with different characteristics, and to investigate the underlying reaction mechanisms. Fuji IX GP[®] was used as the control GIC. The experimental GICs consisted of four HAp-particles with different characteristics added at 8 mass% to Fuji IX-powder. All cements were prepared by mixing with Fuji IX-liquid (P/L=3.6). Four HAp-particles were analyzed, and then the mechanical strengths and the fluoride-ion- release-recharge-behaviors of five GIC groups were evaluated. The results of this study demonstrate that the addition of HAp particles with highly reactive properties such as high specific surface area can enhance the flexural strength and fluoride ion release properties of conventional restorative GIC. Our results further indicate that HAp functions as an adsorbent and an ion exchangeable agent, resulting in improved mechanical and chemical properties of GIC.

Keywords: Glass ionomer, Hydroxyapatite, Particle characteristics, Mechanical properties, Fluoride release

INTRODUCTION

Glass ionomer cement (GIC) (also known as glass polyalkenoate cement) was invented by Wilson and Kent in 1971¹⁾. GIC is widely used as a dental material, due to its ease of use, low coefficient of thermal expansion, good biocompatibility with bone pulp tissue, and long-term bonding to tooth surfaces and metals²⁻⁴⁾. In addition, its unique fluoride ion release characteristics have anticaries, antimicrobial, and remineralization effects⁵⁾. In 2000, the FDI World Dental Federation introduced a new preventive dental treatment concept, known as minimum intervention (MI), that promotes minimal tooth cavity preparation⁶⁾. GIC is the most suitable dental material for MI⁷⁾. Moreover, the World Health Organization (WHO) launched atraumatic restorative treatment (ART), developed in the mid-1980s as a public health program and first implemented, in Africa, by Frencken⁸⁾. ART, which relies on GIC's natural bonding to tooth and its release of fluoride to prevent dental caries, involves the excavation of softened dentin followed by the direct filling of the cavity with GIC. This procedure does not require complicated techniques, dental chairs, rotary instruments, or light curing machines; thus, it is an ideal restorative treatment for use in developing countries. However, research in Syria showed that the cumulative survival rate of ART

restorations after 6.3 years is 66.1%⁹⁾, so the strength and endurance of GIC requires improvement.

The poor mechanical properties of GIC, and its sensitivity to desiccation and moisture¹⁰⁾, have prompted research into overcoming these shortcomings¹¹⁾. For example, the incorporation of amalgam, silver, and metal powders as reinforcements into GIC powder have been reported, but these products have inferior aesthetic appearance and decreased bonding strength to enamel¹²⁾. Light-cured GIC has also been investigated, where resin and a light-curing catalyst are added to hasten the setting and to improve the mechanical strength of GIC¹³⁾. Although light-cured GIC is widely used, resin-reinforced GIC has remarkably high flexural strength¹³⁾ but lower compressive strength than conventional GIC¹⁴⁾. Moreover, resin-modified GIC can irritate dental pulp, has biological side-effects, and causes cytotoxicity and secondary caries; these negative characteristics are not found in conventional GIC^{15,16)}. Mechanical strength could be improved by incorporating SiC whiskers or short fibers into GIC^{17,18)}, but this approach may not be possible because of the fear that these very small fibers could travel to and lodge into vital organs, thus posing a health threat similar to that posed by asbestos fibers.

Hydroxyapatite [HAp: Ca₁₀(PO₄)₆OH₂] has excellent biocompatibility, and its composition and crystal structure are similar to the apatite in human dental

structures and bone tissue. In 1984, Yamamoto¹⁹⁾ added HAp to conventional GIC to improve the biocompatibility of GIC. Yap *et al.*²⁰⁾ later reported that the addition of HAp increased the hardness of GIC and recommended the use of this bioactive cement in orthopedics. Arita²¹⁾ reported improved mechanical strength of GIC, in the absence of resins or fillers, by the addition of HAp whiskers. The addition of HAp granules also strengthened GIC, not by reinforcement but through chemical interactions with the cement matrix²²⁾. However, there has been no report to notice the powder characteristic of HAp in the improving properties of GIC by using HAp.

The primary aim of this study was to evaluate the effectiveness of four HAp particles with different sizes and properties on the mechanical and chemical properties of conventional restorative GIC. We also analyzed the particle characteristics of GIC powder and the four HAp particles, and compared the physical and chemical properties of GIC/HAp mixtures.

MATERIALS AND METHODS

Materials

Conventional posterior glass ionomer restorative cement, Fuji IX GP[®] (Fuji IX, lot nos. 0602021, 0602031, 0701201, GC Corp., Tokyo, Japan) was used as the control GIC group (control-GIC). Fuji IX-powder is mainly composed of fluoro-alumino-silicate glass containing Si, Al and Na, and Sr instead of Ca. Fuji IX-liquid is composed of polyacrylic acid, polybasic carboxylic acid, and distilled water.

Four HAp-particles were used: HAp200 (Taihei Chemical Industrial Co., Ltd., Osaka, Japan), NanoHAp (SANGI Co., Ltd., Tokyo, Japan), HAp100 (Taihei Chemical Industrial Co., Ltd., Osaka, Japan), and HAp100f, which was made by grinding HAp100 to less than 20 μm using an automatic ball mill (Vibration Micro-Pulveriser P-0, Fritsch Japan Co., Ltd., Kanagawa, Japan) in our laboratory. Based on the results of the preliminary experiments, 8 mass percent of the Fuji IX-powder was replaced with individual HAp samples and mixed in 50 mL tubes using a tube mixer (Eddy Mixer S-10, Koike Precision Instruments Co., Ltd, Tokyo, Japan).

In experimental GIC groups, HAp200-, NanoHAp-, HAp100- and HAp100f-added GICs were named A200-, NanoA-, A100- and A100f-GIC, respectively.

Morphology, particle size distribution, microcompressive strength, and specific surface area measurements of Fuji IX-powder and the four HAp-particles

The morphologies, particle size distributions, and microcompressive strengths of Fuji IX-powder and four HAp-particles were analyzed using a scanning electron microscope (SEM; JSM5300, JEOL Co., Tokyo, Japan), a laser diffraction particle size analyzer (SALAD-3100 and 2200, Shimadzu, Kyoto, Japan), and a microcompressive testing machine (MCT-W500, Shimadzu, Kyoto, Japan), respectively. The mean microcompressive strength was calculated using $C=2.8P/\pi d^2$ ²³⁾, where P is the maximum

load (N) and d is the diameter (mm) of the particle ($n=6$).

The specific surface areas of four HAp-particles were measured by a Brunauer-Emmet-Teller (BET) nitrogen gas adsorption method²⁴⁾ using an automated surface area and porosimetry analyzer (TriStar 3000, Micromeritics Instrument Co., Norcross, GA). The BET specific surface area of each sample was calculated from the adsorption and desorption isotherms of nitrogen for each HAp sample.

X-ray diffraction (XRD), transmission electron microscopy (TEM), and selected area electron diffraction (SAED) studies of the four HAp-particles

The crystallite sizes of HAp200, NanoHAp, and HAp100 were analyzed by XRD, TEM, and SAED. HAp100f was excluded since it is the same as HAp100 except for particle size and surface properties. XRD patterns were recorded with a vertically mounted diffractometer system (RINT 2500 VHF, Rigaku, Tokyo, Japan) using CuK α radiation. The scanning range (2θ) was from 1° to 70° at a scan speed of $2^\circ/\text{min}$ and a step size of 0.02° in continuous mode. The crystallite size of the HAp samples was determined by the Scherrer equation (1)²⁵⁾

$$D=0.9\lambda/\beta\cos\theta \quad (1)$$

where D is the crystallite size, λ is the wavelength of the incident X-ray (0.15418 nm), θ is the diffraction angle of the (211) peak, and β is the half-width of the peak. TEM images of the samples were recorded with the HITACHI H-800 ELECTRON MICRO SCOPE (Hitachi High-Technologies Co., Tokyo, Japan) using an accelerating voltage of 200 kV. The TEM samples were finely ground in an agate mortar and dispersed into ethanol by ultrasonication. The crystallite structures of the samples were analyzed by SAED of the TEM images.

Flexural strength test of conventional and HAp-augmented GICs

All cements (control-, A200-, NanoA-, A100-, and A100f-GICs) were prepared by mixing with Fuji IX-liquid using a plastic spatula on a mixing pad at the recommended powder/liquid ratio (P/L) of 3.6. Samples ($n=6$) measuring 3 mm $\times$ 3 mm $\times$ 25 mm were prepared for each group. Samples were clamped for 10 min at room temperature, unclamped and kept for 50 min at 100% humidity at 37°C , then submerged in distilled water and stored for 23 hours at 37°C . The samples were then subjected to a three-point bending test in a universal testing machine (Autograph AG10TA, Shimadzu, Kyoto, Japan) at a crosshead speed of 0.5 mm/min. For each sample group, representative fracture surfaces from the three-point bending test were dried, gold-coated, and observed by SEM (JSM5300, JEOL, Tokyo, Japan).

Compressive strength test of conventional and HAp-augmented GICs

All compressive strength test samples were mixed at a P/L of 3.6 as described for the flexural strength test. Samples ($n=6$) measuring 6 mm in diameter and 12 mm

in height were prepared for the control-, A200-, NanoA-, A100- and A100f-GICs following the procedures outlined in ISO9917-1:2007. After 24 hours of storage, the samples were tested using a universal testing machine (Autograph DSS-500, Shimadzu, Kyoto, Japan) at a crosshead speed of 1.0 mm/min.

Measurement of fluoride ion release and recharge behaviors of conventional and HAp-augmented GICs

All samples for this experiment were mixed at a P/L of 3.6. Six discs (10 mm diameter×2 mm thick) for each GIC group were made using a polyethylene mold for fluoride ion release and recharge measurements. Samples were covered with celluloid strips and pressed with a glass plate under a 500 g load. After 10 min, samples were removed from the mold and stored at 37°C and 100% relative humidity for 50 minutes. Samples were individually suspended by a nylon thread in 10 mL distilled water in sealed containers and stored at 37°C. The concentrations of fluoride released into the water were measured, and the distilled water was replaced every 24 hours for 30 days. For the measurements, each disk was removed from the water, dried on filter paper, and immediately immersed in 10 mL fresh distilled water for further equilibration. The fluoride concentrations in the water samples were measured at room temperature using a fluoride electrode (Model 9609BN, Orion Research, Boston, MA) connected to an expandable ion analyzer (Model 720A, Orion Research). Buffer solution (1 mL, TISAB III, Thermo Fisher Scientific, Beverly, MA) was added to the water sample. After 14, 19, and 24 days, the disks were recharged in 10 mL NaF solution (containing 9,000 ppm fluoride ion) for 5 minutes, rinsed with 5 mL running distilled water, quickly dried, and immediately immersed in 10 mL fresh distilled water. Fluoride ion release concentrations from these recharged samples were measured daily for 30 days.

SEM observation of the fracture surfaces and energy dispersion X-ray spectrometry (EDS) analysis of conventional and HAp-augmented GICs

For each GIC group, representative fracture surfaces from the flexural strength test were dried, gold-coated, and observed under an SEM (JSM5300, JEOL Co., Tokyo, Japan). Elemental analyses of the control- and A100-GICs were carried out for representative fracture surfaces using an EDS detector (IncaPentaFET×3, Oxford Instruments PLC., Oxford, UK) and an SEM (SU-70, Hitachi High-Technologies Co., Tokyo, Japan). The pressure voltmeter was set at 20 kV for 300 seconds. The elemental compositions of the matrix parts of representative fractured surfaces of A100- and A100f-GICs were also determined with an EDS detector (Link Pentafet, Oxford Instruments PLC, Oxford, UK).

X-ray photoelectron spectroscopy (XPS) analysis of conventional and HAp-augmented GICs

The matrices of control-GIC and HAp-added GICs were analyzed quantitatively for chemical composition using

an XPS (PHI5000, ULVAC-PHI Co., Kanagawa, Japan). Samples were prepared by syringe-loading the mixed cement (P/L=3.6) into 6 mm diameter×2 mm high stainless steel split molds, pressing with cellulose acetate sheets and a glass plate, and clamping for 1 hour to obtain matrix-rich surfaces according to Jones' methods²⁶⁾. For XPS, the X-ray source was MgK α , at 400 W and 14 kV. The mass of each element was computed by calculating the peak area for each element, which was then expressed as the XPS peak area ratio of each element to C1s.

Statistical analysis

The mean and standard deviation (S.D.) was calculated for each group. Analysis was performed using Scheffé's *post hoc* F test.

RESULTS

SEM observation, particle size distribution, microcompressive strength, and specific surface area of Fuji IX-powder and four HAp-particles

An SEM image of Fuji IX-powder is shown in Fig. 1A-1. The particles were sharp-edged, polygonal, and ranged from 1 to 20 μ m in diameter, as shown in Fig. 1A-2. In the analysis of particle size distribution, the mean size of Fuji IX-powder was 5.3 μ m, and 10.0% to 90.0% distribution was 1.5 to 18.9 μ m, reflecting a wide range of distribution. The mean ($\pm$ S.D.) microcompressive strength of Fuji IX-powder was 182.8 ± 26.6 MPa.

SEM images of the four HAp-particles are shown in Fig. 1B-1(a-d). HAp 200 (Fig. 1B-1a) comprised hexagonal crystals, which aggregated to form particles with a width of about 0.5 μ m and a length of 2–3 μ m, but could condense to form aggregates about 10 μ m in size. The particle size of NanoHAp (Fig. 1B-1b) was about 10–20 nm, but the crystals could clump together to form particles greater than 10 μ m in diameter. HAp100 (Fig. 1B-1c) comprised columnar crystals about 200–300 nm in diameter, but could condense to form aggregates about 200–300 μ m in size. HAp100f particles (Fig. 1B-1d) were oblong-shaped and 10–20 μ m in diameter, which were round with tiny adhered nano-sized HAp particles. The particle size distributions of the four HAp are shown in Fig. 1B-2. For NanoHAp, even following ultrasonication to separate the clumped particles, the average size was about 3.4 μ m in diameter, with most of the particles in the range of 1–10 μ m. The mean diameters of HAp100f and HAp200 were 11.4 and 13.6 μ m, respectively, and the mode diameter was 17.0 μ m for both, with a range of about 2–40 μ m. HAp100 had the highest mean particle diameter at 236.3 μ m with a range distribution (10.0%–90.0% distribution) of 94.5–422.0 μ m (Fig. 1B-2).

The microcompressive strength values of three HAp are shown in Fig. 1B-3. The small particle size of NanoHAp made measurement of its microcompressive strength impossible using current analysis methods. The mean microcompressive strength of HAp100 and HAp100f (0.76 ± 0.04 MPa and 0.98 ± 0.11 MPa) was significantly lower than that of HAp200 (1.54 ± 0.23 MPa)

Fig. 1 Particle characteristics of Fuji IX powder and four HAp-particles.

A-1: SEM image of Fuji IX powder (x1,500)

A-2: Particle size distribution of Fuji IX powder

B-1: SEM image of four HAp-particles: (a) HAp200 (x20,000), (b) NanoHAp (x50,000), (c) HAp100 (x100) and (d) HAp100f (x3,500)

B-2: Particle size distributions of the four HAp-particles

B-3: Microcompressive strength of HAp200, HAp100, and HAp100f

B-4: Specific surface area of the four HAp-particles

($p < 0.001$).

The specific surface areas of the four HAp-particles are compared in Fig. 1B-4. The values of the mean surface area of the particles were: HAp100 ($62.82 \pm 0.86 \text{ m}^2/\text{g}$) > HAp100f ($59.45 \pm 0.24 \text{ m}^2/\text{g}$) >> NanoHAp ($32.21 \pm 0.01 \text{ m}^2/\text{g}$) >> HAp200 ($6.52 \pm 0.08 \text{ m}^2/\text{g}$). There were significant differences among the groups ($p < 0.001$).

XRD, TEM, and SAED analyses of four HAp-particles

The XRD patterns of HAp200, NanoHAp, and HAp100 (HAp100f) particles are shown in Fig. 2A. The patterns of all samples were in good agreement with the ASTM data (JCPDS: 721243) for hydroxyapatite. The XRD peaks of NanoHAp and HAp100 were broader than those of HAp200. Moreover, the crystallite sizes of NanoHAp and HAp100 were smaller than that of HAp200 (Table

1). TEM images and SAED patterns of HAp200, NanoHAp, and HAp100 are shown in Fig. 2B. The HAp200 sample contained rod-like sharp-edged particles about 40 nm in diameter and 400 nm in length (Fig. 2Ba). The NanoHAp sample consisted of agglomerated nano-particles of diverse shape (Fig. 2Bb). The HAp100 sample showed agglomerated rod-shaped particles, with a particle size of 20 nm in diameter and 30–120 nm in length. SAED of the HAp200 sample provided a clear diffraction pattern with discrete spots, indicating well-formed HAp crystals (Fig. 2Ba inset). The SAED patterns of NanoHAp and HAp100 are shown in Fig. 2Bb and c. The SAED patterns showed spotty ring patterns indicating random orientation in the crystalline phase of HAp; this is particularly pronounced in HAp100 (Fig. 2Bc).

Fig. 2 XRD, TEM, and SAED analyses of HAp200, NanoHAp, and HAp100 particles.
A: XRD patterns of (a) HAp200, (b) NanoHAp, and (c) HAp100
B: TEM image showing typical morphology of (a) HAp200, (b) NanoHAp, and (c) HAp100, and SAED patterns (inset)

Table 1 Crystallite sizes of HAp-particles calculated from the XRD (211) peak

Sample	Crystallite size (nm)
HAp200	41.3
NanoHAp	23.4
HAp100 (*HAp100f)	21.8

* HAp100f is the same crystal as HAp100, since HAp100f is finely ground HAp100.

Flexural strength and compressive strength of conventional and HAp-augmented GICs

The results of the flexural strength test conducted 24 hours after mixing the control-GIC and four HAp-added GICs are shown in Fig. 3A. The flexural strength values of A100f- and NanoA-GICs were significantly higher than that of the control GIC.

The results of the compressive strength test 24 hours after mixing the control-GIC and four HAp-added GICs are shown in Fig. 3B. There was no significant difference between the control- (171.1±7.0 MPa), A200- (176.4±18.6 MPa) GICs, and the control- and A100f-

Fig. 3 Mechanical properties.
 A: Flexural strength of the control-GIC and the four HAp-added GICs after 24 hours from mixing
 B: Compressive strength of the control-GIC and the four HAp-added GICs after 24 hours from mixing
 Significant difference between the control-GIC and HAp-added GICs (* $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$)

(181.0 $\pm$ 19.4 MPa) GICs.

The A100- (131.0 $\pm$ 10.0 MPa) and NanoA- (148.0 $\pm$ 20.0 MPa) GICs showed significantly lower compressive strength than the control-GIC ($p < 0.001$ and $p < 0.05$).

Fluoride ion release and recharge behavior of conventional and HAp-augmented GICs

The mean fluoride ion release values are shown in Table 2. In addition, accumulated fluoride ion release values are shown in Fig. 4. Over a 30-day period, which included three recharges, the HAp-added GICs except the NanoA-GIC exhibited higher fluoride ion release and recharge doses than the control-GIC. In particular, the A100f-GIC showed significantly higher daily fluoride ion release than the other GICs ($p < 0.001$) (Table 2).

SEM observation of fractured surfaces and EDS analysis of conventional and HAp-augmented GICs

SEM images of fractured surfaces of the control-, A200- and A100f-GICs are shown in Fig. 5A(a–c). The control-GIC exhibited an irregular fracture surface. A200- and A100f-GICs exhibited a somewhat smoother

fracture surface with fewer box-shaped glass-particle debonded holes (*i.e.*, holes formed following release of glass particles from the GIC fracture surface) and many fractured glass particles. However, the HAp particles added in the A200- and A100f-GICs could not be observed by SEM.

SEM images (lower and higher magnification) of the fractured segment of HAp100 particle (prior to being added to cement) are shown in Fig. 5B-1a. The result of EDS point analysis in this region of the SEM image is shown in Fig. 5B-1b. SEM images (lower and higher magnification) of the fractured surface, and the result of EDS point analysis of this region in the A100-GIC are shown in Fig. 5B-2a and 5B-2b. The samples of the A100-GIC could only be found in HAp100 particles added into the cement on the fractured surface by SEM. In the high magnification SEM image of the original HAp100 particle, the particles have a rough surface with countless concavo-convex surfaces made by the cohesive nano-size HAp crystals (Fig. 5B-1a). However, in the fractured surface of A100-GIC, the SEM image of HAp100 particle shows a smooth surface made by the penetration of the GIC matrix into the HAp pores by the adsorption ability of HAp (Fig. 5B-2a). EDS point analysis of HAp100 incorporated into A100-GIC provided the distribution of F, Si, Al, and Sr (originating from Fuji IX glass powder), in addition to P and Ca originating from HAp (Fig. 5B-1b and 5B-2b).

EDS and XPS analysis of the cement matrix

The elemental compositions of the matrix phases of the control-, A100- and A100f-GICs are shown in Table 3. The A100- and A100f-GICs included larger amounts of Ca and P in the matrix, whereas little Ca was present in the matrix of the control-GIC. EDS spectra of the matrix in the A100- and A100f-GICs are shown in Fig. 6A. The Ca peak is more clearly evident in the EDS spectrum of the A100f-GIC than the A100-GIC (Fig. 6A-b).

The XPS narrow-scan spectra for Ca2p in the matrices of the control-GIC and HAp-added GICs are shown in Fig. 6B-a. The Ca2p peak was not detected in the control-GIC matrix, but is evident in the matrix layers of the HAp-added GICs. The Ca2p/C1s peak area ratios of the control-, A200-, NanoA-, A100-, and A100f-GICs were 0.00, 0.02, 0.11, 0.04, and 0.07, respectively. Calcium was detected in all HAp-added groups, with higher Ca in the NanoA- and A100f-GICs than in the A200- and A100-GICs. The XPS narrow-scan spectra for F1s in the matrices of the control-GIC and HAp-added GICs are shown in Fig. 6B-b. The F1s peak was clearly detected around 686.0 eV in the control-GIC, but was present as indistinct peaks in HAp-added GICs' matrix. The F1s/C1s peak area ratios of the control-, A200-, NanoA-, A100- and A100f-GICs were 0.16, 0.14, 0.16, 0.30, and 0.33, respectively; the ratio is highest for the A100- and A100f-GICs.

DISCUSSION

The purpose of this study was to improve the mechanical

Table 2 Fluoride ion release from the control and four HAp-added GICs over a 30-day period ($\mu\text{g}/\text{cm}^2$)
Significant difference between the control group and four HAp-added GICs ($*p<0.05$, $**p<0.01$, and $***p<0.001$)
Recharge: After 14, 19, and 24 days, the samples were recharged by exposure to 9,000 ppm F^- ion for 5 min.

Group \ Day	1	2	3	4	5	6	7	8	9	10
Control-GIC	41.3	9.4	6.0	5.3	5.1	4.3	4.1	3.5	5.1	3.0
A200-GIC	69.5	18.4	10.3	6.2	7.2*	8.0	7.5	8.0	6.6	5.1
NanoA-GIC	43.0	15.7	9.7	8.3	5.6	6.3	4.3	4.2	2.7	3.2
A100-GIC	62.0	18.5	11.1	6.6	7.0	8.1	7.7	9.4	6.9	5.0
A100f-GIC	82.8**	27.3**	15.7***	8.3	8.3***	11.7**	10.5**	12.4**	9.9*	7.0**

Group \ Day	11	12	13	14	15	16	17	18	19	20
Control-GIC	2.8	2.4	2.7	2.6	68.6	7.1	2.9	4.1	2.1	29.7
A200-GIC	5.3	4.6	4.2	4.4	167.0*	16.9	5.2	6.4	4.0	60.2
NanoA-GIC	4.86	2.1	4.8	3.0	32.2	11.3	5.7	5.1	3.8	23.8
A100-GIC	5.5	4.6	4.3	4.4	147.3	17.2	5.3	6.3	4.2	59.4
A100f-GIC	7.8**	5.0	5.8**	5.8**	168.6*	24.1*	6.5**	8.1**	5.3**	65.3*

Group \ Day	21	22	23	24	25	26	27	28	29	30
Control-GIC	4.5	3.1	2.2	2.2	28.7	3.7	3.8	2.7	2.6	2.6
A200-GIC	9.4	5.3	3.8	3.6	58.1	7.9	6.7	4.4	4.6	4.2
NanoA-GIC	4.7	2.1	1.9	2.2	36.0	5.6	3.1	2.6	2.4	2.1
A100-GIC	9.6	5.7	4.1	3.6	58.9	8.1	6.7	4.6	4.6	4.1
A100f-GIC	11.9*	6.9**	5.3**	4.7**	68.8*	10.9*	8.4**	5.9**	5.9***	5.4***

($\mu\text{g}/\text{cm}^2$)

Fig. 4 Cumulated fluoride ion release and recharge for the control-GIC and HAp-added GICs over a 30-day period.

Fig. 5 SEM and EDS point analysis of representative fracture surfaces.

SEM images of representative fractured surfaces of (a) control-GIC ($\times 2,000$), (b) A200-GIC ($\times 2,000$) and (c) A100f-GIC ($\times 2,000$). Fractured glass particles (FP), glass-particle-debonded hole (DH)

B-1 (a) SEM images (upper: $\times 1,000$, lower: $\times 15,000$) and (b) EDS point analysis of a HAp100 particle

B-2 (a) SEM images (upper: $\times 1,000$, lower: $\times 15,000$) and (b) EDS point analysis of HAp in the A100-GIC

Table 3 Comparison of the ratio of elements in the matrices of the control-, A100-, and A100f-GICs

Group	Na	Al	Si	P	Ca	Ti	Sr	Total (%)
Control-GIC	3.0 $\pm$ 0.3	33.9 $\pm$ 0.4	36.0 $\pm$ 0.4	8.5 $\pm$ 0.3	0.1 $\pm$ 0.0	1.0 $\pm$ 0.1	17.5 $\pm$ 0.3	100.0
A100-GIC	3.5 $\pm$ 1.7	32.8 $\pm$ 0.3	33.6 $\pm$ 1.7	9.9 $\pm$ 0.3	2.3 $\pm$ 0.4	1.0 $\pm$ 0.1	16.9 $\pm$ 0.5	100.0
A100f-GIC	2.6 $\pm$ 0.1	29.4 $\pm$ 1.6	30.8 $\pm$ 1.8	13.2 $\pm$ 1.4	8.5 $\pm$ 2.6	0.7 $\pm$ 0.1	14.8 $\pm$ 0.6	100.0

and chemical properties of GIC using the chemical reaction behavior of HAp. The mechanism of adhesion of GIC to tooth structure is based on a substitution reaction between the carbonyl anion of polyacrylic acid in the liquid component of GIC, and the hydroxyl groups, Ca ions and phosphoric acid in the HAp which is the main component of tooth. This is followed by the formation of a macromolecular electrolyte-chain in HAp^{11,27}. On the basis of adsorption and infrared spectroscopic studies, Wilson *et al.*²⁸ postulated that, during adsorption,

polyacrylate penetrates the surface of HAp, displacing and replacing surface phosphate. Calcium ions are displaced from HAp along with phosphate as part of a complex series of ionic exchanges. Wilson *et al.* inferred that, as a consequence of those interactions, an “intermediate layer” of calcium and aluminum phosphates and polyacrylates would form at the interface between the cement and HAp^{11,28,29}. This layer is very resistant to acid and is difficult to break²⁸. HAp is a well-known biocompatible functional material for use in

Fig. 6 EDS and XPS spectra of the matrix.

A: EDS spectra of the matrix of (a) A100- and (b) A100f-GICs. Black arrows indicate Ca peaks.

B: Narrow-scan spectra of XPS analysis for Ca2p (a) and F1s (b) in the matrix layers of the control-GIC and HAp-added GICs.

ion exchange and adsorbent materials, and as a catalyst. Therefore, the incorporation of HAp into GIC may improve both the biocompatibility of GIC and enhance its mechanical properties.

We previously demonstrated that the strength of GIC is improved by addition of HAp200 particles³⁰. In the present study, HAp100f particles were generated from commercial HAp100 particles, which is composed of porous particles about 240 μm in size, by mill grinding. Our intention was that the resulting mechano-chemical effects would produce better results than those obtained in our previous study. It has been reported that severe mechanical actions on solid surfaces lead to physical and chemical changes in the near-surface regions where the solids come into contact under mechanical forces³¹. These effects are generally termed “mechano-chemical effects”. HAp100f particles were crushed to about 10 μm in diameter. HAp200 was selected for comparison because its particle size is similar to that of HAp100f. The average diameter of NanoHAp, also chosen because of its extremely small particle size (about 1–20 μm), was the smallest of the four HAp, at about 3 μm . Because the shape of HAp samples in this study had a great difference, it was not recognized the relation between their particle size and their specific surface area. Characterizations of the four HAp-particles showed that HAp100 and HAp100f have higher specific surface area and lower compressive strength than HAp200, and that the particle characteristics of NanoHAp were between HAp100 (HAp100f) and HAp200. In the specific surface area of HAp, it was predicted that HAp100f was smaller than that HAp100 theoretically. However, the result of this study showed the data of the latter was slightly higher than the former. We understood that the surface areas of HAp100f and HAp100 did not have a difference about those data. Furthermore, XRD, TEM, and SAED studies showed that HAp200 had the highest crystallinity, and HAp100 and HAp100f had lower crystallinity than NanoHAp. Thus, HAp100f has the highest reactivity of the four HAp studied in this investigation.

Fuji IX was selected as the base GIC material because it is one of the strongest commercially available conventional restorative GIC, and is recommended for this reason by WHO for ART. GIC glass is mainly composed of SiO_2 , AlO_3 , CaF_2 , Na_3AlF_6 , and AlPO_4 . However, Sr can be substituted for Ca with little change in the GIC structure in order to increase the opacity of GIC to X-rays, because Sr and Ca have similar ionic radii ($\text{Sr}^{2+}=1.13\text{\AA}$, $\text{Ca}^{2+}=0.99\text{\AA}$)¹¹. Fuji IX contains Sr instead of Ca³². In this study, the presence of Sr and the absence of Ca in Fuji IX powders were verified by EDS and XPS analysis. It is therefore advantageous to use Fuji IX for investigating the contributions of Ca to the characteristics of HAp.

Sced and Wilson³³ and Irie¹² improved the flexural strength of GIC by adding amalgam and silver, respectively. However, they also reported decreased resistance to wear and compressive strength. Arita¹⁸ reported that the incorporation of SiC whiskers into GIC

improved transverse strength and fatigue resistance, but decreased compressive strength. Thus, the addition of reinforcements improves some properties of GIC and decreases others, especially compressive strength. Yamamoto¹⁹ and Nicholson³⁴ reported that the compressive strength of HAp-containing GIC decreased as the mass of HAp increased. In this study, all HAp-added GICs showed higher flexural strength than the control-GIC 24 hours after mixing into cements, whereas the compressive strength values of the A200- and A100f-GICs were the same as the control-GIC. Moreover, HAp increased the flexural strength of GIC and helped maintain its compressive strength, even though HAp particle has very poor compressive strength (approximately 1.0 MPa, which is 1/180 that of Fuji IX glass core particle, 182.8 MPa). The demonstrated dramatically improved mechanical strength of A100f-GIC, and its facile reaction with GIC, is likely due to the specific properties of HAp100f particles: 10 μm particle size, high specific surface area, porous surface, lower crystallinity compared to the other HAp, and mechano-chemical effects. It has been reported that the strength of cement is influenced by the size of the particles and the P/L, leading to the recommendation that particles should not be too fine or too large in order to achieve high strength³⁵. The flexural strength of A200-GIC is inferior to that of A100f-GIC, even though the particle size of HAp200 is similar to that of HAp100f. It is possible that the reaction of HAp200 with the GIC components occurs more slowly compared to HAp100f, due to the extremely high crystallinity, low specific surface area, and low porosity of HAp200. Moreover, the flexural and compressive strength values of the NanoA-GIC were lower than the A100f-GIC, although the particle size of NanoHAp is smaller than that of HAp100f. The decreased effects of NanoHAp may be due to the same factors as for HAp200: higher crystallinity and lower specific surface area than HAp100f. The remarkable decrease in the compressive strength of A100-GIC may be due to fracturing of the HAp100, since its particle size was too large to improve the mechanical properties of GIC.

HAp particles were not visualized by SEM observations of the fracture surfaces of the HAp-added GICs, except for the A100-GIC, indicating that the cracks in the matrix are caused by the strongly bonded interface between the HAp and the matrix. Moreover, increased fracturing of the GIC core and decreased glass particle-matrix-debonding surface was seen in the HAp-added GICs compared to the control-GIC. These results indicate that the GIC matrix is strengthened by adding HAp. SEM observation of both HAp100 particles and A100-GIC fractured surface showed that the GIC matrix components penetrate the countless pores throughout HAp100 (Fig. 5B-1, B-2), showing that HAp adsorbs the matrix during the cement hardening reaction.

In the present study, EDS analyses and SEM observations indicated that HAp adsorbed to GIC matrix containing Al, Sr, F, and Si ions. EDS analyses demonstrated the presence of Si in the matrix and, to a

lesser extent, in HAp. Ca could be detected in the matrix phases of the HAp-added GICs by EDS and XPS analyses. The reaction mechanism between HAp and GIC is likely similar to the reaction mechanism between tooth and GIC. Matrices of the A100f-GIC contain more Ca than matrices of the A100- and A200-GICs (Fig. 6). Our results show that HAp100f particles react more easily with polyacrylic acid than HAp100 and HAp200 particles, and that the improved characteristics of HAp100f may be due to a mechano-chemical effect.

GICs can help prevent dental caries by releasing fluoride ions. Approximately 200–300 $\mu\text{g}/\text{cm}^2$ a month of fluoride ion are needed to prevent enamel demineralization³⁶⁾. In the present study, the accumulated amounts of fluoride during the first 14 days from the A100- and A100f-GICs were 161.1 and 218.3 $\mu\text{g}/\text{cm}^2$, respectively, whereas that of the control-GIC was 97.6 $\mu\text{g}/\text{cm}^2$. Thus, the quantity of fluoride released by A100- and A100f-GICs is sufficient for the prevention of enamel demineralization even without fluoride recharge if they are maintained in the oral cavity for one month.

In this study, fluoride ion release and recharge doses of all HAp-added GICs were higher than the control-GIC. Fluoride was included only in the GIC glass powder, so more fluoride ion was released from the HAp-added GICs than from the control-GIC despite the lower fluoride content in the HAp-added GICs. In particular, the fluoride release and recharge behavior of the A100f-GIC was superior to the other HAp-added GICs, indicating that fluoride ion release is improved by adding highly reactive HAp particle.

It has been reported that the fluoride released from GIC is mainly from the matrix³⁷⁾. In addition, Meryon and Smith³⁸⁾ concluded that fluoride released from GIC is not from the GIC core but rather from the matrix. In our study, XPS analysis showed that fluorine contents in the matrices of the A100- and A100f-GICs were higher than in the matrix of the A200-GIC, and that the fluorine content of the A200-GIC was lower than that of the control-GIC. However, the amounts of fluoride ion released from all the HAp-added GICs were significantly higher than from the control-GIC. Moreover, the amount of fluoride ion released from the A200-GIC was similar to that from the A100-GIC over a 14-day period, but the amount of fluoride ion released after recharging the A200-GIC with fluoride ion was higher than for the A100-GIC. These results indicate a discrepancy between the fluoride release dose from HAp-added GIC and the fluoride content in the matrix phase.

Stamboulis³⁹⁾ reported XPS analyses showing the presence of Al-F-Sr(n) and Al-F-Na(n) in Fuji IX-powder. Our study also shows that F1s peaks originate both from organic fluoride (689.0 eV) and metallic fluoride (686.0 eV), suggesting that fluoride will react with Al or Sr in the glass core. Furthermore, Jones²⁶⁾ reported that fluoride ion uptake of GIC based on calcium aluminosilicate glass correlated with the formation of a surface layer rich in Ca and fluoride, and possibly containing CaF_2 . In our study, XPS detected Ca from added HAp in the matrix of four HAp-added GICs. The HAp-added GICs

released and recharged more fluoride ions than the control-GIC, and so it is possible that Ca in the HAp influenced the release of fluoride. Therefore, HAp, GIC glass core, and GIC matrix may react with each other. These findings suggest that the release and recharge of fluoride ion occurs in both the matrix and HAp-added GICs.

CONCLUSIONS

The results from this study demonstrate that the addition of HAp particles with different characteristics may enhance the flexural strength and fluoride ion release properties of conventional restorative GIC. In addition, a novel “apatite glass ionomer cement” with high performance and strength was developed by adding highly reactive HAp particles about 10 μm in diameter to conventional restorative GIC. Our results further indicate that HAp functions as an adsorbent and an ion exchangeable agent, rather than as reinforcement, resulting in improved mechanical and chemical properties of GIC.

The mechanisms underlying these improved properties are thought to be:

- 1) The matrix of HAp-added GIC was strengthened compared to conventional GIC by increased metal ions participating in the cement hardening reaction. The metal ions (Ca^{2+}) are supplied by the dissolution of HAp particles.
- 2) The HAp particles in GIC was reinforced first by the adsorption of GIC matrix and then by the formation of an “intermediate layer” between the surface of the primary HAp crystals and the absorbed matrix.
- 3) HAp-added GIC was reinforced by adhesion of the improved matrix and the improved HAp particles.

ACKNOWLEDGMENTS

This research was supported by the Japan Science and Technology Agency (JST) and Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Scientific Research (A) #20241020.

The authors would like to thank Mr. Katsuhito Kato, Research & Development Dept., GC Corporation, Tokyo, Japan, for EDS analyses and helpful discussions, and Mr. Yosuke Umezaki, Department of Chemical Science and Technology, The University of Tokushima, for his technical support in the XRD, TEM, and SAED analyses.

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