Study on the fluoride-releasing ability of dental GIC materials in deionized water and artificial saliva environments

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Abstract:

Glass ionomer cement (GIC) is a particular type of cement used in dentistry. One of the most critical properties of GIC is the ability to release fluoride, which can prevent recurrent tooth decay. This study simultaneously investigated the release of fluoride, the compressive strength, and the apparent density of three GICs in deionized water (DW) and artificial saliva (AS) environments. GICs with 3 different types of glass powders were used to study. Powder B (the original) was the glass powder based on the SiO_2-Al_2O_3-CaF_2-$AlPO_4$-Na_3AlF_6 system, powder HA5 was powder B supplemented with 5 wt. % hydroxyapatite powder (HA), and powder Si_2 was powder B surface-treated with 2 wt. % silane JH-S69. The results of this study showed the amount of fluoride ion (F^-) released during 28 days in AS was lower in comparison to the DW environment, and the rate slowed down significantly after 1 d. The F^- release rate at 1-d age tended to be high as the compression strength was low. In AS, the powder supplemented with 5 wt.% HA improved the compressive strength and the cumulative amount of F^- released by the GIC. After 28 d, the F^- release of the GIC materials were able to be recharged in a NaF solution with 1,018 ppm F^- concentration for 3 min and further fluoride ions were released in both the DW and AS environments.

Keywords: **dental material, fluoride release, glass ionomer cement.**

Classification number: **2.2**

Introduction

GIC can be defined as a water-based material that hardens following an acid-base reaction. An ordinary glass ionomer cement consists of 2 parts: the ion-leachable glass powder, which is based on a calcium fluoro-aluminosilicate glass, and an acidic polymer solution of a polyalkenoic acid. The setting occurs in concentrated solutions in water. The final structure of a hardened GIC contains polyalkenoate salts with ionic crosslinks and a substantial amount of unreacted glass, which acts as the filler to reinforce the set cement. Since its introduction in 1971 [1], GICs have been successfully applied in dentistry and hold an important role in today's dental materials [2-4]. Although GICs have lower physical and mechanical properties than amalgam and composite resin materials, their advantages of aesthetics, adhesive properties, and biocompatibility make them very attractive to dental applications [5]. Dental caries or tooth decay is one of the most common health problems. The crucial feature of GICs for dental applications is their ability to release fluoride, which has anti-cariogenic effects. Lots of studies have emphasized the importance of fluoride-containing GIC materials to protect existing tooth structures and prevent secondary tooth decay, which places GIC materials in a better position than other materials [5, 6]. The fluoride release of glass ionomers causes the dentin to be less soluble in acid, increases the mineral regeneration, and changes the bacterial plaque composition in the tooth structure around fillings. Besides, GICs also have a fluoride absorption ability when exposed to F-containing sources. This remarkable feature helps to maintain the material's cariostatic capability in the long term [7]. Fluoride is an essential component of the glasses of GICs. This component has several functions within the glass such as lowering the

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fusion temperature, which improves the working behaviour of freshly mixed cement paste by preventing premature gelation. Moreover, fluoride improves the strength of the set cement [8]. However, some previous studies [9] have reported that a high fluoride-release ability could lead to poor mechanical properties. The factors that may affect the release of fluoride are the composition and microstructure of GIC materials (glass powder composition, fluoride content, powder/liquid ratio, substrate composition, and absorption ability of the GIC material), the storage environment (composition, pH, quantity, and frequency of the solution renewal), and regular contact with a local F-source such as toothpaste or mouthwash.

A lot of treatment methods, additives, and/or fillers have been applied to GIC material components to improve or enhance their properties. A mixture of inorganic compounds (glass, mineral, or metal) and organic compounds (rubber, plastic, or polymer) make it difficult to form a fine composite due to surface incompatibility involving the complex interaction of physical and chemical factors. One of the common solutions is the surface modification method using silane coupling agents. These substances are silicon-based chemicals that contain two types of reactivity - inorganic and organic - in the same molecule. The surface treatment of inorganic particles with silanes improves the phase interaction between the substrate and dispersant, thus improving the physical and mechanical properties of materials, and dental GICs are no exception [10-12]. Besides, another way is to increase the density of GICs by the application of various fillers [13] into a polyalkenoate glass component, such as metal powders (silver, stainless steel), carbon fibre, alumino-silicate fiberglass, or inorganic powder (SiO_2, Al_2O_3, ZrO_2, forsterite [14], hydroxyapatite, bioactive glass powder [15]). Among them, hydroxyapatite (HA) [$Ca_{10}(PO_4)_6(OH)_2$] has good biological properties. Therefore, combining HA into GIC may not only improve mechanical properties but also enhance biological compatibility and the fluoride release ability of GIC materials [16, 17].

The modification of GIC components to improve certain properties will no doubt change other properties of the material. The main purpose of this study is to assess the fluoride release from GICs with three different types of glass powders in deionized water and artificial saliva environments, before and after a NaF solution treatment (i.e. fluoride recharge). The change in compressive strength, apparent density, and microstructure of the material was also evaluated simultaneously after immersion periods.

Materials and methods

Materials

Synthesis and characterization of glass powders and liquid of GIC materials: a high-speed lab milling equipment (Ceramic Instruments Ins) with a 1-l ceramic jar and 7-8-mm diameter zirconia ball was used for preparing the glass batch or for grinding the glass frit. The raw materials/ZrO_2 ball ratio was approximately 250 g/1,000 g. The glass batch was prepared by mixing suitable amounts of reagent-grade raw materials (Al_2O_3, SiO_2, $AlPO_4$, Na_3AlF_6, CaF_2) in the ceramic ball mill jar for 10 min. The homogeneous mixture was melted in a platinum crucible in a Carbolite-1600 furnace at 1,300°C for 90 min. Then, the molten glass was quenched in cool distilled water to form a glass frit. The frit was, in turn, dry-milled for 50 min and sieved through a 45 μm mesh sieve to produce the first glass powder denoted as B. The chemical composition of the base glass powder B (mol% of elements, by x-ray fluorescence) is Al: 25.6, Si: 22.9, Ca: 15.2, P: 10.7, F: 15.3, Na: 10.4. The x-ray diffraction (XRD) patterns by Bruker D2 Phaser equipment with Cu - K_α radiation, 2θ scanning from 10 to 70°, step size of 0.03°/2θ, and mean time per step of 42 s, demonstrated that glass powder B was an amorphous material. The average diameter and specific surface area of powder B analysed by laser diffraction were 14.3 μm and 10,358 cm²/cm³, respectively.

The second powder denoted HA5 is powder B supplemented with 5 wt.% HA (synthesized hydroxyapatite powder, a research product of grant number B2012-20-09TD). The XRD pattern of the HA powder showed that the peaks corresponded to the standard hydroxyapatite crystal (ICDD standard, HA: JCPDS No. 09-0432). The crystal size of the nano-HA is determined to be about 51.8 nm by using X'Pert High Score software and the Scherrer equation for the (002) peak. The scanning electron microscope (SEM) and transmission electron microscope (TEM) images showed the particle size of HA to be less than 100 nm [18].

The third powder, denoted Si_2, is glass powder B surface-treated with 2 wt.% silane JH-S69 (chemical name: Bis-(3-triethoxysilylpropyl) tetrasulfide, ChemSpec, Ltd, USA) to improve the surface compatibility with the acidic polymer solution. The glass powder B (100 g) was well mixed with a solution (60 g) of 3.33% JH-S69 in ethanol in a mortar and then dried at 110°C for 2 h in a dryer to obtain the dried silane-treated powder. This dried powder was, in turn, re-dispersed in ethanol at 60°C for 30 min by hot magnetic

stirrer, then vacuum-filtered (using Whatman No.40 filter paper) to remove any non-bonded residual silane. After being dried again at 60°C for 4 h, it was finely crushed in a mortar and passed through a 45 μm mesh sieve to obtain the surface-modified glass powder Si_2.

The main component of the acidic polymer liquid was a poly(acrylic acid) solution $[(C_3H_4O_2)_n]$ (PAA) with average $M_w \sim 100,000$ and 35 wt. % in H_2O (a product of Sigma-Aldrich). To improve the handling, storage, and reactivity characteristics of the polymer liquid, maleic acid $[C_4H_4O_4]$ (5% by mass) and tartaric acid $[C_4H_6O_6]$ (5% by mass) were added to the PAA solution.

Preparation of GIC samples: the GIC powder and liquid were mixed at a powder/liquid (P/L) ratio ~1.4 g/1.0 g and shaped at 23±1°C. Cylindrical specimens were fabricated according to ISO 9917-1:2007's instructions, using stainless steel cylindrical moulds with 4.0±0.1 mm diameter and 6.0±0.1 mm height. Thirty minutes after mixing, the ends of the specimen were ground flat and at right angles to its long axis by using wet 400-grade silicon carbide paper. Then, the specimens were immediately removed from the moulds after surfacing and checked visually for air-voids or chipped edges. Any such defective specimen was discarded. Five GIC cylindrical specimens of each composition (B, HA5, or Si_2) were immediately immersed in closed plastic centrifuge tubes (conical bottom) containing 5 ml of deionized water (pH 7.0) or an artificial saliva solution (pH 5.0) at 37±1°C and 100% humidity for 1, 7, 14, and 28 d in an incubator until testing time. The ingredients of the artificial saliva [19] are shown in Table 1.

Table 1. The ingredients of each 50 g of artificial saliva (AS) solution [19].

Ingredients of AS	Amount in 50 g AS solution
Carboxymethylcellulose sodium	0.5 g
Calcium chloride ($CaCl_2.H_2O$)	0.0073 g
Sodium chloride (NaCl)	0.0422 g
Potassium chloride (KCl)	0.06 g
Sorbitol ($C_6H_{14}O_6$)	1.5 g
Magnesium chloride ($MgCl_2.6H_2O$)	0.0026 g
Potassium monohydrogen phosphate (K_2HPO_4)	0.0171 g
Sorbic acid ($C_6H_8O_2$)	0.025 g
Sodium benzoate ($C_7H_5NaO_2$)	0.0295 g
Deionized water	47.8 g

Compressive strength (CS) test

The CS of the hardened GICs was tested by Testometric M350-10CT equipment (England) at the Faculty of Materials Technology (HCMUT, VNU-HCM), and followed the ISO 9917-1:2007- Annex D with the cross-head speed of 0.75 mm/min. The CS was calculated by using the equation:

$$CS = \frac{4 \times P}{\pi \times d^2} \text{ (MPa)}$$

where P is the maximum force applied (N) and d is the measured diameter of the cylindrical specimen (mm).

Measurement of GICs apparent density

The apparent density, is determined by the Archimedes method:

$$\rho_{ap} = \frac{m_d}{m_d - m_A} \rho_W \text{ (g/cm}^3)$$

where m_d is the dry specimen mass (specimens were dried at 60°C for 3 h) (g), m_A is the saturated specimen mass in water (g), and ρ_W is the density of distilled water (g/cm³).

The microstructure of GICs (Surface examination with scanning electron microscopy)

The surfaces of samples were Pt-sputtered and then analyzed by scanning electron microscope [FE-SEM, Model S-4800 (Hitachi High - Technologies Co., Tokyo, Japan)].

Fluoride release experiment

The environmental conditions may affect the fluoride release ability of GICs. When the storage solution is replaced every day, the releasing ability is higher than in a fixed storage solution. For the test of fluoride release in this study, the storage solutions have to be renewed daily. The cylindrical specimens of the hardened GICs were prepared as shown in above. The average weight and the surface area of each specimen were 0.149±0.005 g and 1.00±0.02 cm², respectively.

The F⁻ concentration of the storage solution after soaking times (expressed as ppm) was analyzed by the Spectroquant® Spectrophotometer Pharo 100 (Merck) at the Centre for Product Evaluation (CPE) of Tra Vinh University (TVU) with a fluoride test kit with measuring range 0.1-20.0 ppm (μg/ml) and code 114598.0001. The cumulative amount of the released fluoride was obtained by the following equation [7]:

Cumulative released F⁻ (µg/g/cm²) = F⁻ concentration (ppm ~ µg/ml) * total volume of storage solution (ml)/total weight of specimens (g)/total surface area of specimens (cm²).

The rate of fluoride release as a function of time is expressed as µg/g/cm²/d.

Fluoride treatment to simulate a fluoride recharge

After 28 d of storage in the DW or AS environment, the GIC samples were soaked in a NaF solution (F⁻ concentration: 1,018 ppm) for 3 min to simulate fluoride recharge during practical applications, which models the F⁻ the GIC could receive from F⁻-containing oral hygiene products. Then, they were rinsed gently with DW and immersed again in the same storage solution at 37°C. The storage solutions also were replaced every day. The sequential F⁻ release was tested at the storage age of the next 1, 2, and 3 d.

Results and discussion

Compressive strength (CS) and apparent density (ρ_{ap}) of GICs

Figure 1 represents the mean CS values and the mean ρ_{ap} values of the hardened GICs at 1, 7, and 28 d of age in the AS and DW storage environment. The CS is an important indicator of strength against mastication forces. The change in compressive strength of each GIC sample, according to the storage time, was similar in the AS and DW environments. The mean CS value of all the GICs increased from 1 d to 7 d, while the 28-d value decreased for the B

and Si₂ specimens. Because of the recent contact (0.5-1 h after the end of mixing) with the soaking solution of the GICs during the prolonged immersion time, the leaching and diffusing ions from the cement to the immersion environment lead to failure in the material structure [20]. This is one of the disadvantages of GICs in return for their F⁻ release capability.

Two important factors affecting the strength of the GICs are the compactness and the interior bondings of the material. The ρ_{ap} reflects the consistency of the hardened GIC samples after the immersion time. With increasing ρ_{ap}, an increase in CS should be expected. A silane coupling agent can provide a stable bond between the two different poorly bonded surfaces as well as better wetting of inorganic substrates, which can help reduce the appearance of voids in the process of mixing and shaping the GIC. Thus, when glass powder B was surface-treated with 2% silane JH-S69, the resulting GIC-Si₂ samples possessed a higher apparent density and a more stable compression strength value at an older age (28 d). In the GIC-HA5 sample, the addition of HA nanoparticles with 5% content leads to a wide particle size distribution of the powder mixture. The glass and HA grains could be intertwined to fill the gap and thus increase the cement density. Moreover, HA is also capable of ion exchange [21]; many research results [17, 22, 23] have shown that HA is able to react with GIC through carboxylate groups in polyacids. That fact contributes to the increase in compressive strength of the GIC-HA5.
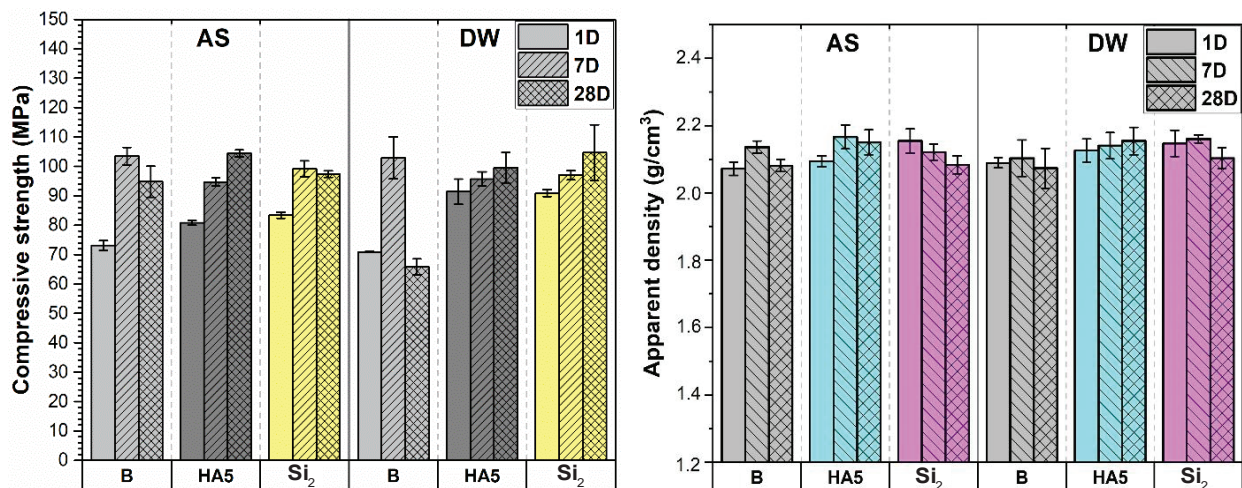

Fig. 1. Mean compressive strength (left) and mean apparent density (right) of GICs in AS and DW environment at 1, 7, and 28 d age.
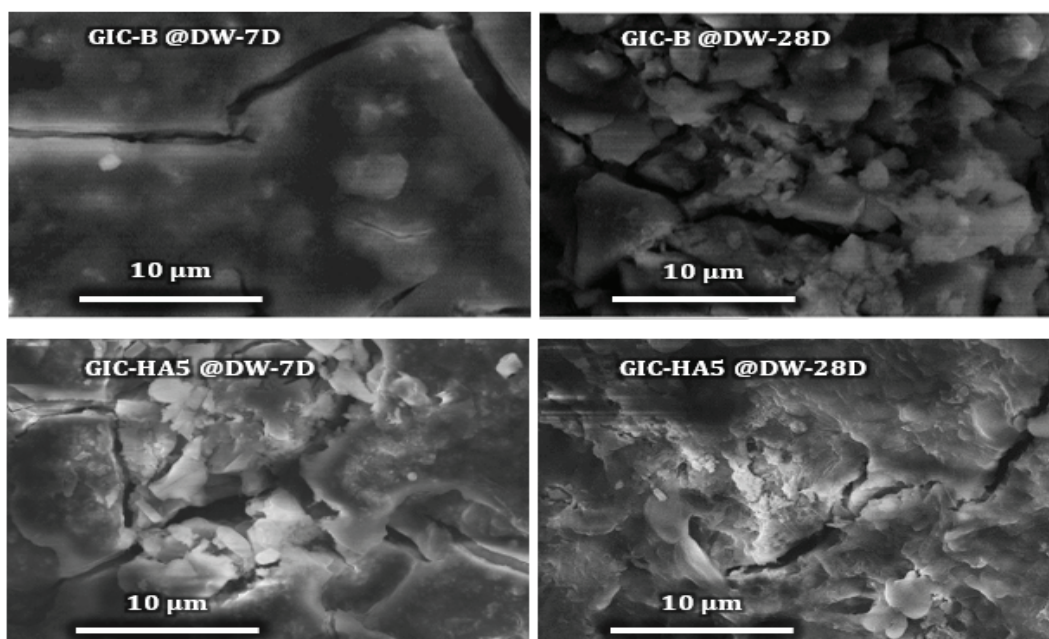
Fig. 2. The SEM images of GIC materials.

The results of SEM

SEM characterization is carried out to analyze the topography and the morphology of the hardened GICs surfaces. As shown in the SEM images (Fig. 2), the compact structure of the hardened GICs could be observed after 7 d.

The unclear borders around the glass powder grains signified that the glass phase reacted with the matrix phase and created mechanical and chemical bonding. Moreover, micro-clefts and pores could be formed by the mixing, shaping, and shrinkage processes. In general, the microstructure of the GIC samples soaked in the AS or DW environment at the same age was not significantly distinguished by the SEM images. It is noteworthy that the structure of the GIC pellet surface became rougher after 28 d of immersion, especially for sample B. The boundary of the unresponsive glass grains was more visible. It is indicated by the SEM images that the partial dissolution of the material on the surfaces occurred over time. This result might also be deduced from the reduction of the bulk density of the sample at the 28-d age compared to the 7-d age. Therefore, the CS of GICs tended to decrease at the 28-d age, except for the GIC-HA5 sample.

Fluoride release

F^- release test data resulting from the GICs studied before and after the F^- treatment in a NaF solution (F^- recharge) are shown in Tables 2 and 3 and Fig. 3. The detailed results showed that the synthetic GICs could release fluoride in both DW and AS environments. The cumulative amount of fluoride release increased with curing time. This phenomenon was caused by the fluoride ions dissolved from the glass powder and those that exist in the glass-ions matrix of the GIC. However, the release rate slowed down significantly after 1 d. The released fluoride in both storage environments was still detectable at 28-d age, but at low levels.

Table 2. The cumulative amount of released fluoride from GIC samples in DW and AS environment.

Environment	Sample	Cumulative released F^- (µg/g/cm²)					1 day after FT	2 days after FT	3 days after FT
		1 day	*7 days*	*14 days*	*28 days*				
AS	B	50.3	54.4	71.4	82.2		484.0	534.6	566.3
	HA5	53.4	100.3	146.3	186.3	*Fluoride treatment (FT) in NaF solution (1,018 ppm)*	375.3	442.2	484.5
	Si_2	45.6	69.7	78.2	93.2		382.4	423.3	450.5
DW	B	204.1	270.4	316.3	389		484.0	534.6	566.3
	HA5	176.9	224.5	244.9	301.4		375.3	442.2	484.5
	Si_2	183.7	224.5	241.5	317.8		382.4	423.3	450.5

Table 3. Fluoride release rate (μg/g/cm²/d) as a function of time of GIC samples in DW and AS environment.

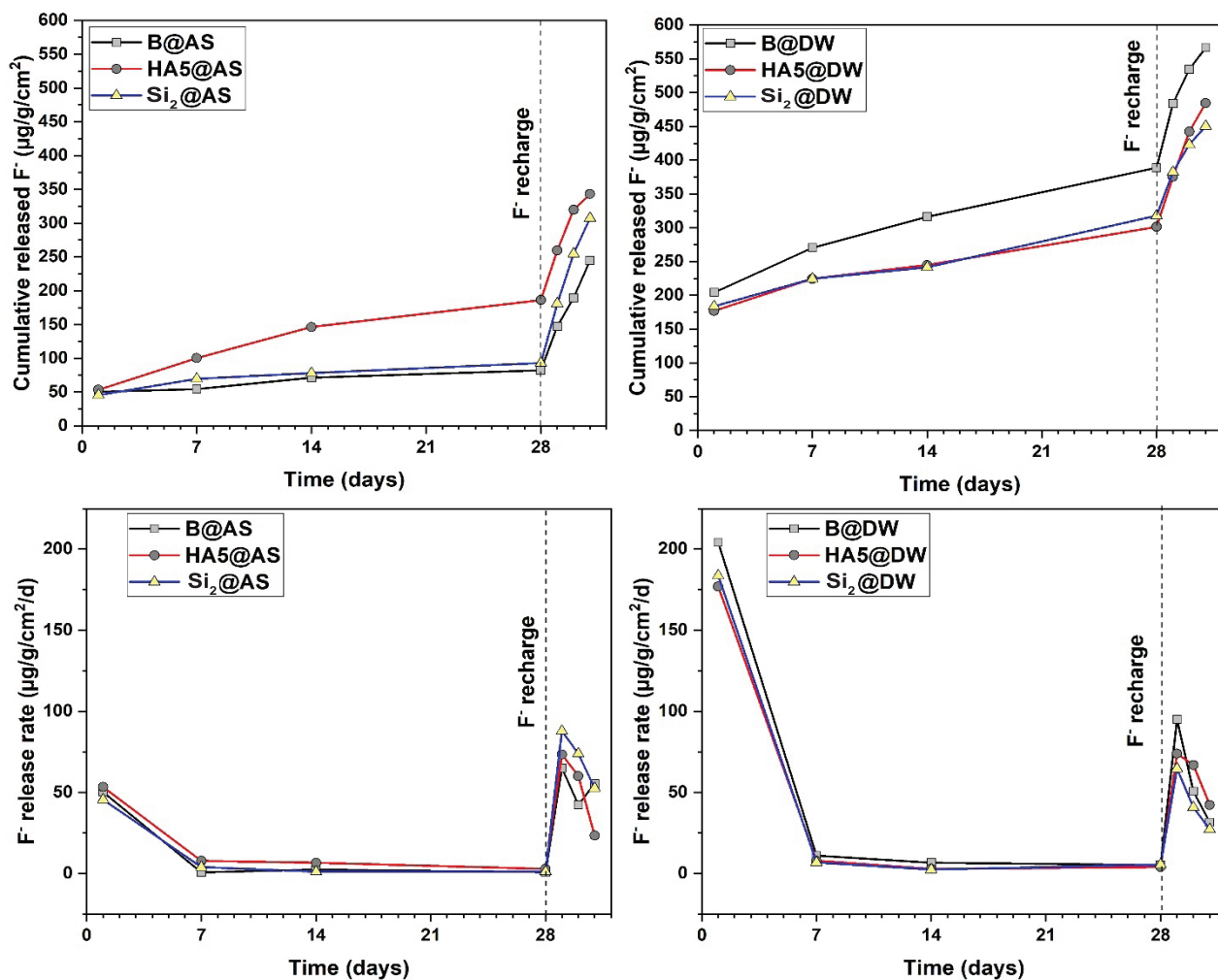| Environment	Sample	F⁻ release rate (μg/g/cm²/d)					1 day after FT	2 days after FT	3 days after FT
		1 day	*7 days*	*14 days*	*28 days*				
AS	B	50.3	0.7	2.4	0.8	*Fluoride treatment (FT) in NaF solution (1,018 ppm)*	65.1	42.3	55.3
	HA5	53.4	7.8	6.6	2.9		73.4	60.1	23.4
	Si₂	45.6	4.0	1.2	1.1		87.8	73.8	52.7
DW	B	204.1	11.1	6.6	5.2		94.9	50.6	31.6
	HA5	176.9	7.9	2.9	4.0		73.9	66.9	42.3
	Si₂	183.7	6.8	2.4	5.5		87.8	40.8	27.2

Fig. 3. The plots of cumulative released F⁻ amount and F⁻ release rate vs time of storage in AS and DW environments of the GIC samples.

Those results could be explained by the mechanism of ion release. Fluoride ions were released first from the surface of the GIC material with a high rate, then the F⁻ diffusion from the inside of the GIC structure extended the releasing process at slower rate [8] due to the tight cross-linkage in the mature cement matrix. After being soaked in a NaF solution (1,018 ppm F⁻) for 3 min, at 28-d age the increase of F⁻ release values over the following days indicated that the GICs could be recharged with fluoride.

In Fig. 4, the cumulative release from the three GICs and their CS after 28 d of immersion in AS and DW is

shown. The linear fitting was performed using the analysis tool of Origin Pro 2015. The cumulative F⁻ release amount of the three GICs observed in AS was less than in the DW environment. That may be explained by the similarity between the ions' composition in the AS environment and the GIC materials, which causes a low diffusion gradient [24]. In the storage solutions, the ions-release phenomena, including F⁻ release, occurred due to the erosion of the GIC.
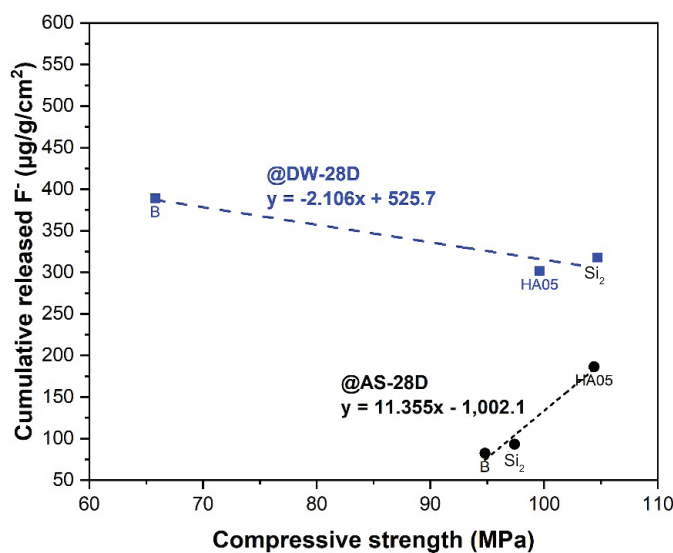

Fig. 4. Plot of cumulative released F⁻ amount vs compressive strength at 28-d age of the GIC samples in AS and DW environments.

In the case of deionized water, a negative value of the slope of the fit line indicates that a mature GIC sample with a high cumulative amount of F⁻ release would have a low CS value. During the GIC immersion process in deionized water, the diffusion of ions took place merely from GIC into the water. Conversely, in the process of storage in the AS environment, the saliva components, including calcium and phosphates, could diffuse into the cement structure and contribute to the strengthening of the GICs' surface [25]. Consequently, the CS values of the GIC-B and GIC-HA5 samples in the AS were higher than those in DW. On the other hand, the presence of HA nano-particles has a role in this aspect as the filler that made the apparent density and the CS of GIC-HA5 higher. However, unlike glass grains, HA particles might disrupt the cross-linking of polysalts. Thus, the fluoride release of GIC-HA5 in AS still occurred quite favourably due to the mobility of the small fluoride ions (like hydroxyl ions) in this GIC matrix without any damage [26].

Figure 5 shows the relationship between the F⁻ release

rate and the compressive strength of the GIC samples in the AS and DW environments at 1-d age and 29-d age (i.e. 1 d after F⁻ recharge). The slopes of the fit lines had negative values. Therefore, for the three GIC samples with different powder compositions, the F⁻ release rate at 1-d age tended to be high when the compression strength was low. This trend was also expressed in the F⁻ re-release value on the first day after the GIC samples were recharged with F⁻. The modification of glass powder B by the addition of HA (HA5) or the silane surface treatment with JH-S69 (Si_2) has increased the CS and the Pap of the GICs. These factors have limited the release of F⁻ from the surface, which is the dominant mechanism in the early stages, as a consequence.
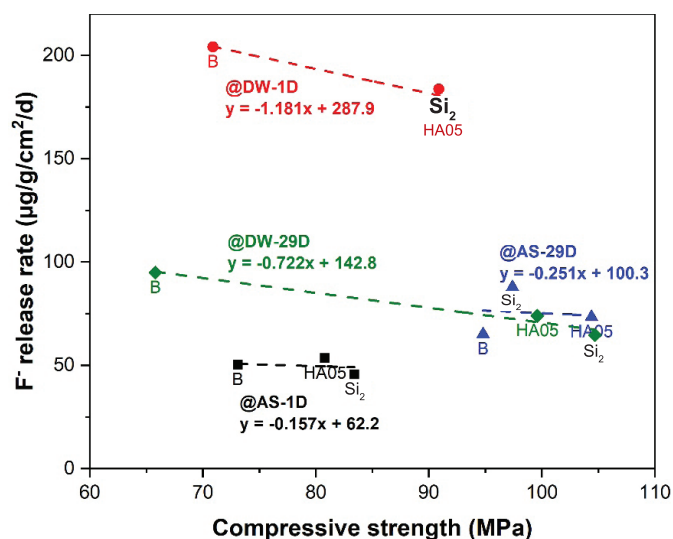

Fig. 5. The F⁻ release rate vs the compressive strength of GIC samples in AS and DW environments at 1-d age and 29-d age (1 d after F⁻ recharge).

Conclusions

The three GICs synthesized in this study showed satisfactory results in their fluoride-releasing ability over time. The releasing capacity in DW was higher in comparison to AS, and the rate slowed down significantly after 1 d of immersion. The modification of glass powder B by the addition of HA (HA5) or the silane surface treatment with JH-S69 (Si_2) has increased the CS and the ρ_{ap} of the GICs, accordingly, and in the early stages, it limited the release of F⁻ from the surface in both environments. In AS, the supplement of 5 wt.% HA can improve not only the CS but also the cumulative F⁻ release amount of GIC. After 28 days of F⁻ release, the GIC materials were able to be recharged and further released fluoride in the DW and AS environments.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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