

REPORT

 OPEN ACCESS

Enhanced bioactivity of glass ionomer cement by incorporating calcium silicates

Song Chen, Yixiao Cai, Håkan Engqvist, and Wei Xia

Applied Materials Science, Department of Engineering Science, Uppsala University, Uppsala, Sweden

ABSTRACT

Glass ionomer cements (GIC) are known as a non-bioactive dental cement. During setting the GIC have an acidic pH, driven by the acrylic acid component. It is a challenge to make GIC alkaline without disturbing its mechanical properties. One strategy was to add slowly reacting systems with an alkaline pH. The aim of the present study is to investigate the possibility of forming a bioactive dental material based on the combination of glass ionomer cement and calcium silicates. Two types of GIC were used as control. Wollastonite (CS also denoted β -CaSiO₃) or Mineral Trioxide Aggregate (MTA) was incorporated into the 2 types of GIC. The material formulations' setting time, compressive strength, pH and bioactivity were compared between modified GIC and GIC control. Apatite crystals were found on the surfaces of the modified cements but not on the control GIC. The compressive strength of the cement remained with the addition of 20% calcium silicate or 20% MTA after one day immersion. In addition, the compressive strength of GIC modified with 20% MTA had been increased during the 14 d immersion ($p < 0.05$).

ARTICLE HISTORY

Received 16 December 2014
Revised 5 October 2015
Accepted 18 November 2015

KEYWORDS

bioactivity; calcium silicate; dental cement; glass ionomer cement; mineral trioxide aggregate

Introduction

Glass ionomer cement (GIC) has been widely used in dentistry since 1970.^{1,2} It is considered superior to other types of water based cements because it has good mechanical properties and transparency.³ In addition, fluoride release over a prolonged period and good biocompatibility make GIC useful as a dental material.⁴ However, GIC has some disadvantages such as relatively high brittleness and it is moisture sensitive during the early stage of setting. Over the past decades, progresses have been made to improve the mechanical strength of GIC, through modification of either polyelectrolyte or glass powder.^{4,5} However the material has relatively high brittleness and it is moisture sensitive during the early stage of setting.⁶ Another disadvantage of GIC is that the bonding between the GIC and tooth is weak.^{7,8} A stronger chemical bond between GIC and teeth could be achieved by rendering a GIC with true bioactive properties, i.e. formation of an apatite interlayer.⁹ The formation of apatite on surface can close gaps between restoration and teeth, improve bonding strength, and enhance bone integration with implant surfaces.¹ However, for conventional GIC, it is considered difficult to form such apatite

layer because the release of polyacrylic acid (PAA) from the GIC lowers the pH and inhibits the formation of apatite.⁷ Thus, it is necessary to develop bioactive GIC that can promote the formation of hydroxyapatite on the surface of GIC.

The invention of bioactive glass by Larry Hench launched the field of bioactive ceramics.^{11,12} The use of bioactive glass to improve the bioactivity of GIC has recently been published. The results show that resin-modified GIC with bioactive glass has an effect on mineralizing dentin both in vitro and in vivo.^{13,14} However, the addition of bioactive glass compromises the compressive strength and surface hardness of GIC.¹⁵ Thus developing bioactive GIC without decreasing its mechanical properties still remains a challenge. One possible strategy is to incorporate silica-based bioceramics into GIC. Silica-based ceramics are important bioactive materials which has gained attention in endodontic applications.¹⁶ Wollastonite, one kind of silica-based ceramics, shows a high bioactivity in vitro with the formation of hydroxyapatite (HAP) on the surface of powder in SBF.^{17,18} Mineral Trioxide Aggregate (MTA), composed of dicalcium silicate (C₂S) and tricalcium silicate (C₃S), also has been demonstrated good cytocompatibility for

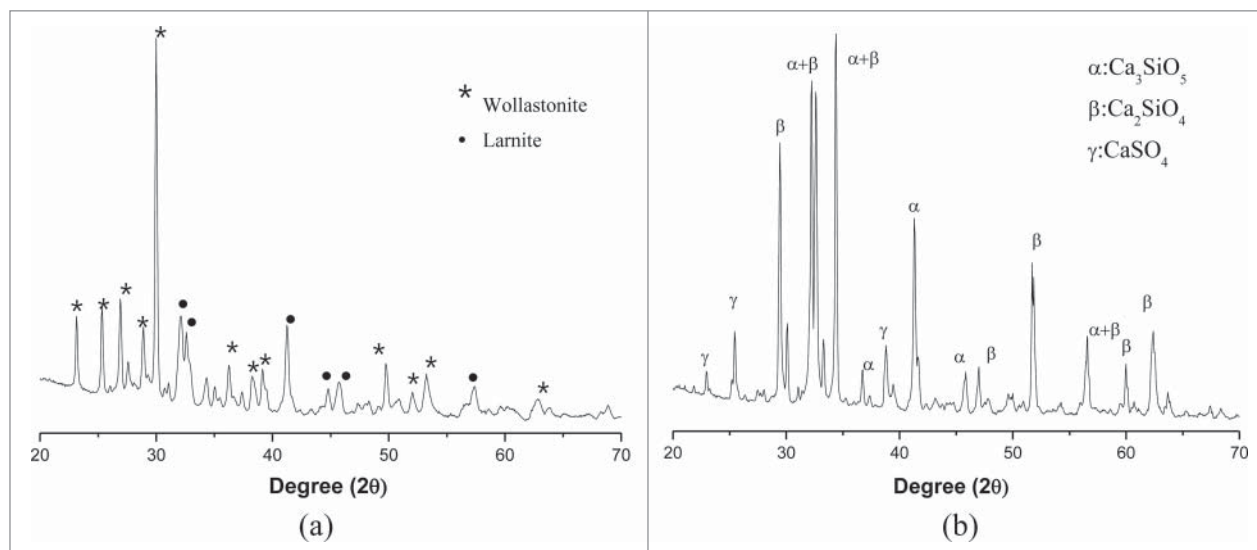


Figure 1. XRD patterns: (A) Wollastonite and (B) MTA powder.

osteoblasts and promotes the formation of crystalline precipitation in phosphate buffer.¹⁹ Via combining the 2 material classes it could be possible to use wollastonite or MTA to form a bioactive GIC. The risk of this strategy is that glass ionomer cement is based on the acid-based reaction in which polyacrylic acid attacks bioactive glass and forms 3 dimensional network. Incorporation of C₂S and C₃S which are high in alkalinity may destroy the 3 dimensional network and decrease mechanical strength.

In this study, both non self-setting (wollastonite) and self-setting (MTA) calcium silicates were chosen to enhance the bioactivity of GIC. The aim of present study is to enhance the bioactivity of GIC by incorporating wollastonite or MTA without decreasing the mechanical strength significantly. The setting time, compressive strength, pH change and in vitro bioactivity of the cements were evaluated.

Results

Characterization of wollastonite and MTA powder

The XRD analysis showed that the synthesized wollastonite powder was mainly composed of wollastonite and larnite, see Fig. 1A. The MTA powder was composed of Ca₃SiO₅, Ca₂SiO₄ and a small amount of CaSO₄, see Fig. 1A. The wollastonite particle formed agglomerates while the MTA powder was irregular sheet like, see Fig. 2.

Setting time of wollastonite and MTA modified GIC

The initial and final setting time of the GIC with and without wollastonite and MTA are given in Table 1 and Table 2. It was apparent that the addition of wollastonite only slightly prolonged the initial setting time from 240 s to 300 s. When increasing the

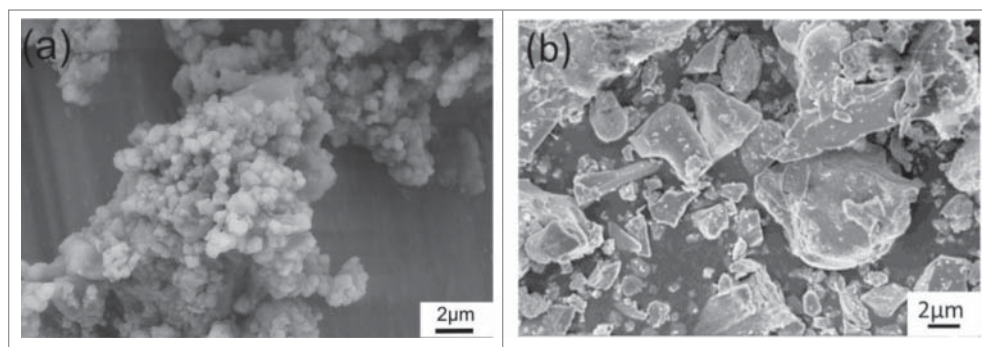


Figure 2. SEM micrographs: (A) Wollastonite and (B) MTA powder.

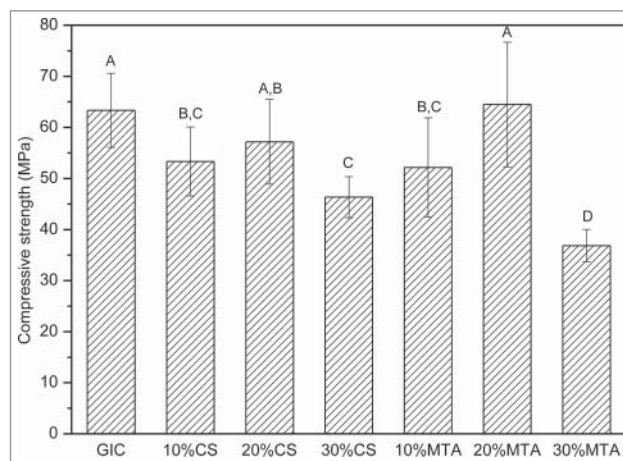
Table 1. Initial and final setting times for wollastonite modified cements.

Cement	Initial setting time (S)	Final setting time (S)
GIC	240	600
10% wollastonite	300	600
20% wollastonite	300	600
30% wollastonite	300	600

amount of wollastonite, the final setting time remained the same. Ten% MTA did not affect initial setting time of the GIC, but slightly increased the final setting time from 600 s to 660 s. Further increasing the amount of MTA, the cement hardened rapidly and it was difficult to continue to mix liquid and powder together homogeneously. In order to enhance the handling property of the GIC, more tartaric acid and water were required. When the amount of MTA was up to 30%, 30% tartaric acid solution (add the concentration of TA solution) was required and the ratio of glass: MTA: PAA was 1:0.4:0.8 in order to form cement which is easily to manipulate. In this case, the initial and final setting times were prolonged to 570 s and 900 s, respectively.

Compressive strength of wollastonite and MTA modified GIC

The addition of 10% and 30% wollastonite in the GIC resulted in slightly decreased ($p < 0.05$) compressive strength (53 (6.7) MPa and 47 (4.1) MPa, respectively, see Fig. 3). However, no significant difference ($p > 0.05$) could be observed between the compressive strength of GIC control (64(7.3) MPa) and GIC with 20% wollastonite (57(8.4) MPa). The addition of 10% MTA resulted in a decrease (18%) of compressive strength ($p < 0.05$), while no significant difference could be observed between control group (64(7.3) MPa) and 20% MTA (65(12.2) MPa).

**Figure 3.** Compressive strength of GIC with wollastonite and MTA. Test groups with the same superscript letter are not significantly different at $P < 0.05$ level (one-way ANOVA, LSD's test).

The compressive strength decreased to 37(3.2) MPa when 30% MTA was added.

pH changes in water and SBF solutions

As shown in Fig. 4A and C, the pH values of SBF solutions soaking with cements decreased during the first 3 d and then increased. For the GIC control, it was less than 7 after 7 d. The pH increased with addition of wollastonite and MTA. For 30% wollastonite modified GIC, the pH was higher than that of 10% and 20% wollastonite at all-time points. It reached to 7.3 after 7 d. GIC with 30% MTA showed a higher value (pH=7.3) after 7 d compared with 10% and 20% MTA.

The pH values after soaking cements in distilled water are shown in Fig. 4B-D. After one hour, all groups showed lower pH values after immersion in distilled water compared with the groups immersion in SBF solution. Then the pH values started to increase after 1 hour. After 7 d immersion in distilled water, the pH value of the group with pure

Table 2. Initial and final setting times for MTA modified cements.

Cement	Concentration of tartaric acid	(Glass+MTA):PAA:Tartaric acid solution (weight ratio)	Initial setting time (S)	Final setting time (S)
GIC control	10%	1:0.4:0.6	240	600
10%MTA	10%	1:0.4:0.6	240	660
20%MTA	10%	1:0.4:0.6	–	–
20%MTA	20%	1:0.4:0.6	240	690
30%MTA	20%	1:0.4:0.6	–	–
30%MTA	20%	1:0.4:0.8	–	–
30%MTA	30%	1:0.4:0.8	570	900

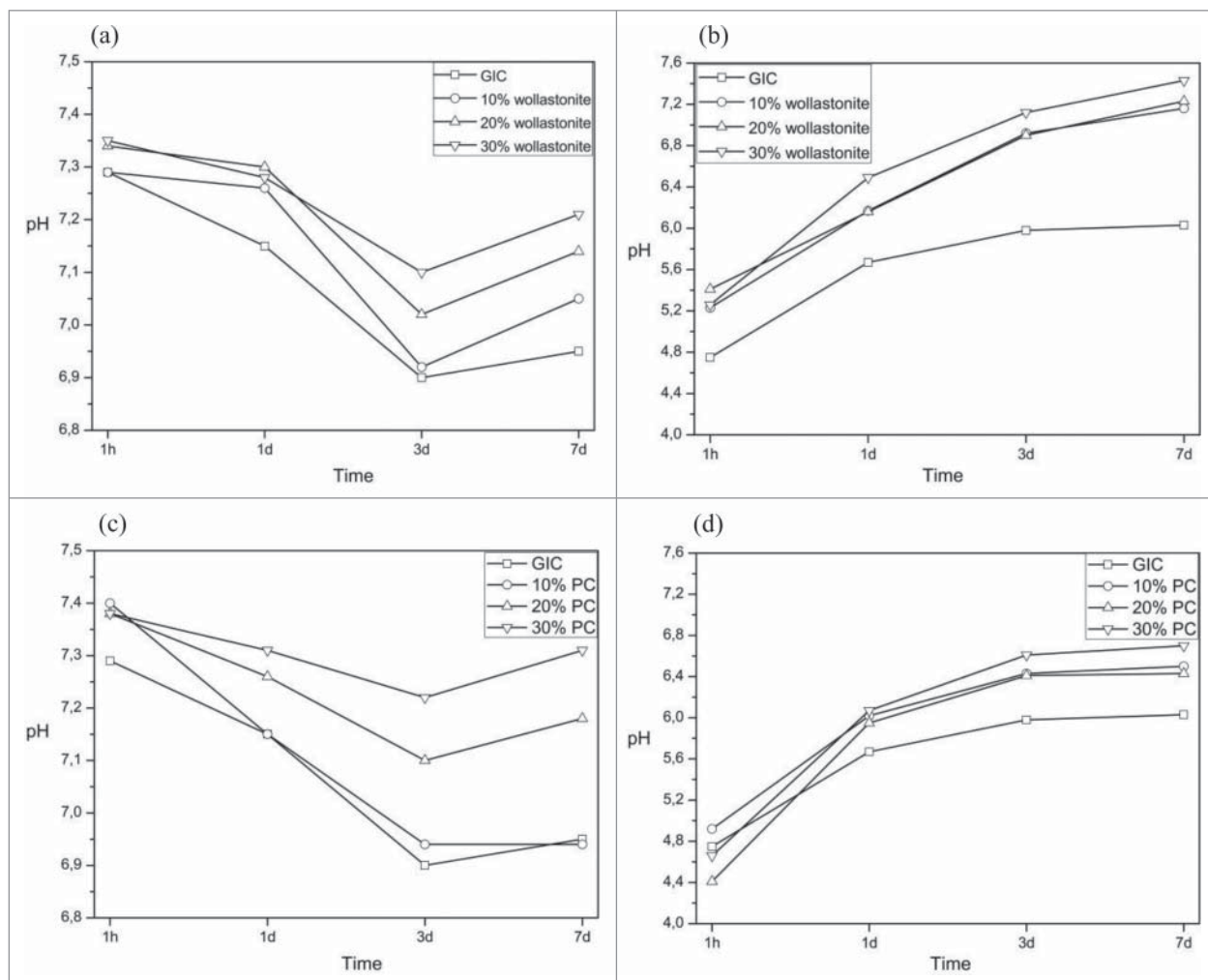


Figure 4. pH changes of solution over a period of 7days. GIC with (A) Wollastonite in SBF (B) Wollastonite in water (C) MTA in SBF (D) MTA in water.

GIC reached a stable value of approximate 6. For GIC incorporated 10%, 20% and 30% wollastonite, the pH was 7.16, 7.23 and 7.43, respectively.

In vitro bioactivity of wollastonite and MTA modified GIC

The GIC control surfaces were similar after 1 h and 7 days' soaking, see Figs. 5 and 6. For samples containing wollastonite and MTA, the surface had the same morphology as the GIC control initially. However, samples modified with wollastonite and MTA showed a new mineralized layer after 7 d EDX analyses of GIC control surface revealed the presence of Ca, Si, Sr, Al and Zn, see Fig. 7. Compared with the control, the test groups displayed a significantly higher P and Ca peak. Cl peak appeared in the modified groups, indicating

chloride ions in SBF could be adsorbed on the surfaces of the cements.

Modification of commercial GIC

Concentration of tartaric acid and powder to liquid ratio are required to adjust in order to form cements with good handling properties, see Table 3. Addition of 20% wollastonite and MTA slightly prolonged the final setting time. After one day the compressive strength of GIC with 20% wollastonite (96 MPa) was lower than GIC control (122 MPa) ($p < 0.05$), see Fig. 8. But after storage for 7 d the strength increased and no significant difference could be found between GIC control and GIC with 20% wollastonite. The compressive strength of GIC with 20% MTA continued to increase during the 14 days' storage. After 14 days, the compressive strength of GIC with 20%

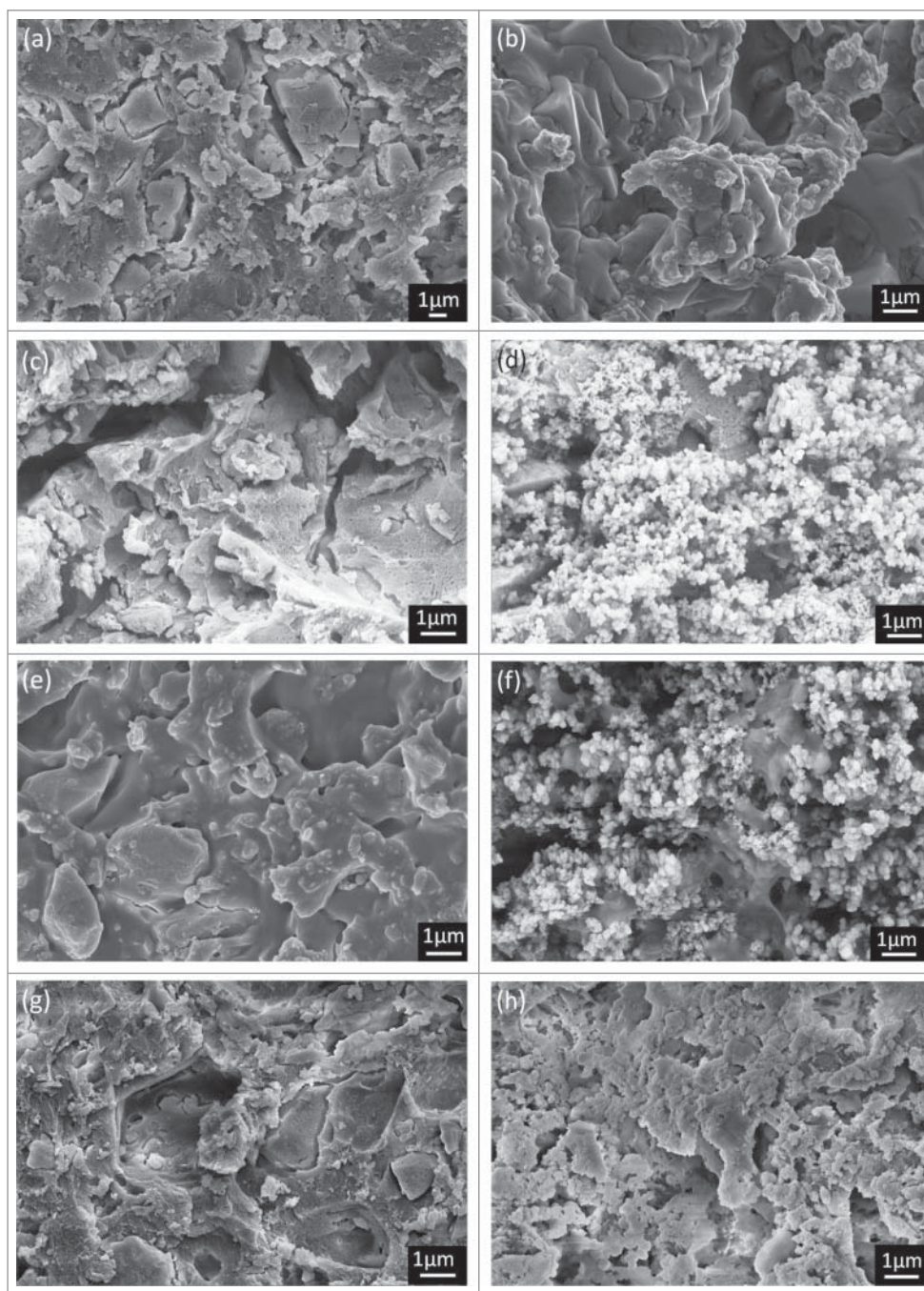


Figure 5. SEM images of the cements with wollastonite after soaking in SBF solution. (A) GIC after 1h, (B) GIC after 7 days, (C) 10% wollastonite after 1 h (D) 10% wollastonite after 7days, (E) 20% wollastonite after 1h, (F) 20% wollastonite after 7 days, (g) 30% wollastonite after 1h, (h) 30% wollastonite after 7 d.

MTA was higher than the samples storage in distilled water for one day ($p < 0.05$). XRD analysis showed that after reaction the cements were mainly amorphous with some calcium tartrate hydrate crystalline, see Fig. 9. Apatite formation can be observed on the surfaces of modified groups after 14 days, see Fig. 10. The EDX spectra showed that the amount of P, Ca and Si on the surface of wollastonite group and MTA

modified GIC were higher compared with GIC control group, while the amount of Al decreased, see Fig. 11.

Discussions

Wollastonite can be prepared by solid state reaction, co-precipitation, sol-gel method and mechanochemical routes.^{20,21} In the current study, sol-gel method

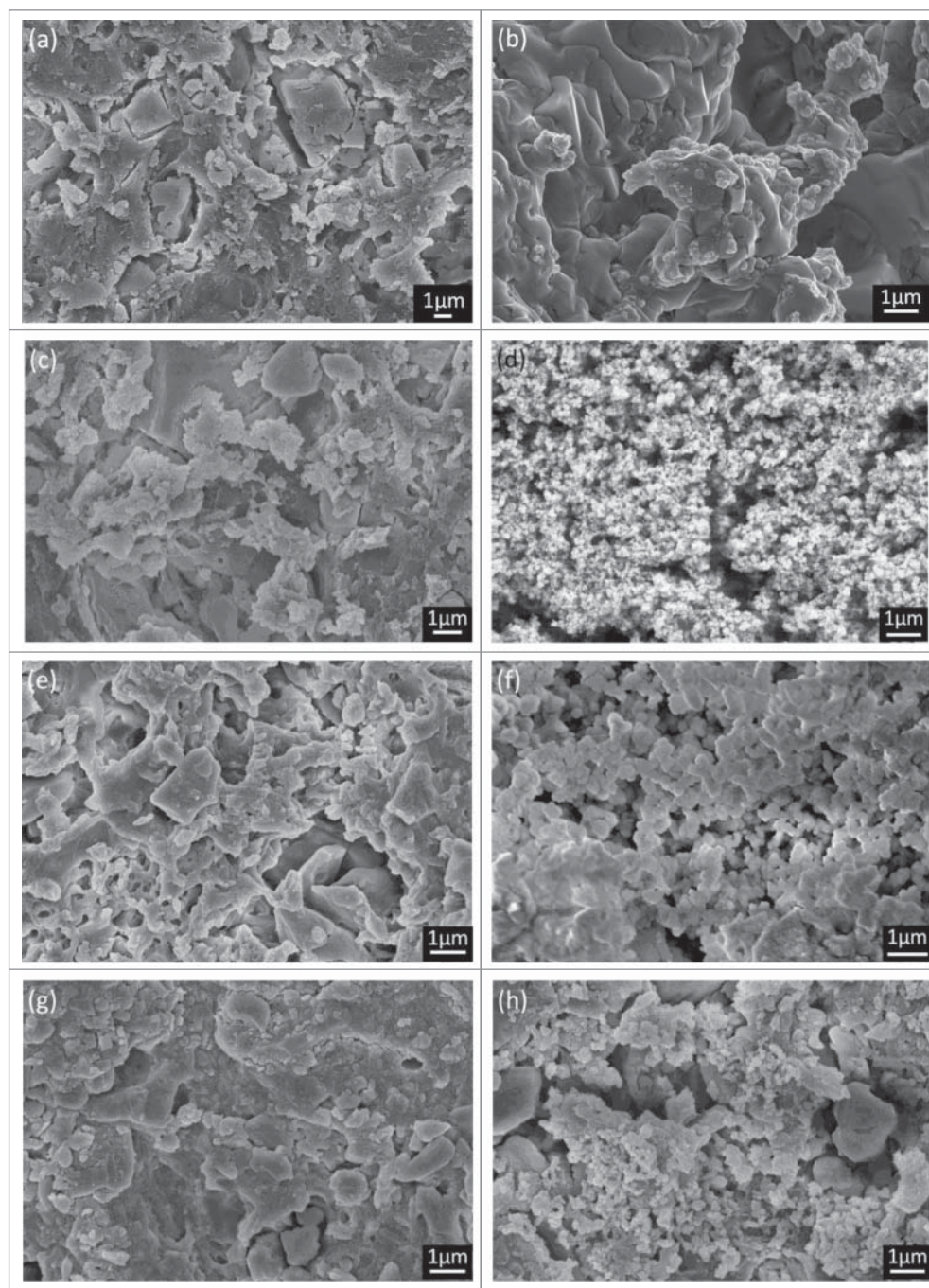


Figure 6. SEM images of the cements with MTA after soaking in SBF solution. (A) 10% MTA after 1 h (B) 10% MTA after 7days, (C) 20% MTA after 1h, (D) 20% MTA after 7 days, (E) 30% MTA after 1h, (F) 30% MTA after 7 d.

was chosen for synthesis because of the homogeneous composition and the low densification temperatures.²¹ XRD spectra in Fig. 1A showed that the powder was crystalline and composed of wollastonite (β -CaSiO₃) and larnite. Similar results have been obtained by other researchers.²² This might be due to the incomplete hydrolysis of TEOS. The un-hydrolyzed TEOS is evaporated during the drying and calcination, which

leads to the increase of Ca/Si ratio. Thereafter larnite might be formed locally. The trace phase of larnite is not a disadvantage, since larnite is also a silica-based material and exhibits good bioactivity.¹⁶

Several studies have shown that fillers in the GIC could have either adverse or beneficial effects on the mechanical performance of cements. It depends on their ability to increase the number of salt bridge and

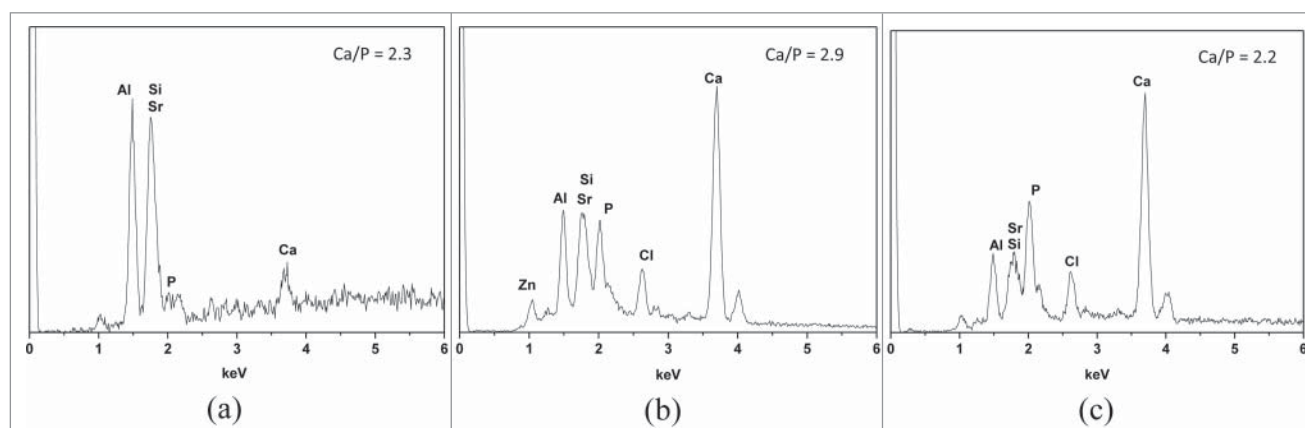


Figure 7. EDX analysis: (A) GIC (B) 20% wollastonite (C) 20% MTA. The specimen was immersed in the SBF for 7 d at 37°C.

cross linking in the hardened cement.³ The additives to increase the bioactivity and antibacterial properties often have adverse effect on mechanical strength. As mentioned above, the compressive strength of GIC decreased with the increasing amount of bioactive glasses.¹⁵ The compressive strength decreased to 36% of its original values when 30% bioactive glass was added. Takahashi et al.²³ incorporated chlorhexidine to improve antibacterial property of GIC. However, the antibacterial agent extended setting time and the compressive strength showed a decrease around 18% when 3 wt% of antibacterial agent was added in the powder. To the best of our knowledge, the effect of wollastonite on the mechanical properties of GIC hasn't been studied yet. The compressive strength decreased slightly when 10% and 30% wollastonite were added, which indicated that wollastonite cannot increase the cross linking of conventional GIC. This is likely due to that wollastonite itself is not a self-setting material. However, compared with the incorporation of bioactive glass and antibacterial agent, the decline in compressive strength was much lower, and might not affect the durability of the restoration. The glass ionomer cement modified with MTA showed increase

in setting time, but did not show decrease in strength. The setting time and compressive strength are determined not only by the amount of water added to the matrix, but also by the concentration of tartaric acid and the reaction between the additives and PAA. The decrease of strength with 10% MTA can be attributed to the high pH of MTA which reduced the release of the ions from the surface of the glass. In this case, the crosslinking of the matrix was weakened. The reaction between PAA and MTA is an acid-based reaction which leads to the inconsistency of the cement. Tartaric acid acted as an accelerator in GIC which helps extraction of ions from glass.²⁴ Meanwhile, tartaric acid acts as strong retardant for the hydration of Portland cement.²⁵ When the amount of MTA is up to 20%, tartaric acid is required to buffer the alkalinity of MTA and slowed down the hydration process to form a good paste. The initial setting time and compressive strength of 20% MTA was almost the same as for the control group. The prolonged setting time and decreased compressive strength of 30% MTA were due to the increase of water and MTA. In this case, the matrix of PAA-glass network might be destroyed by the excess of MTA.

Table 3. Initial and final setting times for wollastonite and MTA modified commercial luting cements.

Cement	Concentration of tartaric acid	P:L(weight ratio)	Initial setting time (S)	Final setting time (S)
GIC control	0%	0.5:0.25	360	540
20% wollastonite	0%	0.5:0.25	–	–
20% wollastonite	0%	0.5:0.3	–	–
20% wollastonite	10%	0.5:0.3	300	660
20% MTA	0%	0.5:0.25	–	–
20% MTA	10%	0.5:0.25	–	–
20% MTA	10%	0.5:0.3	–	–
20% MTA	20%	0.5:0.3	–	–
20% MTA	20%	0.5:0.35	300	720

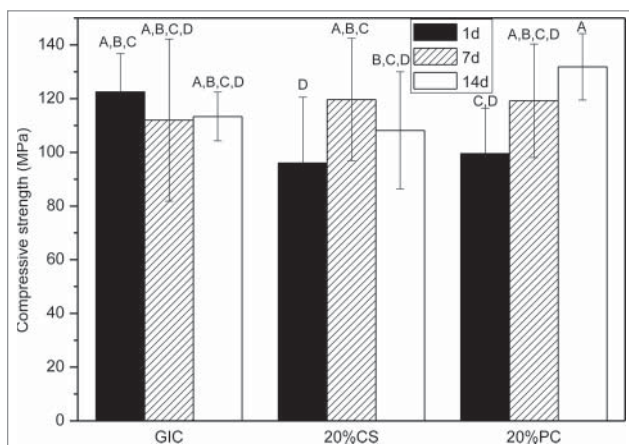


Figure 8. Compressive strength of GIC modified by wollastonite and MTA, after storage in distilled water for 1 day, 7 days and 14 d. Test groups with the same superscript letter are not significantly different at $P < 0.05$ level (one-way ANOVA, LSD's test).

Almost all the modified cements (both with wollastonite and MTA) had higher pH value compared with GIC control group (Fig. 4). This may relate to the hydration of Ca_2SiO_4 and Ca_3SiO_5 during which the calcium hydroxide was produced and resulted in higher pH in both water and SBF solution.²⁷ The increased pH value facilitates the formation of apatite thus can increase the bioactivity of the cements. The pH values were between 4 and 5.5 for control GIC immersed in water for 1 h (Fig. 4 b, d), and increased to 5.7 after 1 day, which is similar to other publications.²⁶ The decline in pH from final setting to the first hour may relate to the release of unreacted polyacrylic acid from the sample. After the rapid release of

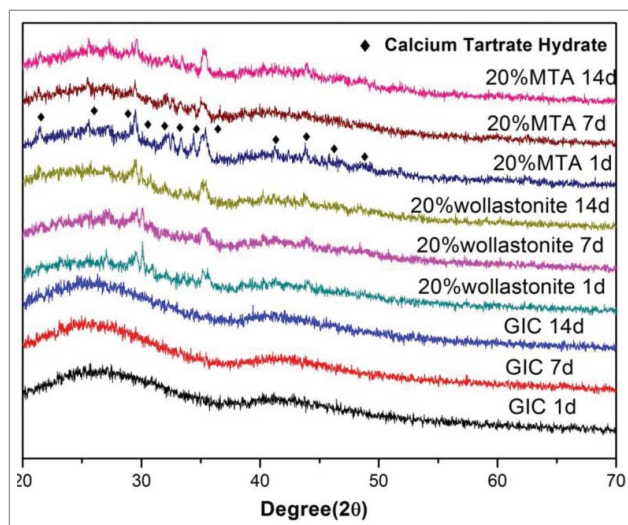


Figure 9. XRD spectra of the cements after hardening for 1 d, 7 d and 14 d in SBF.

unreacted polyacrylic acid, the unreacted glass powders start to release ions from the surface, which resulted in the rise of pH after 1 h. In SBF solution, the acidic cements could be neutralized by the buffer solution. Compared with pH changes in water, the pH decline in SBF were slower and lasted for longer time due to the buffering effect of SBF solution. Little increase in pH in SBF solution after 3 d may attribute to the release of glass powder.

The ultimate aim of incorporating wollastonite and MTA into conventional GIC was to improve bioactivity while without affecting the mechanical and handling properties of GIC. Although some researchers considered the choice of SBF solution for testing the bioactivity of material was arbitrary,²⁸ numerous studies have shown that this method was useful in predicting the in vivo bioactivity of materials.²⁹ In this study, the SEM analysis of the GIC control cement did not demonstrate any HA formation while the formation of apatite could be observed in both wollastonite and MTA added samples. This was further confirmed by EDX analysis (Fig. 7). Maria et al. studied the bioactivity of one light-curable calcium-silicate MTA cement and proved the formation of bone-like apatite just after 1 day immersion in DPBS.³⁰ The mechanism for $\beta\text{-CaSiO}_3$ and MTA promoting the bioactivity of GIC could be interpreted from the increase of pH and the bioactivity of wollastonite and MTA itself. It is believed that increase of solution pH benefits the apatite nucleation since apatite solubility decreases at basic pH and OH^- was required to form apatite.^{31,32} Due to the replacing of SBF solution every day, the pH of the solution remains stable during immersion (Fig. 4). The ion release from $\beta\text{-CaSiO}_3$ may affect the pH on the surface of the sample. This change of pH can facilitate the formation of apatite nucleation on the GIC surface and the release of Ca^{2+} provided enough ions for the apatite crystal to grow. Another reason for the promoted bioactivity may relate to the Si-OH groups from the $\beta\text{-CaSiO}_3$ and MTA which facilitate the nucleation of apatite. It has been reported that negative charge on a material's surface is essential to form bone-like apatite.³³ The negatively charged surface attracts Ca^{2+} ions from the SBF solution, forming calcium compounds like calcium silicate. The positively charged compound attracts the PO_4^{3-} in return.^{10,34} The mechanism of apatite formation on wollastonite was similar to that of CaO-SiO_2 based glass.^{35,36} Ca^{2+} ions are released from $\beta\text{-CaSiO}_3$ and MTA, thus

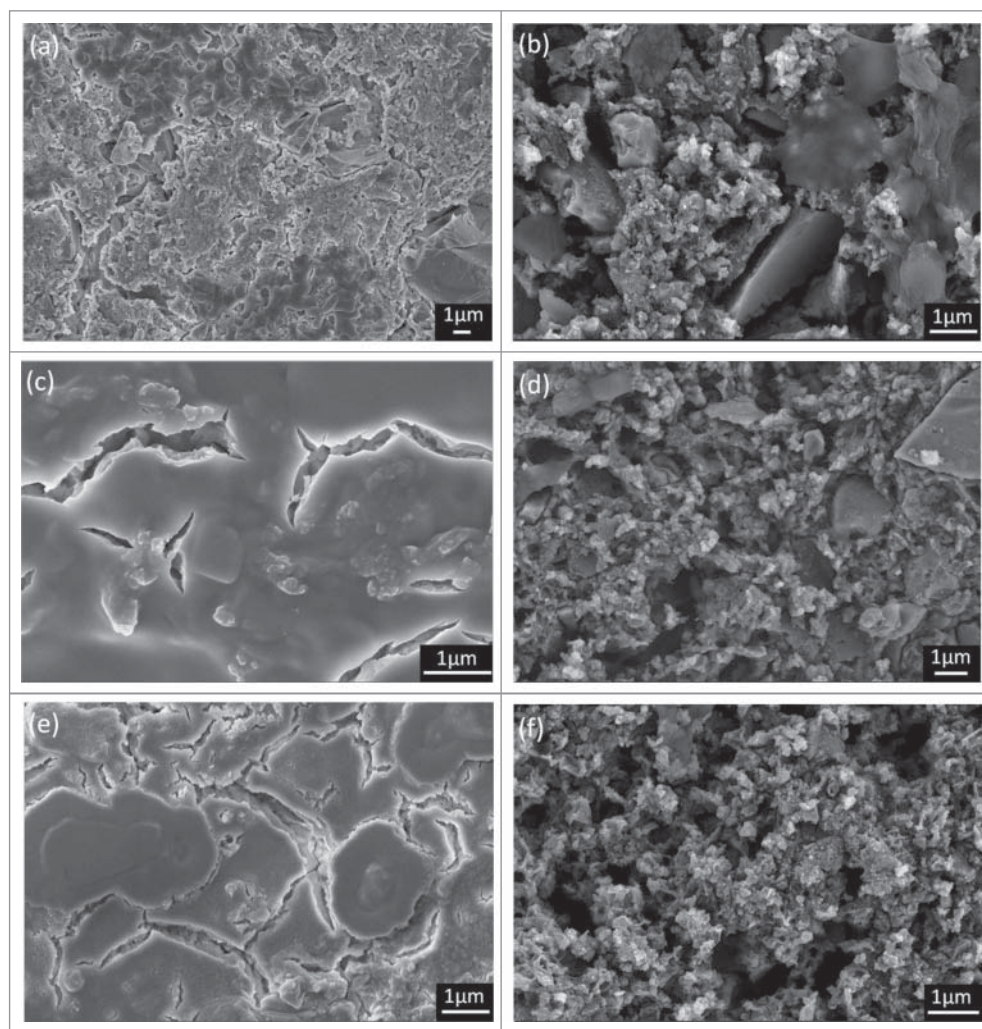


Figure 10. SEM images of the cements after soaking in SBF solution. (A) GIC after 1h, (B) GIC after 14 days, (C) 20% wollastonite after 1 h (D) 20% wollastonite after 14 days, (E) 20% MTA after 1 h, (F) 20% MTA after 14 d.

increased ion activity products in the local solution. In addition, the hydrated silica provided a site for the formation apatite nucleation. After the apatite nucleation, the apatite continues to grow in the SBF solution.

It is very interesting to notice the increase of compressive strength with 20% MTA after 14 d Based on the results, a possible mechanism was proposed to explain the reaction among GIC, MTA and tartaric acid, see Fig. 12. When GIC, tartaric acid and MTA were mixed together, first tartaric acid reacts with C_3S and C_2S to form some calcium tartrate hydrate. The calcium tartrate hydrate covers the surface and inhibits the further reaction between PAA and MTA. After immersion in the water, the unreacted C_3S and C_2S continue to hydrate which strengthens the crosslinking of the cement.

Materials and methods

Precursor powder

Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, Sigma-Aldrich, MKBK6090), tetraethoxysilane (TEOS, Sigma-Aldrich, BCBP9468V), nitric acid (HNO_3 , Sigma-Aldrich, MKBH4658V) and tartaric acid (Sigma-Aldrich, BCBL5409V) were purchased from Sigma. White Portland cement (simulating MTA) was bought from Aalborg Portland as a formulation. Polyacrylic acid (PAA) with $M_w=50000$ was provided by Advanced Healthcare Ltd and the glass was from SCHOTT (G018-090, 30% SiO_2 , 20% SrO_2 , 20% Al_2O_3 , 20% F, $P_2O_5 < 5\%$, $Na_2O < 5\%$). Commercial luting cement was bought from Advanced Healthcare Ltd, UK.

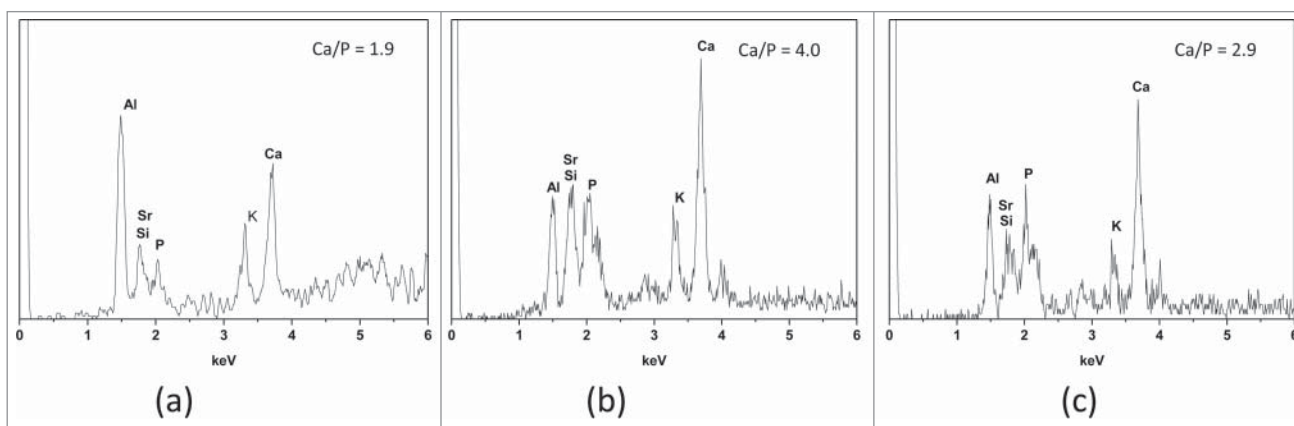


Figure 11. EDX of commercial GIC modified by wollastonite and MTA: (A) GIC (B) 20% wollastonite (C) 20% MTA. The specimen was immersed in the SBF for 14 d at 37°C.

Preparation and characterization of wollastonite and MTA powders

Wollastonite powders were prepared by sol-gel method using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, TEOS, HNO_3 , deionized water and ethanol. Initially, 21.6 ml TEOS, 13.9 ml deionized water and 2.8 ml 2 M nitric acid were mixed and stirred for 1 h at room temperature. Then 22.85 g calcium nitrate tetrahydrate and 50 ml ethanol were added and stirred for another 3 h. Then the solution was stored in oven at 60°C for 1 d for gelation. The obtained gel was further dried at 110°C for 1 d. The dried gel was calcined at 1000°C for 4 h, with the ramping rate of 5°C/min. The calcined gel was milled and sieved (200 μm). The MTA was also sieved (200 μm).

The phase characterization of the wollastonite after calcination as well as the MTA powders was

investigated by XRD (D5000, Siemens, $\text{Cu K}\alpha 1$ radiation ($\lambda=1.5418\text{\AA}$)) at 45 kV and 40 mA. The step size was 0.02, and the scan speed was 2 s per step from 20 degree to 70 degree. The morphology of the powders was studied by SEM (LEO 1550). SEM was also used to check the morphology of cement surface before and after immersion in SBF solution.

Material formulation

The cement was formulated using 2 component system (liquid and powder). The liquid was a water solution of tartaric acid (L (+)). The powder was composed of glass and polyacrylic acid (PAA). The glass and PAA were weighed accurately and mixed by a Turbula mixer (Willy A. Bachofen AG, Switzerland). For wollastonite modified GIC, the weight ratio of (glass + wollastonite): PAA: tartaric acid solution is

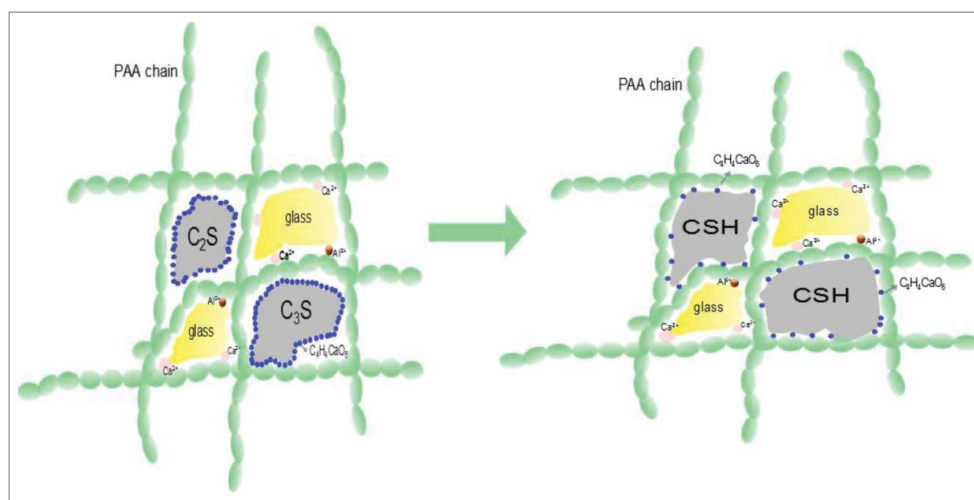


Figure 12. Possible mechanism for the reaction of glass ionomer cement, MTA and tartaric acid.

1:0.4:0.6. Four groups were formulated in this study by adjusting the ratio of wollastonite to glass (1) Control group without wollastonite, (2) Wollastonite: glass = 10%, (3) Wollastonite: glass = 20% and (4) Wollastonite: glass = 30%. For GIC modified with MTA, 4 groups were formulated by adjusting the ratio of MTA to glass: (1) Control group without MTA, (2) MTA: (glass + MTA) = 10%, (3) MTA: (glass + MTA) = 20% and (4) MTA: (glass + MTA) = 30%. The cement was prepared by mixing the powder and liquid part on a plastic pad using stainless spatula.

Modification of commercial glass ionomer cement with wollastonite and MTA

In order to investigate the performance of wollastonite and MTA with commercial GIC product, 20% of wollastonite or MTA was incorporated into commercial GIC (Batch number: 101321–4, glass ionomer luting cement, Advanced Health Care Ltd, UK) to study the potential bioactive effect on the GIC. Twenty% of the glass powder was replaced by wollastonite or MTA. Setting time, compressive strength (1 day, 7 d and 14 days) and bioactivity in SBF solution were studied. The methods were the same as the above.

Setting time

Initial and final setting times were determined by the Gillmore needles.³⁷ A light needle with 113.4 g in weight and 2.12 mm in tip diameter was used to determine initial setting time. A heavy needle with 453.6 g in weight and 1.06 mm in tip diameter was used to determine final setting time. The needle was placed on the surface every 30 s. Initial and final setting times were defined from the start of mixing until the light and heavy needles did not mark on the surface respectively. Two samples were measured for each formulation.

Compressive strength

The cylindrical specimens for compressive strength measurement were 4mm in diameter and 6mm in height. Two samples were made each batch and totally 6 specimens were made for each formulation. The specimens were stored in water at 37°C in an oven for 1 day. The diameters of the specimens were measured using a micrometer screw gauge before mechanical testing. The compressive strength was measured using

a universal testing machine (Autograph AGS-X, Shimadzu) with a crosshead speed of 1 mm/min.

Measurement of pH change in water and in SBF solution

SBF solution was prepared according to the literature. In the tests the samples with diameter of 8mm and thickness of 1mm were immersed in 5 ml of SBF and water, respectively, for 7 d PH is vital in the formation of HA thus the pH changes of water and SBF were measured using a pH meter. The original SBF (pH=7.4) was served as control. Two samples were measured for each formulation.

Surface bioactivity

After final setting, cement samples were polished with 1000 grit silicon carbide paper, washed by deionized water, and stored in SBF solution. The volume of SBF (V_s) was calculated through the equation: $V_s = S_a / 10$. S_a was the apparent surface area of the specimen. The SBF was replaced every day. After 7 days, the samples were removed from the fluid and washed with deionized water. The specimens were dried at 60°C in an oven before SEM analyses. GIC samples without any wollastonite or MTA were used as controls for each group. The morphology of the surface was studied by SEM (LEO 1550). EDX analysis was used to further characterize the surface composition of hardened cements.

Statistical analysis

Statistical analysis was performed using a one-way analysis of variance (ANOVA) followed by LSD post hoc test at $P < 0.05$ level.

Conclusions

In this study, the bioactivity of 2 types of conventional GIC was enhanced by adding the wollastonite and MTA into the glass powder. The pH values started to increase after one hour in distilled water. The pH values for all cements decreased during the first 3 d and then increased in SBF. The final setting time of modified GIC was slightly prolonged. The compressive strength of modified GIC was related to the amount of wollastonite and MTA. When 20% of wollastonite or MTA (or below) was incorporated into the GIC, the compressive strength could be remained the same as

GIC control. In addition, for 20% MTA modified GIC, the compressive strength increased gradually during the 14 days' storage in the distilled water, and was higher than that of the GIC control after 14 days' storage. Therefore, the incorporation of bioactive ceramics can improve GIC's bioactivity and did not decrease the compressive strength. If the ceramic is a self-setting material, such as MTA, the self-setting could enhance the long-term compressive strength.

Abbreviations

GIC	glass ionomer cement
MTA	mineral trioxide aggregate
CS	Wollastonite
SBF	Simulated body fluid
PAA	Polyacrylic acid
EDX	Energy-dispersive X-ray spectroscopy
SEM	scanning electron microscope
XRD	X-ray diffraction

Disclosure of potential conflicts of interest

No potential conflicts of interest were disclosed.

Funding

We gratefully acknowledge support from VR (Swedish Research Council (2011–3399)) and China Scholarship Council (CSC) for the PhD study.

References

- Croll TP, Nicholson JW. Glass ionomer cements in pediatric dentistry: review of the literature. *Pediatric Dentistry* 2002; 24:423-9; PMID:12412956
- Smith DC. Development of glass-ionomer cement systems. *Biomaterials* 1998; 19:467-78; PMID:9645552; [http://dx.doi.org/10.1016/S0142-9612\(97\)00126-9](http://dx.doi.org/10.1016/S0142-9612(97)00126-9)
- Kenneth JCS, Ralph H. Rawls. *Philips' science of dental materials*. 12th ed, 2013
- Moshaverinia A, Roohpour N, Chee WWL, Schricker SR. A review of powder modifications in conventional glass-ionomer dental cements. *J Materials Chem* 2011; 21:1319; <http://dx.doi.org/10.1039/C0JM02309D>
- Moshaverinia A, Roohpour N, Chee WWL, Schricker SR. A review of polyelectrolyte modifications in conventional glass-ionomer dental cements. *J Materials Chem* 2012; 22:2824; <http://dx.doi.org/10.1039/c2jm14880c>
- Moshaverinia A, Roohpour N, Rehman IU. Synthesis and characterization of a novel fast-set proline-derivative-containing glass ionomer cement with enhanced mechanical properties. *Acta Biomaterialia* 2009; 5:498-507; PMID:18640084; <http://dx.doi.org/10.1016/j.actbio.2008.06.011>
- Masanobu Kamitakahara MK, Tadashi K, Takashi N. Effect of polyacrylic acid on the apatite formation of a bioactive ceramic in a simulated body fluid: fundamental examination of the possibility of obtaining bioactive glass-ionomer cements for orthopaedic use. *Biomaterials* 2001; 22:3191-6; PMID:11603591; [http://dx.doi.org/10.1016/S0142-9612\(01\)00071-0](http://dx.doi.org/10.1016/S0142-9612(01)00071-0)
- Yoshida Y, Van Meerbeek B, Nakayama Y, Snauwaert J, Hellemans L, Lambrechts P, Vanherle G, Wakasa K. Evidence of Chemical Bonding at Biomaterial-Hard Tissue Interfaces. *J Dental Res* 2000; 79:709-14; PMID:10728971; <http://dx.doi.org/10.1177/00220345000790020301>
- Kokub T. Bioactive glass ceramics properties and applications. *Biomaterials* 1990; 12:155-63; [http://dx.doi.org/10.1016/0142-9612\(91\)90194-F](http://dx.doi.org/10.1016/0142-9612(91)90194-F)
- Loof J, Svahn F, Jarmar T, Engqvist H, Pameijer CH. A comparative study of the bioactivity of three materials for dental applications. *Dent Mater* 2008; 24:653-9; PMID:17727942; <http://dx.doi.org/10.1016/j.dental.2007.06.028>
- Hench LL. The story of Bioglass. *J Materials Sci Materials Med* 2006; 17:967-78; PMID:17122907; <http://dx.doi.org/10.1007/s10856-006-0432-z>
- Jones JR. Review of bioactive glass: from Hench to hybrids. *Acta Biomaterialia* 2013; 9:4457-86; <http://dx.doi.org/10.1016/j.actbio.2012.08.023>
- Yli-Urpo H, Narhi M, Narhi T. Compound changes and tooth mineralization effects of glass ionomer cements containing bioactive glass (S53P4), an in vivo study. *Biomaterials* 2005; 26:5934-41; PMID:15958240; <http://dx.doi.org/10.1016/j.biomaterials.2005.03.008>
- Yli-Urpo H, Vallittu PK, Narhi TO, Forsback AP, Vaki-partta M. Release of silica, calcium, phosphorus, and fluoride from glass ionomer cement containing bioactive glass. *J Biomater App* 2004; 19:5-20; PMID:15245640; <http://dx.doi.org/10.1177/0085328204044538>
- Yli-Urpo H, Lassila LV, Narhi T, Vallittu PK. Compressive strength and surface characterization of glass ionomer cements modified by particles of bioactive glass. *Dent Mater* 2005; 21:201-9; PMID:15705426; <http://dx.doi.org/10.1016/j.dental.2004.03.006>
- Wu C, Chang J. A review of bioactive silicate ceramics. *Biomed Materials* 2013; 8:032001; PMID:23567351; <http://dx.doi.org/10.1088/1748-6041/8/3/032001>
- PN De Aza, Guitian F, S De Aza. Bioactivity of wollastonite ceramics in vitro evaluation. *Scripta Metallurgica Et Materialia* 1994; 31:1001-5; [http://dx.doi.org/10.1016/0956-716X\(94\)90517-7](http://dx.doi.org/10.1016/0956-716X(94)90517-7)
- Wan X, Chang C, Mao D, Jiang L, Li M. Preparation and in vitro bioactivities of calcium silicate nanophase materials. *Materials Sci Engineering: C* 2005; 25:455-61; <http://dx.doi.org/10.1016/j.msec.2004.12.003>
- Darvell BW, Wu RC. "MTA"-an Hydraulic Silicate Cement: review update and setting reaction. *Dent Mater* 2011; 27:407-22; PMID:21353694; <http://dx.doi.org/10.1016/j.dental.2011.02.001>
- Singh SP. Mechanochemical Synthesis of Nano Calcium Silicate Particles at Room Temperature. *N J Glass*

- Ceramics 2011; 01:49-52; <http://dx.doi.org/10.4236/njgc.2011.12008>
21. Tangboriboon N, Khongnakhon T, Kittikul S, Kunanuruk-sapong R, Sirivat A. An innovative CaSiO₃ dielectric material from eggshells by sol-gel process. *J Sol-Gel Sci Tech* 2010; 58:33-41; <http://dx.doi.org/10.1007/s10971-010-2351-1>
 22. Wang H, Zhang Q, Yang H, Sun H. Synthesis and microwave dielectric properties of CaSiO₃ nanopowder by the sol-gel process. *Ceramics Int* 2008; 34:1405-8; <http://dx.doi.org/10.1016/j.ceramint.2007.05.001>
 23. Takahashi Y, Imazato S, Kaneshiro AV, Ebisu S, Frencken JE, Tay FR. Antibacterial effects and physical properties of glass-ionomer cements containing chlorhexidine for the ART approach. *Dent Mater* 2006;22:647-52; PMID:16226806; <http://dx.doi.org/10.1016/j.dental.2005.08.003>
 24. Hill RG, Wilson AD. A rheological study of the role of additives on the setting of glass ionomer cements. *J Dent Res* 1988; 67:1446-50
 25. Sarita Rail NBS, NP Singh. Tartaric acid with portland cement. *Indian J Chem Tech* 2006; 13:255-61
 26. Roberts HW, Toth JM, Berzins DW, Charlton DG. Mineral trioxide aggregate material use in endodontic treatment: a review of the literature. *Dent Mater* 2008; 24:149-64; PMID:17586038; <http://dx.doi.org/10.1016/j.dental.2007.04.007>
 27. Camilleri J, Montesin FE, Juszczak AS, Papaioannou S, Curtis RV, Donald FM, Ford TR. The constitution, physical properties and biocompatibility of modified accelerated cement. *Dent Mater* 2008; 24:341-50; PMID:17659330; <http://dx.doi.org/10.1016/j.dental.2007.06.004>
 28. Bohner M, Lemaitre J. Can bioactivity be tested in vitro with SBF solution? *Biomaterials* 2009; 30:2175-9; PMID:19176246; <http://dx.doi.org/10.1016/j.biomaterials.2009.01.008>
 29. Kokubo T, Takadama H. How useful is SBF in predicting in vivo bone bioactivity? *Biomaterials* 2006; 27:2907-15; PMID:16448693; <http://dx.doi.org/10.1016/j.biomaterials.2006.01.017>
 30. Gandolfi MG, Taddei P, Siboni F, Modena E, Ciapetti G, Prati C. Development of the foremost light-curable calcium-silicate MTA cement as root-end in oral surgery. Chemical-physical properties, bioactivity and biological behavior. *Dent Mater* 2011; 27:e134-57; PMID:21529922; <http://dx.doi.org/10.1016/j.dental.2011.03.011>
 31. Pan H, Zhao X, Darvell BW, Lu WW. Apatite-formation ability-predictor of "bioactivity"? *Acta Biomaterialia* 2010; 6:4181-8; PMID:20493974
 32. Gandolfi MG, Taddei P, Siboni F, Modena E, Ciapetti G, Prati C. Development of the foremost light-curable calcium-silicate MTA cement as root-end in oral surgery. Chemical-physical properties, bioactivity and biological behavior. *Dent Mater* 2011; 27:e134-57; PMID:21529922; <http://dx.doi.org/10.1016/j.dental.2011.03.011>
 33. Kim HM, Himeno T, Kokubo T, Nakamura T. Process and kinetics of bonelike apatite formation on sintered hydroxyapatite in a simulated body fluid. *Biomaterials* 2005; 26:4366-73; PMID:15701365; <http://dx.doi.org/10.1016/j.biomaterials.2004.11.022>
 34. Hiroaki Takadama HMK, Tadashi K, Nakamura T. Mechanism of Biomineralization of Apatite on a Sodium Silicate Glass: TEM-EDX Study In Vitro. *ChemMater* 2001; 13:1103-8.
 35. Liu X, Ding C, Wang Z. Apatite formed on the surface of plasma-sprayed wollastonite coating. *Biomaterials* 2001; 22:2007-12; PMID:11426878; [http://dx.doi.org/10.1016/S0142-9612\(00\)00386-0](http://dx.doi.org/10.1016/S0142-9612(00)00386-0)
 36. Liu X, Ding C, Chu PK. Mechanism of apatite formation on wollastonite coatings in simulated body fluids. *Biomaterials* 2004; 25:1755-61; PMID:14738838; <http://dx.doi.org/10.1016/j.biomaterials.2003.08.024>
 37. American Society for Testing and Materials. ASTM C266-03: Standard test method for time and setting of hydraulic-cement paste by Gilmore needles. Philadelphia: ASTM; 2000.