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Original article

Setting Characteristics of Hydroxyapatite-Containing Glass Ionomer Cements by Oscillating Rheometer: Phosphate-based Compositions

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Abstract
The purpose of this study was to assess the setting characteristics (working/setting times) of phosphate glass ionomer cement that were reinforced with different concentrations of hydroxyapatite crystals. A series of four ionomer glasses based on increasing in the phosphate content with general formula of $4.5SiO_2\text{-}3Al_2O_3\text{-}xP_2O_5\text{-}3CaO\text{-}2CaF_2$ *(Where* x = *0.75, 1, 1.25 & 1.5) were synthesised using melt-quench route. Thereafter, the glass ionomer cements were prepared by mixing fine glass powder with poly-acrylic acid at specific powder to liquid ratio. The modified samples (hydroxyapatite-containing GICs) were made by adding hydroxyapatite powder to ionomer glass powder on weight substitution basis instead of certain amount of ionomer glass at a specific percentage of 0%, 5%, 10% and 15% respectively. The ionomer cements mixtures were investigated using Wilson's Oscillating Rheometer in order to measure the setting characteristics (working/setting times) of the tested materials. Increasing in both phosphate content and substituted amount of hydroxyapatite for glass powder prolonged working/setting times of the glass ionomer cements significantly. The compositions with higher concentrations (15%) of hydroxyapatite showed adversely effect on handling properties and setting rates of the tested cements. The results suggest that addition of hydroxyapatite crystals has a significant impact on manipulation and setting reaction of the manufactured cements. The tested compositions with low-phosphate (highly reactive) and low-hydroxyapatite contents are more suitable for clinical use. Therefore, the additives concentrations' have to be optimised to produce restorative materials with ideal properties.*

Keywords: *Glass Ionomer Cements, Working Time, Setting Time, Phosphate, Hydroxyapatite.*

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Introduction

Glass Ionomer Cement (GIC) is one of the most widely researched dental restorative materials, since was discovered in 1960s by Wilson and Kent at Laboratory of the London Government Chemist [1]. The GIC invention has been resulted from an experimental study on dental silicate cements, in which the phosphoric acid was replaced with an organic acid of poly-acrylic acid (PAA) that used to produce zinc poly-carboxylate cements. [2-3]. Consequently, the GICs were made as a hybrid of silicate cement powder and zinc poly-carboxylate cement liquid. According to Wilson (1978) research, it found that these hybrid materials with ions release characteristics have a unique ability to form strong chemical bond with tooth surfaces [4].

Chemically, the setting reaction of GICs is based on an acid-base reaction. This reaction occurs when the acid-degradable glasses (calcium fluoro-aluminosilicate glasses) and the aqueous solution of PAA mixed together to form the set cement [5]. Nicholson reported that all techniques used for studying GICs setting reaction have emphasised that the reaction of these water-based cements involves neutralisation of acid by basic glass with formation of metal poly-acrylates (calcium acrylates and aluminium acrylates) [6]. Practically, the changing in the cement's fluidity (viscosity) should be measured through two steps of "dough-forming" stage and "stiffening" stage respectively [7]. Hence, the material should remain in a soft, pliable state to facilitate its placement and contouring easily inside the tooth cavity during the working time; shortly thereafter; it should become rigid within its setting time [8].

Moreover, it is supposed that the first step in the setting reaction of GICs involved the acid hydrolysis of Si-O-Al bonds of the glass network of aluminosilicate glasses, causing the release of (Ca^{2+} & Al^{3+}) cations, associated with formation of a layer of silica gel around the unreacted glass particles [9]. Additionally, increasing in the phosphate content of the original ionomer glasses causes decreasing the susceptibility of Si-O-Al linkages formation, and this will increase Al-O-P linkages as well. It stated that the high solubility of phosphate in water is due to the geometry of PO_4, where the oxygen atom is double bonded with the central phosphorus atom [10]. Accordingly, Al-O-P linkages have lower ability to be hydrolysed during the acid-base reaction of GICs [11].

Hydroxyapatite (HA) is a calcium phosphate bio-ceramic with Ca:P ratio of 1.67, which is similar to an inorganic phase of bones and teeth (formula = $Ca_{10}(PO_4)_6OH_2$). It is widely incorporated into GICs as an additive to improve the cement's properties, which can be beneficial for restorative applications, particularly at high-stress bearing areas [12]. Therefore, this study investigated the setting characteristics (working/setting times) of GICs that were reinforced with different concentrations of HA crystals via assessing the viscosity changes of the cement mixtures during the initial stages of the acid-base reaction using Wilson's Oscillating Rheometer.

Materials & Methods

Preparing of Ionomer Glasses/Cements

A series of ionomer glasses were designed based on LG26 formula, following molar ratios of $4.5SiO_2$-$3Al_2O_3$-xP_2O_5-$3CaO$-$2CaF_2$ (Where x = 0.75, 1, 1.25 & 1.5). The glasses were synthesised in the same manner of melt-quench route that used previously [13].

The mixture of cements were prepared by mixing the glass powders with high molecular weight (80 kDa) freeze-dried PAA (S & C Polymer GmbH, Elmshorn, Germany) and distilled water, with powder/liquid ratios of 5/1 as explained previously [14]. The modified samples (HA-containing GICs) were prepared by adding the dried HA powder to the ionomer glass powder on substitutional basis at a specific percentage of 0%, 5%, 10% and 15% respectively.

Measuring of Working & Setting Times by Wilson's Oscillating Rheometer

The setting characteristics (working/setting times) of GICs with and without incorporation of HA were measured using Wilson's Oscillating Rheometer (Dental Physical Science Unit-QMUL), that was connected with a chart recorder (Linseis GmbH, L200E, Germany) in order to draw the rheometer traces, as displayed in **Figure 1** [9]. The rheometer consists of two plates, approximately 2 mm apart, one of which is fixed while the other oscillates under the action of a driven spring. The fixed plate is connected to a water bath thus enabling measurements at 37°C. The oscillations are noted as a voltage induced by a rod moving in and out of the transducer and plotted to produce a rheogram [15-16].

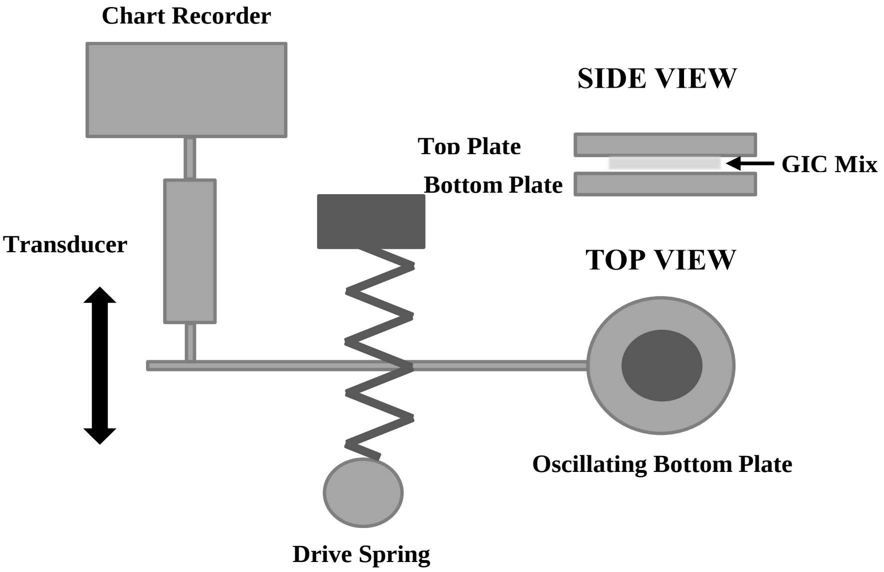

Figure 1: Schematic diagram of an oscillating rheometer. Adopted from [9].

The recorder was switched on from start of mixing, and then a zero-time mark was drawn on the recording paper. After about 40-60 sec the cement paste was transferred to the apparatus at 37°C to mimic the mouth temperature. The mix was placed on the oscillating plate that attached with a coil spring, and then pressed using other oscillated plate [9]. The typical rheometer trace initially showed higher amplitude and then gradually decreased as the mixture sets and thus the shape of traces varies due to the fact that the setting rates within the materials were not identical. The setting time was determined when the amplitude of the trace decreased and became constant.

From the obtained trace, both working/setting times were calculated, as shown in **Figure 2**. The Working time is "the time when the width of the trace is 95% of the original width" (is time of mixing and manipulation of the material before reaching the rigidity state). While, the Setting time is measured when "the width of the trace is 5% of the total width" (is time from starting of mixing until the material becomes completely set) [3-17].

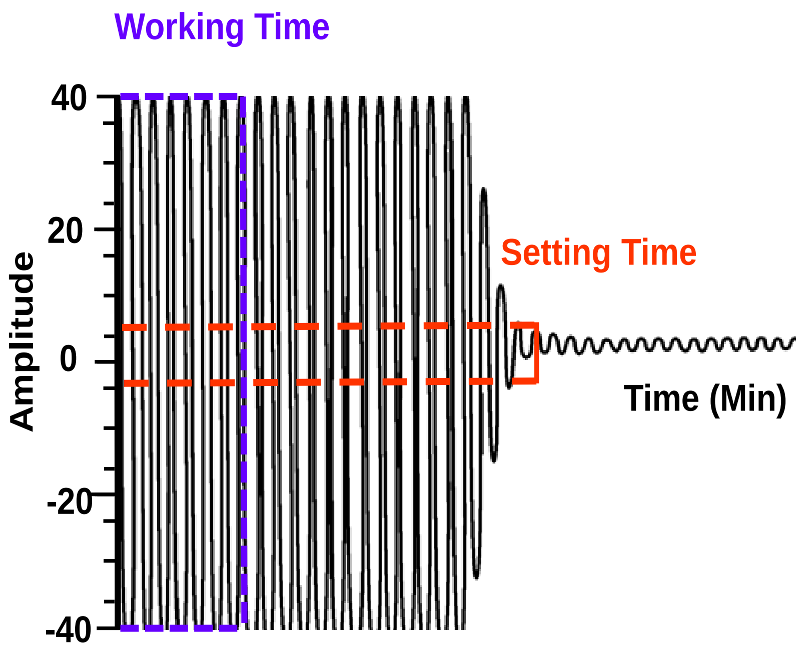

Figure 2: Oscillating rheometer trace, corresponding to working time (95%) and setting time (5%) of oscillation amplitude.

Results

The bar chart in **Figure 3** shows that working/setting times increased with increasing in P_2O_5 proportion in the precursor ionomer glasses. The mixtures of low-phosphate content (highly reactive glasses) yielded workable and more acceptable cements compared to other compositions with high-phosphate contents. The 1.5 P_2O_5 (LG26) cements were set within about 21.9 min, nearly four times more than the 0.75 P_2O_5-based cements that were set faster within 5.3 min.

The bar chart in **Figure 4 & 5** demonstrates that incorporation of apatite crystals of HA caused an additional increase in both working/setting times. Further, Addition of 5% HA did not display a huge difference in the values of working/setting times compared to HA-containing GICs with higher proportions of additives.

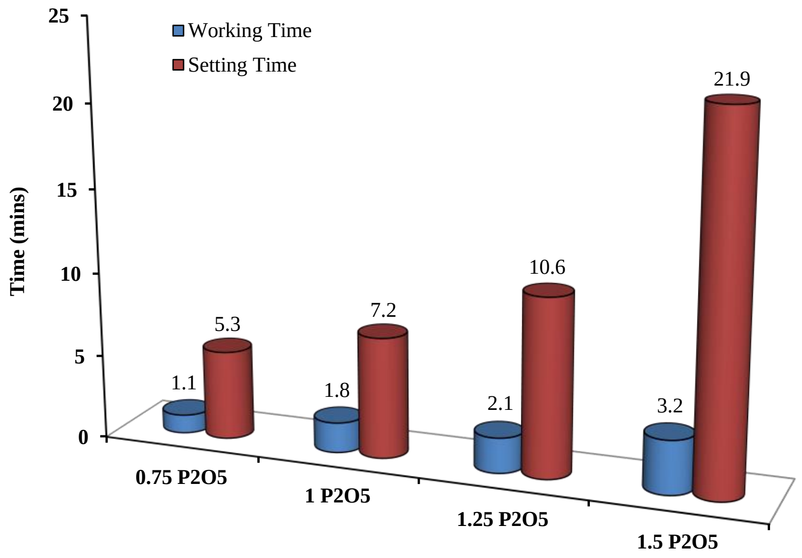

Figure 3: Working & setting times of ionomer cements without addition of hydroxyapatite.

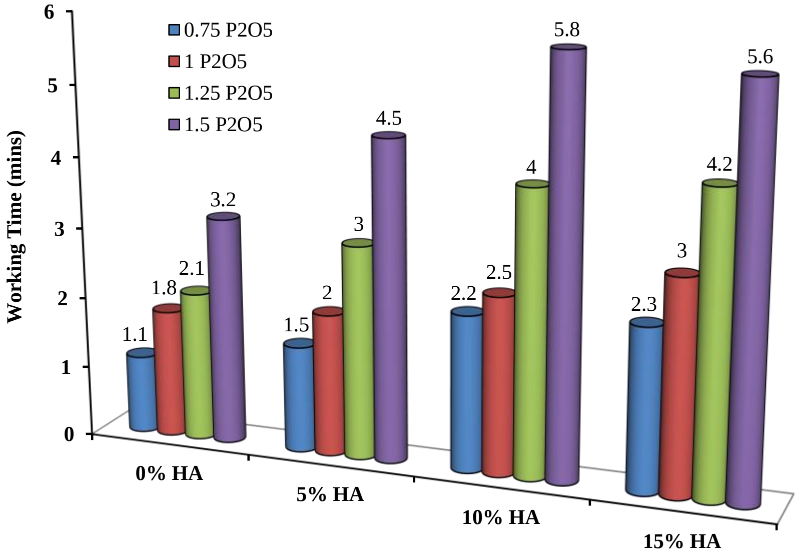

Figure 4: Working time of ionomer cements with/without addition different proportions of hydroxyapatite.

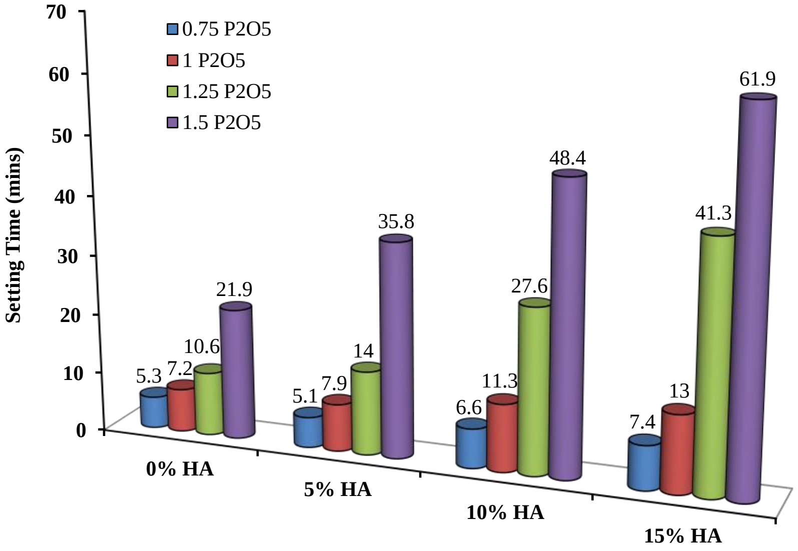

Figure 5: Setting time of ionomer cements with/without addition different proportions of hydroxyapatite.

Discussion

The International Organisation for Standardisation (ISO) determines the minimum values for the glass ionomers (water-based cements) to be allowed onto the market, and also to be well-preformed clinically. The recommended "net" setting time values for luting and restorative cements are proved to be 1.5-8 and 1.5-6 min respectively [18]. The rationale behind the setting behaviour of ionomer cements has been studied extensively using different techniques such as; FTIR, Raman and more recently MAS-NMR spectroscopies, however, the setting mechanism of these materials has not been fully understood yet [19-21]. It is believed that the first step in the setting reaction of GICs involved the acid hydrolysis of Si-O-Al bonds of the glass network, which causing the release of (Ca^{2+} & Al^{3+}) cations [6-22]. On the other hand, the ratio of Al:Si in the glass has a critical role and should not exceed 1:1 to be able to form the glass with four coordinated Al [23]. The high-phosphate containing glasses may also reduce the influence of the Al:Si ratio through phosphorus locally charge balancing four coordinated Al in the original network of silicate glasses [15].

The present results showed that the working/setting times increased with increasing in P_2O_5 amount for the original compositions of ionomer glasses. This is indicated that the phosphate content in the glass has a significant impact on the cement properties. Griffin and Hill (2000) summarised that addition of small quantity of phosphate extended both working/setting times of GICs, due to forming Al-O-P linkages [10]. However, addition of high fraction of phosphate resulted in reduction the compressive strength and Young's modulus of the material. This is because phosphate disrupts the cross-linking process and competes with the carboxylate groups for cross-linking metal cations of (Ca^{2+} & Al^{3+}) [10].

Our finding seems to indicate the strategic importance of LG26 (high-phosphate content = 1.5 P_2O_5) composition associated with the switch in the trend of Al conversion. Additionally, this composition also showed the highest working/setting times in P_2O_5 series. The presence of slowly hydrolysing Al-O-P linkages perhaps can be used to explain the observed trends in working/setting times, though fails to interpret the higher conversion rate that was seen for the compositions with increasing the amount of Al-O-P linkages. If anything it would be expected that the increase in Al-O-P linkages to reduce the amount of the available Al^{3+} cations and thereby this will decrease the reactivity of material and the conversion rate of Al.

On the other hand, increasing in the substituted amount of HA for original glass powder showed a marked slower on the setting mechanism. This is due replacing small amount from the glass powder by powder of apatite crystals and thus leads to lessening the Al^{3+} cations content. The Ca^{2+} ions in apatite crystals are freely available for crosslinking of PAA chains unlike the Ca^{2+} ions in CaF_2, which causes a delay in the first stages of the setting reaction. This also indicates that there are two mechanisms competing to each other within the GIC matrix; they are acid-base reaction process and remineralising process.

The particle size distribution for ionomer glass powder was below 45µm, which is ideal for restorative dental cements [6-16]. Although, any slight variation in the particle size has a distinct impact on the properties of GICs such as; compressive strength and working/setting times. The smaller the particle size is, the larger surface area that would be readily degrading to form silica gel phase and the cations (Ca^{2+} & Al^{3+}) would be leaching more rapidly, resulting in faster cross-linking of GICs [24]. Typically, the changes during mixing are observed as a result of powder cluster phenomena (agglomeration) and deviations from spherical shape of particles.

Well known that incorporation of HA exhibited great improvements in the physical and mechanical properties of GICs, which making it one of the most suitable additives to be approved [12]. This can be also beneficial for the restorative applications, particularly at high-stress bearing areas when the force of mastication has to be withstood. Further studies should be done to optimise the suitable proportion of phosphate and HA to be incorporated into GICs, in order to synthesise an ideal dental material with fully requirements.

Conclusion

Based on the obtained data in this preliminary study, about measuring the setting properties of the experimental GICs, it can conclude that increasing in both P_2O_5 content and substituted amount of HA for glass powder prolonged working/setting times of tested GICs significantly. This study suggests that well-balanced setting characteristics of suitable working/setting times were obtained with the low-phosphate containing GICs (highly reactive formulations). The optimisation of ionomer glass compositions, P/L ratios, concentrations of (phosphate & HA), handling properties and setting behaviours' should be intensely investigated and taken into consideration before launching the newly-formed restorative materials for dental use.

Conflict of Interest

There are no financial, personal, or professional conflicts of interest to declare.

References

1. Smith D. Development of glass-ionomer cement systems. Biomater. 1998;19(6):467-478.
2. Wilson A, Kent B. A new translucent cement for dentistry. The glass ionomer cement. Br Dent J. 1972;132(4):133-135.
3. Wilson A, McLean J. Glass-ionomer cement. 1988:Quintessence Pub. Co.:13-18.
4. Wilson A. The chemistry of dental cements. Chem Soc Rev. 1978:7(2):265-296.
5. Crisp S, Wilson A. Formation of a glass-ionomer cement based on an lon-leachable glass and polyacrylic acid. J Appl Chem Biotechnol. 1973;23(11):811-815.
6. Nicholson J. Chemistry of glass-ionomer cements: a review. Biomater. 1998;19(6):485-494.
7. Ogawa T, et al. Setting characteristics of five autopolymerizing resins measured by an oscillating rheometer. J Prosthet Dent. 2001;85(2):170-176.
8. Anusavice KJ. Phillips' science of dental materials. 2003; Elsevier Health Sciences.
9. Griffin S, Hill R. Influence of glass composition on the properties of glass polyalkenoate cements. Part I: influence of aluminium to silicon ratio. Biomater. 1999;20(17):1579-1586.
10. Griffin S, Hill R. Influence of glass composition on the properties of glass polyalkenoate cements. Part II: influence of phosphate content. Biomater. 2000;21(4):399-403.
11. Ray N. Inorganic polymers. 1978; Academic Press.
12. Murugan R, et al. Effects of nanohydroxyapatite incorporation into glass ionomer cement (GIC). Miner. 2021;12(1):1-10.
13. Hill R, et al. The influence of strontium substitution in fluorapatite glasses and glass-ceramics. J Non-Cryst solids. 2004;336(3):223-229.

14. Albeshti R. A Preliminary Study on pH Changes of Storage Solution and Weight Changes of Ionomer Cements: Influence of Phosphate Content. Libyan J Med Res. 2020;14(2):1-13.
15. Osiro O, et al. Evaluation of dental cements derived from mixtures of highly reactive ionomer glasses and bottle glass: Cement manipulation, mechanical, fluoride ion releasing, radiopaque and setting properties. Dent Mater. 2024;40(11):1981-1990.
16. Osiro O, Hill R, Bushby J. Substitution of strontium for calcium in glass ionomer cements (part 2): effects on the cement mechanical and ion releasing properties. East Afr Med J. 2015;92(10):481-487.
17. Bovis S, Harrington E, Wilson H. Setting characteristics of composite filling materials. Br Dent J. 1971;131(8):352-356.
18. Sidhu S, Nicholson J. A review of glass-ionomer cements for clinical dentistry. J Funct Biomater. 2016;7(3):16.
19. Hill R, Stamboulis A, Law R. Characterisation of fluorine containing glasses by 19 F, 27Al, 29Si and 31P MAS-NMR spectroscopy. J Dent. 2006;34(8):525-532.
20. Young A, et al. Use of Raman spectroscopy in the characterisation of the acid–base reaction in glass-ionomer cements. Biomater. 2000;21(19):1971-1979.
21. Crisp S, et al. Reactions in glass ionomer cements: II. An infrared spectroscopic study. J Dent Res. 1974;53(6):1414-1419.
22. Wilson A, Crisp S. Ionomer cements. Br Polymer J. 1975;7(5):279-296.
23. Kent B, Lewis B, Wilson A. Glass ionomer cement formulations: I. The preparation of novel fluoroaluminosilicate glasses high in fluorine. J Dent Res. 1979;58(6):1607-1619.
24. Kaplan A, et al. Effects of variation in particle size on biaxial flexural strength of two conventional glass-ionomer cements. J Oral Rehabil. 2004;31(4):373-378.

الملخص

كان الغرض من هذه الدراسة هو تقييم خصائص التصلب (أوقات العمل/التصلب) لأسمنت زجاج الفوسفات الأيونومر المقوى بتركيزات مختلفة من بلورات هيدروكسي. أباتيت. تم تصنيع سلسلة من أربعة زجاج أيونومر بناءً على زيادة محتوى الفوسفات بالصيغة العامة $SiO_2-3Al_2O_3-xP_2O_5-4.5$ ($3CaO-2CaF_2$حيث$x = 0.75$ ، 1، 1.25 و1.5 (باستخدام طريقة الإخماد بالذوبان. بعد ذلك، تم تحضير أسمنت زجاج الأيونومر بخلط مسحوق الزجاج الناعم مع حمض بولي أكريليك بنسبة مسحوق إلى سائل محددة. تم صنع العينات المعدلة GICs) المحتوية على هيدروكسي. أباتيت (بإضافة مسحوق هيدروكسي. أباتيت إلى مسحوق زجاج الأيونومر على أساس استبدال الوزن بدلاً من كمية معينة من زجاج الأيونومر بنسبة مئوية محددة من 0٪ و 5٪ و 10٪ و 15٪ على التوالي. تم فحص مخاليط أسمنت الأيونومر باستخدام مقياس ويلسون المتذبذب لقياس خصائص التصلب (أوقات العمل/التصلب) للمواد المختبرة. أدت زيادة كل من محتوى الفوسفات وكمية الهيدروكسي- أباتيت المستبدلة بمسحوق الزجاج إلى إطالة أوقات العمل/التصلب لأسمنت الأيونومر الزجاجي بشكل ملحوظ. أظهرت التركيبات ذات التركيزات الأعلى (15٪) من هيدروكسي- أباتيت تأثيرًا سلبيًا على خصائص المناولة ومعدلات التصلب للأسمنت المختبر. تشير النتائج إلى أن إضافة بلورات هيدروكسي- أباتيت لها تأثير كبير على معالجة وتفاعل التصلب للأسمنت المصنع. التركيبات المختبرة ذات المحتوى المنخفض من الفوسفات (عالي التفاعل) والمنخفض من هيدروكسي- أباتيت هي أكثر ملاءمة للاستخدام السريري. لذلك، يجب تحسين تركيزات المواد المضافة لإنتاج مواد ترميمية ذات خصائص مثالية.