



PHYSICO-CHEMICAL PROPERTIES OF SILICATE BASED BIOMATERIALS

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ABSTRACT

Aim: The purpose of this study was to compare solubility, pH, calcium ion release and setting time of Biodentine, Bioaggregate, and Bioactive glass.

Materials and Methods: For the weight loss, pH changes and calcium ions release, the tested specimens were immersed in distilled water. The evaluations were performed at 1h, 24h and 7 d. The measurement of pH was done using digital pH meter. The measurement for Ca²⁺ ions release was done using atomic absorption spectrophotometry. The setting time was measured by using a Vicat apparatus. Data were analyzed by One Way ANOVA test and the Tukey post-hoc test at P ≤ 0.05.

Results: Biodentine showed the greatest solubility, ultimate increase in pH, and highest calcium ion release at all time intervals and the shortest setting time. Bioactive glass showed alkalinity and moderate Ca²⁺ release after 1 h that were decreased by time. It also showed negative solubility.

Conclusions: Biodentine and Bioaggregate favored proper physico-chemical properties except for solubility it was questionable. Bioactive glass is the best regarding solubility.

KEYWORDS: Bioactive glass, Bioaggregate, Biodentine, Physico-Chemical properties.

Key messages: (1) All materials tested recorded a favorable high pH and Ca²⁺ release. (2) Although Biodentine and Bioaggregate showed high solubility, Bioactive glass showed a negative one. (3) Biodentine has the shortest setting time.

INTRODUCTION

Clearly, the quest for “interactive” or “bioactive” dental restorative materials is not a totally new endeavor^[1]. Bioactivity points to the cement’s ability to produce an apatite-like layer on its surface when it comes in contact with body fluids *in vivo*^[2] or with

simulated tissue fluids *in vitro*^[3]. These materials include, but may not be limited to crystalline calcium phosphate materials including various apatites and hydroapatites, various glasses under the generic terms “bioactive glasses” or “bioglasses,” various glass ceramics such as, calcium silicate-based cements, and calcium aluminate-based cements^[1].

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A new bioactive cement, Biodentine, was recently launched on the dental market by dental materials manufacturer Septodont^[4]. Biodentine contains tricalcium silicate, calcium carbonate, zirconium oxide, dicalcium silicate, calcium oxide and a water based-liquid containing a hydrosoluble polymer and calcium chloride (decreases the setting time)^[5]. Its endodontic indications are similar to those of MTA including; pulp capping and pulpotomy, root perforations, apexification, resorptive lesions, and retrograde filling material in endodontic surgery, with added advantages of being fast-setting and easier to manipulate^[1]

Bioaggregate is a new bioceramic root repair and root-end filling material, developed by Innovative BioCeramix Inc. (IBC), composed of a powder component consisting of tricalcium silicate, dicalcium silicate, tantalum peroxide, calcium phosphate monobasic and amorphous silicon dioxide and a liquid component of deionized water. It utilizes the advanced science of nano-technology to produce hydrophilic ceramic particles that, upon reaction with water produce biocompatible and aluminum-free ceramic biomaterials. BioAggregate powder promotes cementogenesis and forms a hermetic seal inside the root canal. It is also effective in clinically blocking the bacterial infection. It is indicated in repair of root perforation, repair of root resorption, root end filling, apexification and in pulp capping^[6].

Bioactive glass (BG), calcium sodium phosphosilicate, is currently regarded as the most biocompatible material in the bone regeneration field due to its high biocompatibility and remarkable bioactive capability in forming apatite-like structure^[7]. Moreover, the advances in sol-gel technique enable the production of BG with nanometric particle size, which exhibits improved bioactivity accelerating the crystallization of the HA layer as well as the cell differentiation process^[8]. Although BG has not been extensively applied in clinical endodontics, recent studies have shown some potential for its use in endodontic treatments^[9].

The process of tissue repair is directly related to the alkaline potential of the used material and their capacity to release ions into the periapical tissue^[10]. Also, for root repair material, a lack of solubility and short setting time are desired characteristics to facilitate a tight seal between them and the root canal system and the periodontium^[11].

Therefore, it was essential to evaluate the physico-chemical properties (setting time, solubility, pH, and calcium ion release) of dental biomaterials to be considered suitable for endodontic use.

MATERIALS AND METHODS

Materials tested in this study were: Biodentine (Septodont St. Maur-des-Fossés, France, LOT 48059), Bioaggregate (Innovative Bioceramix, IBC, Vancouver, Canada), and Bioactive glass (laboratory made, Faculty of Science, Suez Canal University)

Solubility test

The solubility tests recorded weight loss of the test materials after immersion in distilled water, and followed to a great extent the methodology of the International Standard ISO 6876:2001^[12].

For all sample preparation stainless steel ring moulds having a height of 1.5 mm and an internal diameter of 20.0 mm were used. All moulds were cleaned in an ultrasound bath with acetone for 15 min. Thereafter a copper wire was fixed at each mould in order to hang the specimens in a glass dish in such a way that the surfaces did not touch and the materials remained undisturbed in the dish. Prior to use all moulds were weighed three times and the mean was calculated. All tested materials were mixed according to the manufacturer's instructions. The ring moulds were placed on a glass plate and filled to slight excess with the mixed material avoiding air entrapment. All samples were left to set on a grating for 24 h at 37°C and 95% relative humidity. Excess material was then trimmed to level of the surface of the mould.

From each material, 21 samples were prepared for immersion in distilled water for 1 h, 24 h, and 7 days. Materials in their ring moulds were weighed three times prior to the immersion and the average reading was recorded. All weight measurements were in grams and recorded to four decimal places. Each sample in its ring mould was immersed in a fresh 160 mL aliquot of liquid at 37°C ($\pm 1^\circ\text{C}$) a time for the designed time intervals. The specimens were placed in an airtight dish with 95% - 100% relative humidity such that both surfaces of each sample were freely accessible to the liquid. After the specified immersion period, samples were removed from the dish using a pair of tweezers, touching only the metal mould, washed with 3 mL of double-distilled water and allowed to dry at 37°C for 24 h. Samples were placed on a grating in such way that only the metal moulds touched the grating. Thereafter, they were weighed three times and the mass of the cements was determined to the nearest 0.0001 g. The solubility of the cement was expressed as a percentage of the weight loss compared to the original weight^[13].

pH

The pH of the water in which the samples were immersed in the solubility test was measured at 1 h, 24 h, and 7 days. The measurements were taken using a pH meter (JENWAY, 3505 PH Meter, England) precalibrated against standard solutions of known pH (7.0) and a constant temperature (25°C)^[14].

Calcium ion release analysis

The Ca ion release of the test material was determined using the method recommended by the ISO 9917-1^[15]. A total of 7 discs (8mm in diameter and 1.5 height) were used for each material. Each disc was sealed in a flask containing 10 mL of distilled water, and the amount of calcium ion released was determined at 1 h, 24 h, and 7 days. After each measurement, the discs were moved to new flasks

with fresh distilled water. The measurements were performed with the aid of an atomic absorption spectrophotometer (Model GBCCorp, Melbourne, Australia) equipped with a hollow cathode calcium lamp^[16].

Setting time

The setting time of the test materials was measured using a Vicat apparatus (Humboldt Mfg. Co., Schiller Park, IL, USA) and the method recommended by the ISO 9917-1^[15]. The test materials were mixed according to the manufacturer's instructions and placed in 7 cylindrical stainless steel molds (10 mm in diameter and 5 mm in height). Subsequently, a Vicat indenter of 400 ± 5 g with a flat ended needle of 1.0 ± 0.1 mm in diameter was lowered vertically onto the surface of the test material which initially marked the surface with an indentation. This process was repeated until the mark was no longer visible, and the cement setting time was considered from the start of mixing until this moment^[14, 17, 18].

Statistical analysis

Data presented as mean and standard deviation (SD). pH, Ca ion release and weight changes showed a parametric distribution, so One Way ANOVA test was used to compare between different tested materials and follow up periods, followed by Tukey's post-hoc test for pairwise comparison when ANOVA is significant. The significance level was set at $P \leq 0.05$. Statistical analysis was performed with IBM® SPSS® (SPSS Inc., IBM Corporation, NY, USA) Statistics Version 23 for Windows.

RESULTS

Solubility

The higher solubility was recorded for Biodentine followed by Bioaggregate. They were significantly different at all time intervals except at one hour. The solubility of both materials was significantly increased by time. On the other hand, Bioglass

rather than being soluble, it gained weight which also increased by time (table 1).

pH and Ca Ion release

Biodentine recorded the significantly highest mean values of pH and Ca²⁺ release through all time intervals, followed by Bioaggregate then Bioglass. Regarding the time effect, pH and Ca²⁺ release of Biodentine and Bioaggregate were significantly increased by time to reach the highest value at 7 days. Meanwhile, it decreased by time with Bioactive glass (table 1).

Setting time

Biodentine achieved the significantly most fast setting time, followed by Bioglass and then Bioaggregate which achieved the longest setting time (table 1).

DISCUSSION

Biodentine is a tricalcium silicate-based cement that shares both its indications and mode of action with calcium hydroxide, but does not have its drawbacks [19]. This material has been recently developed to overcome some of shortcomings of white mineral trioxide aggregate, which are difficult handling, long setting time, and potential discoloration. It is a new biologically active cement which has dentine-like mechanical properties. It also can be used as a dentine replacement in the tooth crown and root region.

BioAggregate is another tricalcium silicate-based cement that has been successfully developed as a new generation of dental root end filling material [6]. Bioactive glass is a novel material that dissolves and forms a bond with bone when exposed to body fluids. Bioactive glasses are silicate-based,

TABLE (1) Mean and standard deviation (SD) of solubility %, pH, Ca²⁺ release, and setting time of the tested bioactive materials.

Biomaterials								
Test	Time interval Mean	Bioaggregate		Bioglass		Biodentine		p-value
		SD	Mean	SD	Mean	SD		
Solubility	1 Hr	1.27 ^{aC}	0.084	-5.65 ^{bA}	0.11	1.72 ^{aC}	0.05	0.001*
	24 Hrs	8.0 ^{bB}	0.245	-13.34 ^{cB}	0.09	13.34 ^{aB}	0.30	0.001*
	7 Days	23.46 ^{bA}	0.358	-34.2 ^{cB}	0.45	26.97 ^{aA}	0.34	0.001*
<i>p-value</i>		0.001*		0.001*		0.001*		
pH	1 Hr	11.60 ^a	0.30	10.22 ^{bA}	0.06	11.66 ^{aC}	0.20	0.001*
	24 Hrs	11.83 ^a	0.17	9.52 ^{bB}	0.16	12.04 ^{aB}	0.14	0.001*
	7 Days	12.03 ^a	0.15	8.61 ^{bB}	0.44	12.45 ^{aA}	0.12	0.001*
<i>p-value</i>		0.152 NS		0.001*		0.001*		
Ca Ion release	1 Hr	1.43 ^{bC}	0.12	1.31 ^{bA}	0.12	3.76 ^{aC}	0.04	0.001*
	24 Hrs	2.11 ^{bB}	0.13	0.85 ^{cB}	0.18	4.98 ^{aB}	0.04	0.001*
	7 Days	3.09 ^{bA}	0.08	0.81 ^{cB}	0.25	8.19 ^{aA}	0.08	0.001*
<i>p-value</i>		0.001*		0.002*		0.001*		
Setting time		111.60 ^a	0.55	45.30 ^b	1.52	34.00 ^c	0.71	0.001*

Means with the same uppercase letter within each column are not significantly different at $p \leq 0.05$.

Means with the same lowercase letter within each row are not significantly different at $p \leq 0.05$

*= Significant

with calcium and phosphate in identical proportions to those of natural bone; therefore, they have high biocompatibility^[7].

Because those materials can be used as root end filling materials and thereby getting in direct contact with periapical tissues, they should provide a long-term seal and avoid leakage from the oral cavity and/or the periapical tissue. Consequently, a low solubility in distilled water as proposed in the standards of the International Standard Organisation (ISO) 6876:2001^[12] is required. In addition, a short setting time is helpful to facilitate a tight seal and maintain consistency of the mixture^[11]. Biomaterials induce an alkaline environment which not only neutralizes lactic acid from the osteoclast, thus preventing dissolution of the mineral component of dentine, but could also activate alkaline phosphatase enzyme which is thought to play an important role in hard tissue formation^[20]. The ability to release calcium is a key factor for successful endodontic and pulp capping therapies because of the action of calcium on mineralizing cells differentiation and hard tissue mineralization^[21].

Therefore, the current study assessed the solubility, pH changes, release of Ca ions, and setting time when standard discs of Bioaggregate, Biodentine and Bioactive glass were immersed in distilled water for different time intervals (1 hr, 24 hrs and 7 days).

Solubility

In the present study, all tested materials showed some degree of solubility except bioactive glass which gained weight rather than lose weight, and this gaining weight was increased by time. This could be due to precipitation of calcium carbonate on its surface. When bioactive glass are brought into contact with body fluids a rapid leach of Na⁺ and congruent dissolution of Ca²⁺, PO₄³⁻ and Si⁴⁺ takes place at the glass surface. A polycondensated silica-rich (Sigel) layer is formed on the glass bulk,

which then serves as a template for the formation of a calcium phosphate (Ca/P) layer at its outer surface. Eventually, the Ca/P crystallizes into hydroxyapatite^[22].

On the other hand, both Biodentine and Bioaggregate showed high values of solubility % which also increased by time. However it was higher for Biodentine. This solubility exceeded the limit of ADA tolerance (3%)^[12], except at 1 h interval where BD and BA recorded 1.72 and 1.27% respectively. This was in accordance with other studies where they found unacceptable solubility % of Biodentine^[23, 24]. This finding was not in accordance with **Grech et al.**^[25] who demonstrated negative solubility values for a prototype cement, Bioaggregate, and Biodentine. They attributed this result to the deposition of substances such as hydroxyapatite on the material surface when in contact with synthetic tissue fluids. However cements such like biodentine and Bioaggregate forming calcium hydroxide or calcium oxide during setting should present a certain degree of solubility to improve the mineralization process in contact with vital tissue^[26].

pH and Ca²⁺ release

In the present study, Biodentine showed the highest pH and Ca²⁺ release mean values compared to the other tested materials followed by Bioaggregate and then Bioactive glass. The high alkalinity and Ca²⁺ release of Biodentine and Bioaggregate that were increased by time, might be inferred to the hydration reaction of the calcium silicate particles that triggers the dissolution of their surface with the formation of a calcium silicate hydrate gel and Ca(OH)₂^[27]. In the presence of moisture, calcium hydroxide dissociates to hydroxyl ions, and calcium ions responsible for the increased alkalinity and antibacterial activity, and calcium ions that promote material bioactivity and apatite layer formation^[27-29].

Furthermore, the higher solubility of Biodentine could explain the prolonged alkaline pH and the greater Ca^{2+} release. It was demonstrated that the more the material is soluble, the higher OH^- and Ca^{2+} release [24]. Several studies have compared the calcium release of Biodentine with other bioceramic materials [27, 29, 30], in agreement with this study Biodentine showed a higher level of calcium ion release than BioAggregate [27, 29].

Bioactive glass showed the lowest pH and Ca^{2+} release mean values during all intervals which significantly decreased by time. This might be because Bioactive glass is silicate based material, containing calcium and phosphate [31]. When activated with water it is capable of generating a carbonated hydroxyapatite layer equivalent chemically and structurally to the mineral of bone [32], and an amorphous silicon oxide which reduced the levels of calcium hydroxide produced on hydration [27]. Also, it showed the mineral enrichment efficacy [33]. This was in consonance with Carvalho et al [34] who reported that bioactive glasses presented an alkaline pH immediately in the first 10 min, and over the course of 7 days tended to neutralize. Also, in the first 10 min, Bioglass released more calcium, but from 24 h on, this release was decreased and ceased on the 14th day. bioactive glasses released more sodium and phosphate ions.

Setting time

In the current study, the setting time of Biodentine was significantly shorter than that of the other materials. The shorter setting time of BD is due to calcium carbonate and calcium chloride [25]. Calcium carbonate is a filler component that is often used as a hydration accelerator. It acts as a nucleation site for C-S-H, thereby reducing the duration of the induction period, leading to a faster setting time. Calcium chloride has also been shown to result in accelerated setting time [27, 35]. Bioaggregate showed the highest setting time value, although it is a tricalcium silicate based material as biodentine, but

the amount of tricalcium silicate in Bioaggregate is less than Biodentine leading to a slower reaction rate and more porous microstructure [5].

CONCLUSION

Under the circumstances of this study, it can be concluded that the biomaterials tested can be considered appropriate for endodontic use performing in different ways. For the pH and Ca^{2+} release, Biodentine and Bioaggregate were the best, while for solubility Bioactive glass was the best.

The authors deny any conflicts of interest related to this study.

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I affirm that I have no financial affiliation or involvement with any commercial organization with direct financial interest in the subject or materials discussed in this manuscript, nor have any such arrangements existed in the past three years. Any other potential conflict of interest is disclosed.

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