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Investigation of the physical properties of tricalcium silicate cement-based root-end filling materials

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ABSTRACT

Objective. Tricalcium silicate-based cements have been displayed as suitable root-end filling materials. The physical properties of prototype radiopacified tricalcium silicate cement, Bioaggregate and Biodentine were investigated. Intermediate restorative material was used as a control.

Methods. The physical properties of a prototype zirconium oxide replaced tricalcium silicate cement and two proprietary cements composed of tricalcium silicate namely Bioaggregate and Biodentine were investigated. Intermediate restorative material (IRM) was used as a control. Radiopacity assessment was undertaken and expressed in thickness of aluminum. In addition the anti-washout resistance was investigated using a novel basket-drop method and the fluid uptake, sorption and solubility were investigated using a gravimetric method. The setting time was assessed using an indentation technique and compressive strength and micro-hardness of the test materials were investigated. All the testing was performed with the test materials immersed in Hank's balanced salt solution.

Results. All the materials tested had a radiopacity value higher than 3 mm thickness of aluminum. IRM exhibited the highest radiopacity. Biodentine demonstrated a high washout, low fluid uptake and sorption values, low setting time and superior mechanical properties. The fluid uptake and setting time was the highest for Bioaggregate.

Significance. The addition of admixtures to tricalcium silicate-based cements affects the physical properties of the materials.

1. Introduction

A variety of materials used routinely in dentistry as restorative materials have been utilized as root-end filling materials. Such materials include dental amalgam and intermediate restorative material (IRM). Mineral trioxide aggregate (MTA) has been developed specifically as a root-end filling material and for the repair of furcal perforations [1]. It has been reported that the success rate for the clinical use of MTA and IRM is similar when assessed after 12 and 24 months [2]. More recently materials based on tricalcium silicate cement have been introduced as root-end filling materials. Tricalcium silicate is the main component of MTA [3] and it has demonstrated similar chemical characteristics [4]. The use of tricalcium silicate avoids the presence of trace elements which are inadvertently incorporated in mineral trioxide aggregate from the raw materials and the secondary fuels used during manufacture [5]. Heavy elements have been shown to be present in high amounts MTA and Portland cements [6,7]. The leaching in solution was

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reported to be less but still is a matter of concern [7–9]. Tricalcium silicate-based cements do not leach any contaminants thus are considered safer for use as root-end filling materials [10].

Tricalcium silicate cement has been used alone and with additives, as bone cement [11,12] and as a posterior restorative material [13]. It has been demonstrated that pure tricalcium silicate is a suitable replacement for the cementitious component in MTA due to their similar composition and bioactivity [14], the ability to form hydroxyapatite [15,16] and maintenance of the bone–biomaterial interface once implanted [17]. Tricalcium silicate cement has also proved to have sufficient physical properties [11] to be suitable for use as a root-end filler [15]. In addition, tricalcium silicate cement has been found to have a shorter setting time than MTA, good injectability, good bioactivity and acceptable in vitro degradability (the ability for the implanted cement to be replaced by natural tissue) [17]. Additions of calcium carbonate and calcium sulphate both improve the setting time and the compressive strength of the material [16,17] with calcium sulphate having the added advantage of being bioactive and degradable [16].

Tricalcium silicate is found as the main cementitious component in Biodentine and Bioaggregate. Biodentine has been developed and produced with the aim of bringing together the high biocompatibility and bioactivity of calcium silicates, with enhanced properties such as quick setting time (a function of the calcium chloride added to the Biodentine liquid) and high strength (result of the low water to cement ratio made possible by the addition of a water soluble polymer); properties not usually associated with said cements [18]. Septodont claims to be able to maintain a balance between the two through its water reducing agent in Biodentine thus offering a homogeneous, dense product, with maximized strength. Biodentine uses zirconium oxide as a radiopacifying material. Most of the data available on Biodentine is forthcoming from the manufacturer with few independent researches being conducted.

Bioaggregate contains approximately 41% tricalcium silicate cement and no aluminum content [19,20]. Bioaggregate is similar to white ProRoot MTA in terms of chemical composition, with the major difference being the radiopacifier (tantalum oxide in Bioaggregate as opposed to bismuth oxide in MTA) [19]. The same study found calcium hydroxide in the set form of both materials, which may point to good bioactivity and biocompatibility of the material.

The aim of this study is to assess the physical properties of tricalcium silicate-based root-end filling materials. Prototype radiopacified tricalcium silicate cement, Biodentine and Bioaggregate are investigated and compared to intermediate restorative material.

2. Methodology

The materials used in this study included:

- Tricalcium silicate cement (Mineral Research Processing, Meyzieu, France) replaced with 20% zirconium oxide (ZrO_2; Sigma–Aldrich, Buchs, Germany) – TCS-20-Z;
- Biodentine™ (Septodont, Saint-Maur-des-fossés Cedex, France);
- Bioaggregate™ (Verio Dental Co. Ltd. Vancouver, Canada);
- Intermediate restorative material (Dentsply DeTrey, Konstanz, Germany) – IRM;

The TCS-20-Z was mixed at a water to cement ratio of 0.35 with an effective water to powder ratio of 0.28. The Biodentine, Bioaggregate and IRM were mixed according to manufacturer's instructions. The materials were soaked in Hank's balanced salt solution (HBSS; H6648, Sigma–Aldrich, St. Louis, MO, USA) for 28 days at 37 °C in an incubator.

2.1. *Evaluation of radiopacity*

Radiopacity evaluation was performed using ISO 6876 [21] recommendations. Three specimens 10 ± 1 mm in diameter and 1 ± 0.1 mm thick were used. Specimens were prepared and immediately immersed in gelatinized HBSS. They were radiographed after one day and 28 days. At each time point the specimens were placed directly on a photo-stimulable phosphor (PSP) plate adjacent to a calibrated aluminum step wedge (Everything X-ray, High Wycombe, UK) with 3 mm increments. A standard X-ray machine (GEC Medical Equipment Ltd., Middlesex, UK) was used to irradiate X-rays onto the specimens using an exposure time of 0.80 s at 10 mA, tube voltage at 65 ± 5 kV and a cathode–target film distance of 300 ± 10 mm. The radiographs were processed (Clarimat 300, Gendex Dental Systems, Medivance Instruments Ltd., London, UK) and a digital image of the radiograph was obtained. The gray pixel value on the radiograph, of each step in the step-wedge was determined using an imaging program, Microsoft Paint (Microsoft Corp., Redmond, WA, USA) as a number between 0 and 255 with 0 representing pure black and 255 pure white. A graph of thickness of aluminum vs. gray pixel value on the radiograph was then plotted and the best-fit logarithmic trend line was plotted through the points. The equation of the trend line gave the gray pixel value of an object on the image as a function of the object's thickness in mm of aluminum. This equation was inverted so as to express the object's thickness as a function of its gray pixel value on the radiograph. The gray pixel values of the cement specimens were then determined using the imaging program, and plugged into this equation to calculate the equivalent radiopacity of the cement sample, expressed in mm of aluminum.

2.2. *Determination of washout resistance*

Resistance to washout was determined using the basket drop method [22]. The test set-up (Fig. 1) consisted of a standard-sized test tube with an internal diameter of 14.5 mm which was filled to a height of 120 mm with distilled water and a woven brass mesh cylinder (60 wires per inch with a wire diameter of 0.18 mm) 9.0 mm diameter and a height of 17 mm. The empty mesh cylinder was weighed on an analytic balance with an accuracy of ±0.0001 g (Sartorius AG, Gottingen, Germany) after which it was filled with approximately 1 g of test material and reweighed. The cylinder was released just above the surface of the fluid in the test tube and allowed to sink unhindered. The cylinder was left at the bottom of the tube for 15 s, then brought out of the water in 5 ± 1 s and allowed to drip for 2 min. The cylinder was patted dry

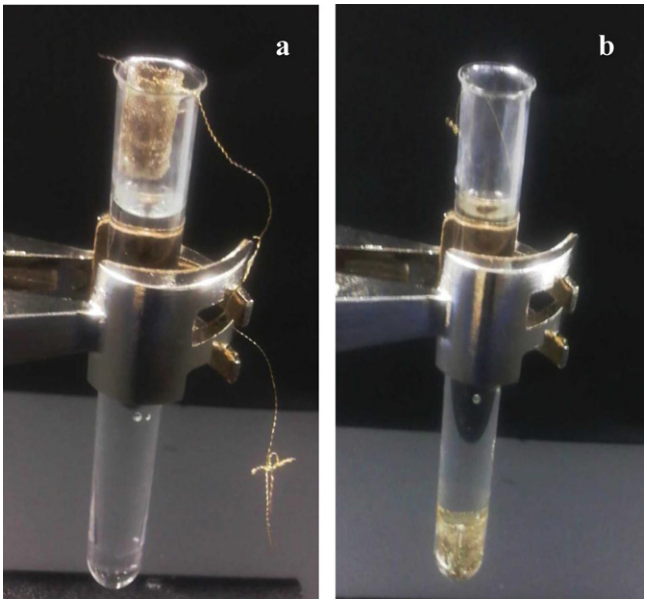


Fig. 1 – (a) Test set-up showing brass mesh cylinder with test material before free-fall immersion in test tube; (b) after free-fall immersion in test solution.

with absorbent paper to remove any remaining water, and weighed. The complete procedure was repeated to give a total of three drop cycles per specimen. Two replicate tests per material were conducted using fresh solution for each replicate. Washout (or loss of mass of the sample) was expressed as a percentage of the initial mass of the sample and calculated using Eq. (1):

$$D = 100 \times \frac{M_i - M_f}{M_i} \quad (1)$$

where D = washout (%), M_i = mass of sample before initial drop, M_f = mass of sample after each drop.

2.3. Evaluation of fluid uptake, sorption and solubility

Specimens for these tests were prepared using disc shaped rubber molds of internal diameter 15 ± 1 mm and a thickness of 1 ± 0.1 mm as specified in ISO 4049; 2009 [23]. The materials were mixed, placed in the molds and allowed to cure for 24 h at 37 ± 1 °C. The specimens were then demolded and weighed in order to record their mass 'm_1' to an accuracy of ±0.1 μg. The mean diameter of each specimen and the thickness of each specimen were measured to an accuracy of 0.01 mm and the volume 'V' of each specimen was calculated. The specimens were then immersed upright in 10 ml of HBSS. The specimens were then removed after 1 day and dried using filter paper. These were then weighed 1 min after being removed from the storage solution to an accuracy of 0.1 μg. Their mass was recorded as 'm'. The fluid uptake of each specimen could be recorded using Eq. (2):

$$F_{uptake}(\%) = \frac{m - m_1}{V} \times 100 \quad (2)$$

This process was repeated to measure the fluid uptake of the specimens after 1, 7, 14, 21 and 28 days. After 28 days, the mass of the specimens (fully saturated) was recorded as 'm_2'. The specimens were stored in a desiccator maintained at 23 ± 1 °C for 24 h using silica gel as desiccant until a constant mass could be recorded. This constant mass was recorded as 'm_3'. Fluid sorption (F_{sp}) for each sample was calculated using Eq. (3).

$$F_{sp}(\%) = \frac{m_2 - m_3}{V} \times 100 \quad (3)$$

Fluid solubility (F_{sl}) for each sample was calculated using Eq. (4):

$$F_{sl}(\%) = \frac{m_1 - m_3}{V} \times 100 \quad (4)$$

2.4. Evaluation of setting time

Setting time was evaluated using the procedure set out in ISO 9917-1; 2007 [24]. The cements were mixed and compacted into stainless steel rectangular molds measuring 10 mm × 8 mm in cross section and 5 mm deep. The specimens were placed at 37 ± 1 °C in different environmental conditions. Testing for setting time was performed using a modified Vicat apparatus (ELE International, Leighton Buzzard, UK), consisting of a weighted needle of square cross-section of side 1 ± 0.01 mm with a total mass of 400 ± 5 g. The final setting time was calculated as the time taken from the start of mixing to the time at which the indenter failed to leave a mark on the set cement surface. The cement was tested for setting initially at 15 min time intervals. The test was conducted by keeping the materials immersed in gelatinized HBSS. The HBSS was gelatinized by adding 20% porcine gelatin (Fluka Biochemika, Fluka Chemie GmbH, Buchs, Germany) and heating continuously until boiling. Once cooled the gelatinized HBSS was poured over the unset specimens.

2.5. Evaluation of compressive strength

Cylindrical specimens 4 ± 0.1 mm in diameter and 6 ± 0.1 mm high were prepared to determine the compressive strength. Twelve cylinders were prepared from each material type and were cured immersed in gelatinized HBSS at 37 °C for 28 days. They were tested in compression using a 15 kN compression testing jig (Controls 50-C0050/CAL; Controls spa, Milan, Italy) attached to a console and data logging system at a loading rate of 50 N/min as suggested by ISO 1997-1; 2007. The compressive strength was calculated using Eq. (5).

$$\text{Compressive strength} = \frac{\text{applied load (N)}}{\text{area (mm}^2\text{)}} \quad (5)$$

2.6. Evaluation of micro-hardness

Discs 10 mm in diameter and 2 mm thick were cast and immersed in gelatinized HBSS for 28 days at 37 °C. Microhardness testing (Mitutoyo, Mitutoyo Asia Pacific Ltd., Singapore) was performed using a diamond shaped indenter. Vickers hardness number (VHN) was recorded.

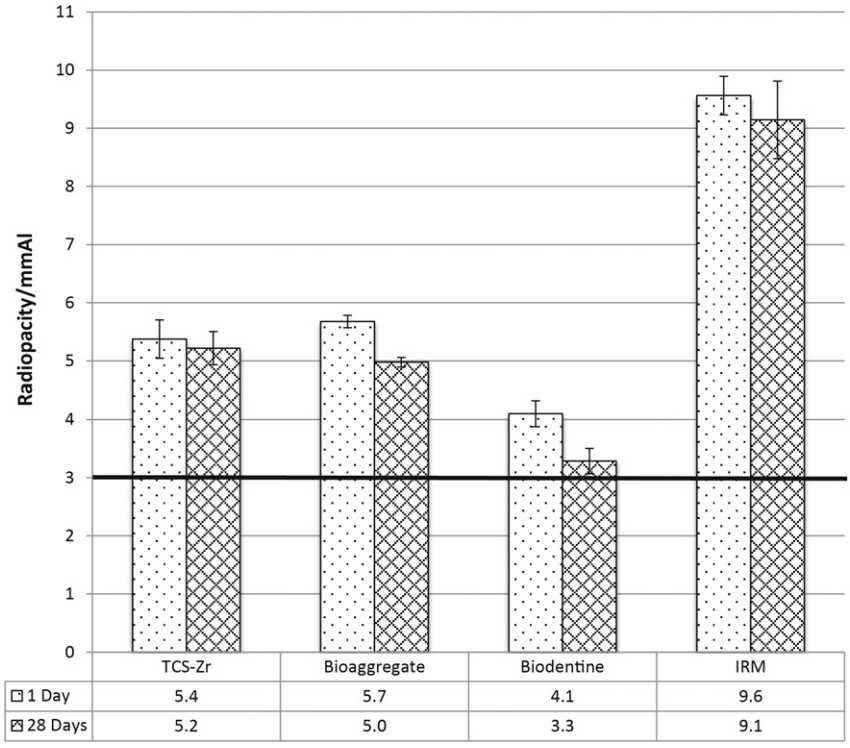


Fig. 2 – Radiopacity evaluation of the cements after immersion in Hank's balanced salt solution for 1 day and 28 days (± SD).

2.7. *Statistical analysis*

The data were evaluated using SPSS (Statistical Package for the Social Sciences) software (PASW Statistics 18; SPSS Inc., Chicago, IL, USA). Parametric tests were performed as K–S tests on the results indicated that the data were normally distributed. Analysis of variance (ANOVA) with $P = 0.05$ and Tukey post hoc test were used to perform multiple comparison tests.

3. Results

3.1. *Evaluation of radiopacity*

The radiopacity evaluations are shown in Fig. 2. All the materials exhibited a radiopacity value higher than 3 mm aluminum suggested by ISO 6786 (2001). All materials lost some radiopacity over time but this was not statistically significant ($p > 0.05$). IRM was the most radiopaque material tested while the calcium silicate cement based materials had a similar radiopacity ($p > 0.05$).

3.2. *Determination of washout resistance*

The results of washout testing are shown in Fig. 3. The radiopacified tricalcium silicate, Bioaggregate and IRM exhibited very low washout ($p > 0.05$). There was also no difference between the consecutive drops ($p > 0.05$). On the other hand Biodentine demonstrated a high washout and there was more material lost with each consecutive drop.

3.3. *Evaluation of fluid uptake, sorption and solubility*

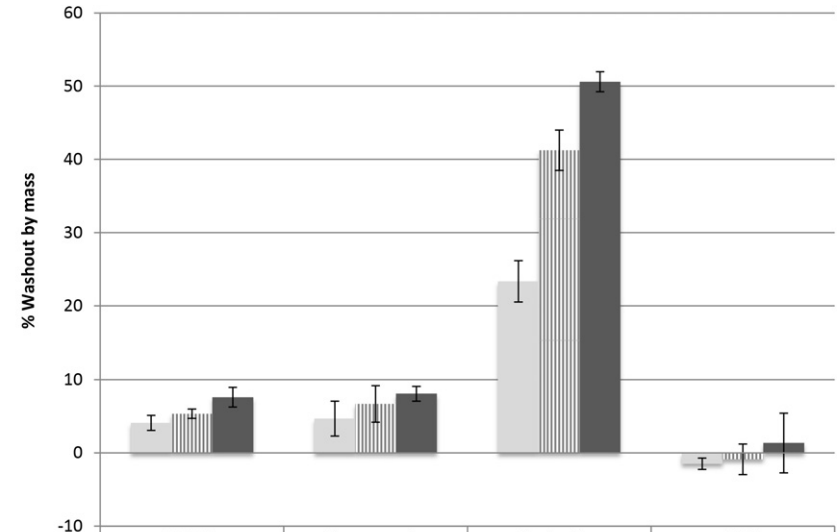
The results for fluid uptake are shown in Fig. 4 and those for percentage sorption and solubility in Fig. 5. The Biodentine exhibited the lowest fluid uptake and was similar to IRM ($p = 0.228$, 0.188, 0.238, 0.153, 0.143 for 1, 7, 14, 21 and 28 days respectively). Bioaggregate had the highest fluid uptake of all the materials tested and this was constant at all time intervals. The results of sorption of the test materials exhibited the same trend with Biodentine being similar to IRM ($p = 0.936$) and Bioaggregate having a very high sorption. The prototype cement, Bioaggregate and Biodentine demonstrated negative solubility values. There was no statistically significant difference between the solubility of the materials tested ($p > 0.05$).

3.4. *Evaluation of setting time*

The setting time of the test materials is shown in Fig. 6. Bioaggregate exhibited the highest setting time of all the materials tested while IRM had the shortest setting time. There was a statistically significant difference between all the materials tested ($p < 0.001$). Biodentine and the prototype dental cement which had similar constituent phases displayed a significant difference in the setting time ($p < 0.001$).

3.5. *Evaluation of compressive strength and micro-hardness*

The results for the compressive strength and micro-hardness testing are shown in Fig. 7. The prototype dental cement and Bioaggregate had similar compressive strength and



	TCS-Zr	Bioaggregate	Biodentine	IRM
1st Drop	4.1022	4.6856	23.3537	-1.4713
2nd Drop	5.3483	6.6855	41.2466	-0.8702
3rd Drop	7.6068	8.0772	50.5970	1.3649

Fig. 3 – Percentage washout by mass of the test materials following three consecutive drops in water.

micro-hardness values to the IRM ($p > 0.05$). The Biodentine exhibited superior strengths than all the materials tested.

4. Discussion

The physical properties of three tricalcium silicate-based cements and IRM were investigated. There is very little published literature on both Biodentine and Bioaggregate which may be due to the novelty of these materials. Although IRM has been in use for several decades very little information is available about this material. The prototype tricalcium silicate based material was similar in composition to Biodentine which is primarily composed of tricalcium silicate and zirconium oxide as suggested by the manufacturer [18]. Regardless of the similarities of these two materials the physical properties were very diverse.

Water sorption (the amount of water adsorbed on the surface and absorbed into the body of the material) and solubility (the amount of that substance that will dissolve in a given amount of solvent) were measured using ISO 4049; 2009 [23]. This standard allows the possibility to test both sorption and solubility and although fluid uptake tests are not included this standard could easily be modified to conduct all tests

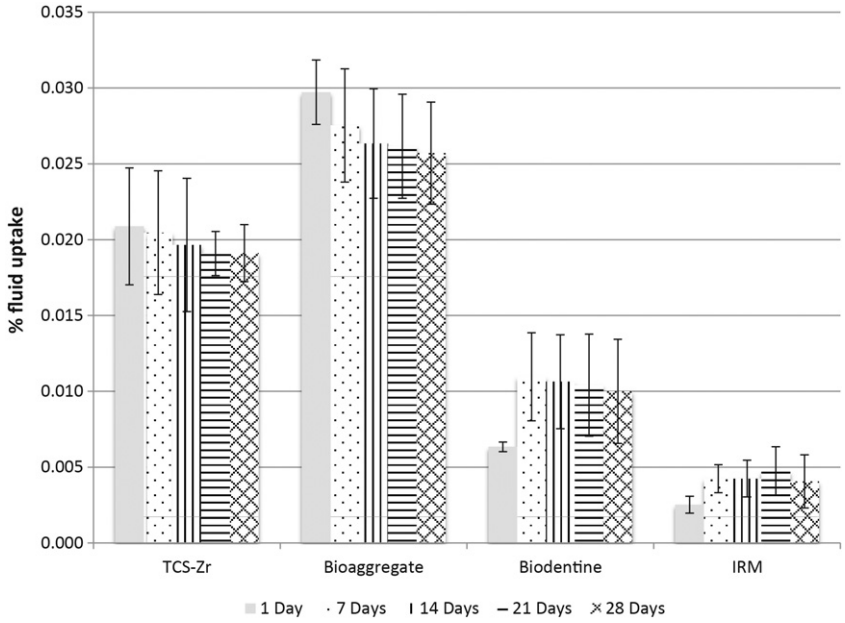


Fig. 4 – Fluid uptake over a period of 28 days for test materials immersed in Hank's balanced salt solution.

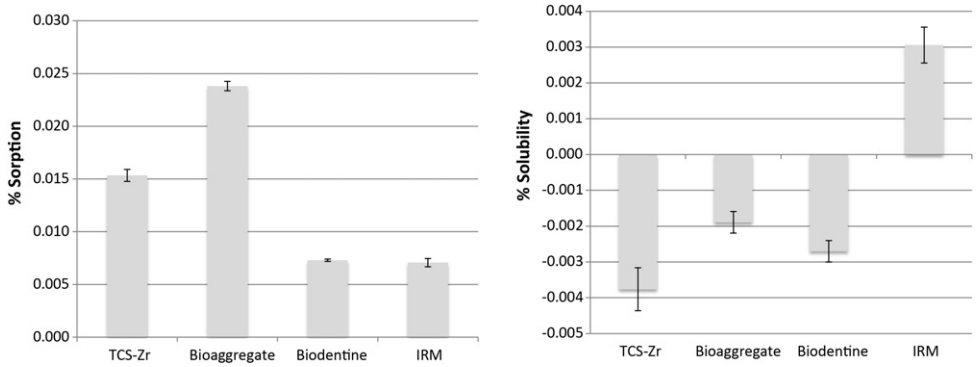


Fig. 5 – Sorption and solubility of test materials immersed in Hank's balanced salt solution for 28 days.

simultaneously and more accurate results could be achieved. The HBSS was used in order to have conditions closely resembling clinical situation.

All the materials exhibited a radiopacity which was higher than the 3 mm aluminum standard suggested by ISO 6867; 2002 [21]. The tricalcium silicate-based materials had a similar radiopacity value which ranged between 4 and 5 mm aluminum while IRM exhibited 9 mm aluminum. The value of IRM is in accordance to previous reports investigating the radiopacity of root-end filling materials [25]. The high radiopacity is a function of the zinc oxide which makes up 80% of the cement with the rest of the powder being composed of polymethyl methacrylate.

The materials were tested for washout resistance. Washout refers to the tendency of freshly prepared cement paste to "disintegrate upon early contact with blood or other fluids" [26]. The method for testing washout has been developed recently [22]. This method gives quantitative evidence of the amount of material lost when subjected to tissue fluids and irrigating solutions during placement. In the current study it has been shown that the radiopacified tricalcium silicate, Bioaggregate and IRM exhibited low washout. Biodentine demonstrated a very high washout tendency with the loss of material increasing with every drop. Although the prototype radiopaque tricalcium silicate and Biodentine had similar constituent phases they did not exhibit similar washout characteristics. The prototype cement did not contain the setting accelerator and the water soluble polymer. These additives to the mixing liquid have been included in the manufacturer's data sheet for Biodentine [18] and have also been verified in a recent report [10]. The radiopacified tricalcium silicate was mixed with water and the liquid provided with Bioaggregate was shown to be water [10]. The water soluble polymer is added to reduce the water/cement ratio without varying the workability of the resultant cement mixture. This principle is adopted in concreting where admixtures are used to increase the concrete flow or to reduce the water to cement ratio thus increasing the material strength [27]. The enhanced material strength is also verified in the current study. The water-soluble polymer has a surfactant effect and thus will disperse the cement particles by applying a charge on their surfaces [28]. This dispersion will lead to a fluid mixture which resulted in the dislodgement of the Biodentine when tested for washout. IRM was mixed with eugenol as liquid. Eugenol is not water miscible thus this allowed for high washout resistance.

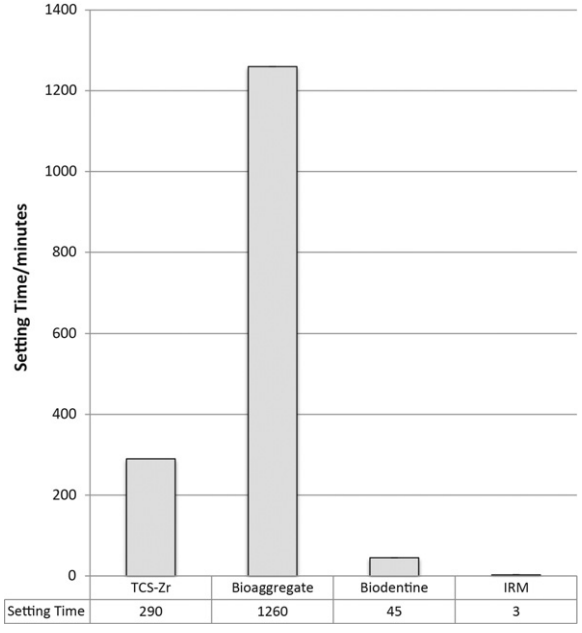


Fig. 6 – Setting time of test materials in minutes.

As already pointed out Biodentine and the prototype radiopacified are both composed primarily of tricalcium silicate cement and zirconium oxide. Regardless this the Biodentine exhibited a shorter setting time, a higher compressive strength and micro-hardness and low fluid uptake and sorption. The setting time is shorter and this is attributed to the addition of calcium chloride to the mixing liquid. Calcium chloride is used with Portland cement mixtures to reduce the setting time [27,28] and has also resulted in accelerated setting time for mineral trioxide aggregate [29–31]. The resultant higher strength and micro-hardness corroborated with the very low water–cement ratios needed for good workability of the material. This was possible with the addition of a water-soluble polymer [10,18]. These additions enhance the material properties as suggested by the manufacturer. The low fluid uptake and sorption indicates that the material is very dimensionally stable, which is an important property for a root-end filling material. The fluid uptake and sorption were similar to IRM which is a eugenol-based cement thus

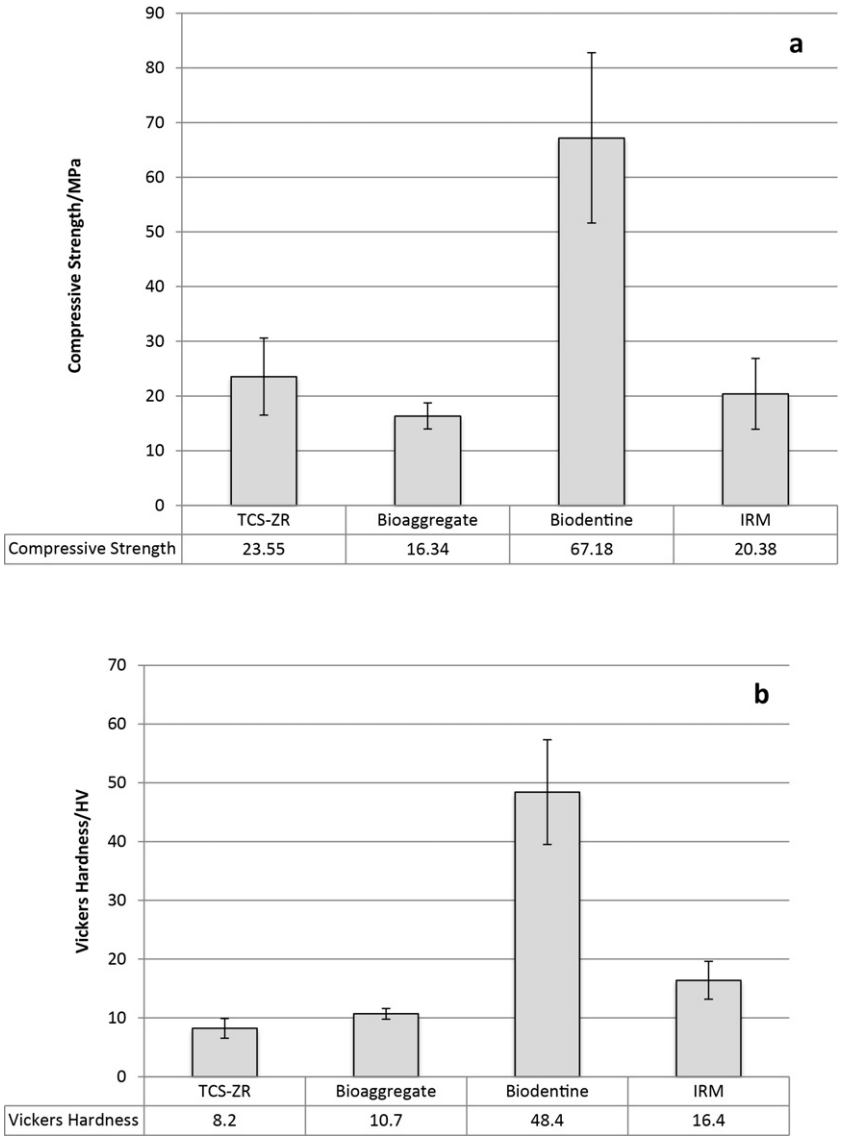


Fig. 7 – (a) Compressive and (b) micro-hardness testing of materials after immersion for 28 days in Hank's balanced salt solution.

expected to be water-repellent. The solubility of the three tricalcium silicate-based materials was negative indicating the deposition of substances on the material. This result could be attributed to the deposition of hydroxyapatite on the cement surface when the material is placed in contact with a simulated body fluid. This deposition of hydroxyapatite has been reported to be present on Portland cement [32,33], mineral trioxide aggregate [34,35] and tricalcium silicate cement [4] and is the reason for the bioactivity of these cements.

Bioaggregate exhibited an extended setting time which was higher than that of the materials tested. In addition it also displayed high sorption and fluid uptake. These characteristics indicate the reduced dimensional stability and poor setting characteristics of this material. IRM exhibited a very low setting time and fluid uptake and sorption. The solubility of IRM was shown to be low and comparable to that of tricalcium silicate-based cements. The solubility was positive thus indicating that the material may lose particulate matter rather than allow the deposition of any substance on it as demonstrated for the other materials tested.

Biodentine was the strongest material tested both in compression and also its surface properties were superior compared to the other materials. The enhanced strength is attributed to the low water/cement ratio used in Biodentine which is permissible as a water soluble polymer is added to the mixing liquid [18]. Radiopacified tricalcium silicate cement, Bioaggregate and IRM exhibited similar mechanical properties. The compressive strength of IRM is in accordance to that reported by other researchers [36] but in contrast to another report indicating a higher value of compressive strength [37]. The brand used for the IRM in these reports could have been diverse as indicated by the different setting times stated with the slow setting IRM having a higher setting time [37]. The mechanical properties of the materials could have been affected by the immersion in HBSS. Radiopacified tricalcium silicate cement using bismuth oxide as radiopacifier exhibited

a reduction in compressive strength when immersed in HBSS [38]. The micro-hardness of IRM was also shown to be affected by contact to fetal bovine serum [39]. In contrast the micro-hardness of MTA seemed to be enhanced when the material was in contact with blood and serum [40].

5. Conclusions

The addition of admixtures to tricalcium silicate-based cements affects the physical properties of the materials.

Acknowledgments

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