The effect of curing conditions on the physical properties of tricalcium silicate cement for use as a dental biomaterial

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Abstract

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Aim To investigate the physical properties of tricalcium silicate (TCS) with and without the addition of a radiopacifier and compare them with that of Portland cement (PC) and radiopaque PC in an mineral trioxide aggregate-like system.

Methodology Tricalcium silicate, PC and radiopacified variants containing 20% bismuth oxide were tested for radiopacity, compressive strength, setting time and dimensional stability. All the testing was performed at 37 °C and under different environmental conditions namely at 100% humidity or immersed in either water or Hank's balanced salt solution (HBSS). Testing was performed after both 1 and 28 days.

Results The cements exhibited radiopacity values equivalent to <3 mm. Addition of 20% bismuth oxide resulted in adequate radiopacity. The strength of TCS was independent of the curing conditions. The cements without radiopacifier had improved strength characteristics when immersed in HBSS, whilst the radiopacified cements exhibited higher strengths when soaked in water. Tricalcium silicate demonstrated the shortest setting time. Addition of bismuth oxide increased the setting time of the cements while HBSS inhibited the setting of bismuth oxide-replaced cements. The PC-based materials exhibited a net contraction higher than that recorded for TCS-based cements in all curing conditions. The dimensional change exhibited by the specimens was generally greater in the first few hours of setting, but then stabilized with time.

Conclusions Tricalcium silicate cement required the addition of a radiopacifying agent to make it suitable for use as a dental material. Tricalcium silicate exhibited adequate physical properties and thus was shown to be a suitable replacement for the PC component in MTA. Bismuth oxide drastically increased the setting time of the test cements in phosphate-containing solutions. Alternative radiopacifiers that do not retard the setting time need to be investigated.

Keywords: mineral trioxide aggregate, Portland cement, tricalcium silicate.

Introduction

Mineral trioxide aggregate (MTA) is composed of 80% by mass Type 1 ordinary Portland cement (PC) and 20% by mass bismuth (III) oxide, the latter being added to increase its radiopacity (Torabinejad & White 1995). MTA is derived primarily from calcium oxide (50–75%), silicon dioxide (15–25%) and aluminium oxide (3–8%), which when clinkered in a kiln during the production process produce a combination of tricalcium silicate (TCS) (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4) and tricalcium aluminate ($Ca_3Al_2O_6$) (Camilleri *et al.* 2005). MTA and PC have been found to have the same elemental constituents with the exception of the bismuth, which was present only in MTA (Funteas *et al.* 2003, Asgary *et al.* 2004). Also, the tricalcium

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aluminate phase present in PC was shown to be scarce in MTA (Camilleri 2007, 2008a). The raw materials and the manufacturing process of both MTA and PC can result in contamination with heavy metals, which result from the production process when the primary fuel used for heating the kiln is substituted with secondary fuels and also the use of wastes as an alternative inorganic raw material in place of the limestone and shale (Achternbosch *et al.* 2003).

Mineral trioxide aggregate, grey and white PC were shown to leach lead, arsenic and chromium when immersed in both water and physiological solution with the industrial PC s exhibiting higher levels of heavy metals than the dental cements (Chang *et al.* 2010). The grey PC and grey MTA exhibited higher acid extractable (Monteiro Bramante *et al.* 2008, Chang *et al.* 2010) and leachable arsenic (Duarte *et al.* 2005) than the white versions of the material, and the white MTA had a similar contaminant level of trace elements to the white PC (Schembri *et al.* 2010). The level of arsenic in MTA was above the limit stipulated by ISO 9917-1: 2007. Conversely, other researchers (De Deus *et al.* 2009, Gonçalves *et al.* 2010, Matsunaga *et al.* 2010) reported levels of arsenic below the limit set by the ISO standard. Heavy metal inclusion can be of concern as MTA is in contact with hard and soft tissues when used as a root-end filling material.

The cement component in MTA has been replaced by various other components that mainly address the extended setting time. Calcium sulphoaluminate cement composed of a mixture of three parts calcium aluminate, eight parts white PC and one part synthetic anhydrite, was found to have faster setting time than MTA, adequate compressive strength (Camilleri 2008b), reduced microleakage when tested using a tracer method (Camilleri 2010b), was not susceptible to acid attack (Camilleri 2011a) and had biocompatibility comparable to glass–ionomer cement (Camilleri 2008c) extending the cement use to a core build-up material. Other components of PC have been used separately as replacements for the PC component in MTA. Dicalcium silicate prepared using a sol-gel method demonstrated bioactivity and biocompatibility together with adequate compressive strength (Chen *et al.* 2009a,b). Radiopacified dicalcium silicate exhibited a reduced setting time when compared to MTA (Chiang & Ding 2010). Calcium aluminates have also been investigated for use in dentistry. A mixture of calcium aluminate cement, polyglycol polymer dispersant, calcium chloride and zinc oxide added to enhance the material radiopacity leached calcium ions in solution, set within 60 min, had adequate compressive strength values and superior handling properties to MTA (Oliveira *et al.* 2010).

The main constituent phase in both PC and MTA is TCS, which makes up 68–74% and 53.1% of the material, respectively (Camilleri 2008a, 2011b). Replacement of the PC component in MTA with pure TCS would allow better control over the impurities and heavy metal inclusions found in the industrial material. Tricalcium silicate is produced using the sol-gel method (Zhao & Chang 2004, Ding *et al.* 2009). Briefly, tetraethyl orthosilicate ($Si(OC_2H_5)_4$) and nitric acid as catalyst are added in water under continuous stirring. Calcium nitrate ($Ca(NO_3)_2.4H_2O$) is then added, and the solution is maintained at 60 °C until gelation occurs. The gel is then dried at 120 °C and calcined for 8 h at 1450 °C. The resultant powder is finally ground and sieved (Zhao & Chang 2004). Tricalcium silicate exhibits the ability to form bone-like hydroxyapatite in simulated body fluid (Zhao *et al.* 2005, 2008, Wang *et al.* 2008, Camilleri 2011b). This layer is essential in maintaining the bone–biomaterial interface when implanted in the body. It exhibited adequate physical properties (Huan & Chang 2008) and a shorter setting time (12–42 min depending on the SiO_2/CaO ratio used) than MTA (Chen *et al.* 2009b), and addition of calcium chloride resulted in a further reduced setting time. The hydrated cement exhibited good biocompatibility with induced cell growth and differentiation and bioactivity (Zhao *et al.* 2005, 2008, Huan & Chang 2008, Wang *et al.* 2008).

Tricalcium silicate is used as bone cement (Huan & Chang 2008, Ding *et al.* 2009) and also as an endodontic material (Wang *et al.* 2008, Chen *et al.* 2009a,b). Tricalcium silicate is also the main constituent phase of Biodentine, which is manufactured by Septodont (Septodont, Saint-Maur-des-Fossés Cedex, France), who claim that the TCS is produced using a novel technological platform called Active Biosilicate-Technology™ (Septodont, Saint-Maur-des-fossés Cedex, France), which guarantees the purity of the material.

The aim of this research was to investigate the physical properties of TCS and a radiopaque TCS and compare them to PC and radiopaque PC in an MTA-like system.

Methodology

Materials used in this study included PC (CEM 1, 52.5 N; LaFarge Cement, Birmingham, UK), TCS manufactured using the sol-gel method (TCS; Mineral

Research Processing, Meyzieu, France) and bismuth (III) oxide, Bi_2O_3 (10 μm 223891-100G; Sigma-Aldrich, St. Louis, MO, USA). The prototype materials created included the cements (PC and TCS) and the radiopacified materials [Portland cement replaced with 20% bismuth oxide (PCB) and tricalcium silicate cement replaced with 20% bismuth oxide (TCSB)], which were prepared by replacement of 20% of the cement component by bismuth oxide. The PC and TCS-based cements were mixed with water at a water-to-cement ratio of 0.3 and 0.37, respectively. All tests were carried out either in an atmosphere of 100% relative humidity using a climatic chamber (Weiss-Gallenkamp, Loughborough, UK) or immersed in either distilled water or Hank's balanced salt solution (HBSS, HBSS H6648; Sigma-Aldrich), at 37 ± 1 °C. The HBSS was used as a simulated body fluid.

Evaluation of radiopacity

For radiopacity evaluation, three specimens 10 ± 1 mm in diameter and 1 ± 0.1 mm thick were used. A total of 24 specimens were prepared. They were tested after 1 and 28 days under the stipulated environmental conditions. The specimens were placed directly on a photo-stimulable phosphor (PSP) plate adjacent to a calibrated aluminium 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 0.48 s at 10 mA and a cathode-target film distance of 300 ± 10 mm. The tube voltage was set at 65 ± 5 kV. The radiographs were processed (Clarimat 300; Gendex

Dental Systems, Medivance Instruments Ltd., London, UK), and a digital image of the radiograph was obtained (Fig. 1). The grey pixel value on the radiograph, of each step in the step wedge was determined using an imaging programme, 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 aluminium versus grey 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 grey pixel value of an object on the image as a function of the object's thickness in mm of aluminium. This equation was inverted so as to express the object's thickness as a function of its grey pixel value on the radiograph. The grey pixel values of the cement specimens were then determined using the imaging programme and plugged into this equation to calculate the equivalent radiopacity of the cement sample, expressed in mm of aluminium.

Determination of compressive strength

Cylindrical specimens 4 ± 0.1 mm in diameter and 6 ± 0.1 mm high were prepared to determine the compressive strength of the materials under investigation. Thirteen cylinders were prepared from each material type and were allowed to cure in the three environmental conditions described for 28 days. Following curing, the specimens were taken out of the solution and dried using filter paper. The top and bottom were lightly sanded using moistened 600-grit sandpaper, and the diameter of each specimen was measured using a micrometer. They were then individually
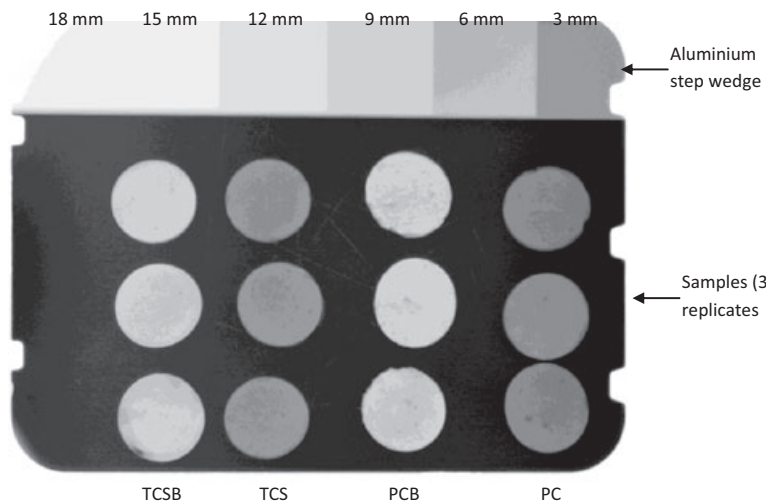

Figure 1 Sample digital radiograph.

tested using a compressive strength testing machine (Controls 50-C0050/CAL; Controls SPA, Milan, Italy) at a loading rate of 50 ± 10 N min^{-1} as per ISO 9917-1 (2007). The compressive test was carried out on the specimen until failure occurred. The compressive loading before failure was recorded, and the compressive strength of each cylinder calculated using the following equation:

$$\text{Compressive strength} = \frac{\text{Force at failure}}{\text{Cross sectional area of specimen}}$$

Evaluation of setting time

Setting time was evaluated using the procedure set out in ISO 9917-1: 2007. The cements were mixed and compacted into stainless steel rectangular moulds measuring 10 mm by 8 mm in cross section and 5 mm deep. The specimens were placed at 37 ± 1 °C either at 100% relative humidity or immersed in distilled water or HBSS. 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 repeated for all four materials under the three environmental conditions indicated, thus generating a total of 12 results.

Determination of vertical (horizontally restrained) dimensional change during setting

The experimental set-up for the determination of dimensional change in the vertical direction is shown in Fig. 2. It included a metal base plate to which was affixed a cylindrical metal mould having an internal diameter of 5 and 10 mm deep. The moulds were coated with a thin layer of mould oil (Separol, Sika, Switzerland). The test materials were prepared and then compacted inside the mould in three incremental stages. The surface of the freshly overfilled mould was flattened with the flat end of a spatula. Five replicates were prepared for each material tested. Prior to testing, all the set-up was left to acclimatize at 37 °C. The cements were allowed to cure for 3 h at 37 °C and 100% humidity before the contact probe of the linear variable differential transducer (LVDT Messotron; Messotron Hennig GmbH & Co, Seeheim-Jugenheim, Germany) was placed in contact with the cement
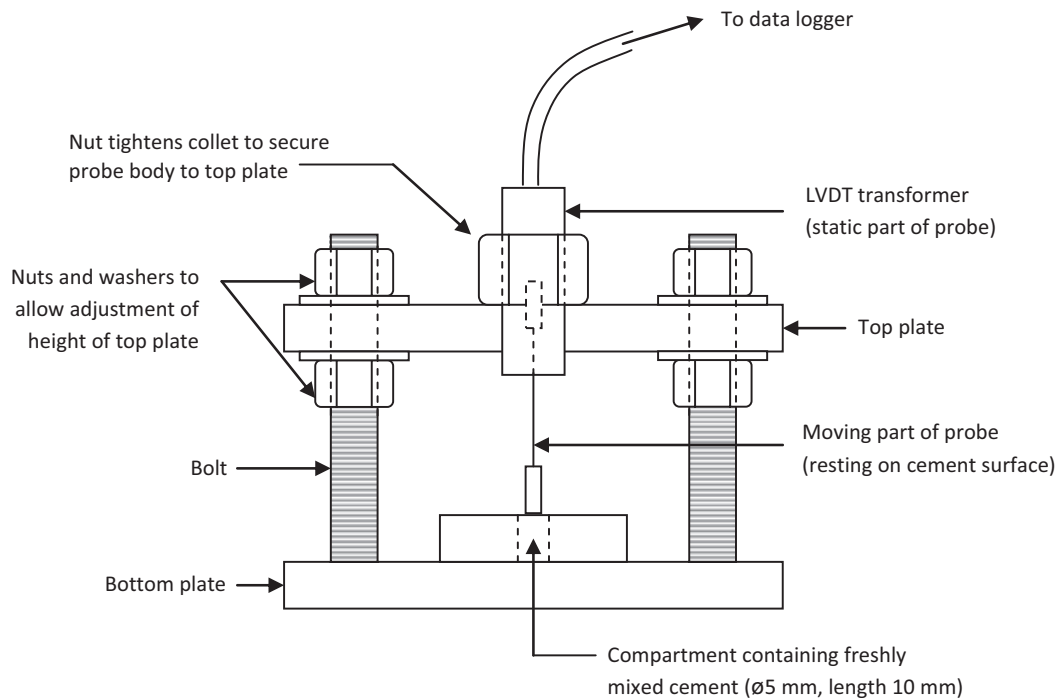

Figure 2 Schematic diagram of the jig used to determine the dimensional stability of the cement specimen.

surface. The experimental set-up was placed inside a climatic chamber. The LVDT was connected to a data logger (Peekel Instruments, Rotterdam, the Netherlands), and the probe position was recorded once every 15 min for 24 h. The dimensional changes of the materials were investigated at 37 °C and at 100% humidity or immersed in water or HBSS.

Statistical analysis

The data were evaluated using Statistical Package for the Social Sciences (SPSS) software (PASW Statistics 18; SPSS Inc., Chicago IL, USA). Parametric tests were performed as K–S tests, and 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.

Results

Evaluation of radiopacity

The results for radiopacity testing are shown in Fig. 3. Both bismuth oxide-containing materials had a radiopacity value of 8-mm aluminium, which was significantly higher ($P < 0.05$) than the pure materials under all environmental conditions and ages tested. The cements without added radiopacifier showed similar radiopacity values ($P > 0.05$), which was lower than the 3-mm aluminium thickness specified by ISO 6876. At 100% humidity, after 1 day, the bismuth oxide-replaced TCS was more radiopaque than the bismuth oxide-replaced PC ($P = 0.013$).

Determination of compressive strength

The compressive strengths of the four materials cured at different conditions are summarized in Fig. 4. When cured at 100% humidity, TCS exhibited the highest strength when compared to the other cements ($P = 0$). In distilled water, the addition of bismuth increased the PC strength ($P = 0.002$), but this increase in strength was not registered with TCS. On the contrary, in HBSS, the addition of bismuth oxide to both the PC and TCS reduced the compressive strength ($P = 0$, $P = 0.024$ respectively). The PC was stronger than the TCS in HBSS ($P = 0$). All the materials except TCS were weaker when kept in 100% humidity compared with the same materials immersed in distilled water or HBSS. In the case of TCS, the strengths were similar and independent of the curing conditions. PC achieved the

highest strength when cured in HBSS, whilst PCB and TCSB were strongest when cured in distilled water.

Evaluation of setting time

The final setting times of the materials under different environmental conditions are illustrated in Fig. 5. The bismuth oxide-replaced cements did not set within 8 h when immersed in HBSS. The bismuth oxide-replaced TCS also failed to set when immersed in water. The TCS exhibited the shortest setting time in all three curing environments. The addition of bismuth oxide resulted in an extended setting time.

Determination of vertical (horizontally restrained) dimensional change during setting

The dimensional changes measured for the four biomaterials during the first 24 h of setting in the different test environments are shown in Fig. 6. The PC-based cements exhibited shrinkage in all curing conditions, whilst TCS showed a net expansion at 100% humidity and in distilled water but shrunk when immersed in HBSS. In all curing conditions, the two PC-based materials (PC and PCB) contracted more than the TCS-based materials (TCS and TCSB). The addition of bismuth (III) oxide reduced the magnitude of the dimensional changes for both PCB and TCSB compared with the pure PC and pure TCS, respectively.

Discussion

Tricalcium silicate has been suggested as an alternative to the PC component in MTA as it is manufactured using raw materials with low levels of impurities in a laboratory. The radiopacity of the TCS cement was lower than the recommended 3-mm aluminium thickness. Thus, the addition of a radiopacifier was mandatory. Bismuth oxide was added in 1 : 4 proportions similar to the quantity used in ProRoot MTA. The radiopacity of the materials under study was assessed using the method suggested by ISO 9917-1 (2007) and ISO 6876 (2001). PSP plates were used, and from the resultant digital image, it was possible to obtain the radiopacity values directly from the grey pixel values of the digital image directly using specialized computer software (Tagger & Katz 2003, Carvalho-Junior *et al.* 2007), thus eliminating the need for a densitometer (Higginbotham 1967). A further development to this technique was the use of common off-the-shelf software that has numerous advantages over proprietary software including a lower
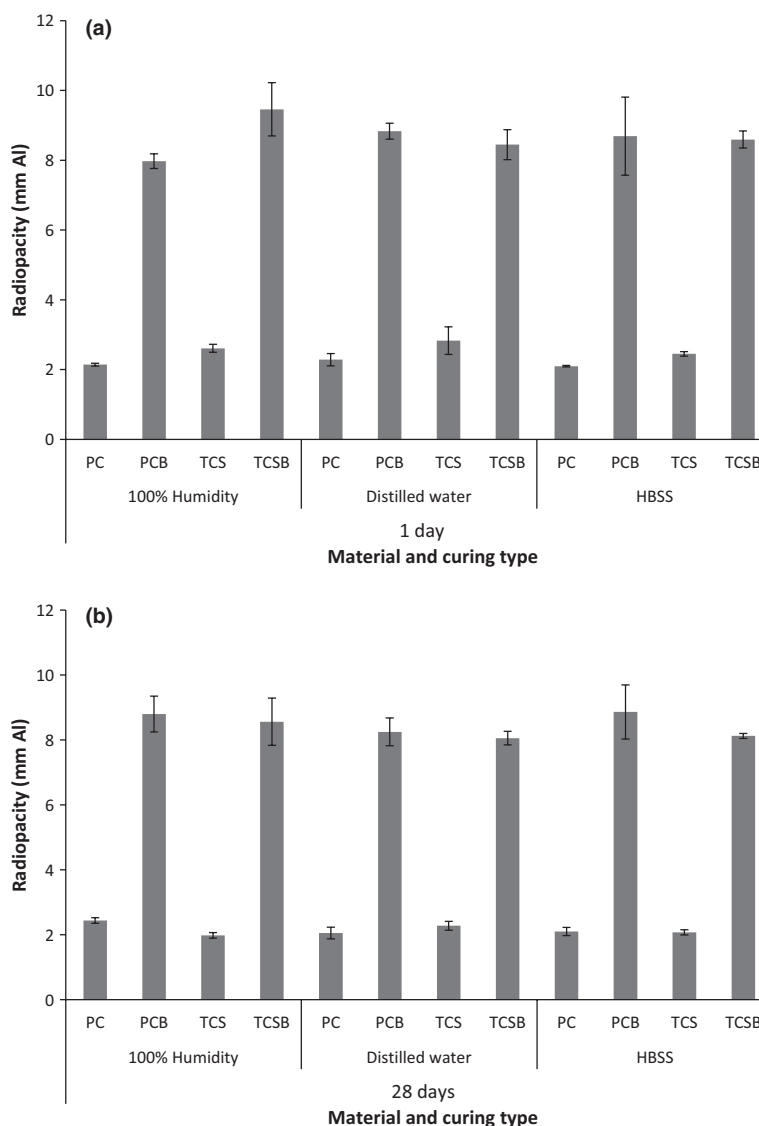
Figure 3 Radiopacity values of the four cements cured at 100% humidity or immersed in water or HBSS (a) after 1 day and (b) after 28 days (±SD). PC, Portland cement; PCB, Portland cement replaced with 20% bismuth oxide; TCS, tricalcium silicate cement; TCSB, tricalcium silicate cement replaced with 20% bismuth oxide; HBSS, Hank's balanced salt solution.

cost of acquisition, more support and compatibility with other users and the ease with which files may be shared. Compressive strength testing was performed in accordance with ISO 9917-1: 2007. Although not specifically intended for PC-based cements, this technique is still suitable for compressive strength testing of any dental material. The aspect ratio of the cylinders was 1.5, which is significant as an aspect ratio greater than 2 would result in a high probability of failure because of bucking, whilst a lower ratio would cause the strength to be influenced by the restraining effect of the loading plates and would necessitate the use of a correcting factor (Neville 1981). Factors affecting compressive strength of cements include water/powder ratio, the shape and size

of the specimen, end preparation of the specimen, the loading rate (Neville 1981) and the packing pressure (Nekoofar *et al.* 2007). The water-to-powder ratio should be set to give a workable mix whilst still ensuring complete hydration for maximum strength. There were no difficulties encountered with the setting of the specimens prepared for compressive strength tests as they were allowed to cure at 100% humidity for the first 24 h rather than immersed immediately in solution as was the case for the setting time testing and also clinically when used as root-end filling materials. All the materials except for pure TCS exhibited low compressive strength (<40 MPa) when cured in 100% humidity, which reinforces the importance of keeping
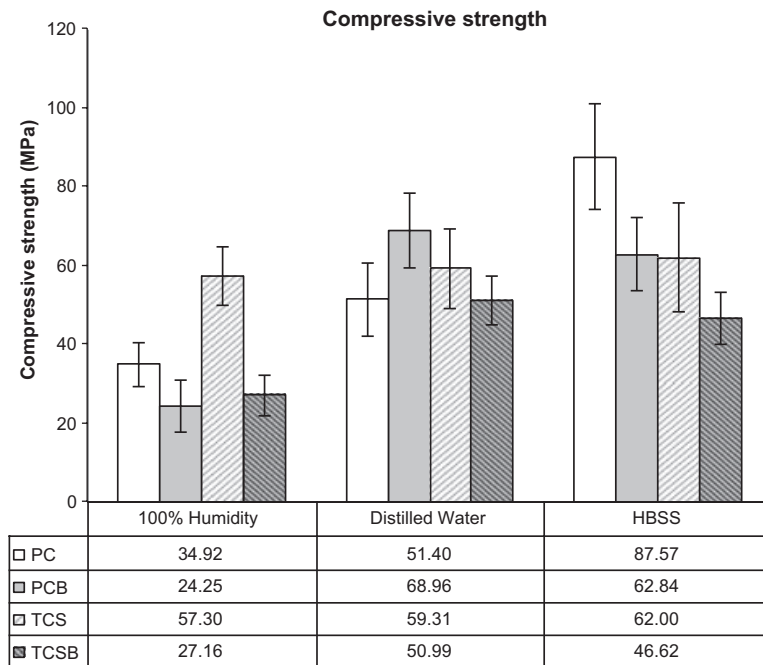
Compressive strength

	100% Humidity	Distilled Water	HBSS
□ PC	34.92	51.40	87.57
▣ PCB	24.25	68.96	62.84
□ TCS	57.30	59.31	62.00
▨ TCSB	27.16	50.99	46.62

Figure 4 Compressive strength values of the cements cured for 28 days either at 100% humidity or immersed in water or HBSS (±SD). PC, Portland cement; PCB, Portland cement replaced with 20% bismuth oxide; TCS, tricalcium silicate cement; TCSB, tricalcium silicate cement replaced with 20% bismuth oxide; HBSS, Hank's balanced salt solution.
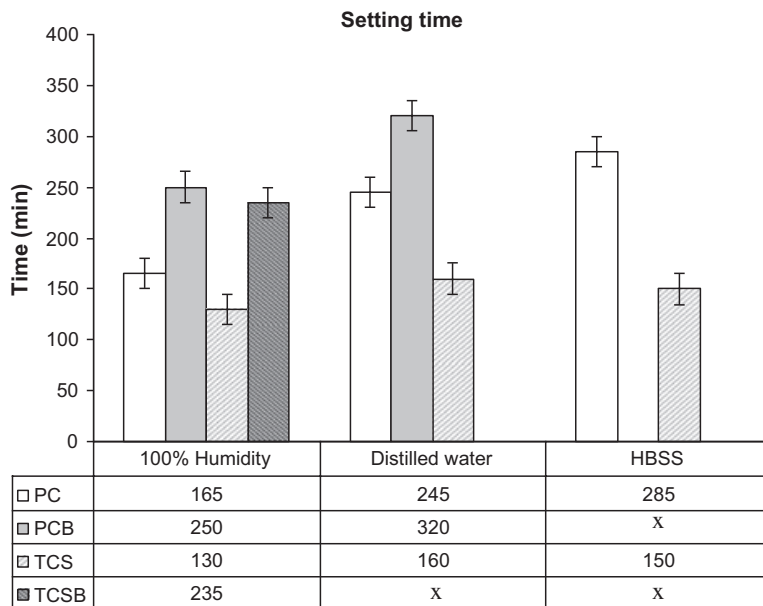
Setting time

	100% Humidity	Distilled water	HBSS
□ PC	165	245	285
▣ PCB	250	320	x
□ TCS	130	160	150
▨ TCSB	235	x	x

Figure 5 Setting times of the cements either at 100% humidity or immersed in water or HBSS at 37 °C. The x signifies failure to set (±SD). PC, Portland cement; PCB, Portland cement replaced with 20% bismuth oxide; TCS, tricalcium silicate cement; TCSB, tricalcium silicate cement replaced with 20% bismuth oxide; HBSS, Hank's balanced salt solution.

the material moist after being applied surgically. This is in accordance with previous research (Chogle *et al.* 2007). The results indicate that pure TCS is stronger than pure PC in 100% humidity and distilled water. It was the only material to exceed the 50 MPa minimum set out in ISO 9917-1: 2007when cured in 100% humidity. The literature investigating the compressive

strength of TCS (Huan & Chang 2008, Wang *et al.* 2008, Chen *et al.* 2009b) indicated a lower strength (around 6 MPa) than that found in the current research. The difference in the results can be attributed to a high water-to-powder ratio, different specimen aspect ratio, the specimen age when tested and the loading rate. All these factors contribute to the differing results. Replacing the
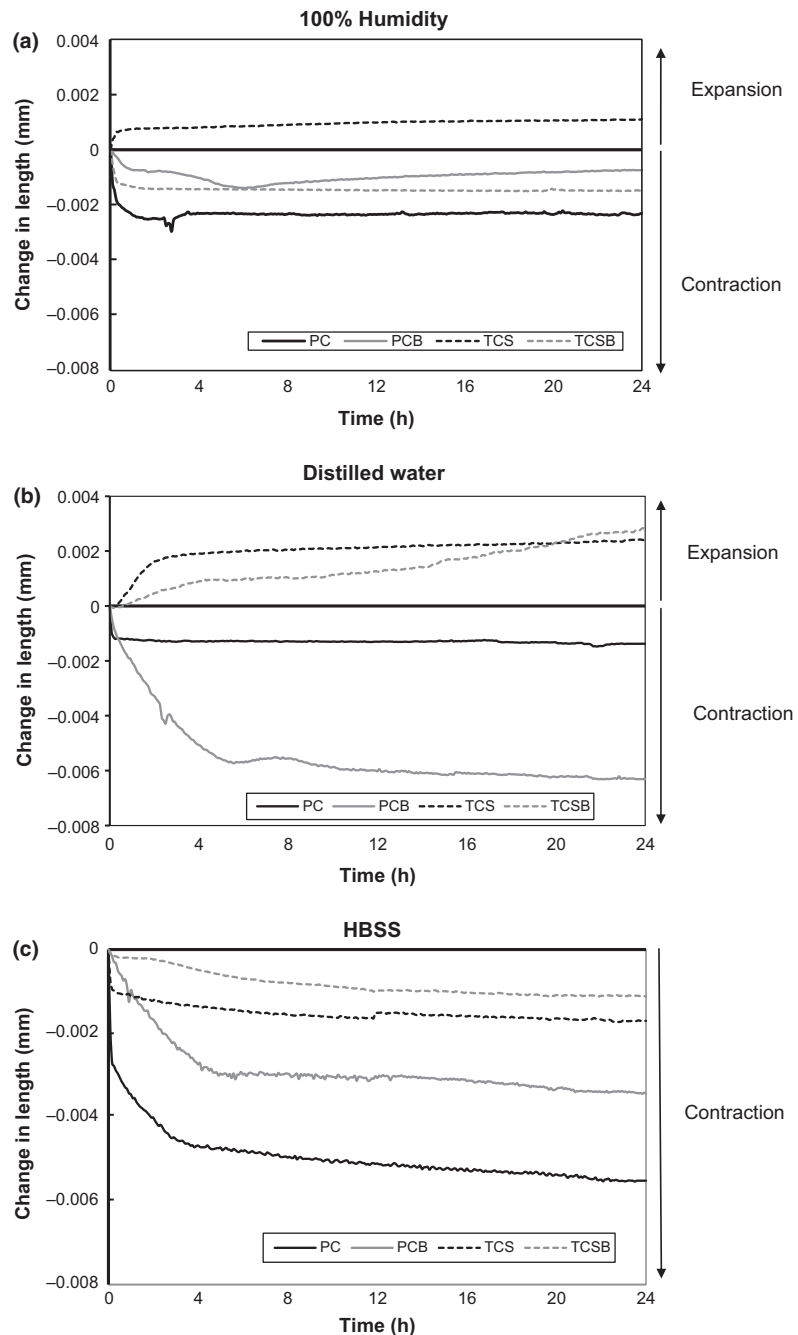
Figure 6 Change in length of cement specimens when cured at (a) 100% humidity, (b) immersed in distilled water and (c) immersed in HBSS for 24 h. PC, Portland cement; PCB, Portland cement replaced with 20% bismuth oxide; TCS, tricalcium silicate cement; TCSB, tricalcium silicate cement replaced with 20% bismuth oxide; HBSS, Hank's balanced salt solution.

cement content with noncementitious fillers such as the bismuth oxide increases the effective water/cement ratio, which explains why the general trend is for the addition of bismuth oxide to reduce the compressive strength (Coomaraswamy *et al.* 2007, Camilleri 2008d). Water/cement ratio was set at 0.37 for TCS to give a workable mix. The use of a high water/cement ratio when

compared to PC was primarily because of the fineness of the powder. The setting time of the materials under study was determined using an indentation method (ISO 9917-1: 2007). Several indentation methods using various needle sizes, needle weights and specimen dimensions exist, including the Vicat and Gilmore needles, of which the Vicat is considered more consistent

for PC as it gives slightly shorter setting times than the Gilmore needle (Neville 1981). The environmental conditions were modified by curing at 37 °C (instead of the 23 °C specified) to closely simulate human body temperature. Tricalcium silicate exhibited a reduced setting time when compared to PC, and the same applied for the bismuth-containing versions of the two materials. This is a significant advantage as the long setting time is one of the main drawbacks of MTA. The bismuth oxide-replaced cements exhibited a longer setting time when compared to their cement counterparts. This is in accordance with studies indicating that MTA had a longer setting time than PC (Camilleri 2010a). In addition, immersion in liquid slowed down the setting of the cement, whilst immersion in HBSS resulted in incomplete setting. Presence of phosphates in solution results in the retardation of setting of cements. The retardation is induced by the formation of insoluble hydroxides in alkaline solution. The insoluble hydroxides form a coating over the cement particles. The adsorption of phosphate ions at the surface of the clinker phase or on the first hydration product is thought to result in the precipitation of calcium phosphates (Ramachandran 1995). This phenomenon is clinically relevant as when the materials are used as root-end fillers, they are in contact with blood and serum immediately when placed. Dimensional stability is an important property for root-end filling materials. A material that is not dimensionally stable can lead to ingress of bacteria *in vivo* or fracture of delicate root ends. LVDTs were used to carry out this test. LVDTs are capable of exceeding the minimum accuracy specified in ISO 6876 and are easy to attach to data-logging equipment. The advantage of this setup was that it allowed the instruments to be left unattended and record data regularly over a lengthy period of time. The setup measured only horizontal displacement. This is a realistic reflection of the *in vivo* situation as the material will be restricted by the sides of the tooth root when it is used surgically. The most significant problem encountered was that when putting the probe on a freshly cast sample, the probe would embed itself into the cement under its own weight and would thus render the results invalid. This problem was mitigated by allowing the cements to set for 3 h in the jig and putting the probe on the surface only after the surface was sufficiently set to resist embedding of the probe. In distilled water, both PC- and the bismuth oxide-replaced formulation contracted, which is consistent with the findings of other studies (Storm *et al.* 2008, Camilleri 2011c). The magnitudes of the dimensional changes were of the same order as those reported in the

literature and fulfil the requirements of ISO 6876 (2001), which gives limits of 1.0 % in shrinkage and 0.1 % in expansion. It was observed that the TCS-based materials had a more consistent magnitude of dimensional change across the different conditions. This may be due to the substance being composed of a single pure phase, as opposed to the complex constitution of PC, which contains a combination of TCS, dicalcium silicate and tricalcium aluminate, each of which may be influenced differently by different environments (Storm *et al.* 2008).

Conclusions

Tricalcium silicate cement requires the addition of a radiopacifying agent to be suitable for use as a dental material. Under the conditions set out in this study, TCS exhibited adequate physical properties and thus was shown to be a suitable replacement for the PC component in MTA. Bismuth oxide drastically increased the setting time of the test cements in phosphate-containing solutions. Alternative radiopacifiers that do not retard the setting time need to be investigated.

Acknowledgements

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