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Evaluation of the strength and radiopacity of Portland cement with varying additions of bismuth oxide

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Abstract

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Aim To study the effect of addition of various proportions of bismuth oxide on compressive strength and radiopacity of Portland cement.

Methodology The compressive strength of white Portland cement and cement replaced with 10, 15, 20, 25 and 30% bismuth oxide was evaluated by testing cylinders 6 mm in diameter and 12 mm high. Twelve cylinders were tested for each material under study. The radiopacity of the cements tested was evaluated using an aluminium step-wedge and densitometer. The optical density was compared with the relevant thickness of aluminium (Al). Statistical analysis was performed using Analysis of Variance (ANOVA) with $P = 0.05$ and Tukey test to perform multiple comparison tests.

Results Various additions of bismuth oxide had no significant effect on the strength of the material when compared with the unmodified Portland cement ($P > 0.05$). The radiopacity of the cements tested ranged from 2.02 mm Al for Portland cement to 9.79 mm Al for the highest bismuth replacement.

Conclusions Addition of bismuth oxide did not affect the compressive strength of Portland cement. All the bismuth oxide cement mixtures had radiopacities higher than 3 mm thickness of aluminium.

Keywords: bismuth oxide, compressive strength, mineral trioxide aggregate, Portland cement, radiopacity.

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Introduction

Mineral trioxide aggregate (MTA) has been used as a root-end filling material for the past decade. The ideal properties of a root-end filling material have been well documented (Grossman *et al.* 1988) and include sufficient radiopacity to be able to distinguish the material from surrounding structures. Clearly a lack of radiopacity when small quantities of material are employed can result in the material not being distinguished from the surrounding anatomical structures (Beyer-Olsen & Orstavik 1981).

Grey MTA (ProRoot™) has been shown to have a radiopacity equivalent to 5.34 mm (Danesh *et al.* 2006) and 6.4 mm (Laghios *et al.* 2000) aluminium (Al), respectively. The prototype version of MTA used by Torabinejad *et al.* (1995) was shown to have a radiopacity of 7.17 mm Al. MTA is less radiopaque than Super-EBA (9.9 mm Al), IRM (9.3 mm Al), gutta-percha (11.0 mm Al) or amalgam (15.6 mm Al) (Laghios *et al.* 2000), but is more radiopaque than Viscosity Enhanced Root Repair Material (4.5 mm Al) (Chng *et al.* 2005). It but is in the same range as zinc oxide–eugenol based canal sealers (Torabinejad *et al.* 1995).

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Most of the materials used in endodontics have radiopacifying materials added to them. These materials usually include barium or bismuth compounds as they are radiopaque. There have been few investigations on the effect that radiopacifiers have on the properties of materials. However, it has been shown that addition of barium sulphate at low concentrations reduced working and initial setting times, but further addition delayed the setting reaction of glass ionomer cements (Prentice *et al.* 2006). Both compressive strength and surface hardness decreased with increasing concentrations of the radiopacifying agent (Prentice *et al.* 2006).

The British Standard for Dental Root Canal Sealing Materials [BS EN ISO 6876 (British Standard Institution 2002)] does not specifically recommend minimum limits for compressive strength. However, there is a minimum recommendation of 50 MPa for compressive strength of low strength dental water-based cements [BS EN ISO 9917-1 (British Standard Institution 2003)]. Compressive strength may not be of paramount importance when MTA is used as a root-end filling, but any subsequent replacement of an associated orthograde root canal filling would require the root-end filling to have adequate strength. The applications for the use of MTA have broadened and sufficient strength must be considered important.

Mineral trioxide aggregate is composed of Portland cement and 4 : 1 addition of bismuth oxide (Torabinejad & White 1995). The main constituent phases in MTA are tricalcium and dicalcium silicates, which are the same phases constituting Portland cement (Camilleri *et al.* 2005). The bismuth oxide added to the MTA has been shown to affect the hydration mechanism of the MTA; it forms part of the structure of calcium silicate hydrate, which is the main by-product of cement hydration and also affects the precipitation of calcium hydroxide in the hydrated paste (Camilleri 2007).

Mineral trioxide aggregate is now widely used to repair lateral root perforations (Lee *et al.* 1993, Pitt Ford *et al.* 1995), for the repair of cervical resumption (Baratto-Filho *et al.* 2005), as a pulp capping agent (Pitt Ford *et al.* 1996, Bakland 2000) and as a dressing over pulpotomies (Holland *et al.* 2001). These extended uses place additional demands on the development of MTA and the compressive strength of the material must be viewed as a more critical property. In addition, it has been demonstrated that additions of bismuth oxide to Portland cement may reduce the compressive strength of the material (Coomaraswamy *et al.* 2007, Camilleri 2008).

The aim of this preliminary study was to investigate the effect of bismuth oxide on the physical properties of Portland cement thus evaluating the effect on the properties of MTA.

Materials and methods

The materials used in this study included white Portland cement [WPC; Italcementi SPA, Bergamo, Italy manufactured to BS EN 197-1; (British Standard Institution 2000), type CEM I, Portland cement strength class 52,5N] and bismuth oxide (Fischer Scientific, Leicester, UK). Bismuth oxide was added to the Portland cement by replacing 10, 15, 20, 25 and 30% of the cement powder by weight. White Portland cement without bismuth oxide was used as a control. The original cement and the cements with bismuth oxide replacements were mixed with water at a powder to water ratio of 1 : 0.37 by weight. This ratio was chosen after performing a standard consistence test [BS EN 196-3; (British Standard Institution 2005)] to determine the amount of water required by this particular cement.

Compressive strength

The compressive strength testing was conducted in accordance to EN 9917-1 (2003) with a modification in specimen dimensions. Cylinders 6 mm in diameter and 12 mm high were cast rather than using the suggested 4 mm diameter and 6 mm height. The cements were cast in three increments and vibrated for a minute per increment to avoid entrapped air. The specimen and mould assemblies were stored in an incubator at 37 °C and 100% humidity for 1 day after which the cylinders were removed from the moulds and cured in water at 37 °C for 28 days. The specimens were tested after 28 days to allow adequate cement curing. Twelve cylinders were prepared for each material tested. The cylinders were compressed using a compression machine (Lloyd Instruments Ltd, Fareham, UK) with a cross-head speed of 1 mm min^{-1} until failure in accordance with BS EN 9917-1 (British Standard Institution 2003). The maximum load required to fracture the samples was noted. Compressive strength was calculated using the formula:

$$\text{Compressive strength} = \frac{\text{Applied load}(N)}{\text{Area}(\text{mm}^2)}$$

Radiopacity

The experimental protocol was based on ISO 6876, Section 7.8 (2002). The Portland cement was mixed with distilled water, at a powder to water ratio of 1 : 0.37

by weight. Cements with different bismuth oxide additions as in the previous experiment were also prepared. The mixes were compacted into stainless steel ring moulds 10 mm in diameter and 1 mm high, and pressed against two glass cover slips to make the specimen 1 mm thick. Two specimens of each material were prepared. The cements were allowed to cure for 24 h at 37 °C covered by a plastic sheet to avoid cement desiccation after which they were removed from the moulds. The cements were placed directly on a cassette loaded with a cephalostat type film with an intensifying screen (Kodak, Rochester, NY, USA) adjacent to an aluminium step wedge with 11 steps each step being 3 mm high (Everything X-ray, High Wycombe, UK) and irradiated with X-rays using a Cephalostat (Orthoralix S, Gendex, Dental Systems, Medivance Instruments Ltd, London, UK) at tube voltage of 64 kV, and current 3 mA and exposure time of 0.5 s. This procedure was used in order to maintain a set target to film distance of 505 mm. Two specimens per material under test were arranged on the cephalostat film and two x-rays were taken of the specimens (Film 1 and Film 2). Eight layers of lead foil were used with each film to ensure that a small section of the film received no exposure. The radiographs were processed in an automatic processing machine (Clarimat 300, Gendex Dental Systems, Medivance Instruments Ltd, London, UK). A photographic densitometer (PTW densix, Freiburg, Germany) was used to take readings of the density of the radiographic image of the specimens, each step of the step wedge and the un-exposed part of the film. Three readings of each material were taken for each radiograph of each specimen and the mean density calculated. The net radiographic density was calculated by subtracting the base and fog value from the gross radiographic density. The base and fog value is the inherent optical transmission density (lowest density) of a film base plus the nonimage density contributed by the developed emulsion. Graphs were plotted for net radiographic density (NRD_{AL}) of the aluminium steps (NRD_{AL}) versus the logarithm of the thickness of aluminium (log d) for each radiograph taken. From the resultant plots, the gradient and the intercept were calculated for each film. Linear regression of the data was obtained using the following formula:

$$NRD_{AL} = m.\log d + I$$

where NRD_{AL} was the net radiographic density of the aluminium step wedge, m was the gradient, log d was the logarithm of the step height, I was the intercept. By rearranging the above equation into:

$$\log d = \frac{(I - NRD)}{-m}$$

the logarithm of the relevant thickness of aluminium for each material could be calculated from its net radiographic density for each film taking into consideration that specimen thickness was 1 mm. Logarithms of step height were then converted to thicknesses of aluminium (Watts & McCabe 1999).

Statistical analysis

The compressive strength data was evaluated using SPSS (Statistical Package for the Social Sciences) software (SPSS Inc., Chicago, IL, USA). The distribution was first evaluated to select the appropriate statistical analysis. The data was plotted and the distribution curve was analysed together with the Kolmogorov–Zmirnov test with $P = 0.05$. A normal distribution was signified by $P > 0.05$, thus parametric tests were performed. Analysis of Variance (ANOVA) with $P = 0.05$ was first performed to evaluate variation between the means. In addition, once a significant variance was detected between the data analysed, the Tukey test was used to perform multiple comparison tests to determine which means differed.

Results

Compressive strength

The results for compressive strength testing of the cements are shown in Fig. 1. All the cements tested including the control showed compressive strength values higher than 50 Nmm^{-2}, which is the minimum recommended by BS EN 9917-1 (British Standard Institution 2003) for dental water-based cements. There is no minimum requirement for root-end filling materials. There was no statistically significant difference between the cements with various proportions of bismuth oxide and the white Portland cement ($P > 0.05$) cured for 28 days. There was a difference between the 10% bismuth oxide replacement and the 30% bismuth oxide replacement with the 30% bismuth oxide replacement showing significantly higher ($P = 0.0006$) compressive strength values.

Radiopacity

The base and fog value for Film 1 was 0.23 and that for Film 2 was 0.24. Subtraction of these values from the gross radiographic density resulted in the net

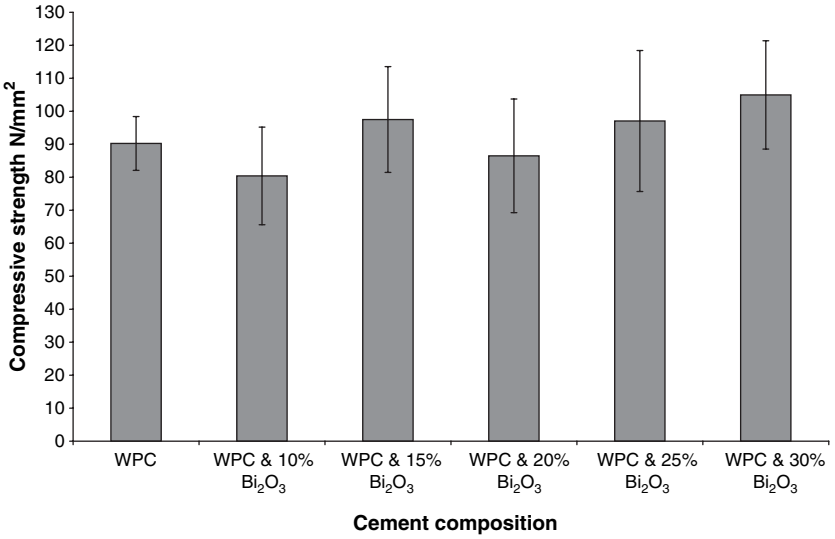

Figure 1 Compressive strength testing of cement cylinders with varying additions of bismuth oxide ± SD (n = 12).

radiographic density of the aluminium step wedge. The plots of resultant net radiographic density against the logarithm of the step height for both films had a gradient: −1.91 for Film 1 and −1.7 for Film 2 with an intercept of 2.74 and 2.4, respectively. The results for mean thickness of aluminium compared with the relevant bismuth oxide replacement cements are shown in Fig. 2. All the cements tested with the exception of un-modified Portland cement had a radiopacity of at least 3 mm Aluminium, which is the minimum recommended by BS EN ISO 6876 (British Standard Institution 2002).

Discussion

In the present study the effect of additions of varying bismuth oxide concentrations to Portland cement was investigated. The main constituent phases of MTA are the same as those of Portland cement (Camilleri *et al.* 2005). MTA is composed of ASTM type 1 Portland

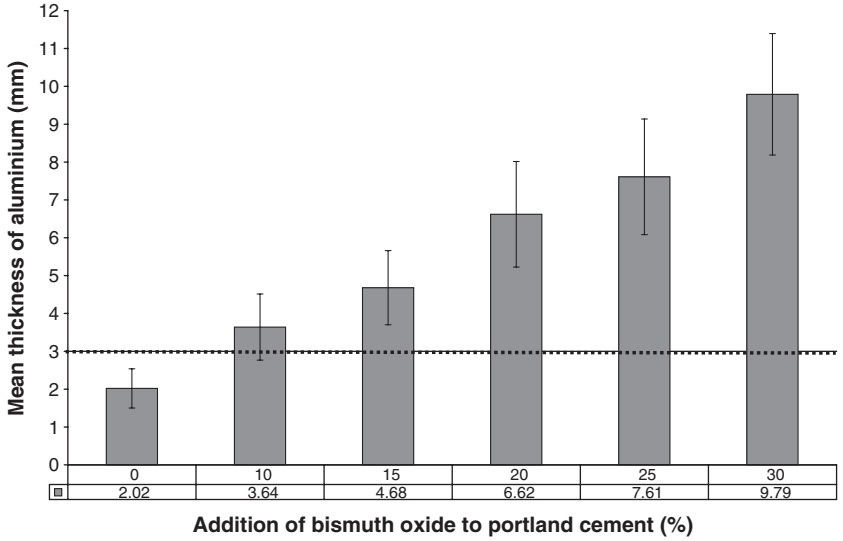

Figure 2 Radiopacity of cement with varying additions of bismuth oxide expressed as mean thicknesses of Aluminium ± SD (n = 2). The dotted line shows the minimum value for radiopaque restorative material.

cement and bismuth oxide (Torabinejad & White 1995). ASTM Type 1 cements and CEM 1 cements are the same; the only difference being the mode of classification (Neville 1981). Thus, the results of the present study have implications for MTA and the likely effects on its physical properties. The bismuth oxide was added by replacing the amount by weight in percentages varying from 10–30%. Mineral trioxide aggregate (ProRoot^{TM}) has been reported as having a 20% replacement of bismuth oxide (Torabinejad & White 1995).

The compressive strength of cements under study was conducted using the method described in BS EN ISO 9917-1 (British Standard Institution 2003). This standard specifies the testing of physical properties of dental water-based cements and advises the use of moulds producing cylinders 4 mm in diameter and 6 mm high. In this experiment, cylinders 6 mm in diameter and 12 mm in height were used giving a height to diameter ratio of 2. This method was adopted in previous studies testing MTA and related materials (Camilleri *et al.* 2006). The strength of cylinders with a height to diameter ratio 2 is not influenced by the restraining effects of the loading plates. Higher values than 2 may lead to buckling of the specimens and lower values require the use of a correction factor when calculating the compressive strength (Neville 1981). No packing material was used to minimize friction between the loading plates and the specimen. If the surfaces tested are not even, the effective contact area between the specimen and the bearing plate can be reduced.

The optical radiographic density of the materials under study was evaluated using a densitometer (Higginbotham 1967) and an aluminium step-wedge as reference (Eliasson & Haasken 1979). The use of digitized X-rays and comparison of the grey pixel value has been reported (Tagger & Katz 2003, Carvalho-Junior *et al.* 2007). The problem with the use of aluminium step wedges lies in the composition of the aluminium as pure aluminium is very difficult to machine due to its softness. The use of aluminium alloys which are easier to machine makes comparisons difficult (Watts & McCabe 1999). Other variables include the target to film distance, although it has been reported that varying the target to film distance does not affect the radiopacity as long as the samples were properly exposed (Gu *et al.* 2006).

Bismuth oxide is added to MTA as a radiopacifying agent in 1 : 4 proportions (Torabinejad & White 1995). In the present study 20% bismuth oxide was added to CEM 1 Portland cement to mimic ProRoot^{TM} MTA. The compressive strength values of the 20% bismuth oxide replacement were similar to that reported by other researchers for white MTA (Islam *et al.* 2006, Holt *et al.* 2007, Nekoofar *et al.* 2007). It has been shown that bismuth affects the hydration mechanism of MTA (Camilleri 2007). SEM analysis of the MTA set structure revealed that bismuth formed part of the structure of silicate hydrate gel, which is the main by-product of cement hydration and also affected the precipitation of calcium hydroxide in the hydrated paste (Camilleri 2007).

The results of this study are at variance with a previous study (Camilleri 2008) where it was demonstrated that 20% addition of bismuth oxide to cement clinker reduced the strength considerably at all curing times. Other researchers (Coomaraswamy *et al.* 2007) also reported a reduction in compressive strength of the cement with increasing levels of bismuth oxide. In this study (Coomaraswamy *et al.* 2007) the specimens were tested after 10 days of curing in comparison to the present study where the specimens were tested after 28 days. In the present study there seemed to be no changes in the results of compressive strength testing on addition of various percentages of bismuth oxide. The variation in the results of compressive strength testing lies in the different testing regimes used. These variables include the use of different specimen sizes, specimen shape, the loading rate and end preparation of the specimen as discussed by Camilleri *et al.* (2006).

Mineral trioxide aggregate has been shown to have a radiopacity equivalent to 7.17 mm (Torabinejad *et al.* 1995), 6.4 mm (Laghios *et al.* 2000) and 5.34 mm (Danesh *et al.* 2006) aluminium. These values are similar to those reported in this experiment for 20% bismuth oxide replaced Portland cement. The values reported for Portland cement in this experiment were also in agreement with other publications (Danesh *et al.* 2006) who reported the radiopacity of CEM 1 cement to be 3.32 mm of Al. All the bismuth oxide replaced cements in this study had radiopacities greater than 3 mm of aluminium, which is the minimum requested by the BS EN ISO 6876 (British Standard Institution 2002). The present study suggests that 20% bismuth oxide is higher than is required for radiopacity whilst maintaining other physical properties of the material at appropriate levels.

Conclusions

Addition of bismuth oxide did not seem to affect the compressive strength of Portland cement. All the

bismuth oxide replaced cements had radiopacities higher than 3 mm thickness of aluminium.

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