The physical properties of accelerated Portland cement for endodontic use

J. Camilleri

Department of Building and Civil Engineering, Faculty of Architecture and Civil Engineering, University of Malta, Malta

Abstract

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Aim To investigate the physical properties of a novel accelerated Portland cement.

Methodology The setting time, compressive strength, pH and solubility of white Portland cement (Lafarge Asland; CEM 1, 52.5 N) and accelerated Portland cement (Proto A) produced by excluding gypsum from the manufacturing process (Aalborg White) and a modified version with 4 : 1 addition of bismuth oxide (Proto B) were evaluated.

Results Proto A set in 8 min. The compressive strength of Proto A was comparable with that of Portland cement at all testing periods (P > 0.05). Additions of bismuth oxide extended the setting time

and reduced the compressive strength (P < 0.05). Both cements and storage solution were alkaline. All cements tested increased by >12% of their original weight after immersion in water for 1 day with no further absorption after 28 days. Addition of bismuth oxide increased the water uptake of the novel cement (P < 0.05).

Conclusions The setting time of Portland cement can be reduced by excluding the gypsum during the last stage of the manufacturing process without affecting its other properties. Addition of bismuth oxide affected the properties of the novel cement. Further investigation on the effect that bismuth oxide has on the properties of mineral trioxide aggregate is thus warranted.

Keywords: improved physical properties, mineral trioxide aggregate, prototype cements.

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Introduction

Mineral trioxide aggregate (MTA) is used mostly in Endodontics. Two commercial forms of MTA are available; ProRoot and White MTA (Tulsa Dental Products, Tulsa, OK, USA) both with similar chemical and physical properties and MTA Angelus (Angelus Soluções Odontológicas, Londrina, Brazil). MTA is Portland cement with 4 : 1 proportions of bismuth oxide added for radio-opacity (Torabinejad & White 1995). Camilleri *et al.* (2005a) have shown using X-ray diffraction analysis that MTA is composed primarily of tricalcium, dicalcium silicate and bismuth oxide, which on hydration produce a silicate hydrate gel and calcium hydroxide, thus rendering the material biocompatible. Cells were shown to proliferate on the elution made up of calcium hydroxide extracted from the material (Camilleri *et al.* 2005b).

One of the main disadvantages when using MTA is its extended setting time (Torabinejad *et al.* 1995, Islam *et al.* 2006) and difficult handling. In industry, the setting time of Portland cement is controlled by grinding the cement with gypsum at the end stage of the manufacturing process (Neville 1981). The gypsum is added by cement manufacturers to retard the setting time of the cement clinker. Removal of gypsum results in a flash-set, which can be controlled by the use of a superplasticizing admixture which makes the material

Correspondence: Dr Josette Camilleri, Department of Building and Civil Engineering, Faculty of Architecture and Civil Engineering, University of Malta, Malta (Tel.: 356 2340 2870; fax: 356 21330190; e-mail: josette.camilleri@um. edu.mt).

more workable (Neville 1981). Superplasticizers are very effective dispersing agents used to reduce the water content of the mix and retain its workability. Water can be reduced at equivalent flow with an increase in compressive strength (Hattori 1978). Significant reduction in setting time could be advantageous when using the material as the number of visits could be reduced.

There is very little experimental evidence on the physical properties of MTA. Only two publications (Torabinejad *et al.* 1995, Islam *et al.* 2006) report the setting time and compressive strength of the material. In the early publication (Torabinejad *et al.* 1995) the experimental evidence is based on the prototype version of the material. There is also limited evidence on MTA Angelus with publications limited to chemical (Duarte *et al.* 2003, Santos *et al.* 2005), and biological (Menezes *et al.* 2004, Ribeiro *et al.* 2005) properties of the material.

The pH of both proprietary brands was reported to be alkaline (Torabinejad *et al.* 1995, Duarte *et al.* 2003, Santos *et al.* 2005). The solubility of MTA in water was shown to be low in some studies (Torabinejad *et al.* 1995, Danesh *et al.* 2006, Islam *et al.* 2006) in contrast to a high solubility shown in other studies (Fridland & Rosado 2005).

Novel cement Proto A was produced by intergrinding the cement clinker without gypsum and mixing it with water and superplasticizer. It has been shown (Camilleri et al. 2005b) that both Proto A and MTA were made of similar constituent elements and phases, namely tricalcium and dicalcium silicate. Both cements were shown to have similar biocompatibility (Camilleri et al. 2005b). The advantage of using the novel cement Proto A is its reduced setting time and better handling properties. The reduced setting time reduces the number of visits per treatment when the cement is used for apexification procedures as the tooth can be restored in the same visit. When used as a rootend filling material the fast set reduces the risk of dislodgement and contamination. The better handling makes it easier to place the material where required. An increased flow can make the material suitable for use as root canal sealer cement.

Mineral trioxide aggregate has a 4 : 1 addition of bismuth oxide which is added to the cement for radioopacity (Torabinejad & White 1995). Bismuth oxide has also been added to Proto A to produce Proto B which is fast setting and has similar biocompatibility to Proto A and MTA (Camilleri *et al.* 2005b). Proto B should have similar physical properties to MTA. The aim of the present study was to investigate the physical properties of the novel fast-setting cements for endodontic use.

Methodology

The materials used in this study included:

1. White Portland cement (WOPC; Lafarge Asland, Valencia, Spain, EN 197-1 (British Standard Institution 2000a): 2000, type CEM 1; strength class 52.5 N),

2. Portland cement clinker (Proto A; Aalborg White, Aalborg, Denmark), which consisted of white Portland cement clinker, inter-ground without gypsum,

3. Portland cement clinker and bismuth oxide (Fischer Scientific, Leicester, UK) in 4 : 1 proportion (Proto B).

White Portland cement was mixed with water at a water to cement ratio of 0.37 whilst both prototype cements were mixed with water and superplasticizer (Glenium Ace 30; Degussa Construction Chemicals, Manchester, UK) at a water to cement ratio of 0.30. The superplasticizer was used to obtain a homogeneous flowable mix as the lack of gypsum tended to flash-set the cement.

Setting time

The setting time of Portland cement, and both prototype cements was determined using the Vicat apparatus (ELE International, Leighton Buzzard, UK). The tests were performed according to EN 196-3 (British Standard Institution 1995). A total of 400 g of the cement were mixed on a moistened aluminum tray with a small trowel. It was then compacted in a twopart brass mould and initial and final setting times were determined. The Vicat assembly was placed in a water bath at 37 °C. The test was repeated three times.

Compressive strength

For testing the materials in compression specimens 6 mm in diameter and 12 mm high were made by casting the cements in brass moulds 6 mm in diameter and 16 mm high with 2 mm caps at both ends (A. Majekodunmi, personal communication). A vibrator was used to avoid entrapped air. The cylinders were stored in an incubator at 37 °C and 100% humidity. Six cylinders were made for each cement type. Compressive strength testing was performed after 1, 7 and 28 days using a Universal testing machine (Instron 1195; High Wycombe, UK) with a cross-head speed of 1 mm min⁻¹.

pН

The pH of the cements was determined during setting and for a period of 28 days. Two grams of cement were mixed on a glass slab. The pH was evaluated using a pH meter (Hydrus 100; Fischer Scientific) with a temperature compensated electrode during mixing. After mixing the materials were compacted into metal moulds producing discs 10 mm in diameter. Six discs were made for each material. The materials were allowed to cure in the moulds for 24 h at 37 °C and 100% humidity by using a chamber with controlled temperature and humidity levels (Climatic Test Chamber; Weiss Instruments Inc., Holtsville, NY, USA). pH determinations were made at 1 and 5 h, and 1 day after mixing before the removal from moulds. pH was determined directly by placing the pH probe on the pre-moistened surface of the cement. The discs were then removed from the moulds and the materials were placed in sealed containers filled with 5 mL distilled water. The containers were kept in an incubator at 37 °C; pH was determined after 7 and 28 days.

Water uptake

Discs 10 mm in diameter were made by mixing 1 g of material and casting it into circular moulds. The materials were allowed to set for 24 h at 37 °C and 100% humidity. They were then removed from the moulds and were cured in water for 28 days at 37 °C. Six samples were made for each cement type. The weight of the samples was recorded after 1, 7 and 28 days.

Statistical analysis

Data was evaluated using SPSS (Statistical Package for the Social Sciences; SPSS Inc., Chicago, IL, USA). The distribution was first evaluated to determine the appropriate statistical test. The data was plotted and the distribution curve was analysed together with the Kolmogorov-Zmirnov test with P = 0.05. P > 0.05signified a normal distribution thus parametric tests could be performed accordingly. With normally distributed data analysis of variance with P = 0.05 was first performed to evaluate any variation between the means. In addition, once a variance was detected between the data analysed, the Tukey test was used to perform multiple comparison tests to determine significant differences.

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Table 1 Setting time of cements \pm SD (n = 3)

The results for water uptake by the cements for a period of 28 days are shown in Table 2. All the cements

revealed high water absorption which rose at 1 day

and remained stable throughout the test period. There

Cement type	Initial set minutes	Final set minutes
White Portland cement	270 ± 8.3	468 ± 12.3
Proto A	5 ± 0.4	8 ± 1.2
Proto B	6 ± 0.4	12 ± 1.0

Results

Setting time

The setting time of the cements are shown in Table 1. Portland cement had an extended setting time in the order of hours as opposed to the prototype cements. Proto A set after 8 min. Proto B had a longer setting time than Proto A but this difference was not statistically significant.

Compressive strength testing

The results for compressive strength testing are shown in Fig. 1. The strength of Proto A was comparable with Portland cement at all time intervals (P > 0.05). Proto B had very low strengths at all time intervals when compared with both Portland cement and Proto A (P < 0.05).

Determination of pH

Water uptake

The pH of the cements at different time intervals are shown in Fig. 2. All the cements were alkaline on mixing with pHs ranging between 10 and 11. After mixing there was a drop in pH in the first hour (9.5 ± 0.5) with a further reduction in pH after 5 h and 1 day. The cylinders showed a rise in pH after 7 days in water. There was no statistically significant difference between pH of the materials at 1 and 5 h and at 7 and 28 days. At 1 day there was a difference in pH between the materials (P < 0.05). Proto A had a lower pH than Portland cement (P = 0.01) and Proto B (P = 0.01). After 1 week the solutions were alkaline with pHs in the range of 12. There was no statistically significant difference between the pHs of the different solutions tested.



Figure 1 Compressive strength testing of cylinders at different time intervals \pm SD; n = 6.



Table 2 Water uptake by cements over a period of 28 days \pm SD (n = 6)

	Water uptake % of original weight		
Material	1 day	7 days	28 days
White Portland cement	13.29 ± 1.2	13.97 ± 1.3	14.88 ± 1.3
Proto A	12.62 ± 3.8	13.54 ± 3.9	13.89 ± 3.8
Proto B	18.65 ± 2.3	18.75 ± 2.3	18.95 ± 2.0

was no statistically significant difference between the water absorption of the Portland cement and Proto A (P > 0.05). Proto B had the highest water absorption (18–19%) when compared with both Portland cement (P = 0.001) and Proto A (P = 0.008).

Discussion

The compressive strength testing of dental cements was performed according to ISO 9917-1 (2003) with some modifications. This standard utilizes moulds 4 mm in diameter and 6 mm high, i.e. a height to diameter ratio of 1.5. In concrete, a height to diameter ratio of two is suggested for testing cylinders (EN 12390-1 [British Standard Institution 2000b]). At this ratio forces developed uni-axially on the specimen are eliminated at the centre of the specimen and also there reduced risk of specimen buckling (Neville 1981). This size of moulds was also used by other researchers (Islam *et al.* 2006) but no reason for the change in mould dimensions from the standard was cited. In addition, these

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moulds also eliminated the problem with end planarity as the caps produced a smooth flat surface that did not require any grinding. End planarity is usually achieved by grinding the ends against a silicon carbide paper (EN ISO 9917-1 [British Standard Institution 2003]). End planarity is important when testing cylindrical specimens as pre-mature contact of any high spots with the platen surface of the testing machine can lead to an abnormal failure pattern with erroneous test results.

The prototype materials had a shorter setting time than the MTA and Portland cement. The setting time of Portland cement was in accordance with the results obtained by previous investigations (Islam et al. 2006). The clinker flash set on mixing with water as the absence of sulphate ions derived from the gypsum allowed the reaction of tricalcium aluminate to produce calcium aluminate hydrate. In the presence of sulphate the tricalcium aluminate reacts to produce ettringite (Lea 1998). The flash setting was controlled by the use of a superplasticizing admixture. This is in contrast to what was reported by other researchers (Dammaschke et al. 2005) who claimed that sulphate present in the cement accelerated the setting time of the cement. Significant reduction in setting time could be useful when using the material as the number of clinical appointments could be reduced.

The recorded strength of Portland cement in the present study was higher than Camilleri et al. (2006) who reported lower values for grey Portland cement when testing cylinders of similar dimensions. In contrast, other researchers reported higher strength values for Portland cement (Islam et al. 2006). Factors influencing the results of compressive strength testing include lack of planarity of the specimen ends, the loading rate, the specimen shape and size, and height to diameter ratio (Neville 1981). In this experiment and in a previous study (Camilleri et al. 2006) the problem of end planarity was eliminated by using moulds with caps at the end thus end trimming was not necessary to produce plane ends. The specimen size and shape and the height to diameter ratio was the same in all the publications reporting the compressive strength of Portland cement (Camilleri et al. 2006, Islam et al. 2006). Only the loading rate is not reported. An increased rate of loading will increase the apparent strength of the cement (Neville 1981).

Bismuth oxide is added to MTA as a radio-opacifying agent. It is added in 1 : 4 proportions (Torabinejad & White 1995). Proto B differed from Proto A in having 1 : 4 proportion of bismuth oxide added to the cement to mimic MTA. It has been shown that bismuth affects

the hydration mechanism of MTA. SEM analysis of the MTA set structure showed 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). Additions of bismuth oxide reduced the strength considerably at all curing times. This is in contrast to reports claiming that MTA had higher compressive strength values than Portland cement. After 28 days of curing MTA was claimed to achieve a compressive strength value of 98.62 Nmm⁻² as opposed to 50.66 Nmm⁻² reported for Portland cement (Islam et al. 2006). Portland cements should comply to EN 197-1 (2000) where the highest value quoted for cements at normal water to cement ratios without the addition of any admixtures to enhance the strength of the cement is 52.5 Nmm⁻² after 28 days of curing. Both publications evaluating the strength of MTA (Torabinejad et al. 1995, Islam et al. 2006) quote higher values for the MTA strength. The strength class of the cement used to produce MTA is not known but as the highest strength class quoted in the standards is 52.5 Nmm⁻² after 28 days of curing (EN 197-1, 2000) then it can be inferred that the bismuth oxide added to the MTA increased its strength. This is again not in accordance with the results obtained in this experiment. MTA used as a root-end filling material has been shown to have lower compressive strengths than amalgam, Intermediate Restorative Material (IRM) and Super Ethoxybenzoic acid (EBA) (Torabinejad et al. 1995). In this publication, the prototype material had been used and bismuth oxide was not mentioned as one of the constituent compounds. Thus, if the bismuth oxide reduces the material strength further as has been demonstrated in the present study then the strength of MTA will be too low for use as a dental restorative material even in nonstress-bearing areas. The limitation in the achievement of high strengths in Portland cement lies in the inherent porosity of the material. Union between grains is attained through reactions with water that produce a hybrid solid phase in the form of a colloidal gel-like material with a high surface area. Porosity results from excess water required for casting, poor dispersion and flocculation of cement particles, and the presence of air in the suspension (Diamond 1976).

The cement showed a high pH on mixing. The pH was lowered during setting until 1 day. After 1 day the cements were immersed in water. Prior to immersion in water the reduction in pH could have been caused by lack of calcium hydroxide in solution as the cements

were kept at 100% humidity rather than in solution. In addition, surface carbonation could have occurred. The calcium hydroxide produced from the hydration reaction of the cement (Lea 1998) could have reacted with the carbon dioxide in air to produce calcium carbonate thus neutralizing the surface pH of the cement. On immersion in water the pH became more alkaline. The pH of the storage solution was always maintained at 12. Further investigations are required to establish what is leached out in solution.

Both prototype materials and Portland cement showed high water uptake. The water was taken up during the first day with practically no changes for the next 28 days. This is in agreement with a previous study (Danesh et al. 2006) where Portland cement was shown to absorb water. Proto B absorbed more water than Proto A, thus the addition of bismuth oxide seemed to increase the water absorption of the material. This is in contrast to previous studies which reported MTA, which is Portland cement with additions of bismuth oxide to absorb no water (Torabinejad et al. 1995, Danesh et al. 2006, Islam et al. 2006) but in agreement with Fridland & Rosado (2005) who reported a high water uptake for MTA. Water absorption will make the material swell thus improving the seal between the material and the dentine with a potential to reduce microleakage. However, as the water is absorbed within the material there will be an increased risk of leakage within the material itself as increased water levels will increase the porosity of the material. The microleakage through dental materials has never been reported. Excessive expansion can also lead to increased risk of root fractures.

The novel cement Proto A had reduced setting time and its use could enable shorter chair-side time and reduce the number of patient visits. Having a material that can set in 8 min can reduce the risk of dislodgement after placement. The addition of a superplasticizing admixture did not seem to interfere with the biocompatibility of the material (Camilleri et al. 2005a). The use of the admixture improved the material handling thus making it easier to place and compact. In addition, the increased flow could enable the use of Proto A as root canal sealer cement which is not possible with MTA. The compressive strength of Proto A are comparable with Portland cement. However, the strength values of Portland cement in this study are different to those reported elsewhere (Camilleri et al. 2006, Islam et al. 2006), and are also lower than strength values reported for MTA (Torabinejad et al. 1995, Islam et al. 2006). The reason for this discrepancy should be investigated. Thus, the novel cement Proto A could replace MTA for use in Endodontics. The addition of bismuth oxide seemed to affect the material properties adversely. The affect of bismuth oxide on MTA should be further investigated together with the possibility of using an alternative radio-opacifying agent.

Conclusions

The setting time of Portland cement can be reduced by excluding the gypsum during the last stage of the manufacturing process without affecting its other properties. The new prototype cement had improved workability and a reduced setting time. This could reduce chair-side time and the number of visits. Addition of bismuth oxide reduced the compressive strength and increased the water uptake of the cement at all ages. Further investigation on the effect of bismuth oxide on the properties of MTA is thus warranted.

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