Physico-chemical properties of MTA and a novel experimental cement

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Abstract

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Aim To evaluate the release of calcium ions, pH and conductivity of a new experimental dental cement (EC) and to compare them with those of mineral trioxide aggregate (MTA-Angelus).

Methodology Five samples of each cement were prepared using plastic tubes 1 mm in diameter and 10 mm long. Each sample was sealed in a test tube containing 10 mL deionized water which was analysed after 24, 48, 72, 96, 192, 240 and 360 h for pH, electrical conductivity and calcium release. The concentration of calcium ions was obtained through atomic absorption spectroscopy technique. The data were analysed statistically using the analysis of variance (ANOVA) and the Student's test (*t*-test).

Results The pH of the storage solutions was not affected by the material and the interaction of material with time ($P > 0.05$). However, the time of immersion was significant ($P < 0.01$) for both materials. For the electric conductivity and calcium release, the interaction of material with time was statistically significant ($P < 0.01$), indicating that EC and MTA-Angelus did not behave in a similar manner.

Conclusions The experimental cement released calcium and increased the pH of the storage solutions in a similar manner to MTA-Angelus. However, EC showed significantly higher calcium release than commercial MTA-Angelus after 24 h.

Keywords: electrical conductivity, mineral trioxide aggregate, pH, Portland cement, release of ions.

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Introduction

Mineral trioxide aggregate (MTA) was described for the first time in the dental literature by Lee *et al.* (1993). Since that time, it has been widely investigated and the results confirm that it has excellent physical (Torabinejad *et al.* 1993, 1995a, Abedi & Ingle 1995, Herzog-Flores *et al.* 2000), chemical (Torabinejad *et al.* 1993, 1995a, Abedi & Ingle 1995, Herzog-Flores *et al.* 2000), and biologic (Abedi & Ingle 1995, Torabinejad *et al.* 1995b, Holland *et al.* 1999, Schawartz *et al.* 1999, Holland *et al.* 2002, Duarte *et al.* 2003) properties. MTA is a white or grey powder of fine hydrophilic particles consisting of compounds of tricalcium silicate, tricalcium oxide, tricalcium aluminate and silicate oxide (Lee *et al.* 1993).

Several studies have reported that MTA is similar to commercial Portland cement (Holland *et al.* 1999, Wucherpfenning & Green 1999, Estrela *et al.* 2000, Holland *et al.* 2001a,b). It is commercially available as ProRoot MTA (Dentsply Tulsa Dental, Tulsa, OK, USA). Recently, a new cement was launched commercially labelled as MTA-Angelus (Angelus Soluções Odontológicas, Londrina, Brazil). This material is composed of 80% Portland cement and 20% bismuth oxide (Duarte *et al.* 2003).

One of the difficulties reported by clinicians when using MTA is its poor handling characteristic and lengthy setting time. On the other hand, there is interest in expanding the applications of MTA as a root canal filling material (Holland *et al.* 1999, Maroto *et al.*

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2003). An experimental endodontic cement (EC) has been developed that is a composition of Portland cement, a gel composed of water, barium sulphate and an emulsifier with the function of improving the handling properties.

Ideally, sealer cements should have an antimicrobial action (Torabinejad *et al.* 1995c) and the ability to stimulate the formation of a mineralized tissue barrier (Holland *et al.* 1999, 2001a,b). Antimicrobial activity is related to the release of hydroxyl ions (Estrela & Pesce 1996), increasing pH and creating an unfavourable environment for bacteria to survive. MTA raises the pH of connective tissue and promotes antibacterial effects (Torabinejad *et al.* 1995c, Estrela *et al.* 2000). On the other hand, the formation of a barrier is promoted by the release of Ca^{2+} in adjacent tissues (Tamburic *et al.* 1993, Holland *et al.* 2002). Holland *et al.* (1999) showed that MTA stimulated hard tissue deposition and suggested that the formation mechanism started with calcium ions release from MTA. These important properties justify the need to know and understand the variation of pH and Ca^{2+} released from sealer cements in aqueous solution.

The aim of this study was to report the results of studies on Ca^{2+} release, pH and electrical conductivity of an experimental cement (EC), and to compare them with those of MTA-Angelus (Angelus Soluções Odontológicas). The conductivity measurements were aimed at confirming whether the calcium in the aqueous solution was predominantly ionic.

Material and methods

Five samples were prepared for each cement (EC and MTA-Angelus), using plastic tubes 1 mm in diameter and 10 mm long. The MTA-Angelus material was mixed with distilled water, manipulated on a glass plate with a steel spatula, in the proportion stipulated by the manufacturer. For EC, the procedure was the same, but the proportion of powder and gel was determined when the mix become a 'putty' consistency. The pastes were inserted into the tubes using a dental motor and handpiece along with a MacSpaddem compactor (Dentsply Maillefer, Ballaigues, Switzerland). In order to standardize the mass placed into each tube, the tubes were weighed before and after filling.

Each filled tube was sealed in a flask containing 10 mL deionized water and stored at 36 °C and a relative humidity between 90 and 100%. After 24 h of immersion, the tubes were carefully removed and placed into another flask with an equal amount of new deionized water for the same period of time. This procedure was repeated for a total of 360 h with the solution changed at 24, 48, 72, 96, 192, 240 and 360 h.

The same stock solution contained in each flask was used to determine the pH, electrical conductivity and calcium release. For measurement of pH, a Q-400 Quimis instrument (Quimis Aparelhos Científicos, São Paulo, Brazil) that was calibrated with standard solutions at pH 4.0 and 7.0 was used. Electrical conductivity was carried out with CD20 Digimed conductivimeter (Digicrom Analítica Ltda, Campo Grande, Brazil) and a standard reference solution of 1.412 mS cm^{-1} at 25 °C was used for calibration. A Spectraa 55B atomic spectrophotometer (Varian, Inc., Palo Alto, CA, USA) was used to determine the Ca^{2+} concentration. Lanthanim oxide was added to all samples to eliminate ionic interference, particularly from phosphate ions. Solutions containing calcium concentrations of 0, 1, 2, 3, 4 and 5 ppm were used to create a standard calibration curve.

The data of the dependent variables (pH, electric conductivity and calcium release) were submitted to analysis of variance, considering a mathematical model with the factors Material (EC and MTA-Angelus), time of immersion (0, 24, 48, 72, 96, 192, 240 and 360 h) and the interaction between material and time. For analysis of the mathematical model and to test the correlation amongst dependent variables the General Linear Model (GLM) and the Student's *t*-test procedures were used, respectively.

Results

Figures 1–3 show the measurements of pH, Ca^{2+} concentration and electrical conductivity data of solu-

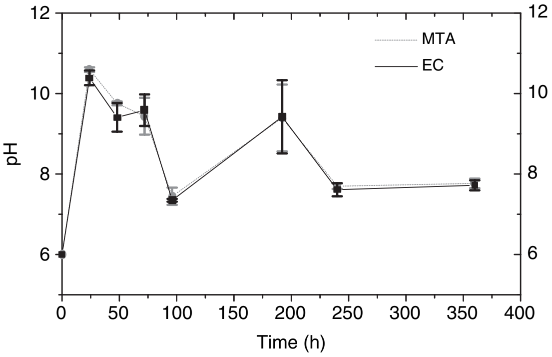

Figure 1 Comparison between EC and MTA of obtained values of pH as a function of immersion time.

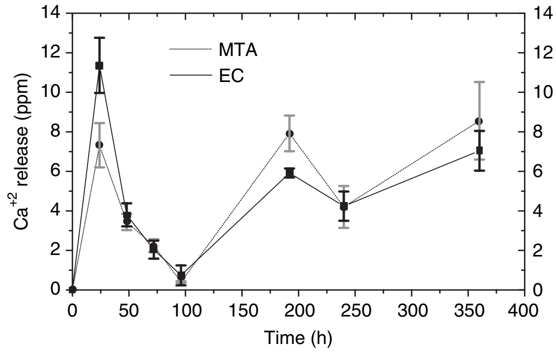

Figure 2 Comparison between EC and MTA of obtained values of Ca^{2+} release as a function of immersion time.

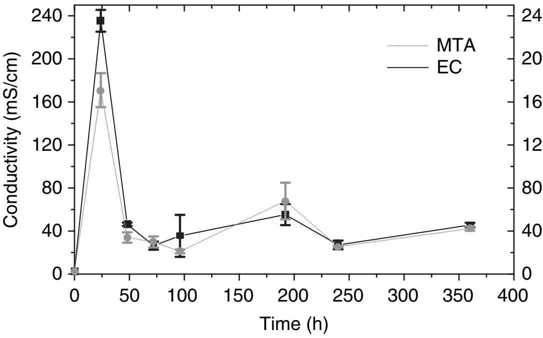

Figure 3 Comparison between EC and MTA of obtained values of electrical conductivity as a function of immersion time.

tions as a function of time for EC and MTA samples. Each point represents the mean value of five measurements. The data corresponding to 0 h refers to the aqueous solution before it received the specimen.

Table 1 summarizes the results of the analysis of variance. Table 2 presents details of analysis of the material/time interaction at each immersion time.

Discussion

A similar methodology was used by Duarte *et al.* (2003) to evaluate the ions released from ProRoot and MTA-Angelus cements. The time of immersion differed from the present study making it difficult to compare the results for pH measurements and calcium release. However, some general comments are possible. For example, in the first 24 h the pH value reported in the present study was higher than that obtained by Duarte *et al.* (2003). An explanation for the observed difference is that the storage solution was changed after the first 3 h in the experiment of Duarte *et al.* (2003). The same variation in the values of pH and of calcium release with time was also observed by Duarte *et al.* (2003). The results they obtained did not show significant difference in the pH values and calcium release between ProRoot and MTA-Angelus cements.

In the pH measurements (Fig. 1) an obvious increase in the first 24 h was observed, indicating that the

Table 1 Analysis of variance

		F		
	DF	PH	Ca^{2+} release	Conductivity
Material (*M*)	1	0.47 ($P > 0.05$)	0.42 ($P > 0.05$)	17.33 ($P < 0.01$)
Time (*T*)	7	189.75 ($P < 0.01$)	164.48 ($P < 0.01$)	555.86 ($P < 0.01$)
$M \times T$ interaction	7	0.48 ($P > 0.05$)	11.42 ($P < 0.01$)	19.86 ($P < 0.01$)

DF, degree freedom; *F*, value of the *F*-test; $M \times T$, interaction between material and time; *P*, minimum level of significance.

Table 2 Analysis of the effect of the material × time interaction (*F*-test) for dependent variables and mean values of the materials at each immersion time

		pH			Ca^{2+} release			Conductivity		
			Mean			Mean			Mean	
Time of storage	DF	*F*-test	EC	MTA	*F*-test	EC	MTA	*F*-test	EC	MTA
Initial time	1	0.00 ($P = 1$)	6.00	6.00	0.00 ($P = 1$)	0.00	0.00	0.00 ($P = 1$)	2.50	2.50
After 24 h	1	0.88 ($P > 0.05$)	10.59	10.39	57.26 ($P < 0.01$)	11.36	7.32	148.00 ($P < 0.01$)	235.40	170.90
After 48 h	1	2.59 ($P > 0.05$)	9.76	9.41	0.45 ($P > 0.05$)	3.80	3.44	5.42 ($P < 0.05$)	46.30	33.96
After 72 h	1	0.47 ($P > 0.05$)	9.44	9.59	0.14 ($P > 0.05$)	2.04	2.24	0.42 ($P > 0.05$)	26.46	29.92
After 96 h	1	0.21 ($P > 0.05$)	7.45	7.35	0.41 ($P > 0.05$)	0.74	0.40	7.40 ($P < 0.01$)	35.50	21.08
After 192 h	1	0.02 ($P > 0.05$)	9.39	9.42	14.03 ($P < 0.01$)	5.92	7.92	5.70 ($P < 0.05$)	55.24	67.90
After 240 h	1	0.16 ($P > 0.05$)	7.70	7.61	0.01 ($P > 0.05$)	4.24	4.2	0.08 ($P > 0.05$)	27.10	25.58
After 360 h	1	0.05 ($P > 0.05$)	7.77	7.72	8.10 ($P < 0.01$)	7.04	8.56	0.37 ($P > 0.05$)	45.54	42.32

cements released OH^-. The same effect was observed in calcium release (Fig. 2). The main constituents of Portland cement are: tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. During setting, hydration reactions take place that result in the production of calcium hydroxide, largely because of the reactions involving dicalcium and tricalcium silicates. When the specimens were introduced into test tubes containing the aqueous solution, the calcium hydroxide dissociated into calcium and hydroxyl ions, increasing the pH and calcium concentrations in the medium.

Table 2 highlights that there was no significant difference between the pH values obtained for the two cements at each immersion time. However, there was a significant difference ($P < 0.01$) between the immersion times. It was also observed that the material/time interaction was significant ($P < 0.01$) for conductivity and calcium ion release (Table 1). In the initial hours, the EC liberated more Ca^{2+} than the MTA, increasing the electrical conductivity more rapidly and also increasing the pH of aqueous solution because of hydroxyl ion release. Both cements behave in the same manner, releasing great quantities of ions initially, with a tendency to release fewer ions between the interval 24–96 h.

The variation of conductivity (Fig. 3) as a function of immersion time had a similar behaviour to the release of ions (Fig. 2). The correlation between electrical conductivity and release of ions was significant ($P < 0.01$), confirming that the calcium ions in aqueous solution were predominantly dissociated. Furthermore, from the statistical analysis, a high correlation was observed amongst the three variables (between pH-conductivity $r = 0.66$ and $P < 0.01$, pH-Ca release $r = 0.56$ and $P < 0.01$, conductivity-Ca release $r = 0.74$ and $P < 0.01$) independent of the type of material.

The similarity observed between the materials which were investigated indicates potentiality to use of the EC as an endodontic cement. However, it is necessary to investigate other properties of the material.

Conclusions

The experimental cement released calcium and hydroxyl ions comparably with those released by MTA-Angelus. After 24 h, the calcium ion release by EC was greater than MTA, but following this initial period, the values were similar. The two cements released calcium ions and hydroxyl ions up to 360 h storage in aqueous solution.

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