Effect of additives on the compressive strength and setting time of a Portland cement

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Abstract: Improvements in strength and setting time of Portland cements (PC) are needed to enhance their performance as endodontic and load bearing materials. This study sought to enhance the compressive strength and setting time of a PC by adding one of the following additives: 20% and 30% poly-methylmethacrylate (PMMA), 20% and 30% irregular and spherical amalgam alloys, and 10% $CaCl_2$. The control consisted of unreinforced PC specimens. Setting time was determined using a Gillmore apparatus according to standardized methods while compressive strength was measured using a universal testing machine after 21 hours or 60 days of water storage. Data were analyzed by ANOVA, Tukey and Games-Howell tests (α = 5%). All additives significantly decreased both initial and final setting times as compared with the PC-control (p < .05). 30% PMMA and 30% irregular alloy had the lowest values of initial setting time. 30% irregular alloy also produced the lowest values of final setting time while 30% spherical alloy yielded the highest (p < .05). No differences were detected between the compressive strength values of 21 hours and 60 days. While 10% $CaCl_2$, 20% and 30% PMMA produced values significantly lower than the PC-control, 30% spherical alloy significantly improved the compressive strength of the reinforced PC (p < .05). In summary, all additives significantly reduced the setting time and 30% spherical amalgam alloy yielded a significant increase in compressive strength for the tested PC, which might represent an improved composition for PCs to expand their use as endodontic and potentially load bearing materials.

Descriptors: Dental cements; Endodontics; Compressive strength; Physical and chemical properties.

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Introduction

Mineral trioxide aggregate (MTA) is an endodontic cement composed of tricalcium silicate, tricalcium aluminate, dicalcium silicate, calcium sulfate dihydrate, and bismuth oxide.[1-3] MTA is a derivative of Portland cements (PCs), both having similar composition except for the presence of bismuth oxide in MTA, which is added for radiopacity.[2,4,5] Dental applications of MTA and PCs have been largely investigated, and it has since been suggested that they fulfill many of the ideal properties of endodontic materials, such as biocompatibility, good sealing and marginal adaptation.[1,6-11] Despite such favorable biological properties, the

indication of MTA and PCs for restorative purposes requires improvements in their chemical and mechanical properties.[4,6] Compressive strength and setting time of endodontic cements are critical for optimized clinical performance, and thus represent a significant advance for their use as restorative materials. Therefore, this study sought to enhance the chemical and mechanical properties of PCs aiming at providing impetus for the development of materials with equal restorative and endodontic capacities.

Commercial forms of MTA have shown extended setting time and lower compressive strength than restorative materials such as amalgam and Intermediate Restorative Material (IRM).[1] Various additives have been proposed to overcome these limitations. A recent investigation evaluated the influence of saline solution, lidocaine, NaOCl, chlorhexidine gluconate, K-Y jelly and different concentrations of $CaCl_2$ on the setting time of MTA and PCs.[12] Although $CaCl_2$, K-Y jelly and NaOCl gel yielded significant improvements in setting time, only NaOCl gel did not decrease the compressive strength of the tested materials.

The successful association of $CaCl_2$ to PCs has been recently reported[12] to reduce setting time and increase compressive strength. The compressive strength of oxide-eugenol cements has also been improved with the addition of poly-methylmetacrylate (PMMA).[13] Similarly, the addition of amalgam alloys to glass-ionomers has long been reported as an effective way to improve properties.[14] However, to the author's knowledge, PMMA and amalgam alloys have never been used to reinforce endodontic cements, and are hypothesized here to improve strength and reduce setting time. Therefore, in the current study PMMA, amalgam alloys and $CaCl_2$ were added to the composition of a PC and tested with the ultimate goal of reducing its setting time and increasing its compressive strength.

Materials and Methods

Materials used in this study are described in Table 1 while groups and their respective concentrations are presented in Table 2.

The concentration of each additive represents the weight percentage added to powdered PC before the addition of water to the mixture.

Setting time

Setting time experiments used a total of 72 specimens (n = 6) which were prepared by carefully pouring the cements into cylindrical metal molds (10 mm diameter x 1 mm) according to standardized procedures.[15] Two glass plates were than positioned at top and bottom of the molds to prevent post-setting expansion. Initial setting time was determined with a Gillmore apparatus one minute after mixing by applying a vertical load (190 g) on the surface of the specimens for 5 seconds. This process was repeated every 30 seconds. Final setting represented the time required from the starting point of mixing to the point when the indenter failed to penetrate the material with a load of 455 g. Results were initially

Table 1 - Materials used in this study.

Material (Brand)	Composition (%)	Manufacturer
Portland Cement (CP V ARI)	60.1 calcium oxide, 18.4 silicon oxide, 5.2 magnesium oxide, 4.3 aluminum oxide, 4.4 insoluble residue, 3.2 phosphorus trioxide, 2.6 iron oxide, 1.6 free calcium oxide	Companhia de Cimentos Itambé, Balsa Nova, PR, Brazil
$CaCl_2$	-	-
PMMA (Jet acrílico®)	Powder: MMA copolymer Liquid: MMA plus cross-linking agent	Clássico, São Paulo, SP, Brazil
Irregular Amalgam (Standalloy F®)	71 silver, 3.3 copper and 25.7 tin	Degussa Hüls, Guarulhos, SP, Brazil
Spherical Amalgam (GS 80®)	40 silver, 31.3 tin, and 28.7 copper	SDI, Melbourne, VIC, Australia

Table 2 - Groups and their respective concentrations.

Groups	Concentrations	
PC – control	-	
$CaCl_2$	10%	
Poly-methylmethacrylate (PMMA)	20%	30%
Irregular amalgam alloy	20%	30%
Spherical amalgam alloy	20%	30%

analyzed using a Kolmogorov-Smirnov test, which allowed a parametric comparison of groups, and subsequently with ANOVA and Tukey HSD with a pre-set signficance level of 5%.

Compressive strength

After mixing, the cements were placed in two-part cylindrical stainless steel molds (12 mm x 6 mm) and the assembly was transferred to an oven (Fanem, São Paulo, SP, Brazil) under a constant temperature of 37°C for 3 h. The specimens were subsequently removed from the molds and examined for voids and chipped edges. Defective specimens were discarded. A total of 10 specimens were selected and stored in distilled water for 21 hours and 60 days prior to testing. Compressive strength tests were performed in an EMIC universal testing machine (EMIC, São José dos Pinhais, PR, Brazil) at a cross-head speed of 1 mm/min. Compressive strength val-

ues were calculated using the equation $C = 4P/\pi D^2$, where P is the applied load and D the diameter of the tested specimen. Results were initially analyzed using a Shapiro-Wilk test, which allowed a parametric comparison of groups. Data analyses revealed that values of 21 hours and 60 days were statistically identical, thus the respective 21-hour and 60-day values of each group were clustered and presented a single value of compressive strength. Subsequently, data were analyzed using a two-way ANOVA followed by a Games-Howell test. Tests were performed using a pre-set significance level of 5%.
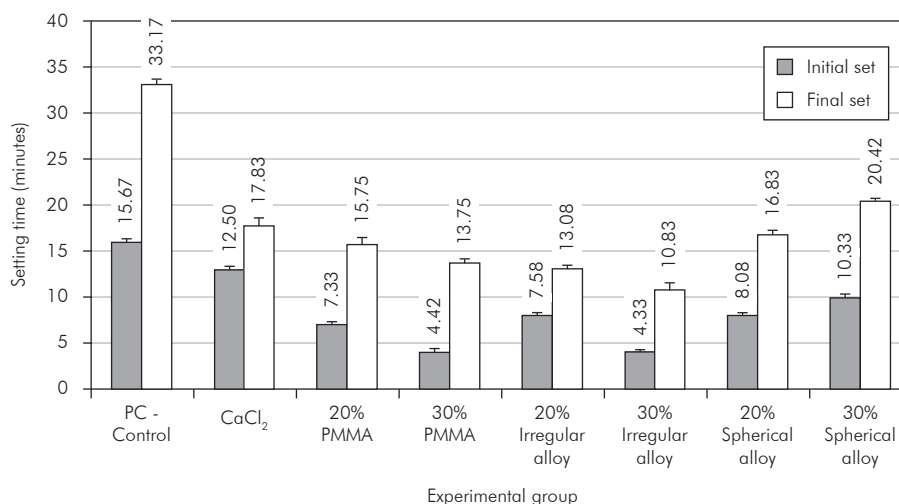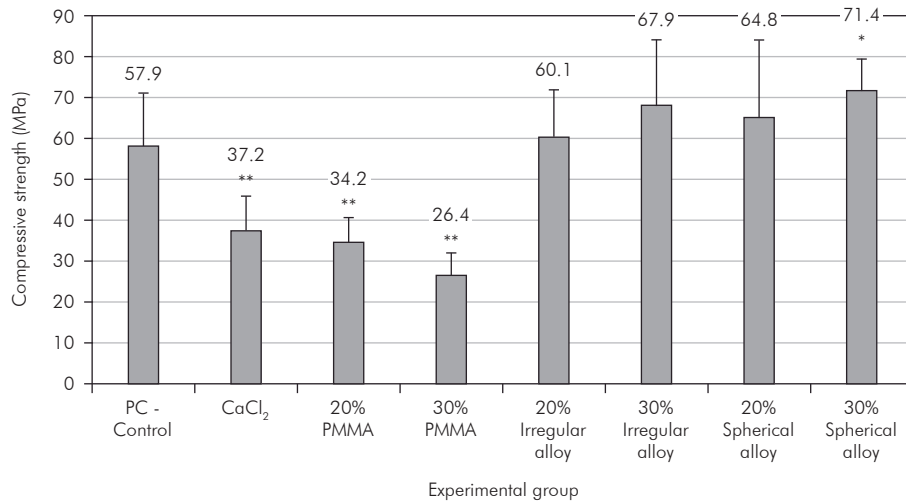
Results

A summary of the results and respective standard deviations for both setting time and the clustered values of compressive strength for both 21 hours and 60 days is shown in Table 3. A graphical depiction of the results of setting time is shown in Graph 1.

Table 3 - Numerical results of compressive strength (MPa) and setting time (minutes).

Additive	Concentration	Compressive strength	Initial Set	Final Set
PC	-	57.92 (13.01)	15.67 (0.41)	33.17 (0.52)
CaCl₂	10%	37.23 (8.63)	12.50 (0.45)	17.83 (0.93)
PMMA	20%	34.24 (6.32)	7.33 (0.41)	15.75 (0.76)
	30%	26.38 (5.42)	4.42 (0.49)	13.75 (0.52)
Irregular amalgam alloy	20%	60.12 (11.54)	7.58 (0.38)	13.08 (0.38)
	30%	67.88 (15.87)	4.33 (0.41)	10.83 (0.82)
Spherical amalgam alloy	20%	64.81 (19.19)	8.08 (0.38)	16.83 (0.52)
	30%	71.35 (7.68)	10.33 (0.41)	20.42 (0.38)

Graph 1 - Results of setting time for all experimental groups.

Graph 2 - Results of compressive strength for all experimental groups. [*: statistically lower than the control group (p < 0.05). **: statistically higher than the control group (p < 0.05)].

All additives decreased significantly both initial and final setting times as compared with the PC-control group (p < .05). Formulations with 30% PMMA and 30% irregular alloy had the lowest values of initial setting time, whereas $CaCl_2$ showed the highest (p < .05). Specimens with 30% irregular alloy also presented the lowest values of final setting time and 30% spherical alloy yielded the highest (p < .05).

A graphical depiction of the clustered values of compressive strength for both 21 hours and 60 days measurements is shown in Graph 2. $CaCl_2$ and both 20% and 30% PMMA had values significantly lower (p < .05) than PC-control. 20% and 30% irregular alloy and 20% spherical alloy did not differ from PC-control (p > .05). The addition of 30% spherical alloy significantly improved the compressive strength vs. the control (p < .05).

Discussion

In this study $CaCl_2$, PMMA, irregular and spherical amalgam alloys were added to a PC with the ultimate goal of enhancing its chemical and mechanical properties. Results showed that the incorporation of $CaCl_2$ and PMMA accelerated setting time, but decreased the compressive strength of PCs, whereas amalgam alloys, specially the spherical type, significantly decreased setting time and at 30% significantly improved the final strength of PCs.

Kogan *et al*. (2006)[12] demonstrated that the addition of 5% $CaCl_2$ to the composition of a MTA reduced its final setting time by 50%, a decrease that was similar to the one reported by Bortoluzzi *et al*. (2009)[16] with the use of 10% $CaCl_2$. A more recent study also showed a reduction of nearly 55% on the setting time of a PC after the addition of 2% $CaCl_2$. In the current study, the addition of 10% $CaCl_2$ reduced the final setting time of the tested specimens by nearly 45%, which is in excellent agreement with the former investigations. It is hypothesized that the $CaCl_2$ particles possibly acted as additional crystallization nuclei for the PC hardening, thus allowing for a similar phenomenon as that observed in gypsum materials enriched with sodium chloride.[17] Sharma and Pandey (1999)[18] found that addition of wastes such as powdered limestone and lime sludge accelerates the hydration of PC, which is related to its setting time. Bortoluzzi *et al*. (2009)[16] suggested that the penetration of $CaCl_2$ in the pores of cements could accelerate the reaction due to the hydration of silicates which reduced their crystallization time, thus hastening the final setting time of the material. $CaCl_2$ as an anhydrous salt is strongly hygroscopic, thus the hypothesis proposed by Bortoluzzi *et al*. (2009)[16] seems reasonable and may be related to the decrease in setting time found for the $CaCl_2$ containing PC in this study. Although the addition of different concentrations of $CaCl_2$ yielded a very similar decrease in setting time, the total time of reaction was remarkably different between the current study and the values reported by Ber *et al*. (2007),[19] which showed an average initial setting

time of 183 min and a final setting time of 83 min. The remarkably higher setting time reported in this former study could be either due to the lower concentration of additive used in their experiments or to the fact that $CaCl_2$ was added to the powder rather than to the liquid of the cement, which was different from the protocol used in the current study and in the investigations of Bortoluzzi *et al*. (2006)[16] and Kogan *et al*. (2006),[12] which had similar results to those found here.

Given the variations observed in the results of studies that used similar materials as the ones used in this study, it is impracticable to suggest an optimal concentration of $CaCl_2$ to be added to the composition of PCs. However, it appears that higher concentrations of $CaCl_2$, such as the one used in the current study (10%), allow for significant improvements particularly with respect to setting time as compared to lower concentrations.

All other additives also significantly reduced the setting time of the tested PC. It is, therefore, suggested that such a decrease occurred due to addition of insoluble solid particles to the experimental cement, henceforth, the final mass of reactive material in the experimental cements was lower than for the PC-control specimens; thus the time required for the reaction to be complete is expected to be lower. Particularly for the PMMA group, it is also suggested that a possible sequestering of the mixing water by the PMMA polymer beads[20] decreased the water-to-powder ratio, thus decreasing the setting time.

Although endodontic materials do not bear any direct occlusal load, and thus compressive strength is assumed to be a non-critical factor, this parameter is of major significance for the indication of PCs and MTA as coronal restorative materials.[4,6] PMMA has been used with success in the reinforcement of zinc oxide-eugenol cements.[13] However, in the current study, 10% $CaCl_2$, and 20% and 30% PMMA additives produced materials with a significantly lower compressive strength than the PC-control group. The lower properties yielded by the PMMA were unforeseen. It is hypothesized that the hygroscopic expansion of the polymer[20] within the initial hours after setting might have induced tension to the final mass of the PC, thus decreasing strength. Further, the ab-

sence of a stable chemical union between the polymer and the cement matrix might have had a negative influence on final strength. Kogan *et al*. (2006)[12] reported a compressive strength of 28.4 MPa for MTA mixed with water after 7 days. The results of our PC-control groups were remarkably higher (57.9 ± 13 MPa) after 21 hours of setting. It has been suggested that several uncontrollable variants, such as pressure used for compaction, environment humidity, variations in the mixing procedure due to intrinsic properties of the additive and the amount of air trapped in the mixture can influence the final properties of reinforced PCs and MTA cements.[1] Moreover, a significant variability between different brands of PC might have a strong influence on the differences found between the results presented here and those presented by Kogan *et al*. (2006).[12]

The addition of metal alloys to dental cements has been reported as an effective way to improve properties.[14] In the past, the addition of metal powder to glass ionomer cements was shown to improve their handling properties and radiopacity.[21,22] In the current study, the addition of amalgam alloys improved the overall final strength of the Portland cement, however a significant increase in compressive strength was found only for the 30% spherical amalgam alloy group. Moreover, no differences in strength were found between amalgam alloy types. It is hypothesized that the amalgam particles reinforced the PC matrix by dissipating energy during crack propagation events, working similar to fillers in resin composites. However, the absence of a stable chemical union between the PC matrix and the alloy particles might have limited the increase in strength. It is possible that the higher properties yielded by the spherical amalgam alloy occurred because the round particles produced less stress concentration than the sharp edges of irregular alloys, thus reducing crack propagation. These observations are rather speculative at this stage and form the basis for future studies.

Although the reinforcement of PCs with different additives may be useful in the development of materials with improved properties as compared to MTAs, one of the arguments against the use of PC is the variable quality of different brands. As previ-

ously mentioned, the presence of impurities in the formulation may interfere with hydration processes during solidification,[23] and may, therefore, jeopardize the structure and function of the final PC. This might represent a limitation for the use of reinforced PCs in future applications. Moreover, this variability limits comparisons between the results found here with results reported elsewhere, since neither the current study nor most of the published investigations provide a more careful analysis of the actual composition of the PC and are rather reliant on the information provided by the manufacturer, which may not always be accurate.

Another limitation of the present study is the fact that although the biocompatibility of PCs and MTAs has been largely investigated, the effects of the additives in combination with the cements on pulp and/or periodontal cells of treated teeth remain unknown. Camilleri *et al.* (2005)[24] found poor cell growth in contact with either MTA or Portland cement, but the calcium hydroxide resultant from the hydration reaction induced cell proliferation. Ideally reinforced PCs should fulfill most of the properties of root-end filling and endodontic materials, which include biocompatibility, good sealing, marginal adaptation, and tissue regeneration potential, as well as those of restorative materials, such as esthetics, high mechanical strength, low solubility, etc. Thus, an additive that facilitates or increases the release of calcium hydroxide from PCs may be a target for future research. Further, since the 30% spherical amalgam alloy additive yielded the most significant improvements in terms of physico-chemical properties in the present study, the potential citotoxic effect of products from corrosion of amalgam particles should be further investigated.

Conclusion

All experimental groups – CaCl$_2$, 20% and 30% PMMAs and 20% and 30% irregular and spherical amalgam alloys – significantly reduced the setting time of the PC. Only the 30% spherical amalgam alloy additive yielded a significant increase in the compressive strength of the reinforced cements. Therefore, the addition of 30% spherical amalgam alloy may be recommended to strengthen and reduce setting time of PCs in future clinical applications.

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