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Influence of Radiopacifier Additives on Calcium Aluminate Cement Properties

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The aim of this study was to determine the best radiopaque additive to be incorporated to calcium aluminate cement (CAC) to promote radiopacity. Measurements of optical density were carried out on white MTA and CAC with and without additives such as: polymeric dispersant, plasticizer and various radiopacifiers. The effects of the radiopacifying addition on some properties of CAC were also evaluated. The radiopacity value for CAC-Bi_2O_3 (25%) was higher than the other radiopacifying agents tested. The addition of ZnO (25%) and 15%ZnO:10%Bi_2O_3 increased the compressive strength of CAC, whereas for Bi_2O_3 (25%) containing samples the strength was lower than for the CAC. The ZnO (25%) and 15%ZnO:10%Bi_2O_3 additions also reduced the apparent porosity. CAC does not have sufficient radiopacity to be distinguished from adjacent anatomic structures, such as dental tissues and bone. The addition of 15%ZnO:10%Bi_2O_3 can be suggested as the most suitable one to obtain the best compromise between good physical and mechanical properties and ideal radiopacity for clinical purposes.

Keywords: *dental cement, radiopacity, physical and mechanical properties*

1. Introduction

Mineral Trioxide Aggregate (MTA) has been considered as the ideal root-end filling material because of its low solubility, low cytotoxicity, good tissue tolerance and induction of mineralized tissue formation[1]. MTA is a white or grey powder which sets when there is moisture[2,3]. MTA primarily consists of tricalcium silicate ($3CaO.SiO_2$), dicalcium silicate ($2CaO.SiO_2$)[4,5] as binder phases, and bismuth oxide to increase its radiopacity[1].

Calcium aluminate cement (CAC) has been studied as root-end filling material to overcome some MTA drawbacks such as the long setting time and its negative implications for the clinical needs[6-12]. CAC has suitable physical and mechanical properties[10], biocompatibility[7,12], ability of stimulating hydroxyapatite deposition in simulated body fluid solution[13] and acts as a barrier against bacterial microleakage[8]. Calcium aluminate-based cement showed no inflammatory and less tissue reactions than MTA, and it was biocompatible when tested in rat subcutaneous tissue[6].

A key physical property for these endodontic materials is the radiopacity. Most endodontic materials contain radiopacifying agents to visualize the root canal filling and to check the healing evolution over time[14]. The root-end filling material should have enough radiopacity to be distinguished from adjacent anatomical structures, such as bones and teeth[1,14,15].

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The radiopacity of material is changed by adding particles containing heavy metals such as bismuth (Z=83), barium (Z=56), zirconium (Z=40), strontium (Z=38) or zinc (Z=30)[16,17].

Bismuth oxide is a well-known radiopacifying agent. However, previous studies pointed out that Bi_2O_3 affected the hydration mechanism of MTA, reducing the precipitation of calcium hydroxide in the hydrated paste[18] and it was slightly leached out with the calcium hydroxide[4].

The use of Bi_2O_3 with calcium silicate has been shown to be deleterious to the physical properties of the final material, affecting particularly the compressive strength[19]. The bismuth oxide is not inert and retards the hydration of the cement by decreasing its calcium ions release rate, changing its reparative capacity and its physicochemical properties[15].

Barium sulphate and zinc oxide are applied extensively in medical devices[19]. However, according to Vivan et al.[14], $BaSO_4$ itself does not provide suitable radiopacity to Portland cement. Zinc and zirconium oxides are used in dental materials for prosthetic and implant purposes and do not present toxicity[15].

The extensive use of these materials indicates that they present favorable interaction with the tissues. However, adding them even at minimal amounts can affect the physical properties of the final compound. Besides its

importance, there have been few investigations on the effect of radiopacifiers on the material's properties[19].

Therefore, the aim of this study was to determine the best radiopaque additive to be incorporated to CAC to promote sufficient radiopacity for clinical purpo*ses* and the influence of this addition on some of its properties such as compressive strength, apparent porosity and setting time.

2. Experimental Procedures

White-MTA (Angelus, Londrina, PR-Brazil) and CAC (Secar 71, Kerneos, Neuilly sur Seine-France) were tested. The additives used are presented in Table 1.

The characteristics of the ZnO and Bi_2O_3 radiopacifiers, such as morphology and size distribution of particles, were analyzed by using the equipments scanning electron microscope (EVO MA10; Zeiss) and Sedigraph (5000D, Micromeritics) as showing in Figure 1. Further characterization of the materials was based on optical density, compressive strength, apparent porosity and setting time.

Aqueous suspensions of CAC (82 wt% solids) were prepared in the presence of a dispersant (D), plasticizer (P) and radiopacifying agents. Adding the dispersant and plasticizer reduced the water required to produce a workable mix of the calcium aluminate cement paste, resulting in a denser structure and, therefore, a stronger material[10]. Also, higher liquid to powder ratio was necessary to prepare the MTA suspension (75 wt% solids) used as control. The coagulated nature of the MTA particles does not result in fluid suspensions, unless they are diluted[20].

The CAC or MTA suspensions were cast into circular metallic molds (10 mm diameter × 1 mm thick). Four specimens per each studied composition were prepared. The samples were cured for 24 hours at 37°C in a stove (MA033, Marconi) in a moisture-saturated environment (~100% RH). After that, the samples unmolded were kept at 37°C for 24 more hours.

One sample of each composition was placed on an occlusal radiographic film (Kodak Insight, Manaus, Amazonas, Brazil) (Ref 1169143, Lot 39500204). At their side, a 99% pure aluminum step wedge with ten steps (1 to 10 mm) was also placed on the radiographic film as shown in Figure 2. The radiographs were obtained using 70 KVp, 8 mA X-ray apparatus (ION 70X, Procion, Ribeirão Preto, São Paulo, Brazil) and exposed for 0.25 seconds at a focus-film distance of 20 cm. The films were manually developed in a darkroom following the time/temperature recommendations of the manufacturer. The optical density value (OD) was measured with a photodensitometer (MRA; Indústria de Equipamentos Eletrônicos Ltda, Ribeirão Preto, São Paulo, Brazil). Optical density of the samples and each thickness of the aluminum step wedge were measured in triplicate for each film. The results of optical density represent the average of twelve measurements for each composition (3 measurements for each sample × 4 samples for each composition). The optical density data of cements tested were submitted to a polynomial regression to obtain the equivalence in radiopacity (mm Al)[15].

Aqueous suspensions of CAC (82 wt% solids) were also prepared in the presence of dispersant, plasticizer and the radiopacifying agents ZnO (25%), Bi_2O_3 (25%) and 15%ZnO:10%Bi_2O_3 and cast into 16 mm diameter × 18 mm height cylinder moulds for measurements of compressive strength and apparent porosity. Eight specimens per each studied composition were prepared (five for compressive strength and three for apparent porosity). Samples were cured at 37°C in a stove (MA033, Marconi, São Paulo, Brazil) in a moisture-saturated environment (~100% RH) for 12 hours. The samples were unmolded and placed into containers with simulated body fluid (SBF) solution at 37°C (100% RH) for 3, 7, 15 or 30 days.

The compressive strength of the samples was measured as a function of the exposition time in SBF, whereas others were dried at 110°C for 48 h and their apparent porosity was evaluated. The SBF solution was prepared according to the procedure described in the literature[21].

The compressive strength was measured with the help of an EMIC Test Machine (Model DL 10.000, Curitiba, Brazil). A constant displacement rate of 0.15 mm/min was used. The compressive strength was calculated as:

$$\sigma_R = \left[\frac{4P}{\pi D^2} \right] \quad (1)$$

where, σ_R was the rupture stress (MPa); P was the ultimate load (N); and D (mm) was the diameter of the samples.

Table 1. Additives used as dispersant, plasticizer and radiopacifying agents.

	Additives	Content (wt%) based on the cement	Suspension composition
Dispersant (D)	Polyglycol[1]	0.6	CAC-DP
Plasticizer (P)	$CaCl_2.2H_2O$[2]	2.8	
Radiopacifiers	$BaSO_4$[3]	25	CAC-DP-$BaSO_4$
	Bi_2O_3[3]	25	CAC-DP-Bi_2O_3
	ZrO_2[4]	25	CAC-DP-ZrO_2
	ZnO[2]	25	CAC-DP-ZnO (25%)
	ZnO[2]	30	CAC-DP-ZnO (30%)
	ZnO[2]	35	CAC-DP-ZnO (35%)
	ZnO:Bi_2O_3	22.5%ZnO:2.5%Bi_2O_3	CAC-DP-22.5%ZnO:2.5%Bi_2O_3
	ZnO:Bi_2O_3	20%ZnO:5%Bi_2O_3	CAC-DP-20%ZnO:5%Bi_2O_3
	ZnO:Bi_2O_3	15%ZnO:10% Bi_2O_3	CAC-DP-15%ZnO:10%Bi_2O_3

[1]Bayer, Trostberg, Germany; [2]Labsynth, Diadema, SP, Brazil; [3]Vetec, Duque de Caxias, RJ, Brazil; [4]Sigma-Aldrich, USA.

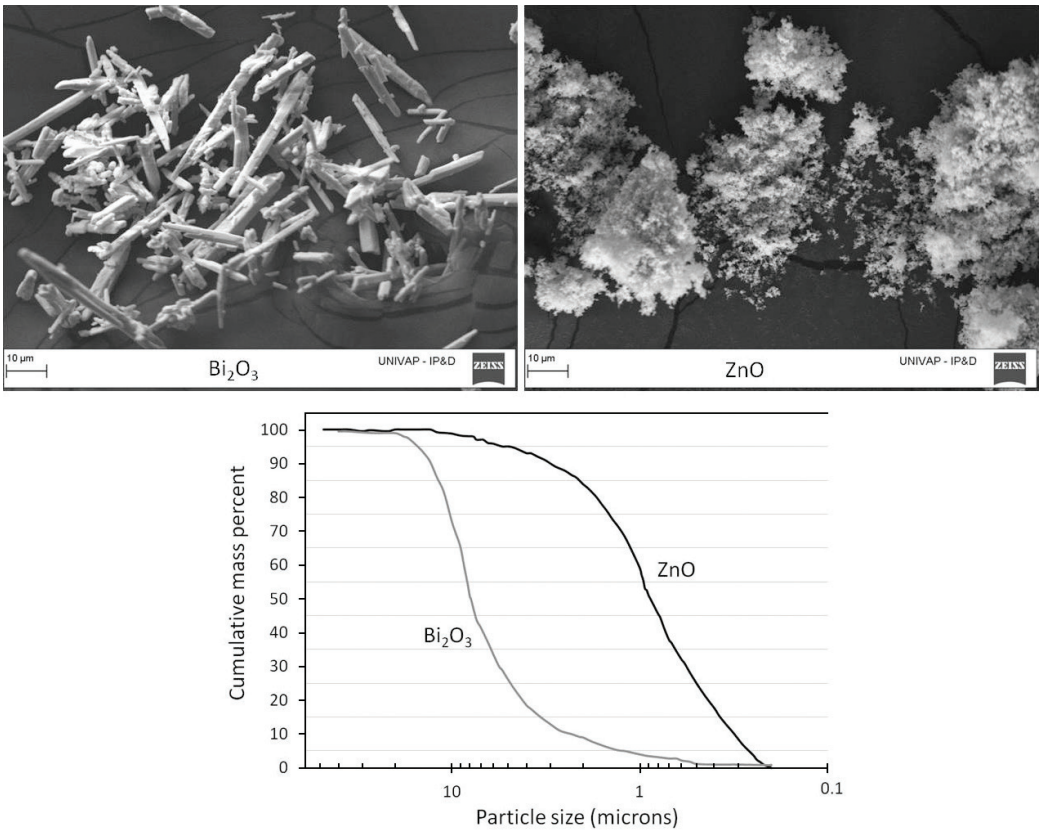

Figure 1. Characterization of radiopacifiers ZnO and Bi_2O_3 as morphology and size distribution of particles.

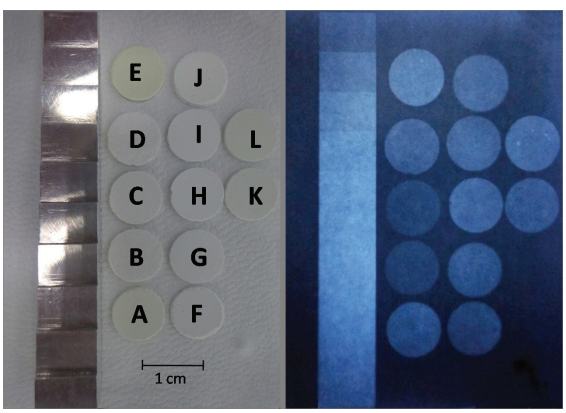

Figure 2. Example of the radiographic procedure. A) white-MTA (WMTA), B) CAC, C) CAC-DP, D) CAC-DP-$BaSO_4$ (25%), E) CAC-DP-Bi_2O_3 (25%), F) CAC-DP-ZrO_2 (25%), G) CAC-DP-ZnO (25%), H) CAC-DP-ZnO (30%), I) CAC-DP-ZnO (35%), J) CAC-DP-22.5%ZnO:2.5%Bi_2O_3 K) CAC-DP-20%ZnO:5%Bi_2O_3 and L) CAC-DP-15%ZnO:10%Bi_2O_3 (D and P, indicates dispersant and plasticizer, respectively).

The apparent porosity was evaluated according to the immersion test (Archimedes principle), using kerosene. This principle states that a body immersed in a fluid is buoyed up by a force equal to the weight of the displaced fluid. The buoyant force is measured by the difference, expressed in grams, between the weight of the body in air and when submerged in kerosene[22].

The samples are initially weighed in dry conditions (W_d). After 1 hour of immersion in the liquid under vacuum, the sample is weighed both suspended in the immersion liquid (W_i) and humid (W_h). Thereby, the apparent porosity (A.P) of the sample is calculated considering the mass of liquid retained in its open pores:

$$A.P. = \left(\frac{(W_h - W_d)}{(W_h - W_i)} \right) \times 100 \quad (2)$$

Aqueous suspensions of CAC (82 wt% solids) were also prepared using a standard laboratory mixer (Marconi, Piracicaba, Brazil) under 2000 rpm. The setting time of CAC suspensions was evaluated in the presence of dispersant, plasticizer and radiopacifying agents ZnO (25%), Bi_2O_3 (25%) and 15%ZnO:10%Bi_2O_3. After mixing for 1 min, the suspensions were poured into a container (180 mL) where the setting time was measured with an automatic recording Vicat apparatus (Vicatronic E044, Matest, Italy). A needle is inserted in the suspension every 1 min. The time for which the penetration distance was zero indicated the setting time of the sample.

3. Results and Discussion

3.1. *Radiopacity tests*

The optical density of the aluminum step wedge measured for different radiographs is shown in Figure 3.

The constancy of the optical density on the 4 radiographs showed the precision of the measurement. As expected, a decrease in OD was observed with increasing the step wedge thickness, as the image progressively became more radiopaque[15].

The radiopacity for each tested material is expressed in millimeters of equivalent aluminum as shown in Figure 4. The radiopacity value for CAC-DP-Bi_2O_3 (25%) was higher than the other radiopacifying agents tested, including the commercial material (WMTA) which includes bismuth oxide in its composition. The CAC-DP-15%ZnO:10%Bi_2O_3 composition presented sufficient radiopacity for clinical purposes, similarly to MTA.

Bi_2O_3 is used as a radiopacifying agent for dental material such as acrylic resin and some MTAs imparting the sufficient radiopacity to them[15,19]. Among all additives evaluated, Bi_2O_3 addition resulted the lowest optical density (OD).

ISO 6876:2012[23] standard establishes 3 mm Al as the minimum radiopacity for the root canal sealers. When the OD values obtained for each material were converted into radiopacity, results higher than 3 mm Al were obtained mainly for CAC-DP-Bi_2O_3 (25%). This composition presented higher radiopacity than all other radiopacifying agents tested. CAC-DP-ZnO (25%) resulted in a lower value than that required (2.2 mm Al, Figure 4) to allow radiographic differentiation among the cement and dental structures. Based on that, higher contents of ZnO were evaluated and also the mixture with Bi_2O_3 in different proportions. CAC-DP-15%ZnO:10%Bi_2O_3 compositions presented suitable radiopacity (3.5 mm Al), similarly to MTA.

Figure 3. Optical density of the aluminum step wedge measured for four radiographs.

Aguilar et al.[15] also pointed out that Bi_2O_3 was efficient radiopacifier for cement based calcium aluminate cement, providing suitable results for all studied thicknesses. However, the present authors highlight that further research was required to evaluate the effect of the addition of this radiopacifying agent on other physicomechanical and biological properties of cement because it has been reported that bismuth is toxic and induces cell death[24]. Other authors also affirmed that the effect that particle shape and particle size distribution of a cement-replacing material have on the properties of the resultant material still needs to be investigated[19].

Therefore, the influence of ZnO (25%), Bi_2O_3 (25%) or their mixture (15%ZnO:10%Bi_2O_3) on some properties of CAC such as compressive strength, apparent porosity and setting time, was evaluated.

3.2. *Compressive strength and apparent porosity tests*

Results of compressive strength and apparent porosity as a function of the curing time, for samples of calcium aluminate cement containing additives (dispersant, plasticizer, and radiopacifier) are shown in Figures 5a and b, respectively.

The addition of ZnO (25%) and 15%ZnO:10%Bi_2O_3 increased the compressive strength of CAC-DP, whereas to Bi_2O_3 (25%) the values were lower than the CAC-DP. The

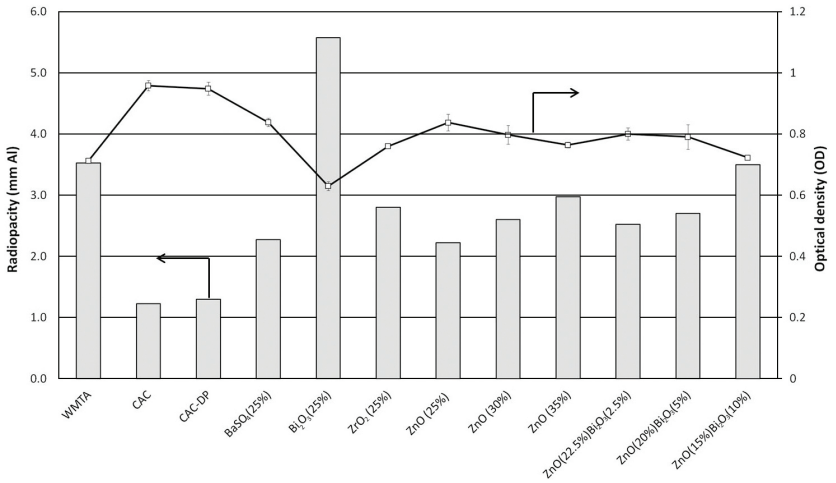

Figure 4. Mean radiopacity values expressed as aluminum thickness (mm Al) and the optical density for the tested materials: white-MTA, main calcium aluminate cement (CAC) or containing additives dispersant (D), plasticizer (P) and radiopacifiers.

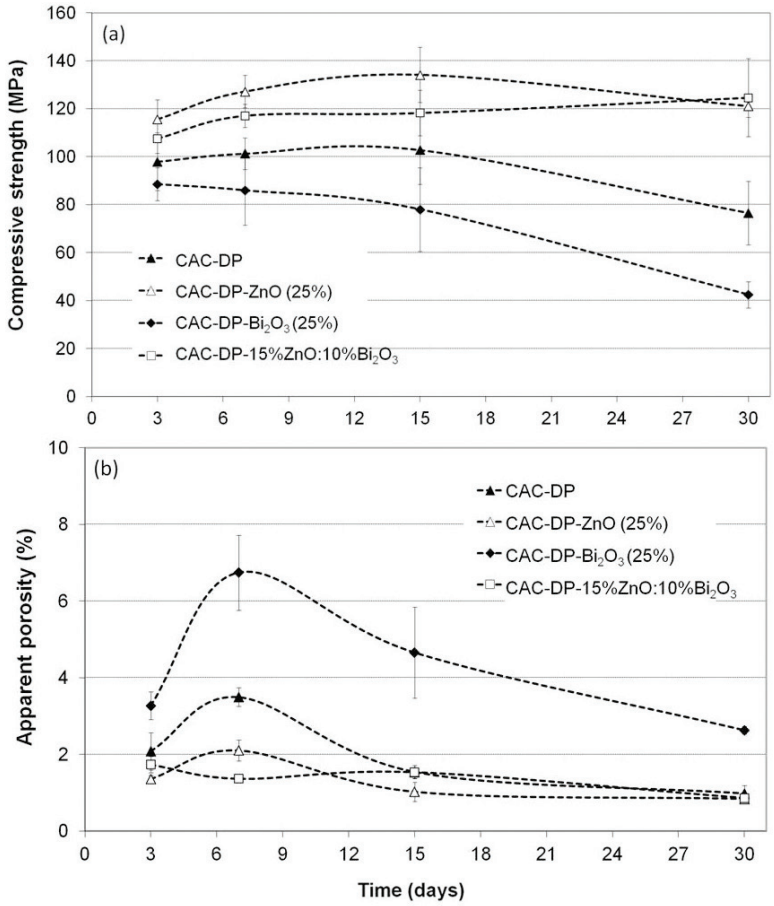

Figure 5. (a) Compressive strength and (b) apparent porosity as a function of the curing time for samples of calcium aluminate cement (CAC) containing additives dispersant (D), plasticizer (P) and radiopacifiers. Error bars represent variation of measurements among the samples (five of them for compressive strength and three for apparent porosity).

ZnO (25%) and 15%ZnO:10%Bi_2O_3 addition also decreased the apparent porosity compared to the Bi_2O_3 (25%) ones.

An important feature that must be considered when choosing a radiopacifier additive is the mechanical strength of the resulting material. Compressive strength is an important factor to consider when the filling material is placed in a cavity that bears occlusal pressure, such as a root canal filling[3], or even a restorative base. The addition of ZnO (25%) increased the mechanical strength of CAC-DP when compared to Bi_2O_3 (25%) as shown in Figure 5a. ZnO comprises finer particles than Bi_2O_3 (Figure 1) positively affecting the particle packing, resulting in lower porosity (Figure 5b) and consequently higher mechanical strength. On the other hand, Bi_2O_3 increases the porosity and decreases the mechanical strength of calcium aluminate cement as their particles that have wide size range and elongated shape. The addition of 15%ZnO:10%Bi_2O_3 mixture to CAC resulted in close values of compressive strength compared to ZnO (25%) and also lower apparent porosity than the Bi_2O_3 (25%) one. Both ZnO (25%) and 15%ZnO:10%Bi_2O_3 mixture additions also resulted in a lower decrease of the mechanical strength over time.

Camilleri and Galdolfi[19] also showed that ZnO (Fischer Scientific) presents very fine particles (lower 3 μm) which are difficult to be distinguished by SEM even at high magnification. On the other hand, Bi_2O_3 (Fischer Scientific) shows elongated needle like shape particles and showed a wide particle size range (5-100 μm).

The calcium aluminate cement dissolution in contact with water promotes the release of Ca^{2+} and $Al(OH)_4^-$ ions, which is followed by precipitation of calcium aluminate hydrate (CAH) and aluminium hydroxide (AH) due to the saturation of the solution[25]. The type of hydrate formed determines the material properties such as mechanical strength and porosity. The time favors conversion of less stable hydrates (CAH_{10}, less dense) to a more stable one (C_3AH_6, more dense) which may explain the decrease in mechanical strength. The precipitation of AH_3 gel occurs simultaneously inducing the decrease in apparent porosity with time.

3.3. *Setting time tests*

Measurements of setting time using Vicat apparatus were taken for CAC suspensions with dispersant, plasticizer and the following radiopacifying agents ZnO (25%), Bi_2O_3 (25%) and 15%ZnO:10%Bi_2O_3, as shown in Figure 6. ZnO slightly retarded setting, whereas Bi_2O_3 accelerated setting.

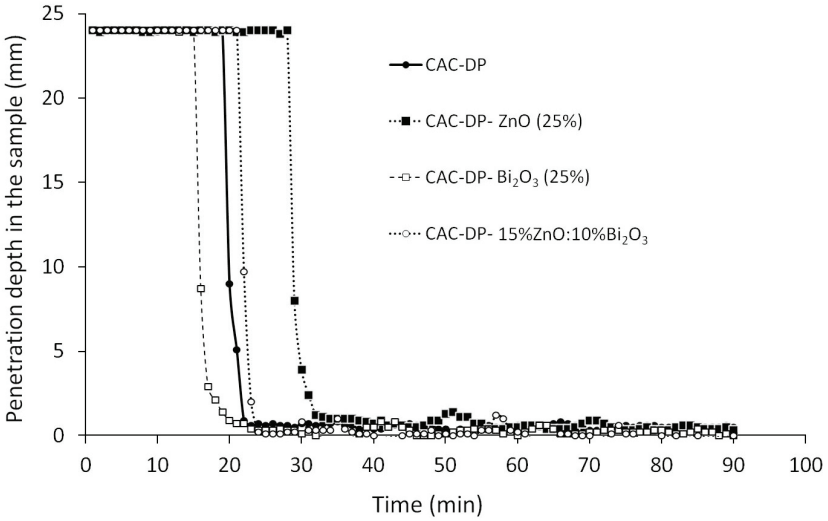

Figure 6. Evaluation of setting time of aqueous suspensions of calcium aluminate cement (CAC, 82 wt% solids) containing additives dispersant (D), plasticizer (P) and radiopacifiers.

Another important feature for application of CAC as dental material is the setting time. CAC-DP showed a reduced value (close to 20 min.), which matched to the clinical requirements. Additionally, the additives showed little influence on the setting time of CAC-DP compositions [25 wt% of ZnO (close to 29 min.), 25 wt% of Bi_2O_3 (close to 16 min.) and 15%ZnO:10%Bi_2O_3 (close to 23 min)]. The advantage of using cement with a reduced setting time is the less likelihood of constant professional procedures during the treatment. When used as a root-end or root-canal filling material the faster hardening should also reduce the risk of contamination and dislodgement after placement[20,26].

It is noteworthy that similar tests of compressive strength, apparent porosity and setting time using CAC-DP when compared with MTA were previously shown by the authors[10]. The CAC presented better fluidity, improved handling properties, greater mechanical strength, and reduced porosity with lower pore size when compared with MTA Angelus.

4. Conclusions

The effect of different additives not only on radiopacity but also on some physical and mechanical properties of calcium aluminate cement used in endodontic treatments was compared. The radiopacifier compound that leads to a higher benefit is Bi_2O_3 but it increases the porosity and decreases the mechanical strength of calcium aluminate cement due to their wide particle size range and elongated shape. On the other hand, the ZnO is comprised by much finer particles than Bi_2O_3 which positively affected the particle packing resulting in the increase of mechanical strength of CAC. Nevertheless, ZnO results in a lower value of radiopacity than that required by ISO 6876:2012. This work shows that it is possible to attain suitable radiopacity for clinical purposes using lower additive content besides the better compromise between physical and mechanical properties by using the mixture ZnO with Bi_2O_3, specially 15%ZnO:10%Bi_2O_3.

Acknowledgments

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