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ORIGINAL ARTICLE

Optimisation of hardness and setting time of dental zinc phosphate cement using a design of experiments

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Abstract The main objective of this study is to demonstrate the application of strategy of an experiment design to optimize the compressive strength and setting time of zinc phosphate cement used in the dental application. For this work, the extreme vertices design was chosen. Its factors are components of the mixture forming a ternary system: zinc oxide, aluminum phosphate and orthophosphoric acid ($ZnO–AlPO_4–H_3PO_4$). The local region of dental cement – in simplex space-explored and limited by upper and lower limits of the three components of the mixture. The optimization of each response and then all both together by graphical methods allowed us to obtain the adequate cement.

1. Introduction

Zinc phosphate dental cements were discovered over a century ago (Boston and Jefferies, 2009; Loher et al., 2009; Fakiha et al., 1992), and their development has continued since then (Wagh and Arun, 2004). A lot of formulations are described and made available to dentists (O'Brien, 2002; Neira et al., 2009; Dickens and Flaim, 2008; Londono et al., 2009). Its principal applications are for pulp protection under restorations made of metal or plastic (Nicholson et al., 2001). Thus, it can be used as cement for fixation of crowns and bridges, inlays, orthodontic bands and ligaments (Nicholson et al., 2001).

This class of cements has a short setting time and can develop high mechanical strength (Li and White, 1999), these advantages contribute to good practice in dentistry. The solid phase of zinc phosphate cement is generally formed by a zinc oxide heated at higher temperatures (> 1000 °C) (Fakiha et al., 1992). However, the liquid phase is formed by a phosphoric acid diluted by water. The acid–base reaction between zinc oxide and orthophosphoric acid is responsible of setting and hardening of these cements (Pawlig and Trettin, 1999). The setting of cement is due to formation of acidic zinc phosphate forms, as a primary, secondary and tertiary salt (Hopeite) of zinc phosphate (Czarnecka et al., 2003). While, Hopeite is of considerable importance since it has been observed as a stable phase growing on the surfaces of zinc phosphate dental cements (Herschke et al., 2006). Crowell et al. described in

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addition to Hopeite, the presence of non-reacted Zinc oxide (Margerit et al., 1996).

The role of aluminum in the zinc phosphate cements was considered very important. In fact, the incorporation of aluminum ions in the liquid phase of cement prevents and delays the formation of crystalline hydrates of zinc (Park et al., 1998; Pawlig and Trettin, 1999). Aluminum oxide greatly moderated the reaction of zinc oxide and phosphoric acid, and this effect was attributed to the formation of an aluminum phosphate gelatinous coating on zinc oxide particles. In fact, (Wilson and Nicholson, 1993) believe that the gelatinous substance may even be zinc aluminophosphate phase, which subsequently crystallizes into Hopeite and aluminophosphate amorphous gel ($AlPO_4 \cdot nH_2O$). However, (Pawlig and Trettin, 1999) described that the presence of aluminum ions is important for improvement the hardness of cement. In this case, final cement consists of excess zinc oxide coated and bonded by possibly aluminum phosphate and zinc phosphate gels (Wilson and Nicholson, 1993).

Currently, a lot of ions form part of zinc phosphate dental cement, such as calcium which combined with a phosphate can form calcium phosphate bonded cement. Other approach consists to insert calcium phosphate compounds to zinc phosphate cement for improvement their biocompatibility (Jabri et al., 2010).

In our laboratory, intensive effort to highlight the natural phosphate to several uses, then in previous work (Abbaoui et al., 2004), we showed that it was possible to work out cement which cash up in vivo, while evolving to the hydroxyapatite. The cement is composed of tricalcium phosphate a type (α-$Ca_3(PO_4)_2$), calcium hydroxide ($Ca(OH)_2$) and phosphoric acid (H_3PO_4). The latter has a close structure to that of the mineral phase of the bone what supports the osseous push back. The preparation process and application of this kind of dental cement has been patented (Mejdoubi et al., 2002).

For improving the physical and mechanical properties, it is indispensable to make the optimization techniques. In this study, we adopt the strategy of design of experiments to explore the area of cement in the ternary system ($AlPO_4$, nH_2O–ZnO–H_3PO_4) and optimize each individual response: mechanical hardness and setting time. Tracing the curves of equal response provides all mixtures that meet both objectives.

2. Materials and methods

The solid phase of cement is based on aluminium phosphate and zinc oxide, the liquid phase consists of distilled water and orthophosphoric acid (1.71% and 85%). The experimental tests (Table 1) are organized by using an Extreme Vertices Designs with upper and lower constraints for the three components.

The design matrix generates 10 tests represented in the Fig. 1. The response of setting time is determined by Vicat needle apparatus. The form of mould for Vicat test is cylindrical, it has the following dimensions 20 mm for length and 8 mm for diameter. This mould is filled by cement paste.

As for measuring the compressive strength, we used a Controlab press mark with a maximum force of uniaxial compression is 250 KN. This force is applied on small cylindrical specimens who have 10 mm for length and 5 mm diameter.

The report liquid to solid is fixed at 0.42. The amount of acid in the liquid for cement paste is given by the matrix experiment in Table 1. The temperature test is set at 24 °C.

For the compression test, when the making of moulds is completed, all samples are introduced in an oven at 37 °C for a week.

3. Results and discussions

The local area of cement is limited by the upper and lower limits of the composition of various components in the ternary system (Fig. 1). Although outside this zone, the cement loses its physical and mechanical properties. Then, our study will be made in this limited region (green points). The statistical calculations and graphs were done by using (N.E.M.R.O.D) software. The mathematical model chosen for medelisation the two responses such as the setting time and mechanical strength is an incomplete cube regression model of third-order, his equation as follow:

$$\mathbf{Y} = b_1 * \mathbf{X}_1 + b_2 * \mathbf{X}_2 + b_3 * \mathbf{X}_3 + b_{12} * (\mathbf{X}_1 * \mathbf{X}_2) + b_{13} * (\mathbf{X}_1 * \mathbf{X}_3) + b_{23} * (\mathbf{X}_2 * \mathbf{X}_3) + b_{123} * (\mathbf{X}_1 * \mathbf{X}_2 * \mathbf{X}_3).$$

with $\mathbf{X}_i$ are a the coded factors of components i $\mathbf{X_1}$ for $AlPO_4$, nH_2O; $\mathbf{X_2}$ for ZnO and $\mathbf{X_3}$ for H_3PO_4. And b_1, b_2, b_3... are the regression coefficients of model.

3.1. Optimisation of setting time

The regression equation to model setting time (Y_s) in pseudo-component variables has the following form:

$$\mathbf{Y_s}(\text{min}) = 27.83\ \mathbf{X_1} + 2.01\ \mathbf{X_2} + 6.10\ \mathbf{X_3} + 15.68\ (\mathbf{X_1} * \mathbf{X_2}) + 35.87\ (\mathbf{X_1} * \mathbf{X_3}) - 117.50\ (\mathbf{X_1} * \mathbf{X_2} * \mathbf{X_3})$$

Table 1 Matrix experiment and results of measuring setting time and hardness.

N	$\%\mathbf{X}_1$	$\%\mathbf{X}_2$	$\%\mathbf{X}_3$	$V(\mathbf{X}_3)$/2 g of cement	V(liq phase)/2 g	Hardness (MPa)	Setting time (min.)
1	0.192	0.372	0.436	0.6	0.84	45	28
2	0.028	0.536	0.436	0.6	0.84	12	2
3	0.028	0.372	0.6	0.83	0.84	18	6
4	0.11	0.454	0.436	0.6	0.84	68	19
5	0.11	0.372	0.518	0.71	0.84	100	26
6	0.028	0.454	0.518	0.71	0.84	17	5
7	0.0827	0.4267	0.4907	0.68	0.84	48	14
8	0.1373	0.3993	0.4633	0.64	0.84	72	23
9	0.0553	0.4813	0.4633	0.64	0.84	28	8
10	0.0553	0.3993	0.5453	0.75	0.84	42	12

$\%\mathbf{X_1}$ = % $AlPO_4$, nH_2O; $\%\mathbf{X_2}$ = % ZnO and $\%\mathbf{X_3}$ = % H_3PO_4.

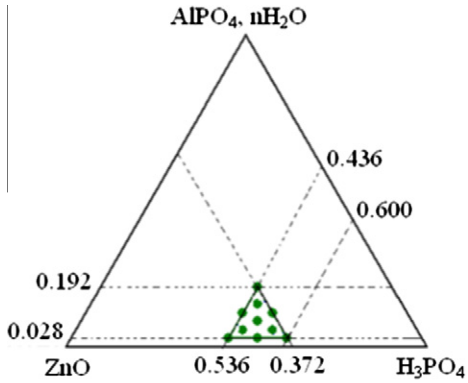

Figure 1 Local region of cement in the tertiary system ($AlPO_4$, nH_2O–ZnO–H_3PO_4).

The analysis of variance shows that the regression model explains perfectly the experimental results. Indeed, the value of Snedecor factor calculated experimentally is $F = 784.9469$, it is greater than or equal to the critical value of theoretical factor ($F_{0,001}$ (6, 3) = 132.8475), with a significance level of 0.1%. So for a confidence level of 99.9%, the regression is significant. In addition, it has good statistical characteristics, such as the R^2 and R^2 adjusted ranging respectively 0.999 and 0.998. This allows us to use this model to present the results and make forecasts.

A check of lack of fit of the regression model in control points has shown that the regression model is adequate with 95% confidence. So for this value alone coefficient b_{23} of regression model is not significant.

To explain the influence of three factors on the response of setting time of cement, we analyzed the Piepel curve (Fig. 2). The geometric interpretation of effects for three components of mixture has revealed that the variation of setting time of cement according to the variation of percentage of aluminum phosphate presents a positive slope. This shows that when the percentage of aluminum phosphate increases, the setting time increases. We can conclude that the effect of the percentage of aluminum phosphate on the response time is positive. In contrast the effects of two other components such as zinc oxide and phosphoric acid are negative (slope of curves is negative), so when the percentages of these components increase, the setting time decreases.

On light of these results we can draw the following assumptions:

– The aluminum phosphate has a retarding effect on the cement.
– The essential reaction responsible for setting cement is between zinc oxide and orthophosphoric acid.

The geometric interpretation in the form of isoresponse graphs (Fig. 3) for regression model of setting time can provide many opportunities to choose the optimum compositions (depending on the value of setting time) of ternary mixture for several types of dentistry intervention. While for good practice in dentistry, the Zinc phosphate cement should have a setting time less than 10 min, this suggestion corresponds to the area where the variation margins of real compositions for the three components are as follow:

$$3 < \%AlPO_4, nH_2O < 6.60$$

$$37.3 < \%ZnO < 53.34$$

$$37 < \%H_3PO_4 < 58.7$$

3.2. Optimization of mechanical strength of cement

The mathematical model adopted in this study is similar as the setting time. We choose an incomplete cube regression model of third-order. So, the response of cement hardness ($\mathbf{Y}_H$) in function to pseudo-component variables of three components of tertiary system can take the following form:

$$\mathbf{Y}_H(MPa) = 45.73\ \mathbf{X}_1 + 11.27\ \mathbf{X}_2 + 17.64\ \mathbf{X}_3 + 158.01\ (\mathbf{X}_1 * \mathbf{X}_2) + 274.74\ (\mathbf{X}_1 * \mathbf{X}_3) - 720.84\ (\mathbf{X}_1 * \mathbf{X}_2 * \mathbf{X}_3)$$

The analysis of variance shows that the regression model explains perfectly the experimental results. Indeed, the value of Snedecor factor calculated experimentally is $F = 230.4299$, it is greater than or equal to the critical value of theoretical factor ($F_{0,001}$ (6, 3) = 132.8475), with a significance level of 0.1%. So for a confidence level of 99.9%, the regression is significant.

On the other hand, this regression model has good statistical properties, such as: R^2 = 0999; R^2 adjusted = 0.998. We

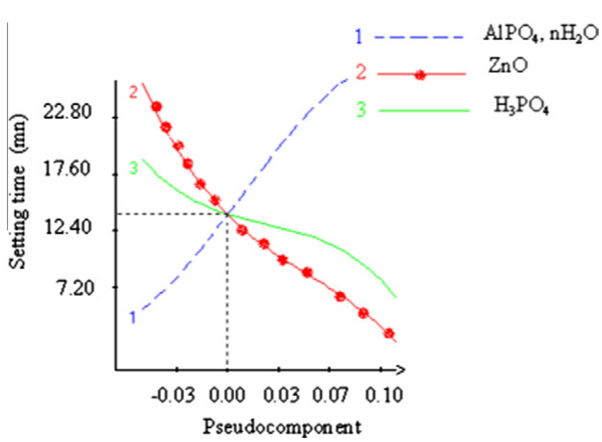

Figure 2 The plotted effects of pseudo-components on the response of setting time according to Piepel direction.

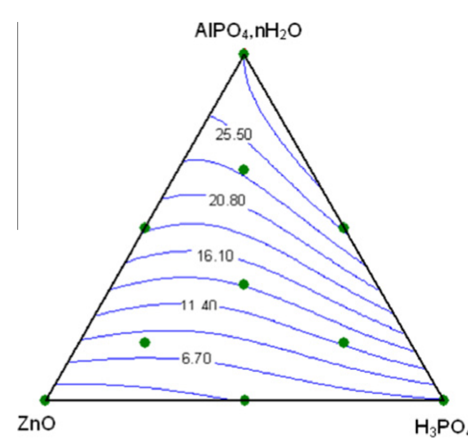

Figure 3 The isoresponses graph for regression model of the setting time (in pseudo-components).

will use it for interpretation of results and make graphs presentation of isoresponse contours.

The curves of effects for three components of the mixture on the mechanical strength are plotted in form of Piepel direction (Fig. 4). The interpretation of these curves leads the following explanations:

The variation of mechanical hardness of cement in function to the percentage of aluminium phosphate shows that the strength of cement increases when the percentage of the latter increases. This increase pass by a maximum, whose composition is: $AlPO_4$, nH_2O = 11.9%; ZnO = 37.2%; H_3PO_4 = 50.9%. And the response of hardness cement at this point is 100.6 MPa. Thus, after this maximum, the curve descent when the percentage of aluminium phosphate continues to increase.

The addition of aluminium phosphate at the cement powder has increased considerably the mechanical hardness of the cement. We search by technical methods of analysis, the mechanism of action of this compound on the mechanical strength. In contrast, the curves representing the variation of cement resistance are decreasing when, the percentage of the other two components such as zinc oxide and orthophosphoric acid is increasing.

The contour plot of isoresponses in function to pseudo-component variables (Fig. 5) leads to choose the convenable strength of cement for several interventions in dentistry.

In terms of chemical composition of cement and for its better practices, the both responses must be met simultaneously. We superimpose the isoresponses curves for both objectives together (Fig. 6), and eliminate prohibited areas for getting mixtures that meet the objectives. For example, the maximum hardness of a cement composition is 100.6 MPa which involves a setting time of 26.90 min.

4. Conclusion

The optimization of the mechanical hardness and setting time of cement by the strategy of experiment design, allows us to meet the following results:

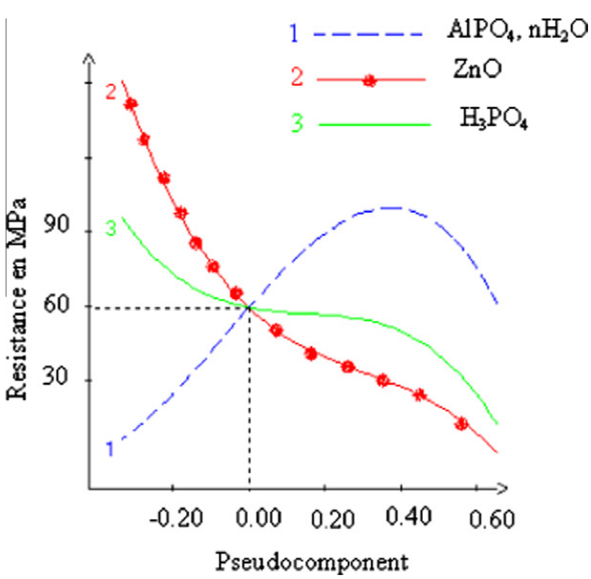

Figure 4 The plotted effects of pseudo-components on the response of cement hardness according to Piepel direction.

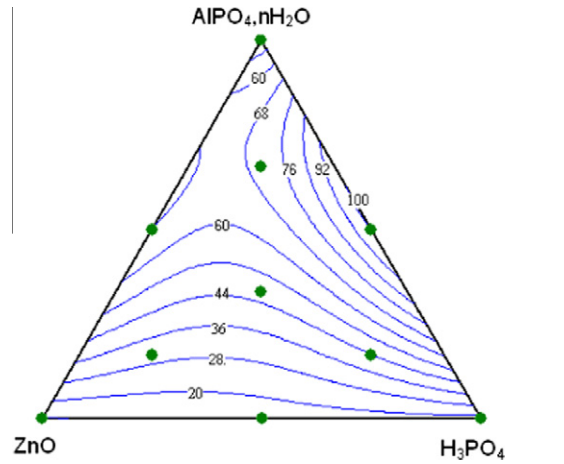

Figure 5 The isoresponses graph for regression model of the cement hardness (in pseudo-components).

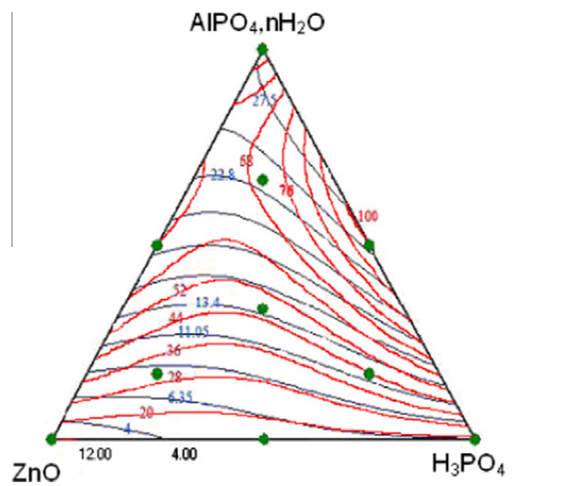

Figure 6 Graphic of areas which the specifications are met for both responses such as the setting time and strength of cement.

- Exploration of the local area of cement in the tertiary system ($AlPO_4$, nH_2O ZnO–H_3PO_4), which is limited by the margins of compositions following:
- 2.80% < $ALPO_4$ < 19.2%
- 37.2% < ZnO < 53.6%
- 43.6% < H_3PO_4 < 66%
- The setting reaction of cement is mainly due to the reaction between orthophosphoric acid and zinc oxide
- The aluminium phosphate delays the setting reaction of cement.
- The aluminium phosphate, in addition to its role retarder, has contributed to the increase in mechanical hardness of cement.
- The plotted of isoresponses curves allowed us to identify areas of compromise for both responses and there by broaden the scope of use of cement according to each composition.

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