56º Congresso Brasileiro de Cerâmica
1º Congresso Latino-Americano de Cerâmica
IX Brazilian Symposium on Glass and Related Materials
03 a 06 de junho de 2012, Curitiba, PR, Brasil

MODIFICATIONS ON THE PROPERTIES OF A CALCIUM PHOSPHATE CEMENT BY ADDITIONS OF SODIUM ALGINATE

Coelho, W. T.[1,a], Fernandes, J. M.[1,b], Vieira, R. S.[1,c], Thurmer,, M. B.[1,d], Santos, L.A.[1,e]

[1]*Universidade Federal do Rio Grande do Sul – PPG3M –LABIOMAT - BRAZIL*
[a] trajano@ufrgs.br, [b] julianafernandes2@yahoo.com.br, [c] rsvieira.eng@gmail.com,
[d] monicathurmer@yahoo.com.br, [e] luis.santos@ufrgs.br

Keywords: calcium phosphate cement (CPC), sodium alginate, compression resistance.

Abstract. The Calcium Phosphate Cement (CPC) are bone substitutes with great potential for use in orthopedics, traumatology and dentistry due to its biocompatibility, bioactivity and osteoconductivity, and form a paste that can be easily shaped and placed into the surgical site. However, CPCs have low mechanical strength, which equals the maximum mechanical strength of trabecular bone. In order to assess the strength and time to handle a CPC composed primarily of alpha phase, were added sodium alginate (1%, 2% and 3% wt) and an accelerator in an aqueous solution. The cement powder was mixed with liquid of setting, shaped into specimens and evaluated for apparent density and porosity by Archimedes method, X-ray diffraction and compressive strength. A significant increase in compressive strength by adding sodium alginate was verified.

Introduction

Currently the interest in verifying the new opportunities generated by the use of Calcium Phosphate Cement (CPC) [1] and the wide range of compounds that can be added in the formulation to provide different properties [2-4], has aroused the research for compositions that show results similar to the porosity of bone tissue and with high mechanical strength [5]. Thus, there was the need to maximize the mechanical properties of Tricalcium Phosphate (TCP), suitable for biomedical applications. Several authors suggest the addition of polymers as catalysts of this purpose [6-8], among them are the hydrogels, specifically sodium alginate [9, 10] by presenting an excellent biocompatibility. Due to its viscosity when diluted, was chosen concentrations of 1, 2 and 3% by weight of Sodium Alginate to be added to the accelerator Disodium Hydrogen Phosphate (Na_2HPO_4) and verified the influence of this addition in the cement setting time, apparent porosity and compressive strength. Cured after 24 hours in an environment with 100% humidity, was verified the formation of Calcium Deficient Hidoxyapatite (CDHA) through XRD patterns and scanning electron microscopy (SEM).

Materials and methods

Initially it was prepared Calcium Pyrophosphate (γ-$Ca_2P_2O_7$) by burning Dibasic Calcium Phosphate, DCPD ($CaHPO_4.2H_2O$), at 550°C for 5 hours. Calcium Carbonate ($CaCO_3$) was added, in proportion to the Calcium Pyrophosphate Ca/P equal to 1.5 mol/mol. The mixture was heated at 1500°C for 3 hours. To identify the crystalline phases present in the CPC was used a diffractometer Phillips XPERT MPD, with tubes with copper target ($\lambda CuK\alpha$ = 1.5418 A) at 40 kV and 40 mA. The diffraction patterns were obtained using the geometry $\theta/2\theta$ in the range of 20-50° (2θ), with an increment of 0.05 ° in a time of 3 sec/step. The distribution and average particle size were determined using the technique of Laser Diffraction Particle Size CILAS 1180. To the CPC powder was added 40% by weight of liquid solution containing

56º Congresso Brasileiro de Cerâmica
1º Congresso Latino-Americano de Cerâmica
IX Brazilian Symposium on Glass and Related Materials
03 a 06 de junho de 2012, Curitiba, PR, Brasil

2.5% Disodium Hydrogen Phosphate (Na_2HPO_4), to accelerate the setting time, and 0, 1, 2 and 3% sodium alginate (w/v) . The specimens were prepared for compression test according to ISO 5833 [11]. For the setting time test, the powder and liquid were mixed in a beaker for one minute and the initial and final setting time for the cement paste were determined with Gillmore needles according to ASTM C266 [12]. The setting time was recorded when the needle failed to create an indentation depth of 1 mm in three distinct areas. Tests of Bulk Density and Apparent Porosity were performed according to ASTM C20-00(2010) [13]. After curing of the cement, the compression specimens were kept in 100% humidity for 24 hours and tested at the traction machine 1105C Applied Test System, with a speed of 0.5 mm/min using a load cell ALFA Instruments Z100 100kg. After testing, some specimens were separated to perform SEM in the JEOL SEM - JSM 6060 and others specimens were crushed and sieved to perform XRD patterns in order to identify phases in cement.

Results and discussions

The distribution of particles sizes by sedimentation of CPC after grinding in an alcoholic medium was ranged from 25.0 to 1.50 μm, with a mean size of 12.0 mm (Fig. 1), which are similar to that reported in literature [14, 15], with a distribution of 25.2 micrometers. The amount of liquid containing 2.5 wt% Na_2HPO_4 (0.4 ml / g) used is the same as reported in the literature [16,17] to produce consistency of a paste. The size distribution of powder particles in all types of cement is a key reason to the liquid/powder needed to produce a paste with the proper consistency [18].
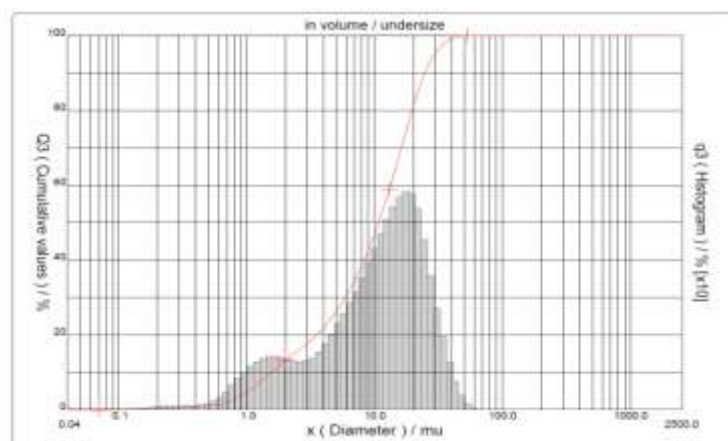

Fig. 1 - Size and particles distribution

The measurements of setting times of the samples, shows that the addition of Sodium Alginate decreases the initial and final time of hydraulic setting for CPCs, according to the literature [19-22]. These results suggest that the polymerization reaction of Sodium Alginate is responsible for the initial increase in mechanical strength or increases the setting process.

% Sodium Alginate	0%	1%	2%	3%
Initial setting [min]	30 +/- 3	20 +/-3	23 +/-3	25 +/-3
Final setting [min]	65 +/- 5	45 +/-5	47 +/-4	50 +/-5

Tab. 1 – Setting times

The amount of pores existing in the specimen can be evaluated by Apparent Porosity, which is a favorable factor for the developing tissue, allowing tissue growth into the pores [20], but decrease compressive strength [21]. According to the data, for samples with additons of 1, 2

56º Congresso Brasileiro de Cerâmica
1º Congresso Latino-Americano de Cerâmica
IX Brazilian Symposium on Glass and Related Materials
03 a 06 de junho de 2012, Curitiba, PR, Brasil

and 3% wt sodium alginate there are increase of 10% on Apparent Porosity and Bulk Density decreases. These results are according to the literature [7, 8, 10].

Sample	AP (%)	BD [g/cm^3]
0% Alg	30,23 ±1,43	1,80 ± 0,05
1% Alg	33,25 ± 1,37	1,76 ± 0,05
2% Alg	33,16 ± 0,86	1,74 ± 0,02
3% Alg	33,54 ± 0,81	1,67 ± 0,02

Tab. 2 - Values of Apparent Porosity (AP) and Bulk Density (BD).

The introducing of Sodium Alginate increases the viscosity of the liquid added, with increasing the distance between particles, as compared with the control sample, which has only the accelerator Disodium Hydrogen Phosphate. The composition CPC with 2% Sodium Alginate has the highest value of mechanical strength, 14.75 MPa. Based on the sample without addition of Sodium Alginate as a reference, 12.5 MPa, the value of strength was similar to the literature [1, 2, 6, 22, 23]. The sample with 2% Sodium Alginate presented a compressive strength 17% higher and the sample with 3% Sodium Alginate presented 22%. Lower than sample control.
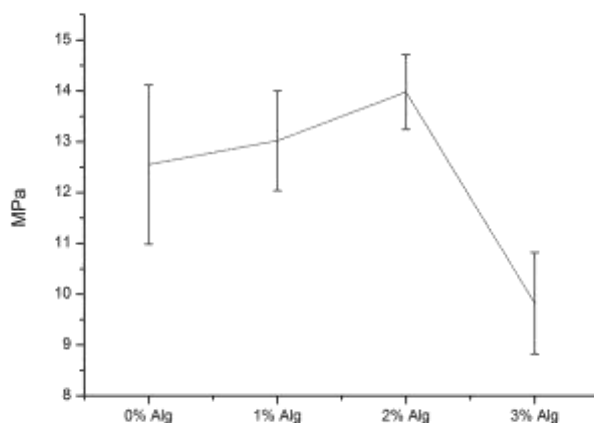

Fig. 2 - Sodium Alginate influence on compressive strength

As you add the Sodium Alginate in the liquid mixture of cement, is the removal of particulate, which can be verified in their Bulk Densities. Probably the addition of 2% Sodium Alginate was the composition that optimizes this removal, providing a better locking the microstructure due to the emergence of CDHA, which appears in acicular form. By increasing this distance, appear pores that cannot be perfectly filled by the CDHA needles, weakening the material's microstructure. Due to the ceramic process variables, we obtained a value of standard deviation for samples, compatible CPC, which are prepared, in most cases, in situ [13].

56º Congresso Brasileiro de Cerâmica
1º Congresso Latino-Americano de Cerâmica
IX Brazilian Symposium on Glass and Related Materials
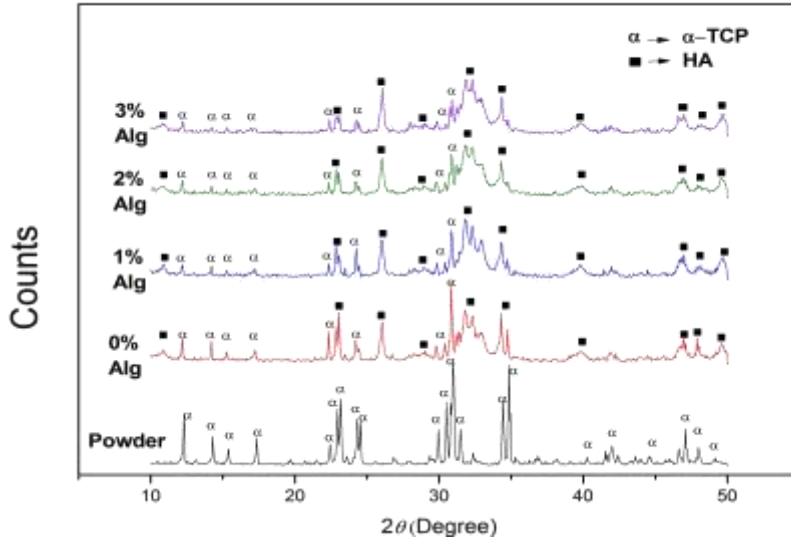03 a 06 de junho de 2012, Curitiba, PR, Brasil

Fig. 3 – XRD patterns from the samples

In XRD patterns is possible to identify the presence of CDHA in samples that were processed with Disodium Hydrogen Phosphate, with or without Sodium Alginate. The XRD pattern shows the formation of CDHA in CPC after 24 hs in an atmosphere with 100% humidity, consistent with the literature [1-4]. There was only a partial transformation of α-TCP into CDHA, showing that reaction is influenced by time. Can be noted a decrease on α-TCP diffraction peak at $2\theta = 30,7º$, showing a setting acceleration with increase of Sodium Alginate content.
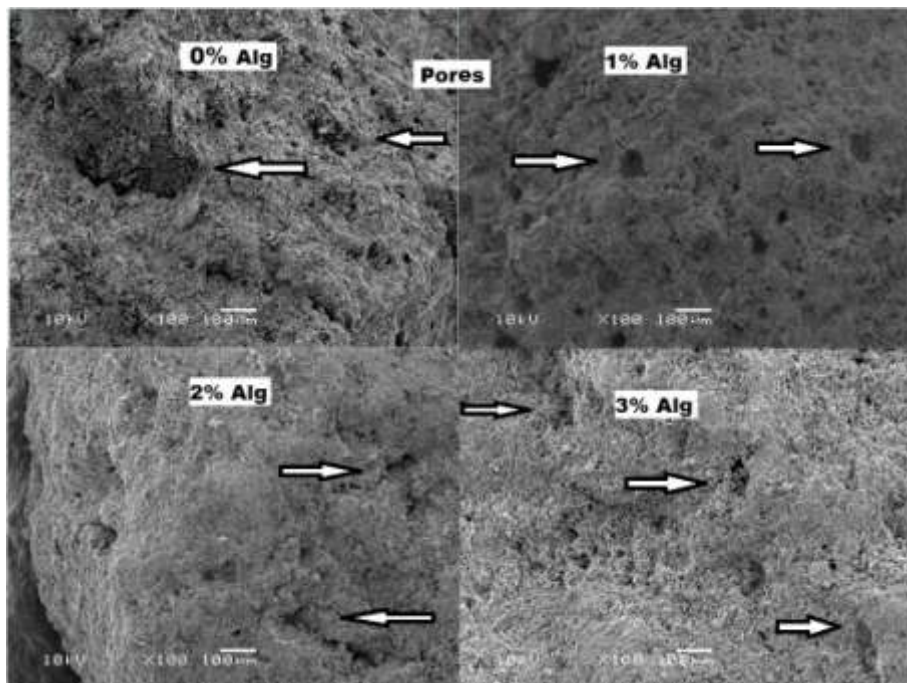

Fig. 4- SEM fracture surface, showing pores

It can be seen in Fig. 4, the porosity characteristics of TCP cements, this is a determinant factor of its low mechanical strength and apparent porosity consistent with previously presented.

56º Congresso Brasileiro de Cerâmica
1º Congresso Latino-Americano de Cerâmica
IX Brazilian Symposium on Glass and Related Materials
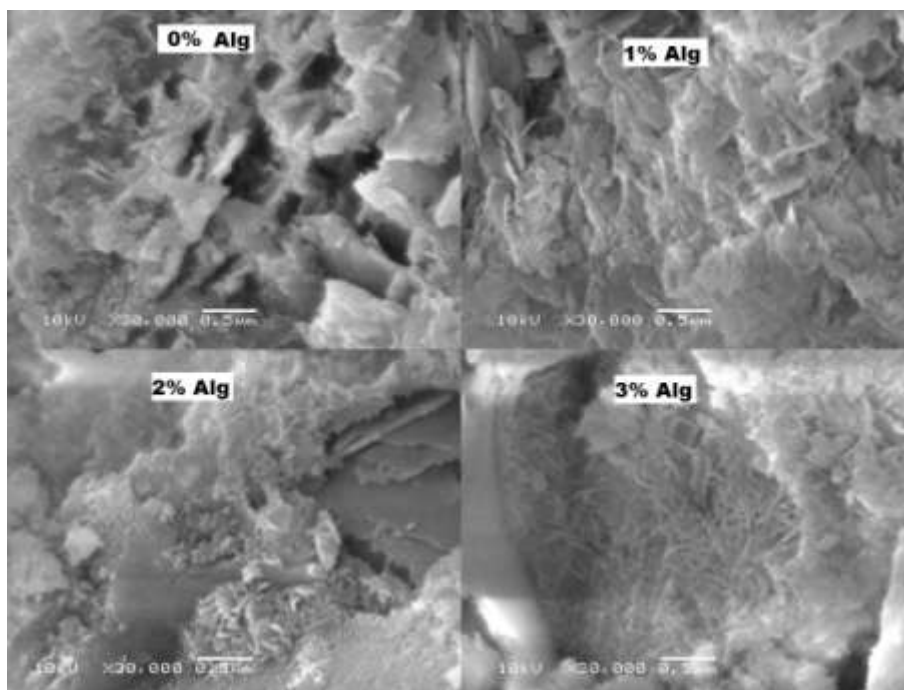03 a 06 de junho de 2012, Curitiba, PR, Brasil

Fig. 5 - SEM fracture surface showing the CDHA needles.

The presence of CDHA (fig. 5) is the essential factor for the increase of CPCs in the mechanical strength [1-4]. There were not evident differences on the microstructure of all samples.

Conclusions

The addition of sodium alginate increased the apparent porosity and decreased the apparent density in all samples. The addition of 2% sodium alginate showed an increase of 17% in compressive strength, even with a high porosity. The addition of 3% sodium alginate showed a reduction in compressive strength of 22%. The XRD patterns showed the presence of CDHA in all samples tested, which was confirmed by scanning electron microscopy.

Acknowledgements

References

[1] L.A. Santos: *Cimento de Fosfato de Cálcio Reforçado por Fibras*, Campinas: Faculdade de Engenharia Mecânica, Universidade Estadual de Campinas, 2001. 249 p. Tese (Doutorado)
[2] H. L. Alves, in: *Influência de aditivos na injetabilidade de cimento ósseo de fosfato tricálcico* (2006). Dissertação de Mestrado.
[3] S. Ming-you, C. David, W. Chuan-yeh, C. Ting-yi and D. Shinn-jyh, in: *Immersion behavior of gelatin-containing calcium phosphate cement, Acta Biomateriali*a, Volume 4, Issue 3, May 2008, Pages 646-655.
[4] Y. Atsuro, K. Takao and N. Masanori, *Development of calcium phosphate cement using chitosan and citric acid for bone substitute materials, Biomaterials, Volume 23, Issue 4*, 15 February 2002, Pages 1091-1101.
[5] M.Y. Shie, D. C. Chen, C. Y. Wang, and S. J. Ding in: *Immersion behavior of gelatin-containing calcium phosphate cement.(2008) Acta Biomaterialia*, 4 (3), pp. 646-655.

56º Congresso Brasileiro de Cerâmica
1º Congresso Latino-Americano de Cerâmica
IX Brazilian Symposium on Glass and Related Materials
03 a 06 de junho de 2012, Curitiba, PR, Brasil

[6] Y. Fujishiro and K. Takahashi in: *Preparation and compressive strength of a-tricalcium phosphate/gelatin gel composite cement. J. Biomed Mater Res* 2001;54:525–30.

[7] A. Bigi, B. Bracci and H. Panzav in: *Effect of added gelatin on the properties of calcium phosphate cement. Biomaterials* 2004;25:2893–9.

[8] L. A. Santos, L. C. Oliveira, E. C. S. Rigo, R. G. Carrodeguas, A. O. Boschi and A.C. Arruda in: *Influence of polymeric additives on the mechanical properties of α-tricalcium phosphate cement. Original Research Article Bone, Volume 25, Issue 2, Supplement 1*, August 1999, Pages 99S-102S

[9] I. Kunio, M. Youji, Y Masa, N. Masaru and A. Kenzo. In: *Non-decay type fast-setting calcium phosphate cement: composite with sodium alginate, Biomaterials, Volume 16, Issue 7,* May 1995, Pages 527-532.

[10] S. Tajima, N. Nishimoto, Y. Kishi, S. Matsuya and K. Ishikawa in: *Effects of added sodium alginate on mechanical strength of apatite cement. Dent Mater J* 2004; 23:329–34.

[11] ISO 5833:*2002 Implants for surgery - Acrylic resin cements.*

[12] C266-08 *Standard Test Method for Time of Setting of Hydraulic-Cement Paste by Gillmore Needles*

[13] C20-00(2010) Standard Test Methods for Apparent Porosity*, Water Absorption, Apparent Specific Gravity, and Bulk Density of Burned Refractory Brick and Shapes by Boiling Water.*

[14] M. P. Ginebra, F. C. Driessens and J.A. Planell in: *Effect of the particle size on the micro and nanostructural features of a calcium phosphate cement: a kinetic analysis, Biomaterials, Volume 25, Issue 17*, August 2004, Pages 3453-3462.

[15] L. C. Chow, M. Markovic, S. Tagaki and M. Cherng in: *Injectable calcium phosphate cements: effects of cement liquid on the physical properties of the cement. Innov Tech Med 18*, 1997.

[16] F. C. Driessens, M. G. Boltong, O. Bermudez and J. Planell in: *Effective formulations for the preparation of calcium phosphate bone cements. J Mater Sci Mater Med 5* (1994), pp. 164–170.

[17] E. Fernández, M. P. Ginebra, O. Bermudez, M. G. Boltong and F. C. Driessens in: *Dimensional and thermal behaviour of calcium phosphate cements during setting compared to PMMA bone cements. J Mater Sci Lett 14* (1995), pp. 4–5.

[18] Y. Fukase, E. Eanes, S. Tagaki and L. S. Chow in: *Setting reactions and compressive strengths of calcium phosphate cements. Journal of Dental Research, v. 69, n. 12, p. 1852-1856*, 1990.

[19] Y. Miyamoto, K. Ishikawa, H. Fukao, M. Sawada, N. Masaru and M. Y. Asaoka in: *In vivo setting behaviour of fast-setting calcium phosphate cement, Biomaterials, Volume 16, Issue 11, July* 1995, Pages 855-860.

[20] J. L. Machado in: *Desenvolvimento de Cimento ósseo de Fosfato de Cálcio como suporte para o crescimento de tecidos, Porto Alegre: Programa de Pós-graduação em Engenharia de Minas, Metalurgia e de Materiais, Universidade Federal do Rio Grande do Sul, 2007. 101 p. Dissertação de Mestrado.*

[21] E. Fernandez, M. Vlad, M. Montserrat, J. Lopez, R. Torres and J. Cauich in: *Modulation of porosity in apatitic cements by the use of [alpha]-tricalcium phosphate-calcium sulphate dihydrate mixtures, Biomaterials, Volume 26, Issue 17, June* 2005, Pages 3395-3404.

[22] A. Bigi, B. Bracci and S. Panza in: *Effect of added gelatin on the properties of calcium phosphate cement, Biomaterials, Volume 25, Issue 14, June* 2004, Pages 2893-2899.

[23] Q. Yang, T. Troczynski and D. Liu in: *Influence of apatite seeds on the synthesis of calcium phosphate cement, Biomaterials, Volume 23, Issue 13, July* 2002, Pages 2751-2760.