

THE HARDENING PROCESS AND MECHANICAL PROPERTIES OF CALCIUM PHOSPHATE CEMENT BY APPLICATION OF $\text{KH}_2\text{PO}_4\text{-H}_3\text{PO}_4$ HARDENING LIQUID

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Abstract

The hardening mechanism and influence modification of 1.5 M KH_2PO_4 hardening liquid by H_3PO_4 on compressive strength and setting characteristics of calcium phosphate cement were studied. The brushite was formed in a very short period from the addition of KH_2PO_4 hardening liquid to the cement mixture by the interaction between TTCP and KH_2PO_4 . Final product of the hardening process is nanocrystalline calcium deficient hydroxyapatite. The hardening process of cements in SBF was studied. Addition of phosphoric acid to KH_2PO_4 caused a rapid increase in setting times of cements and lowering of the resistance to disintegration in SBF. Cements prepared with KH_2PO_4 as a hardening liquid were resistant to wash out immediately after mixing. Maximum of compressive strength was around 80 – 100 MPa in cements soaked in SBF.

Keywords: calcium phosphate cement; compressive strength; setting time; $\text{KH}_2\text{PO}_4\text{-H}_3\text{PO}_4$

INTRODUCTION

Calcium phosphate cements (CPC) are highly compatible with soft and hard tissues because of the apatitic nature of the setting reaction products. The combination of setting and biocompatibility makes calcium phosphate cements useful materials in a great variety of medical and dental applications. The transformation of CPC components – tetracalcium phosphate (TTCP) and dicalcium phosphate anhydrous (DCPA) – with phosphoric acid (1M) as hardening liquid showed the gradual transformation of these phases to nanocrystalline hydroxyapatite in Hank's solution. Compressive strength of cement increased with soaking time [1]. HAP particles were formed after partial dissolution of TTCP in phosphoric acid solution as hardening liquid of cement [2]. Comparison of hardening process of $\text{Ca}(\text{OH})_2\text{-KH}_2\text{PO}_4$ and TTCP-DCPA cements, where 1M KH_2PO_4 was used as hardening solution, indicates that transformation of components in cement mixture to nanocrystalline HAP was faster in cement on $\text{Ca}(\text{OH})_2$ basis and peaks corresponding to starting compounds have been found in XRD patterns in tetracalcium phosphate cement after 45 minutes from the beginning of mixing [3].

In our work we studied the mechanism of hardening process of TTCP-DCPA cement with KH_2PO_4 solution as hardening liquid and the effect of phosphoric acid addition into hardening liquid on setting characteristics, compressive strength and cement microstructure after soaking in SBF solution.

EXPERIMENTAL PROCEDURE

Tetracalcium phosphate (TTCP) was prepared by annealing an equimolar mixture of calcium carbonate (CaCO_3 (analytical grade), Sigma Aldrich) and dicalcium phosphate anhydrous (DCPA (Ph.Eur.), Fluka) at 1450°C for 5 hours. The cement powder mixtures were composed of TTCP and DCPA in equivalent molar ratio. As hardening liquids, 1.5 M KH_2PO_4 and 1.5 M $\text{KH}_2\text{PO}_4 + 8.5\% \text{H}_3\text{PO}_4$ (1+1) solutions with the same phosphorus content were used. CPC (calcium phosphate cement) powder and hardening liquids were mixed with P/L = 2:1 in a glass mortar. Cement (or cement pastes) were signed as 1, 2 according to used hardening liquid (1 - 1.5 M KH_2PO_4 , 2 - 1.5 M $\text{KH}_2\text{PO}_4 + 8.5\% \text{H}_3\text{PO}_4$ (1+1)). The resultant paste was placed into a stainless steel mould (6 mm D \times 12 mm H). The force applied to the rod during packing was 6 MPa or 0.7 MPa. The specimens were immersed into simulated body fluid (SBF) (prepared according to [4]) at 37°C for 1, 2, 4, 24 hours. The compressive strengths were measured on a universal testing machine (LR5K Plus, Lloyd Instruments Ltd.) at a crosshead speed of 1 mm/min for each experimental group (3 samples). The setting time (ST) of the cement pastes were evaluated by using a 1 mm tip diameter of Vicat needle with a 400g load (according to ISO standard 1566), which fails to make a perceptible circular indentation on the surface of the cement.

RESULTS AND DISCUSSION

In the microstructure of cement (1) after 30 minutes of hardening in 100% humidity, Fig.1a, smooth particles with average size of 6 μm and pores with sizes between 5 – 10 μm can be visible. The presence of fine-grained phase in close environment to TTCP particle is clearly visible in Fig.1a. Nontransformed core of TTCP particle in cement (1) after 7 days of hardening in 100% humidity is shown in Fig.1b. In this figure, the needle-like particles of apatitic phase can be found. In microstructure of cement (2) after 7 days of hardening in 100% humidity, Fig.1c, the same pore distribution (1-5 μm) was observed and pores had irregular shape. Differences in microstructures of cements are clear from the comparison of apatite particle morphologies, where particles in cement (2) had more plate-like and coarser shape, particles in cement (1) were more rod shaped. The porosities of all types of cements after 7 days hardening in 100% humidity were around 40%. No effect of compaction pressure (0.7 and 6 MPa) on porosity of cements was found and cements had porosities around 40%. The change in compaction pressure from 0.7 to 6 MPa caused 20-30% increase of compressive strength in cement (1) for all used soaking times, Fig.2. The compressive strength rose with hardening time in SBF, being approximately 30 MPa after 1 hour. This is sufficient from the point of view of practical application of cements as bone defect filler. The maximum compressive strength (80 MPa) in cement (1) was achieved after 24 hours of hardening in SBF and no changes in compressive strength of the cement are found after prolongation of hardening. The compressive strengths of cements hardened in 100% humidity were lower than of those soaked in SBF during 7 days, Fig.3. In the microstructure of cement (2) after 14 days of soaking, hydroxyapatite particles with plate-like morphology predominate, being 200-300 nm in length and thickness of tens of nm. The highest values of compressive strength were found in cements with rod-like shaped particles of 200 nm length (100 MPa in cement (2)). Setting time of cement (1) equals 4 minutes and this value is markedly (4 times) lower than that for cements (2). Note, the cement paste (1) can be immersed to water solutions without desintegration practically immediately after mixing with hardening liquid (in 2-3 minutes). Cement paste (2) is resistant to wash out after 10 and 15 minutes from the addition of the hardening agent.

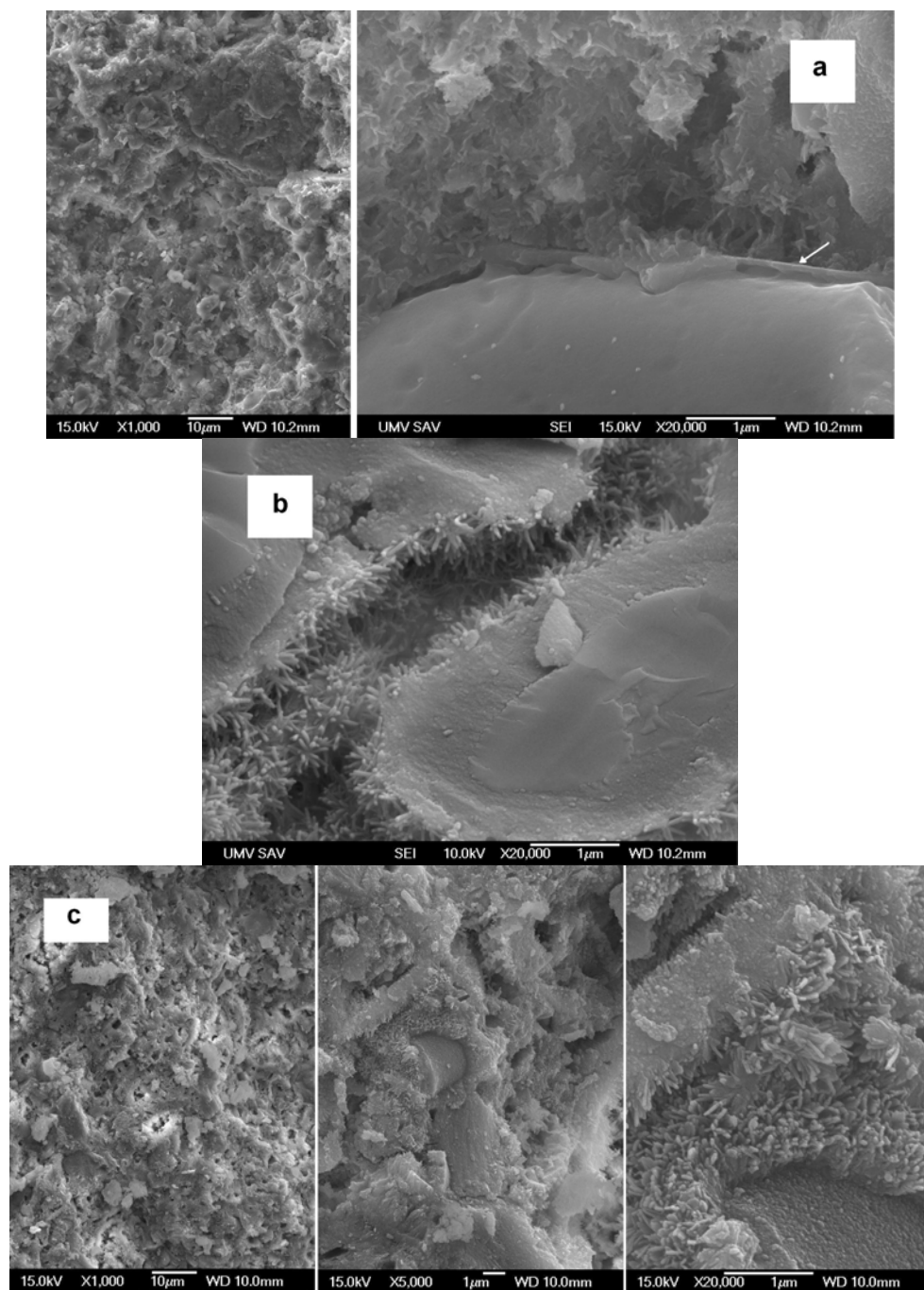


Fig.1. Microstructure of cement (1) after 30 minutes of hardening in 100% humidity (a), nontransformed core of TTCP particle in cement (1) after 7 days of hardening in 100% humidity (b), microstructure of cement (2) after 7 days of hardening in 100% humidity (c).

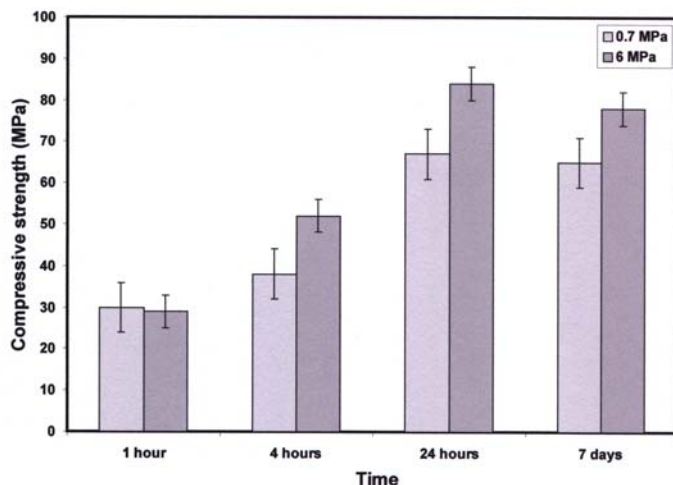


Fig.2. Effect of compaction pressure 0.7 and 6 MPa on compressive strength of cement (1) after soaking in SBF for 1, 4, 24 hours and 7 days.

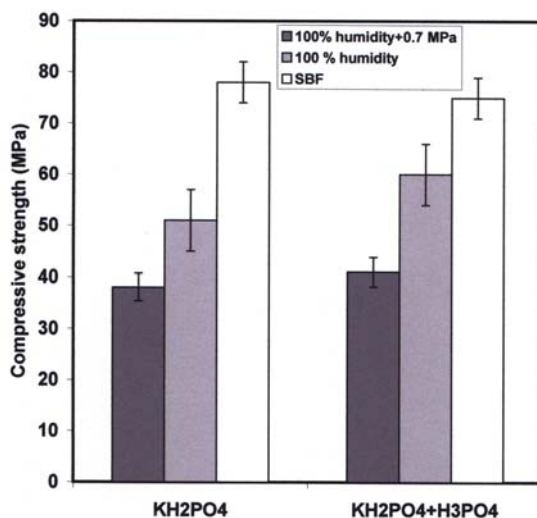


Fig.3. Comparison of compressive strength of cements (1,2) hardened in 100% humidity during 7 days without and after compaction with 0.7 MPa and in SBF.

CONCLUSION

Brushite was formed by interaction between TTCP and KH₂PO₄ in a very short period after addition of KH₂PO₄ hardening liquid to TTCP-DCPA cement mixture. Addition of phosphoric acid to KH₂PO₄ caused a rapid increase in setting times of cements and lower resistance to desintegration after immersion into SBF. Cement with pure KH₂PO₄ hardening liquid was resistant to wash out immediately after mixing (around 2 minutes). Compressive strengths were around 80-100 MPa in cements soaked in SBF.

Acknowledgements

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