

Calcium Phosphate and Gypsum Composite Set with Hydroxypropyl Methylcellulose for Control of Degradation Rate

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Statement of Purpose: In order to control degradation rate of scaffolding materials, tricalcium phosphate-gypsum [1] or hydroxyapatite-gypsum [2] composite materials have been tried in resorbable bone regeneration area. However, fast resorption of gypsum involves some degradation debris, which may give birth to rapid decrease of mechanical strength of 3-dimensional scaffold during resorption in case of gypsum coating on porous calcium phosphate scaffold. Hydrosoluble polymer such as hydroxypropyl methylcellulose (HPMC) or its derivatives have been used in injectable bone substitute or bone cement area with calcium phosphates as a carrier of granules and a good spacer for angiogenesis and osteoconduction [3]. HPMC is also used as a binder in industrial field, and may play a role in preventing degradation debris of gypsum during degradation. In this study, degradation rate of different types of gypsum and calcium metaphosphate (CMP)-gypsum composite was investigated in terms of weight loss in revised simulated body fluid (r-SBF) for 21 days. In order to evaluate the effect of HPMC on preventing degradation debris of gypsum, half of CMP-gypsum composites were set with HPMC.

Methods: Calcium sulfate dehydrate (CSD) and hemihydrate (CSH) powders were used from Duksan Chemical Co., Korea (98%, respectively) and calcium sulfate anhydrite (CSA) powder was prepared by calcination of CSH at 300°C for 3 hours. These powders were mixed with water at a ratio of 1:1 and the slurries were set in a plastic mold with a diameter of 15 mm in diameter. CSH200 and CSH600 were prepared by heat-treatment of self-hardened CSH disks at 200°C and 600°C, respectively. CMP-CSA composite disks with 5, 10, 20, 30, 50, and 70 vol% of CSA were prepared by powder compaction and sintering at 900°C. In order to evaluate the effect of HPMC on prevention of debris, CMP-CSA composites were set with 0.25% HPMC solution with a ratio between gypsum and water was 1:1 and amount of CMP for self-hardening was 5, 10, 20 wt% to gypsum. The prepared samples were soaked in r-SBF for 1, 3, 7, and 21 days. The crystallographic phases of each disk were investigated by XRD and surface morphology changes with soaking time in SBF were examined by SEM. The degree of degradation of samples was measured in terms of percentage weight loss compared to that before soaking in r-SBF.

Results / Discussion: From the XRD patterns, CSD, CSH and CSA powders was all transformed into CSD after setting with water. But CSH200 appeared the same in phase after setting, and CSH heat-treated at 600°C showed CSA from XRD patterns. In CMP-CSH sintered at 900°C showed quite dissimilar patterns; CMP for 5 vol% CSH, $\text{Ca}_4\text{P}_6\text{O}_{19}$ for 10~30 vol%, $\text{Ca}_2\text{P}_2\text{O}_7$ for 50 vol%, and $\text{Ca}_2\text{P}_2\text{O}_7$ /CSA mixture for 70 vol%,

respectively. From weight loss data in r-SBF, all of gypsums were highly degraded by 1 (CSH200) ~13 % (CSD) even at 1 day, 4~34 % at 3 days, 34~61 % at 7 days, and 74 (CSH200)~99 % (CSA) at 21 days. For CMP-CSA composites, the degradation was considerably retarded compared to those of gypsums. The weight of some CMP-CSA composites increased slightly at 1 day above initial weight, which was considered by a little weight increase due to phase transformation of CSA into CSD in r-SBF. There was no significant weight loss by 50 vol% of CSA because the added CSA transformed already into $\text{Ca}_4\text{P}_6\text{O}_{19}$ or $\text{Ca}_2\text{P}_2\text{O}_7$ which were less degradable phases than gypsum. CMP-70%CSA composite was degraded by about 10.12 % at 7 days and 36.5 % at 21 days due to presence of resorbable CSA phase. In case of CMP-gypsum composite set with HPMC, the samples with above 30wt% of CMP to gypsum would not set fully, in contrast, gypsum with CMP less than 20 wt% was set harder than the case without HPMC. Gypsum debris in CMP-gypsum composite was considerably decreased in r-SBF due to HPMC addition, but its efficacy need to be followed up for extended time period because the samples were only self-hardened and not heat-treated at elevated temperature.

Conclusions: Various phases of gypsums were studied in terms of degradation rate in r-SBF to control degradation rate. All gypsums were degraded so fast for 21 days, however, the degradation of CMP-CSA composite was affordably retarded compared to gypsums. With HPMC, gypsum debris was decreased during degradation. It is thought that the degradation of CMP is able to be controlled properly with the addition of gypsum.

References:

- [1] M. Bohner: Biomaterials 25 (2004), p. 741-749.
- [2] S. Sato, T. Koshino, and T. Saito: Biomaterials 19 (1998), p. 1895-1900.
- [3] G. Daculsi, P. Weiss, J.M. Bouler, O Gauthier, F. Millot and E. Aguado, Bone, 25 (2) (1999), p. 59S-61S.

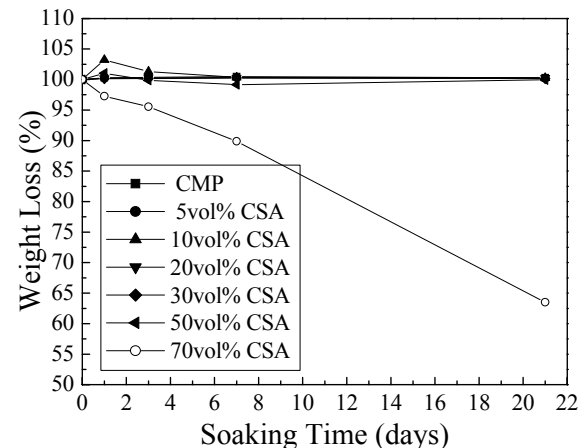


Fig. 1. Weight loss curves of CMP-CSA disks with different CSA contents in r-SBF.