DIAMETRAL TENSILE STRENGTH OF POLYMER-CONTAINING CALCIUM PHOSPHATE CEMENTS

KENJI MUROYAMA, KIMIHIRO YAMASHITA, and TAKAO UMEGAKI

Department of Industrial Chemistry, Faculty of Engineering,
Tokyo Metropolitan University,
1-1 Minami-Ohsawa, Hachioji, Tokyo 192-03

Abstract The effect of additives such as polyvinylalcohol, polyacrylamide, acrylamide and acrylic acid on the mechanical properties of calcium phosphate cement was investigated, measuring the diametral tensile strength of the hardened cement made by pressing the cement paste. Of the additives tested, the combined use of acrylamide monomer and acrylic acid was effective to improve the mechanical properties of the hardened cement. For the cements made by pressing at various pressures (72.8 - 291MPa), the addition of acrylamide and acrylic acid resulted in an about 30% increase of the diametral tensile strength and an about 7% increase of the bulk density compared to the control (no additives). The hardened cement with acrylamide and acrylic acid exhibited a diametral tensile strength of 15.4 MPa as the largest values obtained.

Introduction

A number of studies have been performed on calcium phosphate cements in recent years. Calcium phosphate cements are expected to be used as biomaterials due to their biocompatibility and self-setting capability. However, one of the problems encountered on practical applications is that their mechanical strengths are relatively low compared to bone and teeth. We have studied the effect of addition of polymer on preparation of hardened calcium phosphate cements to improve their mechanical strength. In the previous study we described that the addition of acrylamide led to improving the mechanical properties of the calcium phosphate cements.¹⁾ Recently, we found that the use of a small amount of

acrylic acid in addition to acrylamide was more effective than the use of acrylamide alone for strengthening the hardened cement. In this study the bulk density of the hardened cements with additives, water-soluble polymers, was increased by pressing the cement paste, and the effect of the additives on the diametral tensile strength of the hardened cement was examined.

Experimental

The thermal decomposition product of hydroxyapatite (HAp) was used as a cement. Hydroxyapatite (HAP200, Taihei Kagaku Sangyo, Ltd.) was decomposed at 1450°C for 3 hours and cooled under nitrogen. The slightly sintered product was ground in a mortar and sieved to a size of less than 75 μ m. The additives used and the compositions of the cement paste are shown in Tables 1 and 2, respectively. Additives were dissolved in deionized water to be a solution. The cement was added to the solution and the resulting paste was mixed using a spatula in a ultrasonic cleaner for three minutes. Discs (6 - 7 $\times$ 13mm ϕ) were made by pressing the paste uniaxially in a cylindrical die at various pressures for

Table.1 Additives used for the preparation of calcium phosphate cement .

Additives	Abbreviation
Polyvinylalcohol *	PVA
Polyacrylamide * *	PAAm
Acrylamide	AAM
Acrylic acid	AA
N,N'-methylenbisacrylamide	Bis
Ammonium persulfate	APS

* Saponification degree 86.5~89 mol%

Average molecular weight 24,300~24,800

* * Average molecular weight

700,000~1,000,000 (10% in Water)

Table.2 Compositions used for the preparation of calcium phosphate cement pastes.

Additives	Additive/Cement(w/w)	Cement/Water(w/w)
PVA	0.1	2.0
PAAm	0.056	2.0
AAM+Bis	(AAM+Bis)/Cement=0.1 Bis/AAM=0.01	3.3
AAM+AA+Bis	(AAM+Bis)/Cement=0.1 Bis/AAM=0.01 AA/AAM=0.1	3.3
no additives		2.5

0.5 min. The discs were stored in 100% relative humidity at 60°C for 45 h. After curing, the samples were tested for wet diametral tensile strength at crosshead speed of 1 mm/ min. The bulk densities of the samples dried in a vacuum desiccator were determined. For each set of conditions, 5 samples were tested. Some samples dried in a vacuum desiccator were examined using XRD, FT-IR , and SEM.

Results and discussion

The effect of additives on the diametral tensile strength of the hardened cements was examined by preparing discs using a compaction pressure of 146 MPa. The diametral tensile strengths are shown in Fig.1. The diametral tensile strengths of PVA and AAm cements were nearly equal to that of the control (no additives). That of PAAm cement was slightly higher than that of the control. The AAm+AA cement had the highest value of 11.9 MPa. In the previous study the addition of PVA considerably decreased the flexural strength of the hardened cement compared to the control (no additives) because large pores were incorporated into the cement paste.²⁾

However, excluding large pores by pressing improved the mechanical properties of the cement with PVA in this study. XRD analysis showed that α -TCP of the initial cement converted to HAp and tetracalcium phosphate (TeCP) of the initial cement remained in hardened cements for all compositions tested.

For the addition of AAm+AA, which had showed the highest values of diametral tensile strength, the effect of compaction pressure on the diametral tensile strength and the bulk density of the hardened cement was examined. The compaction pressure used were 72.8, 146, 218 and 291

Fig.1 Effect of additives on diametral tensile strength of the hardened cement. (mean ± s.d.). AAm and AAm+AA containing Bis.

MPa. The diametral tensile strength and bulk density are shown in Figs.2 and 3, respectively. The diametral tensile strength and bulk density of both the AAm+AA cement and the control (no additives) increased with increasing of compaction pressure. The diametral tensile strength and bulk density of the AAm+AA cement were higher than those of the control at all compaction pressure examined. An increase of the fluidity of cement paste by the addition of acrylamide seemed to result in the increase of the bulk density of the AAm+AA cement. Further, the increase of the bulk density by the additives led to improving the mechanical strength of the hardened cement at all compaction pressure examined.

X-ray diffraction patterns of the AAm+AA cement and the control had the peaks of HAp and TeCP. The peaks of HAp of the AAm+AA cement were broader than those of the control. The result indicated that the additives lowered the crystallinity of HAp formed in the hardened cement.

Fourier transform infrared spectra of the AAm+AA cement and the control showed PO_4^{3-} bands, OH stretching at 3570 cm^{-1} and OH librational mode at 630 cm^{-1} . The P-OH band at 870 cm^{-1} was also observed in those spectra, indicating that the HAp formed in the hardened cement was calcium deficient. For

Fig.2 Effect of compaction pressure on the diametral tensile strength of the hardened cement: ●; AAm+AA, ■; no additives. (mean $\pm$ s.d.).

Fig.3 Effect of compaction pressure on the bulk density of the hardened cement: ●; AAm+AA, ■; no additives. (mean $\pm$ s.d.).

Table.3 Polymer content in the AAm+AA cement estimated by the FT-IR.

Fig.4 FT-IR spectra of the AAm+AA cement compacted at 146 MPa (a), compacted at 291MPa (b). (KBr disk method)

the AAm+AA cement, the absorption bands of polymer were found as shown in Fig.4 : the C=O band at 1670 cm⁻¹, the N-H band at 1617 cm⁻¹ and the COO- band at 1565 cm⁻¹. The COO- band suggested the bonding between the carboxylic units of polymer and the calcium ions of cements

Polymer content in the AAm+AA cement was estimated by the FT-IR spectral data as a part of the water solution of additives was lost on pressing ; the ratio of peak intensity of C=O (1670cm⁻¹) to that of P-O (1040cm⁻¹) of the samples compacted by pressing was compared with that of the standard sample made without pressing. The polymer content is shown in Table.3. Although the cement paste had contained 9.9 wt% additives when being prepared, half of the additives was lost by pressing. The SEM micrographs of samples prepared by pressing at 291MPa are shown in Fig.5. Needle-like apatite crystals were observed in both the AAm+AA cement and the control. However, the apatite crystals of the AAm+AA cement showed thinner shapes compared to those of the control. This finding was consistent with the XRD results about the crystallinity of HAp.

Fig.5 SEM micrographs
of the fracture surfaces
of the hardened body of
the AAm+AA cement
(a) and the control (no
additives) (b) compacted
at 291MPa.

a

b

Summary

The effect of water-soluble polymers on the diametral tensile strength of the calcium phosphate cements made by pressing was investigated. The addition of acrylamide and acrylic acid brought about improving the mechanical properties of hardened cements; an about 30% increase of the diametral tensile strength for the cement with the additives compared to the control (no additives) was observed.

Acknowledgment

The authors wish to express their appreciation to Taihei Kagaku Sangyo Ltd. for providing hydroxyapatite.

References

1. K.Muroyama, T. Matsumoto, K.Yamashita and T.Umegaki, Inorganic Mater., 3, 380 (1996).
2. T.Matsumoto, K.Yamashita, T.Umegaki and H.Monma, Proceedings of the 33th Symposium of Basic Science of the Ceramic Society of Japan (1995) p.238.