The Effects of Excess Calcium and Aging Media on The Mechanical Properties of Calcium Phosphate Filling Materials

A.S.F. Alqap[1, a], I. Sopyan[2,b] and Suryanto[2,c]

[1]Mechanical Engineering Study Program, Faculty of Engineering, University of Bengkulu, Bengkulu, Indonesia

[2]Department of Manufacturing and Materials Engineering, International Islamic University Malaysia, PO Box 10 Kuala Lumpur, Malaysia

[a]asepsofwan4@gmail.com, [b]sopyan@iium.edu.my, [c]surya@iium.edu.my

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Abstract. The effect of excess calcium and aging media on calcium phosphate biomaterials mechanical strength was studied. The variation of excess calcium and sample type has shown different performance when they are being aged in the moist environment (ME) and the simulated body fluid (SBF). The calcium phosphates were synthesized via low temperature hydrothermal method and sampled to two types of powder-water (3:2) mixture and paste for 90 days of the aging time. Two mechanical tests were applied, compression and diametrical tensile test, while XRD to evaluate phases. Scanning electron micrograph showed the paste samples that soaked in SBF was better entanglement of the particles, better compression strength but with degradation and diametrical tensile strength improvement by aging. Calcium hydroxide and ammonium di-hydrogen phosphoric was traced in all the samples along with calcium deficient hydroxyapatite as the main phase.

Introduction

The ability to form apatite at physiological temperature is essential if a biocompatible, biodegradable bone replacement is to develop. It has been demonstrated that apatite can be formed at low temperature by a cement-like reaction [1]. This occurs by an acid-base reaction involving tetracalcium phosphate or α-tricalcium phosphate with an acidic calcium phosphate, such as monocalcium phosphate monohydrate, anhydrous dicalcium phosphate, or dicalcium phosphate dihydrate.

Regardless the advantage of the products mechanical properties, bone is smart environment, into which biocompatible non-toxic material being implanted is coordinative with the host hard tissue then modifies and substitutes as a new hard tissue. Once filler is put in bone tissue the filler strengthening is accomplished by bone remodeling. It even was noted that an interface as result of bone remodeling between the host bone and the ceramic implant may have strength greater than the host bone and the implant [2]. Beside, the positioning of the implant determines success of biomaterial application [2,3]. Less crystalline hydroxyapatite and Ca-deficient hydroxyapatite (CDHA) play important roles in bone remodeling and bone formation. These considerations and flexible needs in application make research on this material always interesting.

Single pot technique that is meant as straightforward introduction of the filler material from single synthesis process to characterization or application is here introduced. CP materials in the use of filler are in the form of its mixture with water. The effect of the excess CaO of the samples as the mixture of water after different aging times in both moist environment and SBF media were evaluated in terms of mechanical and physical properties.

Materials and Methods

The CP biomaterial was prepared from calcium oxide granules (CaO) (Techno Pharmchem, India) and ammonium di-hydrogen phosphate ($NH_4H_2PO_4$) (Systerm, Malaysia) as the precursors with distilled water as the solvent. For the preparation of the solution, a stoichiometric weight of calcium oxide was mixed with distilled water with vigorous stirring to get a soluble suspension. Into this suspension, ammonium di-hydrogen phosphate powder on the base of 1.67 Ca/P was then added dropwise. The synthesis temperature was between 80-100°C up to paste was obtained. Four synthesized pastes of different excess Ca were prepared: 0, 1, 2, 10 and 20% excess CaO (labeled as CP0, CP1, CP2, CP10 and CP20 respectively). The products were than treated as shown in Fig. 1.

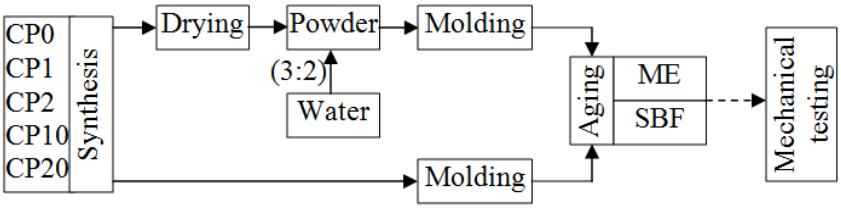


Fig. 1: Flow diagram of the work

The paste was divided into two groups: with drying and without drying. The first, it was dried overnight at 80°C in an oven, then mixed with water as the ratio of powder and water of 3:2. Filled and loaded by hand through steel bar without specific loading force in 6 mm D x 12 mm H and 6 mm D x 3 mm H Teflon moulds, ejected and put in a closed polyethylene box containing moist (moist environment, ME) and being aged for 7d, 15d, 30d and 90d (d is short form of days) in the room temperature. The second, the paste was kept as paste and when the weight was 80% of yield (with the range of - 0% / +10%) the synthesis process was stopped and it was molded by the same procedure, then left as such in the moulds and put in the polyethylene box containing Kokubo's SBF controlled in 37.5°C with initial pH 7.25. After the same aging times the samples were released out, ejected, dried at 50°C over night before the mechanical tests performing by using a Lloyd LR 10 K+ Universal Testing Machine under 1 mm/min crosshead rate of compression and 0.5 mm/min of diametrical tensile tests.

Results and Discussion

Fig. 2 and 3 show phase changes of the (3:2) p/w and Paste samples, respectively, after different aging times as observed from an XRD test with the procedure was described elsewhere [4]. In general the phases that obtained were Ca-deficient hydroxyapatite (CDHA) with two specialties listed in the column **m**, the type that consisted of two adjacent peaks by similar intensity in the range of 31-33 2θº is coded as A, and when the only one as dominant peak in this range is coded as B. The figure also described the traces of $Ca(OH)_2$, CH, with the intensity at **34** 2θº and Ammonium di-hydrogen phosphate, ADP, at **38.3** and **44.5** 2θº. Fig. 2a showed that the intensity of the main peak as shown in the column **cps**, i.e. 31.7 2θº, improved by aging of the (3:2) p/w sample in the moist environment (ME) but not in SBF (Fig. 2b). The excess CaO improved the CDHA pattern when B frequently observed in the samples however this was more after aging in SBF. CH and ADP appeared in all the samples and the times, however, they commonly increased with times when being aged in ME, not in SBF. Fig. 3 shows the Paste samples got more perfect of the CDHA pattern with the excess CaO as the column **m** listed B frequently. The phase intensity (**cps**) improved with aging times in ME and not in SBF. The contaminants intensities generally reduced with aging times.

a: In the moist environment (ME)

	CP0					CP1					CP2					CP10					CP20				
	m	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**
7D	A	70	19		7	A	80	25	7		B'	65	20			A	55	20			B	72	67		
15D	B'	85	20			B'	79	20	10		B'	90	25			B'	55	25			B	60	48		
30D	B'	48	15			B	57	15			C	165	40	17	30	C	165	50	20	45	C	145	62		
90D	B	145	40	30	50	C	160	40	5	10	C	155	35	20	40	C	155	50	7	7	C	135	70	15	35

b: In the SBF media

	CP0					CP1					CP2					CP10					CP20				
	m	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**
7D	A	115	30	125	175	B	152	36	48	78	B	170	45	36	52	B	175	38	22	50	B	175	40	40	60
15D	B	175	40	32	45	A	168	57	102	170	B	165	40	40	68	B	182	43	35	58	A	107	55	180	200
30D	B	130	34	37	36	B	128	27	23	20	B	135	28	52	40	A	145	47	152	118	B	136	30	37	27
90D	B	145	35	-	-	B	144	32	-	-	B	118	27	-	-	B	145	35	-	-	B	140	35	-	-

m is phase pattern as described in the paragraph with **cps** is the tallest peak in intensity at range of 31-34 2θ°.
34 refers to the intensity of 2θ° peaks position of CH and **38.3**, and **44.5** of ADP.

Fig. 2: Phase changing of the (3:2) p/w samples over aging times

a: In the moist environment (ME)

	CP0					CP1					CP2					CP10					CP20				
	m	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**
7D	A	74	130	71	123	A	78	138	28	55	A	81	123	68	149	C	124	55	43	67	C	113	90	27	40
15D	B	80	134	10	24	B	70	130	16	45	B	80	120	5	5	C	130	59	7	18	C	134	78		10
30D	B	77	121	10		C	100	67	5	5	B	108	95	10	28	C	127	67	4		C	135	50	7	4
90D	C	169	35			C	109	50	6	18	C	120	83	5	17	C	150	57	5	5	C	135	60	5	7

b: In the SBF media

	CP0					CP1					CP2					CP10					CP20				
	m	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**	**m**	**cps**	**34**	**38.3**	**44.5**
7D	A	102	23	175	140	B	165	40	76	60	B	162	35	45	32	B	162	36	52	52	B	175	40	35	23
15D	B	126	32	40	43	B	126	28	40	35	B	123	32	45	43	B	123	30	47	32	A	94	12	155	143
30D	A	95	40	175	115	B	128	25	40	28	A	80	20	175	144	B	125	27	55	55	B	132	27	-	-
90D	A	93	20	-	-	A	98	15	15	-	B	123	28	45	35	B	130	25	-	-	A	80	10	162	97

m, **cps**, **34**, **38.3**, and **44.5** are as described in Fig. 1.

Fig. 3: Phase changing of the Paste samples over aging times.

a: CS, ME

MPa	CP0			CP1			CP2			CP10			CP20		
	Min	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**
7D	1.60	1.99	2.34	0.86	1.24	1.43	0.70	1.28	1.59	0.46	0.88	1.10	0.55	0.71	0.90
15D	1.11	1.48	1.67	0.67	0.74	0.85	0.71	0.97	1.33	0.20	0.36	0.48	0.38	0.55	0.77
30D	1.27	1.52	1.75	0.79	1.09	1.43	0.58	0.79	1.16	0.29	0.64	0.95	0.66	0.83	1.02
90D	0.65	1.32	1.65	0.27	0.54	0.83	0.45	0.65	0.88	0.33	0.39	0.45	0.36	0.66	0.88

b: CS, SBF

MPa	CP0			CP1			CP2			CP10			CP20		
	Min	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**
7D	1.09	1.34	1.53	0.70	0.90	1.25	0.44	0.51	0.55	0.62	0.80	0.94	0.32	0.45	0.60
15D	0.40	0.92	1.19	0.17	0.36	0.50	0.35	0.55	0.67	0.56	0.66	0.80	0.26	0.40	0.69
30D	0.45	0.84	1.18	0.57	0.69	0.99	0.42	0.52	0.62	0.50	0.63	0.95	0.28	0.38	0.56
90D	0.68	1.12	1.39	0.64	0.84	1.06	0.38	0.44	0.53	0.50	0.62	0.69	0.21	0.42	0.69

c: DTS, ME

MPa	CP0			CP1			CP2			CP10			CP20		
	Min	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**
7D	0.27	0.32	0.37	0.21	0.31	0.40	0.13	0.26	0.38	0.11	0.13	0.15	0.08	0.13	0.19
15D	0.21	0.33	0.49	0.20	0.30	0.45	0.20	0.26	0.39	0.07	0.11	0.12	0.12	0.15	0.19
30D	0.23	0.38	0.52	0.17	0.27	0.32	0.21	0.30	0.41	0.09	0.14	0.16	0.07	0.14	0.25
90D	0.21	0.28	0.39	0.11	0.14	0.19	0.24	0.33	0.39	0.03	0.09	0.15	0.03	0.06	0.07

d: DTS, SBF

MPa	CP0			CP1			CP2			CP10			CP20		
	Min	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**
7D	0.06	0.13	0.20	0.06	0.11	0.16	0.07	0.09	0.13	0.06	0.08	0.10	0.12	0.15	0.20
15D	0.17	0.20	0.22	0.07	0.12	0.21	0.08	0.09	0.10	0.08	0.10	0.13	0.11	0.17	0.22
30D	0.14	0.18	0.24	0.09	0.12	0.20	0.12	0.14	0.16	0.11	0.14	0.16	0.06	0.15	0.22
90D	0.22	0.27	0.32	0.12	0.15	0.18	0.13	0.16	0.21	0.09	0.14	0.22	0.19	0.25	0.29

Fig. 4: Mechanical changing of the (3:2) p/w samples over aging times.

Fig. 4 shows the effect of aging on the compression and diametrical tensile strengths of the (3:2) p/w samples. The excess CaO reduced the strength of (3:2) after aging in ME and SBF as well (Fig. 4a-b). The soaking in SBF was not helpful to improve the strength, additionally no improvement after aging was observed from these two media. DTS of the samples were low (Fig. 4c-d) however soaking in SBF showed some improvements. This improvement may be due to SBF entered in the thinner samples thoroughly.

It is shown that the strength of the Paste (Fig. 5) was higher than that of the (3:2) p/w (Fig. 4) and this was attributed with better particles entanglement within the sample (see Fig. 6). Degradation of the (3:2) strengths by ME was higher than that by SBF, however, it was not clear for the degradation of the paste ones. The superior strength was achieved by the paste CP2 when soaked in SBF (Fig. 5). The mechanical strength data indicated that the technique can be applied for non load bearing bone implant. The advantage of the paste system also was from excellent injectability as reported elsewhere [5].

a: CS, ME

MPa	CP0			CP1			CP2			CP10			CP20		
	Min	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**
7D	1.58	1.80	2.06	1.80	2.02	2.38	0.71	1.32	1.77	1.21	1.85	2.66	1.40	2.05	3.08
15D	1.38	1.80	2.21	1.07	1.30	1.59	1.61	2.04	2.47	0.77	1.34	1.69	1.75	2.27	3.25
30D	1.08	1.42	1.77	1.01	1.14	1.50	1.02	1.19	1.40	1.30	1.74	2.33	1.26	2.08	2.48
90D	0.61	1.52	1.93	0.49	0.61	0.67	0.99	1.42	1.67	0.64	1.30	2.08	1.16	1.48	1.74

b: CS, SBF

MPa	CP0			CP1			CP2			CP10			CP20		
	Min	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**
7D	1.13	1.47	2.28	1.51	1.73	2.45	1.58	2.69	3.37	1.36	1.70	1.85	0.47	0.66	1.04
15D	0.87	1.21	1.69	1.01	1.94	2.71	1.70	2.06	2.97	1.12	1.33	1.59	0.70	0.80	0.91
30D	0.60	1.09	1.62	1.22	1.51	1.84	0.97	1.28	1.87	1.24	1.43	1.60	0.30	0.58	0.84
90D	0.89	1.15	1.89	1.31	1.71	2.11	0.94	1.89	3.23	0.92	1.07	1.35	0.81	0.92	1.01

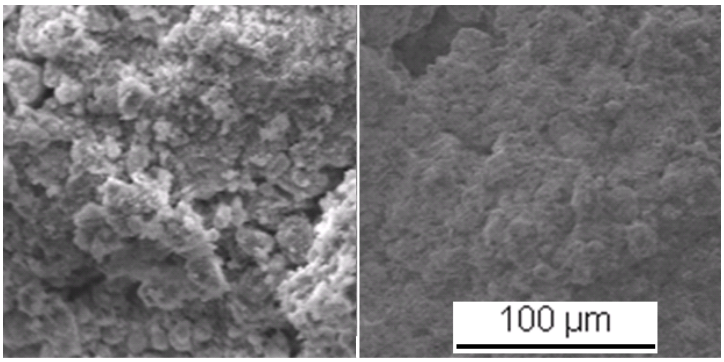
c: DTS, ME

MPa	CP0			CP1			CP2			CP10			CP20		
	Min	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**
7D	0.66	0.72	0.75	0.55	0.62	0.67	0.67	0.78	0.87	0.80	0.91	1.00	0.80	1.00	1.22
15D	0.46	0.54	0.68	0.41	0.47	0.52	0.33	0.62	0.84	0.42	0.63	0.88	0.69	0.95	1.19
30D	0.48	0.57	0.66	0.35	0.41	0.47	0.59	0.96	1.11	0.36	0.54	0.76	0.52	0.73	0.98
90D	0.30	0.38	0.48	0.16	0.27	0.39	0.36	0.47	0.58	0.21	0.35	0.44	0.63	0.75	1.02

d: DTS, SBF

MPa	CP0			CP1			CP2			CP10			CP20		
	Min	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**	**Ave**	**Max**
7D	0.44	0.46	051	0.43	0.54	0.68	0.45	0.53	0.66	0.25	0.39	0.47	0.09	0.23	0.35
15D	0.27	0.39	0.46	0.19	0.36	0.47	0.69	0.84	0.94	0.30	0.50	0.66	0.19	0.24	0.35
30D	0.16	0.32	0.42	0.25	0.34	0.41	0.34	0.57	0.87	0.30	0.49	0.65	0.22	0.26	0.35
90D	0.23	0.31	0.43	0.32	0.46	0.54	0.40	0.49	0.60	0.11	0.19	0.28	0.19	0.23	0.26

Fig. 5: Mechanical changing of the Paste samples over aging times.



(3:2) p/w Paste

Fig. 6: Mechanical changing of the Paste samples over aging times.

Summary

The mechanical test of CP biomaterial prepared by single pot technique has been successfully done to elucidate the effects of excess CaO, preparation technique and aging condition. The results show that the increase in the excess CaO reduces the strength but not in the case of Paste. The preparation technique of paste results in better entanglement of the particles. For examples, the compression strengths (MPa) of CP0, CP1, CP2, CP10 and CP20 are 1.99, 1.24, 1.28, 1.10 and 0.71 respectively for 7D aging samples made of powder, and 1.80, 2.62, 1.32, 1.85 and 2.05 for those made of paste; meanwhile their diametrical tensile strengths (MPa) are 0.32, 0.31, 0.26, 0.13 and 0.13 respectively for the former group samples, and 0.72, 0.62, 0.78, 0.91 and 1.00 for the laters.

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