

D. A. CORTÉS***, P. J. HOGG**, K.E. TANNER*, J.C. ESCOBEDO***

MECHANICAL PROPERTIES OF A NOVEL BIOACTIVE CERAMIC SYSTEM

WŁAŚCIWOŚCI MECHANICZNE NOWYCH BIOAKTYWNYCH MATERIAŁÓW CERAMICZNYCH

A basic ceramic system was developed by mixing the low temperature form of wollastonite ceramics, sodium silicate and aluminium phosphate. In some cases, UHMW polyethylene powder has been added to the ceramic system during the mixing. The effect of maturation time and aluminium phosphate and polyethylene contents on the mechanical properties has been evaluated. By using four-point bending and double torsion tests the mechanical characterisation has been performed. The mechanical properties, with the exception of the maximum strength, are of the order of human cortical bone. This system allows other constituents to be added to the basic formulation to improve mechanical properties due to the presence of liquid sodium silicate that decreases the interfacial energy of ceramics. Thus, from the mechanical point of view, the materials developed may be suitable for the repair and reconstruction of bone.

Podstawowy skład badanego materiału ceramicznego został otrzymany w procesie mieszania wolastonitu, krzemianu sodowego oraz fosforanu glinowego. W niektórych kompozycjach, w procesie mieszania dodawano proszek polietylenowy. Badano wpływ ilości dodawanego fosforanu glinowego i polietylenu oraz czasu dojrzewania na własności mechaniczne produktu. Własności te określano czteropunktowym testem zginania oraz skręcania ze zmianą kierunku obrotów. Wyniki badań wskazują, że z wyjątkiem maksymalnych własności wytrzymałościowych otrzymane materiały charakteryzowały się własnościami mechanicznymi rzędu wartości dla kości człowieka. Uzyskanie żądanych wartości własności mechanicznych okazało się również możliwe przez dodawanie innych składników, gdyż dzięki obecności ciekłego krzemianu sodowego, obniżeniu ulegała energia oddziaływań międzyfazowych. Na podstawie wyników przeprowadzonych badań można stwierdzić, że otrzymane materiały mogą być używane w procesach rekonstrukcji i łączenia kości człowieka.

* IRC IN BIOMEDICAL MATERIALS, QUEEN MARY UNIVERSITY OF LONDON, MILE END ROAD, LONDON, E1 4NS, UK

** DEPARTMENT OF MATERIALS, QUEEN MARY UNIVERSITY OF LONDON, MILE END ROAD, LONDON, E1 4NS, UK

*** CINVESTAV-UNIDAD SALTILLO, APDO.POSTAL 663, 25000 SALTILLO, COAH.MÉXICO

1. Introduction

Nearly inert materials are encapsulated by a fibrous tissue when implanted into bone defects. As a result a lack of bonding between the material and bone is obtained leading to implant rejection. A new generation of biomaterials started with the emergence of Bioglass® in 1971 [1]. Bioglass® is highly bioactive and is able to bond with natural tissue. Since then, several kinds of inorganic materials have also been found to bond to living bone. Apatite and wollastonite containing glass-ceramic called A-W [2,3], and pseudo-wollastonite ceramics [4] are typical examples of bioactive materials.

In the attempt to match the natural components of bone and collagen, isotropic composites of hydroxyapatite in polyethylene, HAPEX™, were developed [5]. HAPEX™ is already clinically used and exhaustive work has been done regarding the biocompatibility and the mechanical properties of these isotropic composites [6–8]. Composites of Bioglass® and two polymeric matrices have also been developed to mimic bone, polyethylene [9, 10] and polysulphone [11].

This work consists of the development and characterisation of a basic matrix system obtained by mixing the low temperature form of wollastonite ceramics, liquid sodium silicate and aluminium phosphate. The advantages of this system in comparison with the conventional bioactive materials are its mouldability and the feasibility to process it in the form of an aqueous gel at low temperature. Furthermore, this system allows the addition of different fibres and fillers to the ceramic system due to the presence of liquid sodium silicate that decreases the interfacial energy of the ceramics.

The ceramic system is based on liquid silicates that have the capability to be chemically cross-linked by hardeners (such as aluminium phosphate) at low temperatures (<200°C). Thus, the matrix is liquid initially and, via a curing process, the matrix becomes solid by transformation of the silicate into a cross-linked three-dimensional structure. However, even at room temperature and immediately after the mixing of the compounds, the slurry starts to polymerise and, with time (maturation time), the initial slurry becomes a mouldable dough material. The bioactivity of this system was previously evaluated by the present authors [12] by immersion of the samples in simulated body fluid (SBF) at 37°C for different periods of time. The system showed a highly potential *in vitro* bioactivity. The biocompatibility, using an *in vitro* cell culture model, was also evaluated [13]. No evidence of cytotoxic effect was obtained.

The mechanical characterisation of the ceramics was performed using double torsion and four-point bending tests in air at room temperature. The effect of maturation time and aluminium phosphate and polyethylene contents on the maximum strength, maximum strain, modulus, fracture toughness and energy to fracture of the wollastonite based materials have been evaluated.

2. Materials and methods

2.1. Raw materials

To achieve the minimum water content in the final product, a sodium silicate solution grade 079 has been selected as the base liquid for the ceramics. The hardener used was a fine powder of $Al_2(P0_4)$. Quantitative chemical analyses of seven of the small particles were performed by using Energy-Dispersive X-ray analysis (EDX). The mean values of weight percentage and their corresponding standard deviations are shown in Table 1. For the physical characterisation of the aluminium phosphate powder,

TABLE 1

Quantitative chemical analysis of the aluminium phosphate powder

Element	Wt.(%)	Std. dev.
Al	12.74	0.1501
P	31.96	0,5692
Fe	0.099	0.0662
Zn	0.432	0.2700
Ca	0.173	0.1285
S	0.238	0.0124
Na	0.178	0.0050
O	53.25	0.5483

particle size analysis has been performed by using the Mastersizer X, polydisperse model, with Version 1.0 software. An obscuration of 20.39% was used. The particle size with the highest frequency is 12 μm and the 75% of the particles are below 26 μm in diameter. As the main compound in the preparation of the materials the triclinic low temperature form of wollastonite ceramics, $\alpha\text{-CaSiO}_3$, supplied by Cornelius Chemical Company, was used. The chemical characterisation of the wollastonite powder was done by using X-Ray Fluorescence Spectroscopy (XRF). Two fused glass disks of wollastonite powder and lithium tetraborate were made using a fluxer according to SOP/CSF-22 of the IRC in Biomedical Materials, QMW. The results obtained are presented in Table 2. For the physical characterisation of the Wollastonite powder, particle size analysis has been performed. An obscuration of 17.91% was used. The particle size with highest frequency is 18 μm and the 75% of the particles are below 26 μm in diameter. The UHMW polyethylene used was a powder supplied by Himont (Himont 1900 was the commercial name). The size of the particles varied from 100 to 250 μm .

TABLE 2

XRF spectrometry results of the wollastonite powder

Compound	Concentration	Abs. Error
Na ₂ O	0.874 wt%	0.051
MgO	0.601 wt%	0.015
Al ₂ O ₃	0.371 wt%	0.033
SiO ₂	51.73 wt%	0.09
P ₂ O ₅	<0.011 wt%	–
K ₂ O	0.0967 wt%	0.0098
CaO	46.10 wt%	0.07

2.2 Preparation of samples

The basic formulation was prepared by mixing from 70 or 74.6 wt% of wollastonite powder with 25wt% of sodium silicate. The aluminium phosphate was added at different weight percentages, 0.4, 1.0, 1.5, 2.0, 2.5 and 5wt% (compounds FF0.4 to FF5.0 on Table 3). A blender was used to mix the three components. In some cases 15wt% of UHMW polyethylene powder was added to the basic formulations during the mixing (compounds GF0.4 to GF5.0 on Table 3) decreasing the wollastonite content in 15wt%. Once an homogeneous slurry was obtained through the mixing, the slurry was placed into an airtight plastic container and stored. A partial polymerisation occurs with time and a dough moulding compound is obtained. One, 504 or 1176 hours (one hour, three weeks or seven weeks) after the mixing of the compounds (maturation times), once a partial maturation of the pastes was obtained, the materials were processed in a Palamina press at 140°C and at 3.45 MPa for 1.5 hours to obtain laminates 270 mm × 270 mm × 2.5 mm.

TABLE 3

Identification of the processed materials

Identification	Aluminium phosphate content (wt.%)	UHMWPE powder (wt%)	Maturation time (hours)
FF (0.4, 1, 1.5, 2, 2.5, 5)	0.4, 1, 1.5, 2, 2.5, 5	0	0, 504, 1176
GF (0.4, 1, 1.5, 2, 2.5, 5)	0.4, 1, 1.5, 2, 2.5, 5	15	0,504, 1176

Summarising, the variables in the processing of the materials, as indicated in Table 3 were the maturation time, that is the time period between the preparation of the ceramic pastes and the curing of the laminates (1 hour, 3 weeks and 7 weeks), the aluminium phosphate content (0.4, 1, 1.5, 2, 2.5 and 5wt%) and the polyethylene content (0 and 15wt%). The processing temperature and pressure were kept constant at 140°C and 3.45 MPa respectively.

2.3. Four-point bending method

To evaluate the modulus, the elongation to fracture and the maximum strength of the materials four-point bend testing in air and at room temperature was performed. Rectangular specimens approximately 10 mm×2.5 mm×80 mm were prepared from the laminates. The bending properties were evaluated at air at room temperature according ASTM C674, D6272 and D790 at a crosshead speed of 0.2 mm min⁻¹ and using a span length of 64 mm. An MTS model 830 test machine was used. Five measurements were made for each material prepared.

2.4. Double torsion method

Fracture toughness, K_{IC} , was evaluated by double torsion method [14]. The compliance analysis of a pre-cracked DT specimen indicates that the applied stress intensity factor, K_I , is independent of crack length [14,15].

The specimen was a plate 3 mm×35 mm×100 mm into which a groove 0.6 mm wide and 1.5 mm was machined deep along the length of the specimen at the centre. Into this groove, a small crack 2 mm wide and of different lengths was also machined in the specimen to initiate the fracture. The compliance analysis was performed using five different crack lengths (3, 6, 9, 12 and 15 mm) for each material to corroborate that the range of crack length selected to test the SS-W materials is that in which K_I is independent of crack length. The specimen was supported on four ball bearings. An Instron model 6025 computer controlled test machine was used. Once proved that K_I was independent of crack length, fracture toughness, K_{IC} , was calculated using the following equation [16]:

$$K_{IC} = PW_m \left[\frac{3(1+\nu)}{Wd^3d_n} \right]^{\frac{1}{2}} \quad (1)$$

where P is the load, ν is the P o i s s o n ' s ratio and the other terms are the specimen dimensions illustrated in Figure 1. Five measurements were performed at air at room temperature for each material.

The fracture surface energies (γ) were calculated according to the following expression:

$$K_{IC} = \left[\frac{2E\gamma}{(1-\nu^2)} \right]^{\frac{1}{2}} \quad (2)$$

where, E is the modulus. The value of 0.26 was used for P o i s s o n ' s ratios [17].

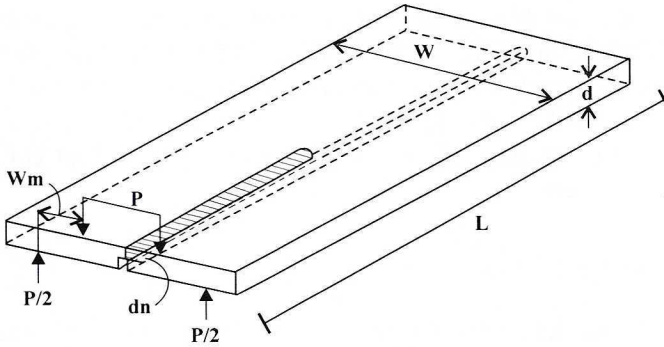


Fig. 1. A double torsion specimen (Reproduced from [16])

3. Results

The effect of maturation time on the mechanical properties for the materials with 2.5 and 5.0 wt% of aluminium phosphate and with and without polyethylene is presented in Figure 2. The processing temperature and pressure were kept constant at 140°C and 3.45 MPa respectively. Table 4 shows the effect of maturation time on the mechanical properties presented in Figure 2, but including the standard deviation. The maturation time has a considerable effect on all the properties evaluated with the exception of the maximum strain. Maximum strength, maximum strain, modulus and fracture surface energy increase remarkably as the maturation times is increased. The material identified as FF5.0 (5.0wt% aluminium phosphate and no polyethylene added) showed the higher modulus. On the other hand, the material identified as FF2.5 (2.5wt% aluminium phosphate and no polyethylene added) showed the higher fracture toughness and the maximum energy to fracture.

The effect of the aluminium phosphate content on the mechanical properties of the ceramic materials and the polyethylene modified compounds is shown in Figure 3. The other processing variables were kept constant; the processing temperature at 140°C, the pressure at 6.9 MPa and the maturation time at 7 weeks (1176 hours). As expected, since the aluminium phosphate increases the polymerisation rate, the strength and modulus increase as the metal phosphate is increased in materials without polyethylene (compounds FF), while the strain to failure decreases. For these compounds FF, the fracture toughness and energy to fracture also increase, however in the compound with 5wt% of metal phosphate a decrease in these properties is observed. Thus, the maximum values for fracture toughness and fracture surface energy are obtained by adding to the formulation 2.5wt% aluminium phosphate. During the preparation of the slurries, when no polyethylene powder was added to the ceramics, a difficulty in mixing the different compounds was observed and this difficulty in the mixing was increased when increasing the aluminium phosphate.

In contrast, the effect of metal phosphate on the strength of the compounds containing polyethylene powder is not significant, although the compounds are stiffer

TABLE 4

Effect of maturation time on the mechanical properties of the materials with 2.5 and 5wt.% metal phosphate and the corresponding polyethylene modified compounds.

Data shown in Figure 2, but including standard deviations. The pressure and the temperature were kept constant at 3.45 MPa and 140°C respectively

$\sigma_{\text{Max}}/\text{MPa}$								
Maturation time (hours)	FF2.5	Std. Dev.	FF5.0	Std. Dev.	GF2.5	Std. Dev.	GF5.0	Std. Dev.
1	10.25	0.9145	11.26	1.74	9.52	1.29	11.88	1.1
504	19.09	1.2348	19.98	2.54	15.14	1.19	17.47	1.42
1176	28.88	1.2915	30.99	2.97	22.65	1.27	23.98	1.35
Max. Strain/%								
Maturation time (hours)	FF2.5	Std. Dev.	FF5.0	Std. Dev.	GF2.5	Std. Dev.	GF5.0	Std. Dev.
1	0.118	0.025	0.1104	0.023	0.2433	0.017	0.2331	0.017
504	0.110	0.032	0.1058	0.027	0.2202	0.016	0.2294	0.011
1176	0.103	0.023	0.0966	0.023	0.2196	0.012	0.2263	0.015
Modulus/GPa								
Maturation time (hours)	FF2.5	Std. Dev.	FF5.0	Std. Dev.	GF2.5	Std. Dev.	GF5.0	Std. Dev.
1	10.25	1.1895	15.26	1.65	9.6	0.975	10.2	0.9874
504	16.38	2.3564	20.35	1.87	13.12	1.110	14.5	1.074
1176	23.23	1.9018	26.73	1.734	19.24	0.999	20.0	1.0258
$K_{\text{IC}}/\text{MPa m}^{1/2}$								
Maturation time (hours)	FF2.5	Std. Dev.	FF5.0	Std. Dev.	GF2.5	Std. Dev.	GF5.0	Std. Dev.
1	1.23	0.3214	1.2	0.41	1.07	0.38	1.14	0.19
504	2.35	0.4120	1.8	0.31	1.74	0.28	1.89	0.25
1176	4.08	0.4201	3.31	0.36	2.25	0.19	3.07	0.24
$\gamma/\text{J m}^{-2}$								
Maturation time (hours)	FF2.5	Std. Dev.	FF5.0	Std. Dev.	GF2.5	Std. Dev.	GF5.0	Std. Dev.
1	69	12.64	44	9.25	56	7.41	59	6.5
504	157	17.25	74	11.2	108	12.3	117	10.2
1176	334	28.58	191	16.14	123	14.2	219	15.6

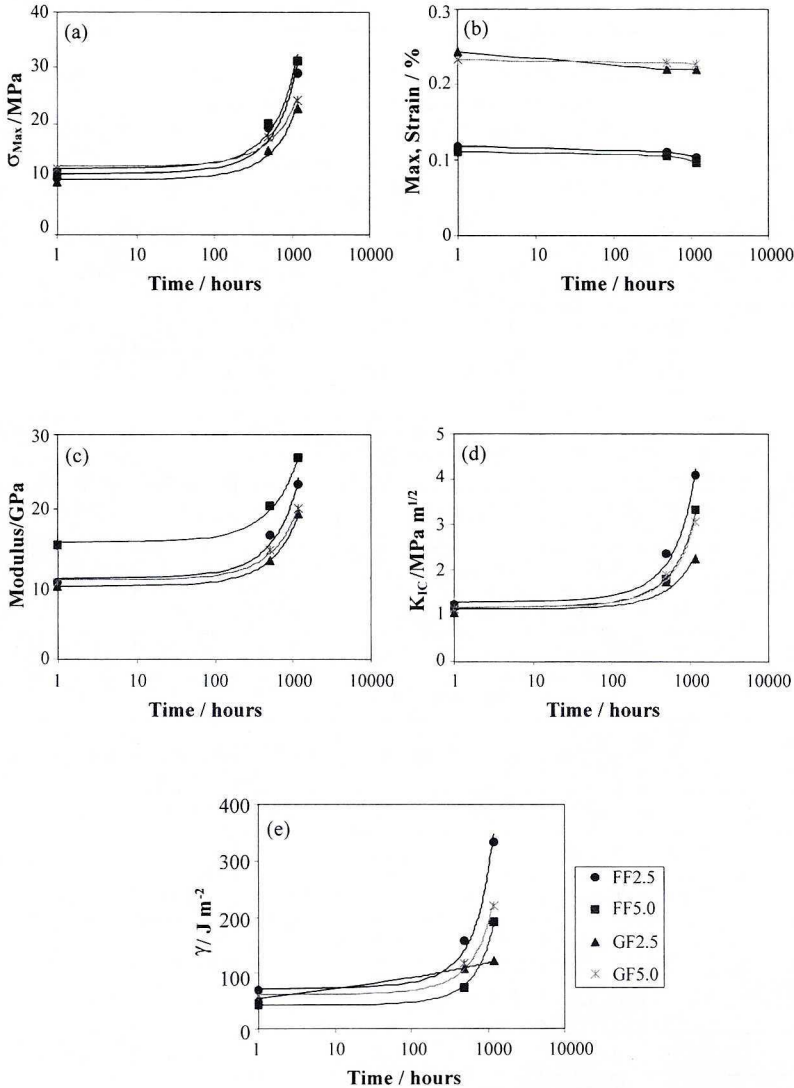


Fig. 2. Effect of the maturation time on the mechanical properties of the materials with 2.5 and 5.0wt% metal phosphate and the corresponding polyethylene modified compounds, (a) maximum stress, (b) maximum strain, (c) Modulus, (d) fracture toughness and (e) energy of fracture. The pressure and the temperature were kept constant at 3.45 MPa and 140°C respectively

when the aluminium phosphate content is increased. At lower phosphate contents (0.5–1.5 wt%) fracture toughness and fracture surface energy do not change considerably, but start to increase at 2.0 wt%, however at 5 wt% a substantial decrease is obtained. For the materials with polyethylene, the strain to failure increases slightly, mainly

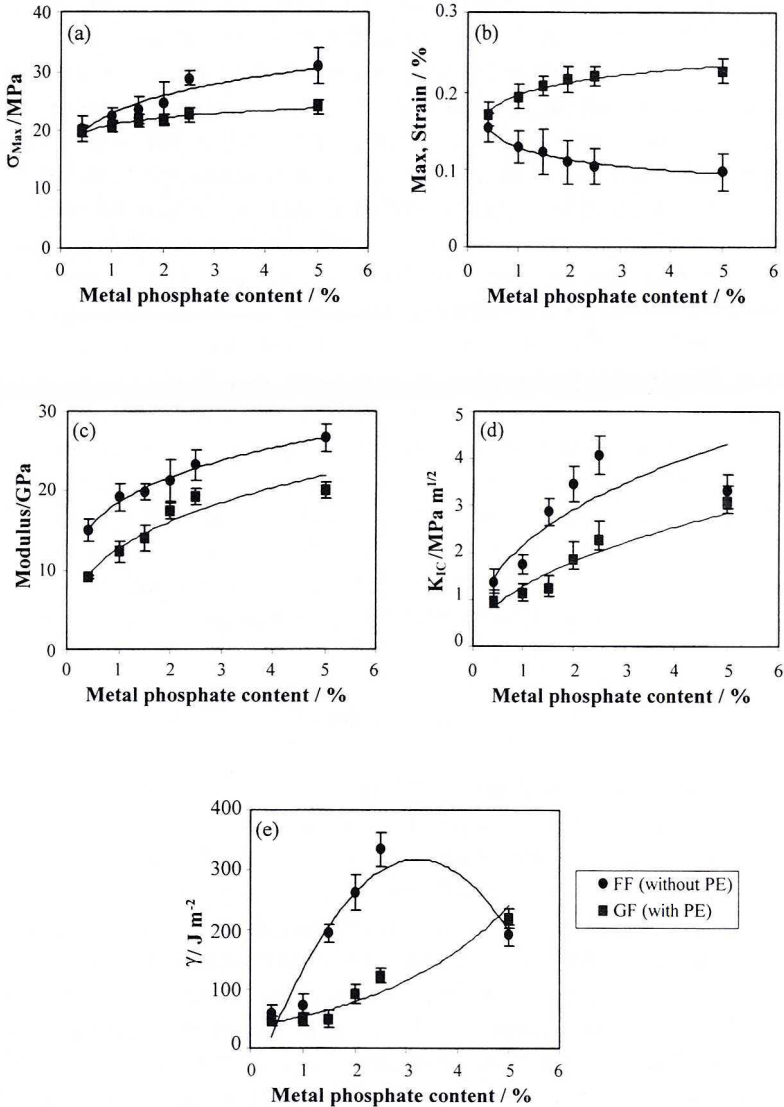


Fig. 3. Effect of aluminium phosphate content on the mechanical properties of the materials and the corresponding polyethylene modified compounds, (a) maximum stress, (b) maximum strain, (c) Modulus, (d) fracture toughness and (e) energy of fracture. The pressure, the temperature and the maturation time were kept constant at 3.45 MPa, 140°C and 7 weeks (1176 hours) respectively

between 0.4 and 2.0 wt% aluminium phosphate, which is the opposite to that observed in compounds without polyethylene.

In a generalised observation of the results obtained, the mechanical properties of the materials at different contents of aluminium phosphate decrease with the addition of

15% of polyethylene. At lower content of wollastonite ceramics, by adding 15 wt% polyethylene to the formulation, a decrease in the strength was expected.

Furthermore, when considering fracture toughness and fracture surface energy, in the case of materials without polyethylene powder, 2.5 wt% aluminium phosphate (FF2.5) seems to be the optimal while 5 wt% is optimal in the polyethylene modified compounds (GF5).

Comparing the mechanical properties of these wollastonite based materials with those of bone and of existing bioactive systems, with the exception of the maximum strength, the mechanical properties of the materials developed in this project, are closer to those of bone than the properties reported for the bioactive systems. *A-W* glass-ceramic [16], shows the highest mechanical properties however, Young's modulus of *A-W* glass ceramic is 124 GPa, substantially higher than that of cortical bone, which has a maximum of 30 GPa [18]. The fracture toughness of *A-W* glass ceramic is 2.6 MPa m^{1/2}, while that of bone is up to 6 MPa m^{1/2}. In the materials of this study, the highest modulus was 26 GPa and the maximum fracture toughness was 4 MPa m^{1/2}. The maximum strength did not exceed 30 MPa while that of bone is about 50 to 150 MPa [18]. However, due to the presence of liquid sodium silicate that decreases the interfacial energy of the ceramics, the system allows fibres and fillers to be added to the basic formulation to improve mechanical properties. Thus, from the mechanical point of view, these wollastonite based materials may be suitable for the repair and reconstruction of bone.

4. Conclusions

Among the processing conditions tested, the most important effect is the maturation time. A remarkable increase in the mechanical properties is obtained by processing the laminates 7 weeks after the preparation of the dough moulding compound. In the wollastonite based materials the polyethylene decreases all the mechanical properties, apart from the maximum strain. The strength and modulus are slightly increased as the aluminium phosphate content is increased. At lower aluminium phosphate contents fracture toughness and fracture surface energy also increase however, at 5 wt% a substantial decrease is observed. For the materials with polyethylene, the strain to failure increases slightly as increasing the aluminium phosphate content, which is the opposite to that observed in compounds without polyethylene. On the other hand, the mechanical properties of the wollastonite based materials obtained are closer to those of bone with the exception of the maximum strength. However, mechanical properties can be optimised by material formulation and hence, this ceramic system is potential implant material for bone replacement or augmentation.

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