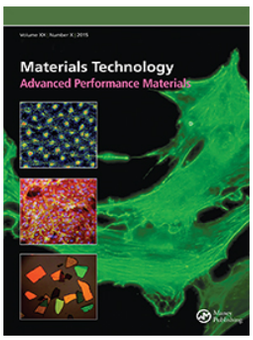

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A ceramic composite derived from high-grade rock phosphate as a substitution for human bone

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ABSTRACT

This study is focused on to find out chemical and structural suitability of newly synthesised ceramic-embedded polymer composite as bone cement. Synthesised ceramic is derived from high-grade rock phosphate and is a form of hydroxyapatite prepared using sol–gel technique, alcoholic route. A mixture of commercially available bone cement and its liquid monomer, commercially available methyl methacrylate (MMA) and a mixture of sol–gel-synthesised Eppawala hydroxyapatite (SGHAp) powder with commercially available MMA was prepared. Then physical and chemical properties including composition, crystallinity, presence of functional groups, thermal stability, surface morphology and microstructural features were examined compared to human bone. Results show that there is a close similarity between newly synthesised product and human bone. Also it has credent high thermal stability and good crystalline properties than the commercial product. The study concluded that newly synthesised SGHAp-embedded MMA composite can be used directly as a substitution for human bone.

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KEYWORDS
Eppawala hydroxyapatite; bone cement; methyl methacrylate; orthopaedics; human bone

Introduction

Eppawala rock phosphate deposit is one of the non-renewable phosphate sources situated in Eppawala village near Anuradhapura, which was the ancient capital of Sri Lanka. It usually contains 34–40% total phosphorus expressed as a percentage of phosphorus pentoxide (P_2O_5) [1–5].

Amongst so many phosphate products, currently 'Eppawala' high-grade rock phosphate mineral is only considered as the raw material for fertiliser in Sri Lankan agriculture industry.

High-grade rock phosphate has a low commercial value in Sri Lanka. Therefore, we have value added by chemically converting it into the hydroxyapatite, a well-known bioceramic, using sol–gel technique under the alcoholic route. In considering the sol–gel technique under alcoholic route, its ability to replace chlorine in chloroapatite with hydroxyl groups at high temperature due to the increase of reactivity as its chlorine positions is under strain in the structural framework [2,3].

Hydroxyapatite is a widely used bioceramic which has a close chemical and structural similarity with human hard tissues and performs several outstanding properties: biocompatibility, non-inflammatory in nature, osteoconductivity, non-toxicity, bioactivity etc. [6–11]. As a result, it has a range of biomedical applications mainly in the fields of orthopaedics and dentistry [2,12–24].

This study mainly focussed to find out the suitability of sol–gel synthesised Eppawala hydroxyapatite with (methyl methacrylate [MMA]) monomer as bone cement, by comparing and contrasting it with human bone as well as commercially available bone cement, which is currently used in orthopaedic surgeries. Selected commercial product containing two main parts as bone cement majorly consists of zirconium dioxide and a liquid monomer MMA. It is currently used as fast-curing bone cement in Sri Lankan government hospitals for stable attachment of total or partial joint endoprostheses in bone, filling, stabilisation of bone defects within the scope of internal fixation treatment or for endoprosthesis revision surgery and a primary/secondary coverage of skull bone defects. It is prepared directly before the medical use, by mixing its powder component with the liquid monomer component clinically in the hospital. Resulted ductile dough cures within a few minutes [25].

This study is designed to find out the possibility of substituting commercial bone cement with the newly synthesised ceramic powder into the commercial liquid monomer MMA product and to find out its structural suitability as bone cement.

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Experimental procedure

Sample preparation

As the first step, sol–gel-synthesised Eppawala hydroxyapatite (SGHAp) was prepared under sol–gel technique using Eppawala high-grade rock phosphate, ethanol and diluted acid as the raw materials [2]. Then the synthesised ceramic powder was mixed with commercially available MMA liquid monomer until the ductile dough forms. In the second step, commercial cement powder and its liquid monomer with MMA were mixed together until the ductile dough forms.

Sample characterisation

Before mixing with the MMA, commercial bone cement and Eppawala hydroxyapatite were examined under X-ray fluorescence spectroscopy (Rigaku [XRF] Spectrometer) to find out its elementary composition and presence of impurities. Liquid monomer was examined with Fourier transform infrared spectroscopy (Bruker – Alpha [FTIR] spectroscopy) attenuated total reflection mode to confirm its composition. Then sample mixture of newly prepared bone cement and the sample mixture of commercial bone cement were characterised using X-ray diffraction spectroscopy (XRD), FTIR, thermogravimetric analysis (TGA) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM with EDS) techniques together with the human bone sample. The crystallographic phases of samples were determined by X-ray diffractometer (Rigaku – Ultima. IV diffractometer) in reflection mode with Cu$K\alpha$1: 0.154 nm radiation. Scanned speed of 1.5° min^{-1} was used to collect data within 15°–80° ranged angles as 2θ values. The presence of functional groups was confirmed by using FTIR spectroscopy (Bruker – Alpha FTIR spectroscopy). The FTIR spectra were obtained over the region 400–4000 cm^{-1} using KBr pellet technique. The resolution of the spectrometer was 4 cm^{-1}. The surface morphology and microstructural features of samples were studied using Hitachi SU6600 Analytical variable pressure field emission-scanning electron microscope and Oxford Instruments EDS, with AZtec software. Furthermore, TGA was done using a thermal analyser (SDT Q600) with N environment, 10°C min^{-1} heating rate and 1450°C maximum temperature to find out the thermal stability of samples.

Results and discussion

XRF analysis

Table 1 shows that commercial bone cement sample only contains Zr in higher amount and then S and Hf accordingly. Human bone and sol–gel-synthesised Eppawala hydroxyapatite (SGHAp) do not contain Zr, Hf or S in composition. There is a difference between commercial bone cement with bone ash meal, as it contains 54.14% CaO, 38.03% P_2O_5 and 0–0.9% Fe_2O_3, SiO_2, Al_2O_3 and a similarity between SGHAp and bone ash in composition according to previous research findings [2,25].

SEM with EDS analysis

Considering Figures 1–3, SEM images of all mixtures and human bone show that there are good correlations of particles. SGHAp with MMA mixture consists of irregular shape micro-size crystalline particles as shown in Figure 1. Presence of some different particles shaped in ball with some rough surface can be found in commercial bone cement mixture which may lead to have higher surface area as mentioned in Figure 2. According to Figure 3, both crystalline property and porosity can be found in human bone sample.

As indicated in Table 2, it can be clearly stated that human bone and SGHAp with MMA mixture have identical Ca, P, O as well as C levels than commercial product with MMA mixture. Even though Fe is taken as an impurity in SGHAp, Fe level of presence is related with the human bone. When comparing SEM with EDS results, newly synthesised SGHAp with MMA mixture is compatible with natural human bone due to its similarity in composition. Therefore, it is more suitable as bone cement.

FTIR analysis

As shown in Figure 4, all peaks for phosphate groups in the 560, 640, 963, 1028 and 1110 cm^{-1} wave no range and characteristic peak for OH^-/hydroxyapatite nearly 3572 cm^{-1} wave no appeared in the human bone as well as in the SGHAp with MMA mixture [2].

Figure 5 shows that the resulted graph for liquid monomer has coincided with the FTIR characteristic graph for MMA monomer, interpreting several peaks related to stretching vibrations including the broad

Table 1. XRF results for commercial bone cement, Eppawala hydroxyapatite and for human bone.

	Commercial bone cement (wt%)		Human bone (wt%)		SGHAp (wt%)	
Element	Avg. value	SD	Avg. value	SD	Avg. value	SD
16 S	9.58	0.74	Not detected	Not detected	Not detected	Not detected
40 Zr	96.40	0.14	Not detected	Not detected	Not detected	Not detected
72 Hf	3.54	0.053	Not detected	Not detected	Not detected	Not detected

SGHAp: Sol–gel-synthesised Eppawala hydroxyapatite; SD: standard deviation.

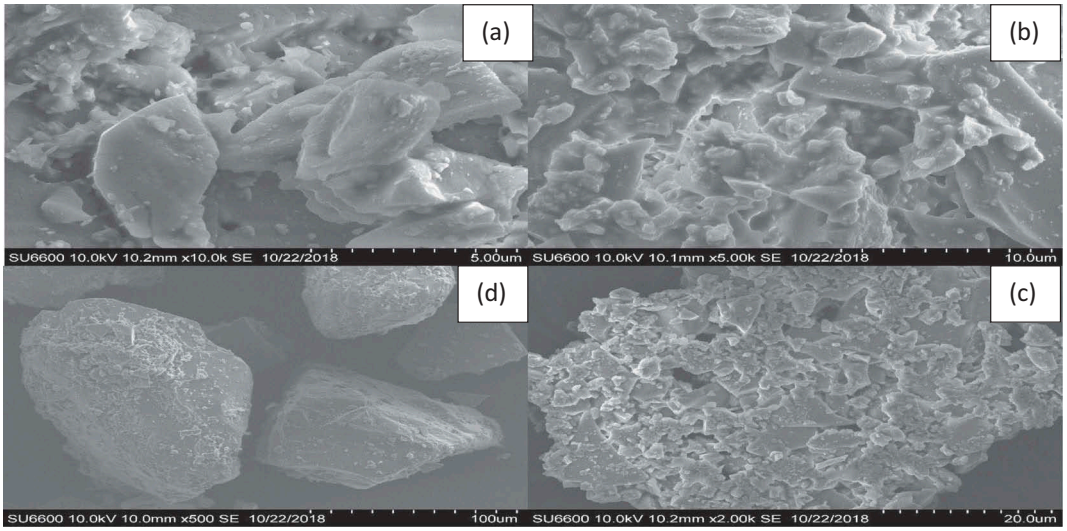

Figure 1. SEM images for SGHAp ceramic with MMA mixture, 10.0 kV, (a) 10k, (b) 5k×, (c) 2k×, (d) 500×.

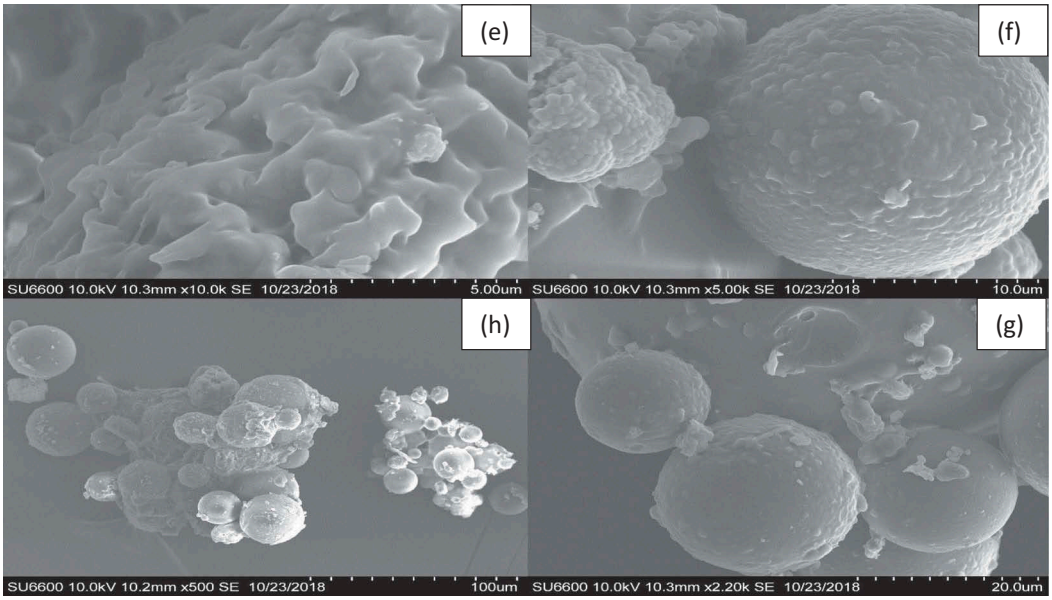

Figure 2. SEM images for commercial bone cement with MMA mixture, 10.0 kV, (e) 10k (f) 5k×, (g) 2.2k×, (h) 500×.

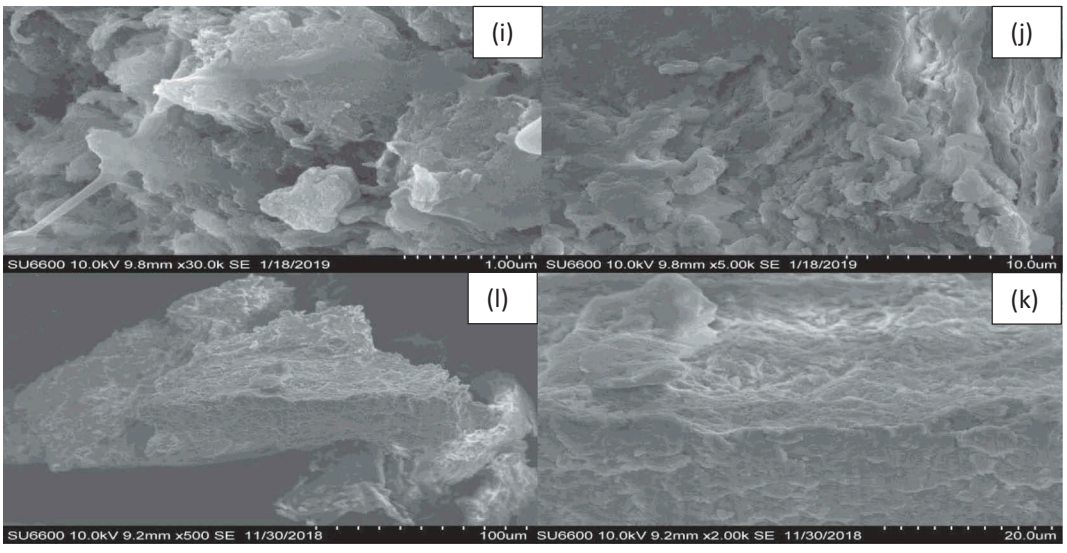

Figure 3. SEM images for human bone, 10.0 kV, (i) 30k×, (j) 5k×, (k) 2k× (l) 500×.

peak ranging from 3100 to 2900 cm^{-1}, the sharp intense peak at 1731 cm^{-1} related to the presence of ester carbonyl group, broad peak nearly 1150 cm^{-1} due to the C–O (ester bond) and a peak nearly 800 cm^{-1} is due to the bending of C–H. When comparing figures, characteristic peaks for MMA appeared commonly in both commercial bone cement with MMA mixture and SGHAp with MMA mixture except in human bone confirming that both commercial product and SGHAp mixed with MMA [26].

XRD analysis

Figure 6 explains even after mixing MMA monomer, XRD results of SGHAp mixture all characteristic peaks related to the crystallographic phases 002, 210, 211, 112, 300, 202, 310, 222, 213 and 004 of hexagonal hydroxyapatite, which shows similarity to human bone [2,27,28]. Also, it interprets 96% crystallinity. Comparing those results with Figure 7, it has shown that commercial product also has crystalline properties but its structure does not coincide with hexagonal hydroxyapatite. It interprets 84.1% crystallinity with monoclinic crystal structure of zirconium dioxide including peaks related to 110, 111, $\bar{1}11$, 002, 200, $\bar{1}02$, $\bar{2}11$, 022, 122, 300, 013, 302, $\bar{1}13$ and $\bar{3}22$ crystallographic phases.

TGA analysis

As shown in Figure 8, 14.5730 mg product sample was used to analyse under thermal analyser. There is a small drop in weight nearly at 200°C that may occur due to the elimination of moisture in the sample. Then up to 678.25°C, 1.006% (0.1466 mg) weight loss was observed. That may occur due to the elimination of some gas from the sample. Then again from 678.25 to 1432.97°C, there is a weight loss indicating 0.7% (0.1020 mg) which has occurred due to the incipient transformation of produced hydroxyapatite in β-TCP. Therefore, it indicates the formation of hydroxyapatite in products. Final weight remained at 1432.97°C was 98.03% of in original weight (14.2859 mg).

As shown in Figure 9, 14.0710 mg of commercial product mixture was subjected to TGA. Nearly up to 200–400°C, considerable amount of weight loss was occupied representing 85.14% from initial weight (11.96 mg). Basically up to 400°C, weight losses may occur due to the dehydration of sample/moisture removal. Therefore, it can be predicted that first weight

Table 2. EDS results for SGHAp with MMA mixture, commercial bone cement with MMA mixture and human bone.

	SGHAp with MMA mixture (wt%)		Commercial product with MMA mixture (wt%)		Human bone (wt%)	
Element	Avg. value	SD	Avg. value	SD	Avg. value	SD
O	61.3	0.15	72.03	0.46	63.1	0.28
Ca	18.2	0.09	0.1	0.081	19.46	0.14
C	16	0.16	26.86	0.262	17.1	0.23
P	8.46	0.13	0.033	0.0001	8.93	0.13
Cl	0.6	0.03	–	–	–	–
Zr	–	–	0.9	0.74	–	–
Fe	0.1	0.06	–	–	0.033	0.0471
S	–	–	0.1	0.081	0.033	0.0471
Na	–	–	–	–	0.26	0.1886
Mg	–	–	–	–	0.13	0.0943

SD: standard deviation.

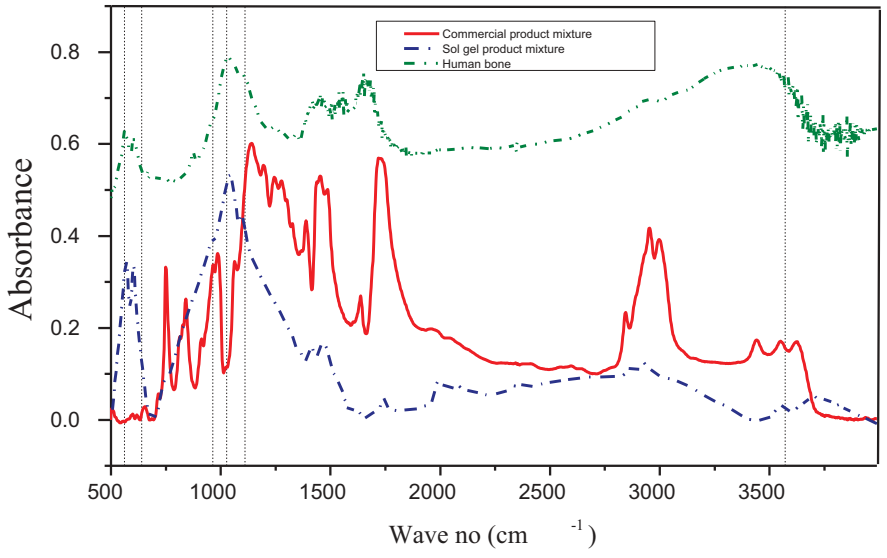

Figure 4. FTIR comparison for commercial bone cement with MMA mixture, SGHAp with MMA mixture and human bone.

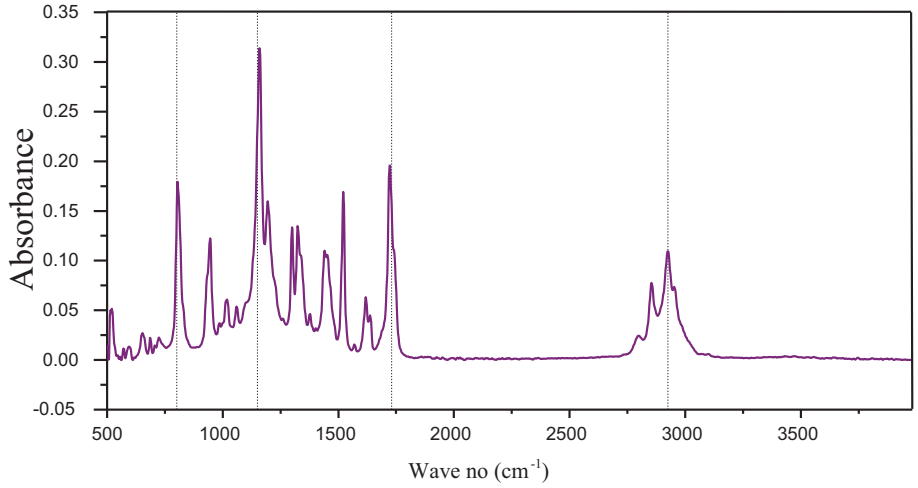

Figure 5. FTIR graph for liquid monomer.

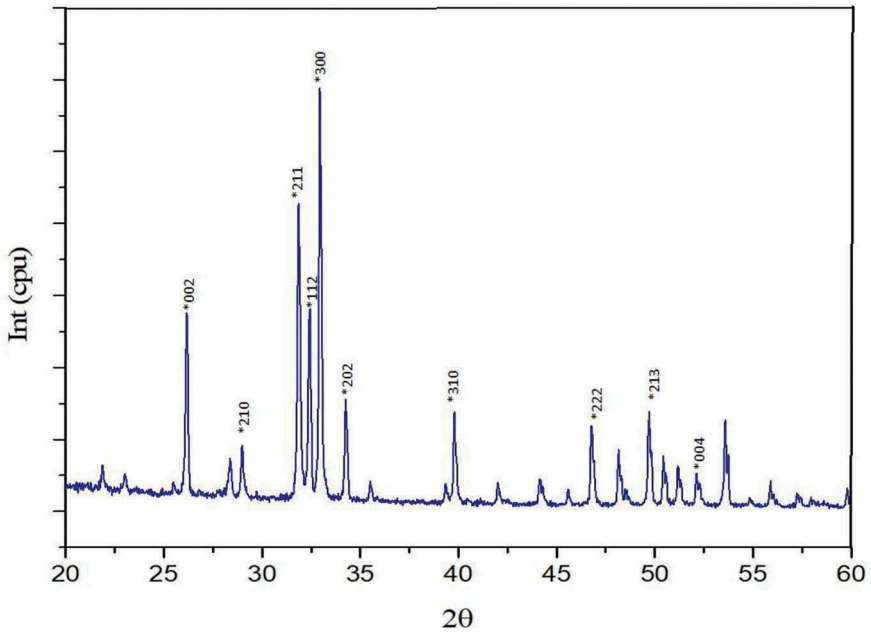

Figure 6. XRD pattern for SGHAp with MMA mixture.

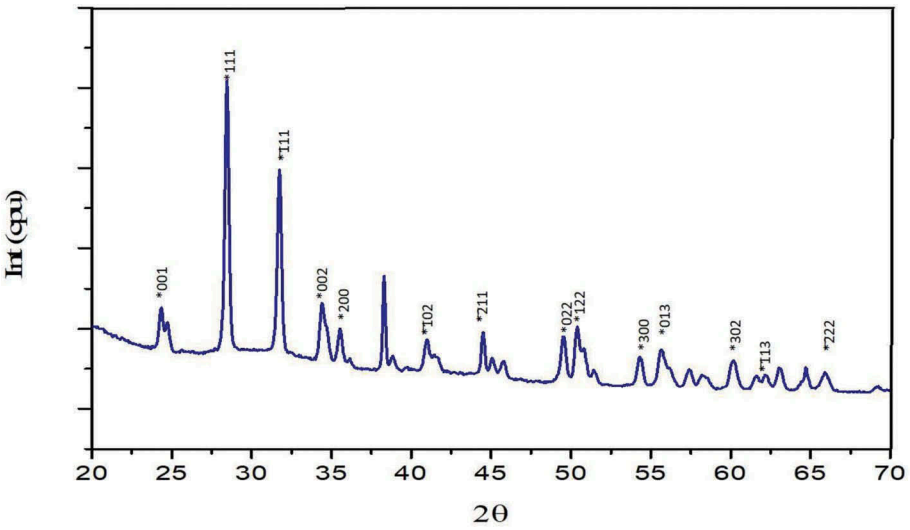

Figure 7. XRD pattern for commercial bone cement with MMA mixture.

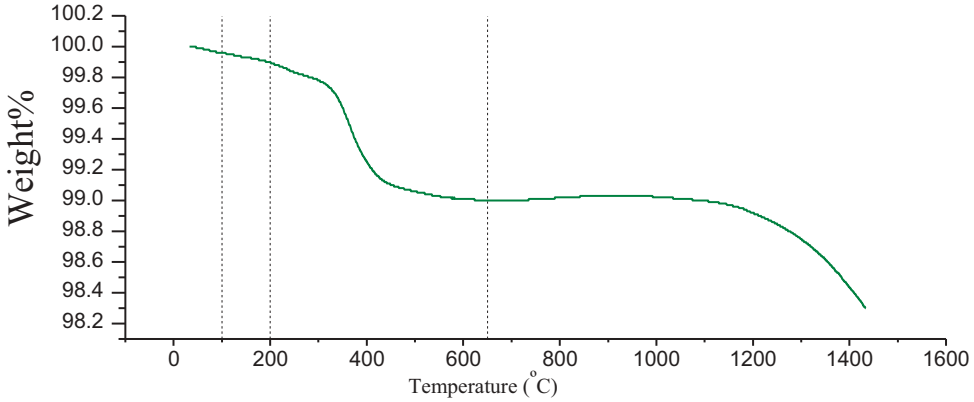

Figure 8. TGA curve for SGHAP with MMA mixture.

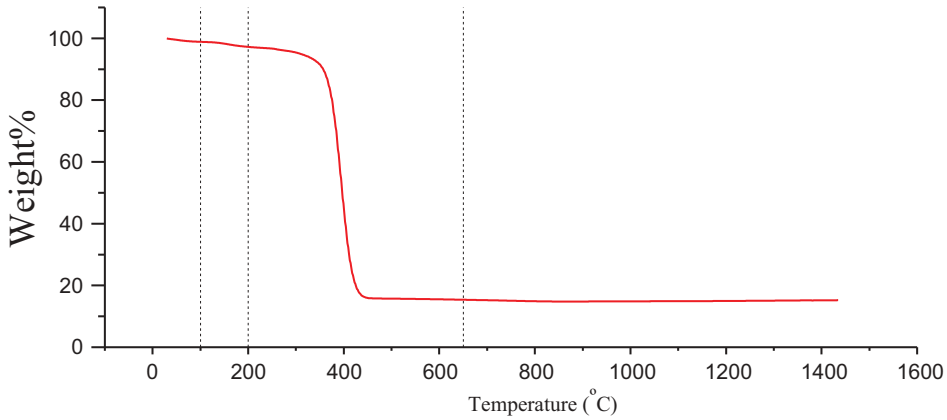

Figure 9. TGA curve for commercial bone cement with MMA mixture.

loss may occur due to moisture removal of the product, but there may be some other reasons also such as structural degradation or deformation. After that, weight loss rate has become slower and then a constant value. At 1435.98°C, 15.23% of initial weight remained.

According to Figure 10, 10.115 mg human bone sample was subjected to TGA. As mentioned in the literature, first significant weight loss which occurs nearly at 200°C (0.9112 mg), representing 9.008%, may associate with the dehydration of the sample. Following that interval, the sample reduced its weight nearly 5.6358 mg at 650°C; it has occurred due to the bone structure collagen elimination. This reaction continues up to 936.88°C, with a lowered rate. Above that temperature, a fine TGA curve descending slope is observed up to the maximum analysed temperature of 1432.97°C with the total weight loss of 54.79%, this being associated with the collagen remains removal and the incipient transformation of hydroxyapatite in β-TCP [2,27,29].

When comparing human bone with commercial bone cement with MMA mixture and SGHAp with MMA mixture, according to Figure 11, the mixture of human bone and the SGHAp has shown a similar pattern of weight loss, which was slightly different from commercial product mixture. That may happen due to the composition similarity of human bone and SGHAp with MMA mixture, as they were containing hydroxyapatite. Also due to the least amount of weight loss in synthesised SGHAp mixture sample than bone and commercial product mixture, it can be concluded that the synthesised SGHAP with MMA mixture performs high thermal stability and good material stability in nature and application.

Conclusion

Study concludes that, sol–gel synthesised Eppawala hydroxyapatite embedded with MMA mixture can be used as a direct substitution for bone cement as it performs chemical and structural similarity with human bone. Synthesised product interprets highly crystalline structure with 99.41% crystallinity and good thermal stability. Also when synthesising composites, the brittleness of hydroxyapatite varieties as ceramics has been reduced by increasing ductile properties via addition of MMA.

Further work as ageing properties, mechanical properties including tensile and impact strengths of these synthesised hydroxyapatite composite to be studied in future. Also 3D printing technique will be

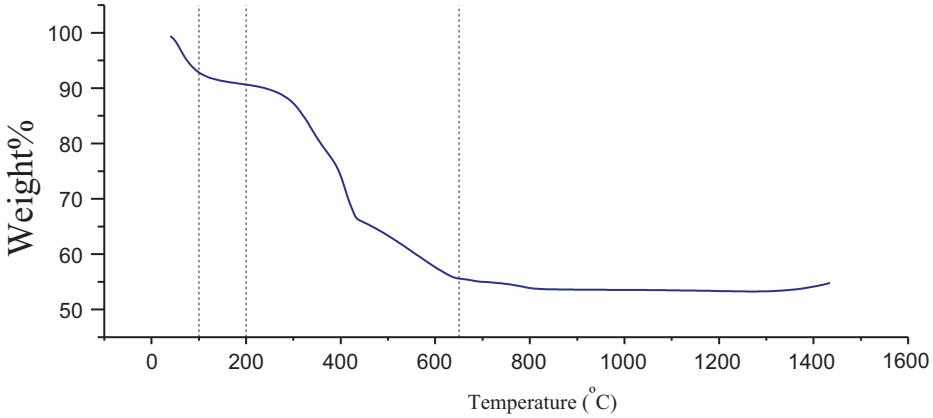

Figure 10. TGA curve for human bone.

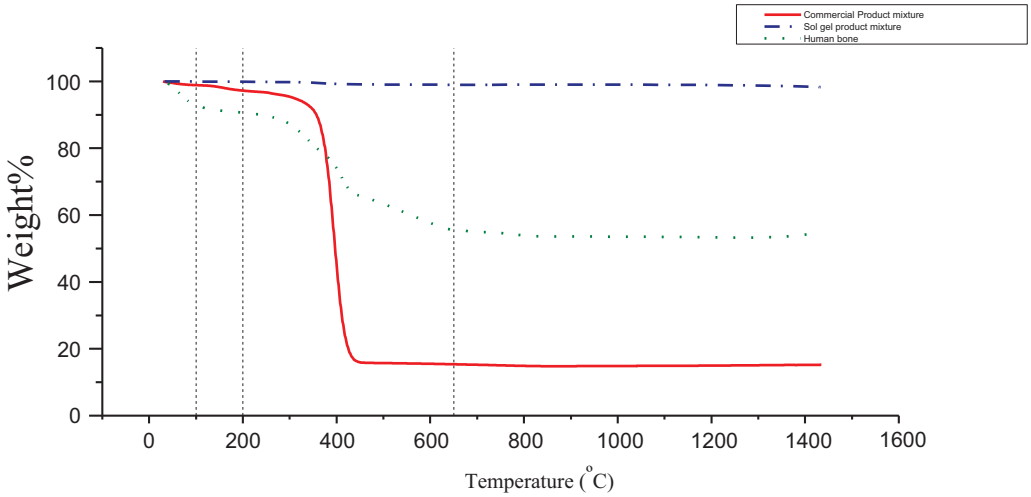

Figure 11. Comparison between TGA results of human bone, commercial bone cement mixture, and sol–gel product mixture.

applied to build implants from these materials to be explored in future.

Disclosure statement

No potential conflict of interest was reported by the authors.

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