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EFFECT OF SODIUM ALGINATE ON THE PROPERTIES OF CALCIUM PHOSPHATE FOR BONE IMPLANT APPLICATION

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ABSTRACT

Calcium (CaP) is a bioceramic material which limited in mechanical strength. Due to the limitation, Sodium Alginate (SA) was reinforced in CaP matrix composite with different ratio of CaP/SA weight percentage (100/0, 99/1, 97/3, 95/5, 90/10 and 80/20). The composite was prepared by using the precipitation method and the compacted powder was sintered at 1000°C. The sintered samples are characterized through x-ray diffraction (XRD). The physical and mechanical properties were determined by density, shrinkage and hardness test. Microstructure and grain size of the samples were examined under scanning electron microscope (SEM). Tricalcium phosphate (TCP) was detected in XRD analysis after sintered at 1000°C. The grain size and shrinkage of the CP were increased with SA as well as hardness and density. SA reinforcement has improved the density and hardness of CaP with with 2.90g/cm^3 and 4.71GPa respectively. The grain size and the crystallite size were also increased with SA. Due to the improved properties, CaP/SA composite can be proposed as one of biomaterials for bone implant application.

Keywords: Calcium phosphate, bioceramic, hardness, sodium alginate.

1.0 INTRODUCTION

Calcium phosphate (CaP) is an inorganic material that mostly been used in bone treatment or bone replacement due to the chemical structure close to the natural bone. CaP shows a positive effect as bone substitution since it has high developing bonding with bone tissue exhibits a good osteo-conductive as well as bio-resorption behavior [1]. CaP also known as an excellent material in biocompatibility and bioactivity [2]. Even though, the composition is suitable for human bone, the mechanical strength of the CaP was not suitable with the natural bones. Since that, application of the CaP limited in artificial bone implant due to lower in mechanical strength [3,4,5]. In order to improve the mechanical properties of sintered CaP, composite of SA/CaP was prepared. SA was used as a reinforcement that can improve biodegradation of CaP without releasing any toxicity in human body. [6,7]. SA is a natural polymer extracted from brown algae [8].

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The properties of SA that is biocompatible, low toxicity and low cost have led this material in many biomedical applications such as wound healing, drug and protein delivery[9]. Among of biopolymer materials, alginate is one of biopolymer that usually been used in bone tissue engineering due to it easily modified in any form [10]. Based on the previous studies, the addition of SA can improve the properties of CaP. Some of studies showed that the formation of tricalcium phosphate (TCP) in hydroxyapatite (HA) has improved the mechanical properties of the HA sample [11]. Formation of α-TCP after sintering was observed by Coelho (2012) where the intensity decreased with addition of SA [12]. Mechanical strength of the CaP cement was improved with the addition of SA compared to the pure CaP cement [12]. Rajkumar et al., (2011) were observed that the addition of SA in HA has improved the hardness and density of the green body sample [13]. In this study, SA was choose as a reinforecemnet in CaP and sintered at 1000°C in order to enhance the mechanical and physical properties of CaP.

2. MATERIAL & METHODS

2.1 Powder Preparation

Calcium phosphate ($CaHPO_4$) (Fisher Scientific) was mixed with sodium alginate (SA) (R&M Chemical) in different weight percentages (1.0, 3.0, 5.0, 10 and 20 wt%) by using a precipitation method. CaP was stirred for 2 hours at 80°C with distilled water by using a magnetic stirrer. After that, SA was added slowly with vigorously stirring. The solution then was stirred for another 2 hours with similar temperature until paste-like solution was formed. The paste was aged at ambient room temperature for another 24 hours. Thereafter, the paste was oven dried for another 24 hours at 80°C and the powder formed was ground by using mortar and pestle to produce fine powders.

2.2 Samples Preparation

The fine powders were compacted into 13 mm diameter of disc shape. The green bodies were then sintered at 1000°C with 2°C/min for 2 hours. Samples were grinded and polished with nylon cloth by using diamond paste prior to hardness test and SEM examination [14].

2.3 Samples Characterization and Testing

Sintered samples were characterized by using x-ray diffraction (XRD) (Bruker D8 Advance). The analysis was set at 40 kV and 40 mA with diffraction angles (2θ) between 25° and 60° with step size of 0.02° per second [15]. The crystallite size was calculated based on Scherrer's equation. The microstructure and grain size were examined under SEM (Hitachi, SU 1510) with 15kV. In order to get a better microstructure, the samples were polished and thermal etched at 950°C for 30 minutes. The grain sizes were revealed by using intercept method. Straight lines were drawn at the diagonal of the microstructure and the intercept lines between grain boundaries were measured. The measurement must be taken at two lines that were drawn at diagonal and the average values were recorded [14]. The Archimede's principle was applied to measure the bulk density of the sintered samples. The hardness of the sample was performed by using the Vicker's hardness (Shimadzu) according to the ASTM C1327-15. At least 10 indentations with constant load 0.2Hv (1.961N) for 10s loading time was used. The diameter of the samples was recorded before and after the sintering process to calculate the shrinkage.

3.0 RESULTS AND DISCUSSION

XRD analysis of different ratio of CaP/SA is shown in Figure 1. Based on the analysis, two phases were observed after sintered that belongs to calcium phosphate ($Ca_2P_2O_7$) (JPDS no. 71-2123) and whitlockite ($Ca_3(PO_4)_2$) (JPDS no. 03-0713) peaks. SA reduced the intensity of CaP ($Ca_2P_2O_7$) peak. However, the intensity of whitlockite ($Ca_3(PO_4)_2$) increases with SA. Whitlockite also known as tricalcium phosphate (TCP) [16] was observed on the sample probably due to the dehydroxylation where it was occurred during sintering process between 800 to 1350°C [17]. This is in line with Ou et al., (2013), the β-TCP and tetracalcium phosphate (TTCP) phases were appeared after sintering process at 1100°C [18]. TCP peak was also observed in HA sample after sintered at 1250°C [11]. Some other studies on HA/TCP have shown that the samples completely transformed β-TCP to α-TCP when sintered above 1200°C [19]. Dehydroxylation that occurred due to sintering process can influenced the density and strength of the sample [17]. Slosarcyk et al., (1998) have proved that dehydroxylation phenomenon that formed HA into TCP resulted best mechanical property compared to the pure HA [11]. According to Rajkumar et al., (2011), the absence and the presence of (SA) in HA has provided a significant effect on the crystal growth of HA [14]. The formation of sharp peaks of HA was due to the increase of sintering temperature and crystallinity of the sample [20, 21].

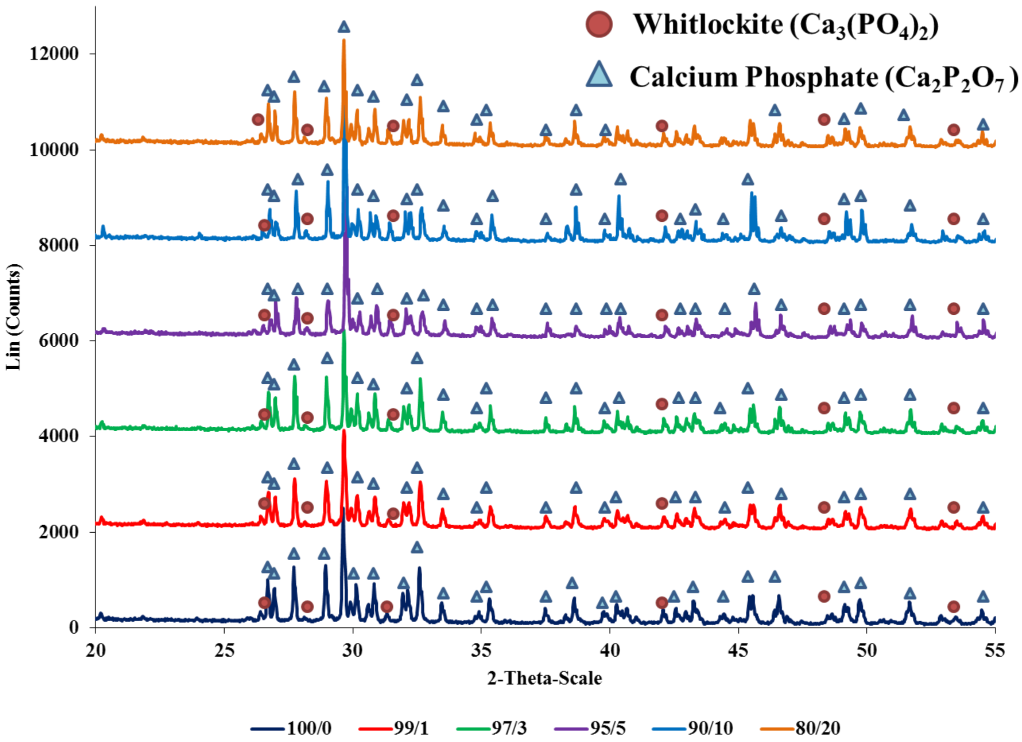

Figure 1. XRD Analysis of CaP/SA at different ratio

Average crystallite size of the sample taken at 32° at 2θ scale is shown in Figure 2. Maximum crystallite size was observed at 3wt% SA with 143.53nm. Based on the result, it shows that the addition of (SA) has increased the crystallite size of CaP. This is in agreement with Rajkumar et al. (2011) where the average crystallite size was increased with (SA) until 1.5wt% [13]. Based on the result, it proves that the present of (SA) in CaP can increase the crystallite size of the CaP.

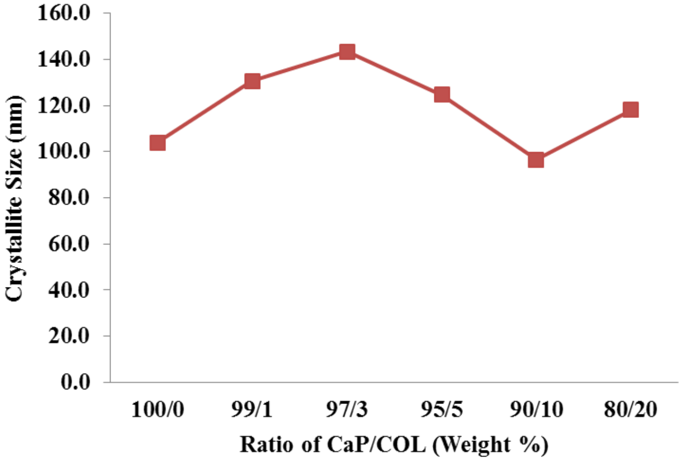

Figure 2. Crystallite Size of CaP/SA at Different Ratio of Weight Percentages

The density and hardness can be observed in Figure 3 (a) and Figure 3 (b). Both curves reveal that the hardness and density increased with SA content. Maximum density and hardness were observed at 5wt% of SA with 2.90g/cm^3 and 4.71GPa respectively. While minimum density and hardness were found in pure CaP with 2.05g/cm^3 and 0.06 GPa respectively. This result proves that the addition of SA in CaP has improved the hardness and density which similar with the results reported by Rajkumar (2011) [13]. Based on results, the hardness was relatively related to density of sintered sample [22], where the hardness gradually increased with increasing the density of the sample. Gibson et al. (2001) was reported that the density of the sintered sample were clearly influenced the hardness of sample [23]. The density was increased until 5wt% of SA but further addition has led to the decrease of density. According to Gibson et al. (2001), increasing the density of the sample was influenced by large grain growth and low porosity [23]. Meanwhile the decreasing of the density was occurred due to larger pores presented [24]. This can be proved in this study, based on Fig that shows the addition of SA has led to less porosity until 5wt% of SA, further addition of SA was observed formation of pores that leads to decreasing the density. Hoepfner et al., (2003) observed that the grain size is one of the factors that influenced the HA hardness [22]. This can be seen in Figure 5 shows that the increasing of the grain size was in line with the hardness until 5wt% of SA. However, further increment of the grain size has led to decreasing of the hardness [25]. Thangamani et al., (2002) also reported that the decreasing in hardness was occurred due to retarded densification of the HA [25].

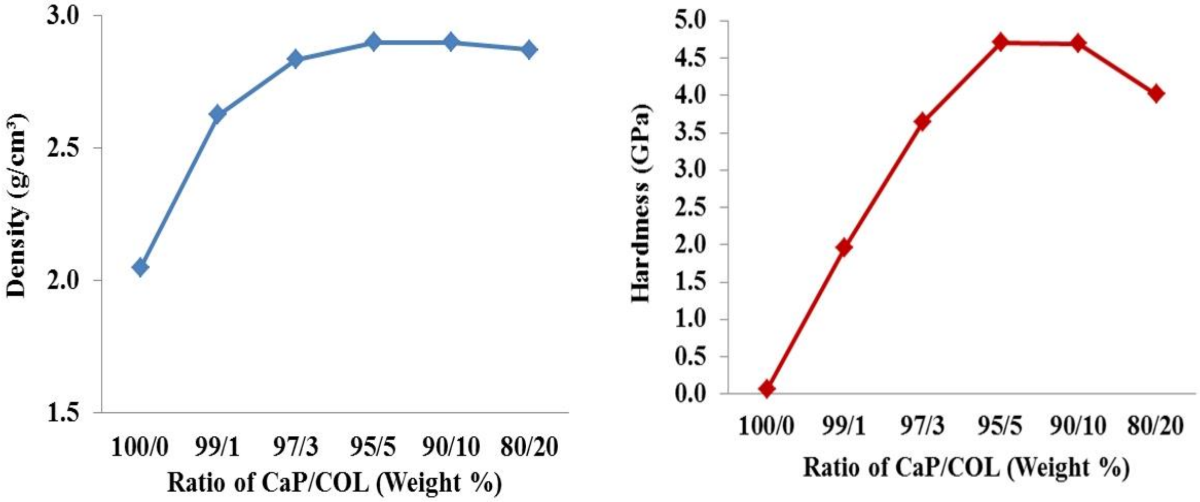

Figure 3. (a) Density and (b) Hardness of CaP/SA at Different Ratio of Weight Percentages

Figure 4 shows the shrinkage happened after sintering process. The diameter of the sample shrinks rapidly when increasing the addition of SA. Maximum shrinkage was occurred at 20wt% of SA addition with 17.36%, while the minimum shrinkage happened at pure CaP with 4.27%. Shrinkage was directly influenced by the dense structure of the composite. This result can be observed in the microstructure of the composite in Figure 6, where the formation of dense structure was occurred with the addition of SA. The shrinkage was occurred due to reduction of porosity and where the particle extend to be more large to fill the porosity between the particle that cause reduction size of sample [26].

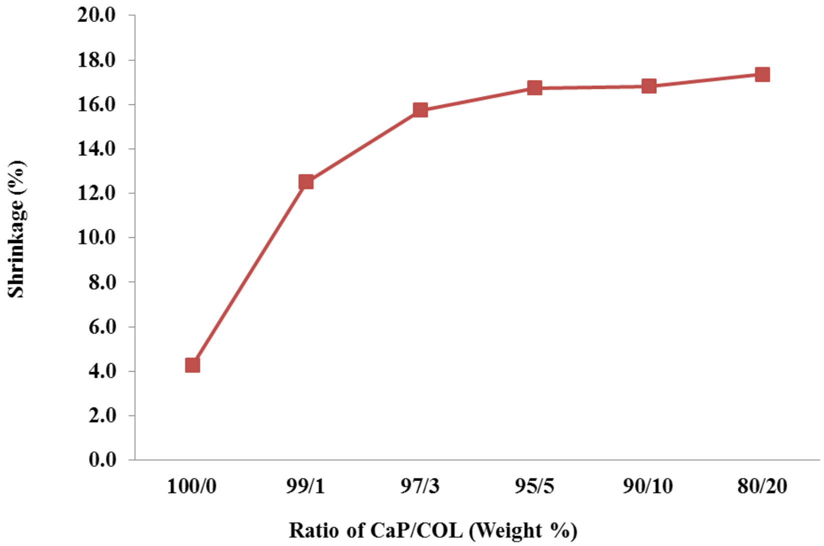

Figure 4. Shrinkage of CaP/SA at Different Ratio Weight Percentages

The grain size and the surface microstructure of the CaP/SA composite are illustrated in **Error! Reference source not found.** and Figure 6 respectively. Figure 5 shows the maximum grain size was obtained at 80/20 ratio of CaP/SA with 1.82µm. While the minimum grain size was observed at 100/0 sample with 0.84µm. Based on Muralithran et al., (2000), grain size was influenced the density and hardness of HA sample [24]. Based on Figure 6, the porosity of the sample was reduced when increasing the addition of SA and formation of larger grain was observed. Formation of large and small grain that observed at 95/5 sample was formed highest density and hardness of CaP sample. This is in agreement with Adzila et al., (2016) combination of small and large grain was formed strong bonding between the grain size which enhanced the density and hardness of CaP sample [27]. However, close the porosity and larger the grain size were led to decreasing the density as well as hardness of the CaP sample [23, 27]. The grain size was also linearly increase with the crystallite size from XRD analysis with equiaxed hexagonal and cubic structure.

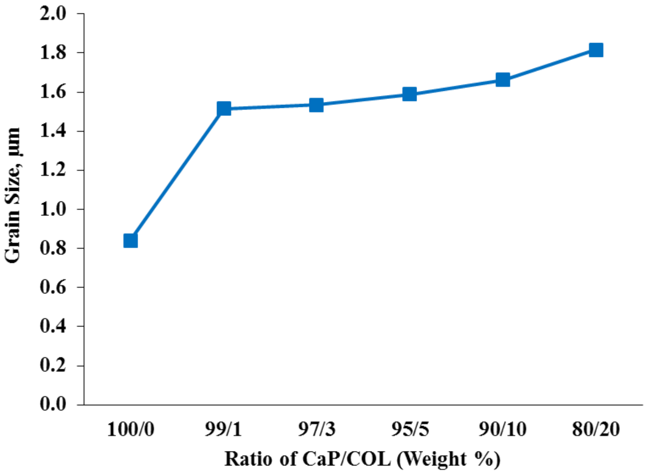

Figure 5. Grain Size of CaP/SA at Different Ratio of Weight Percentages

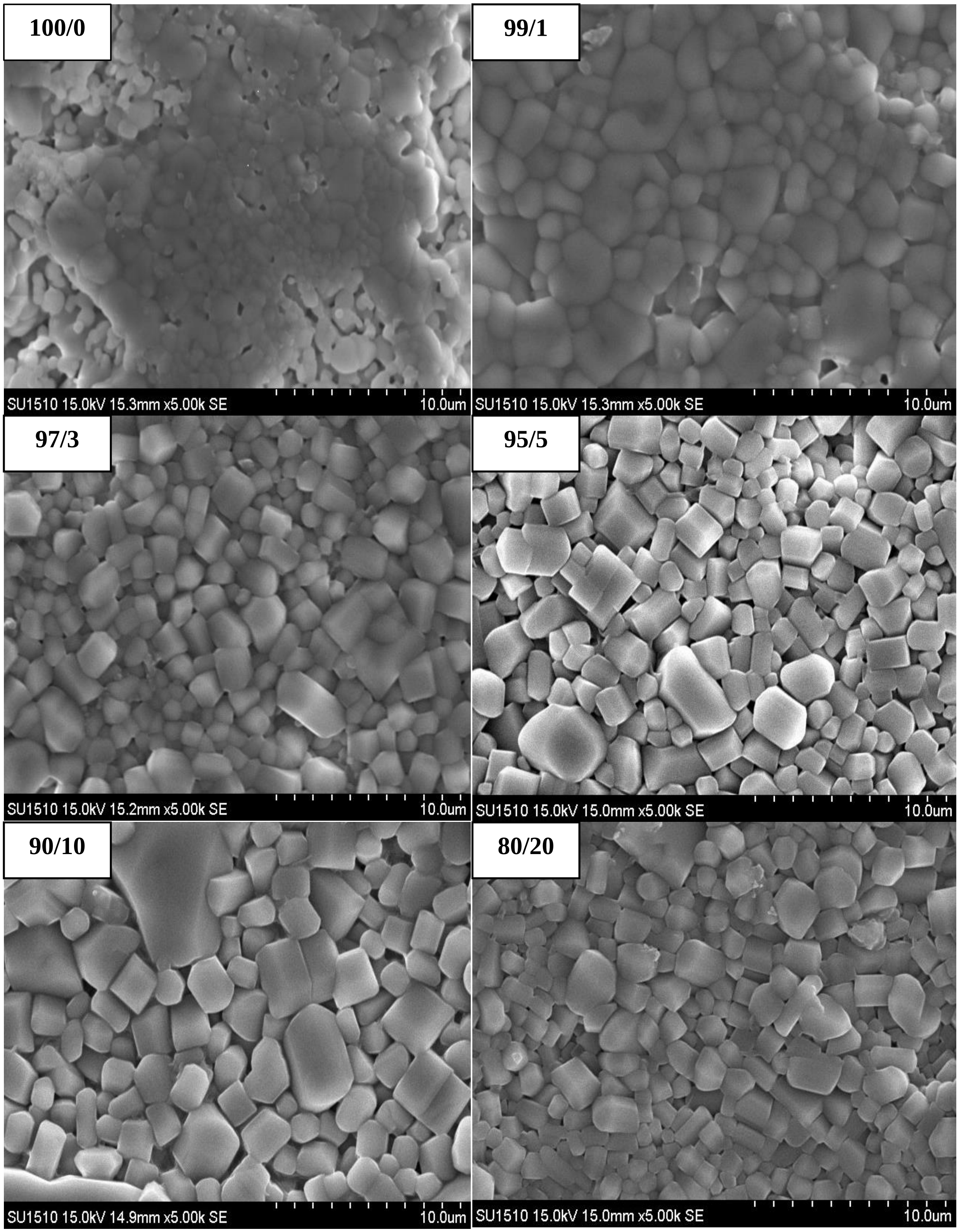

Figure 6. Microstructure of CaP/SA at Different Ratio of Weight Percentages

4.0 CONCLUSION

From this study, the XRD analysis has showed the formation of whitlockite phase (TCP) after sintering process and the intensity increased with the addition of SA. CaP/SA biocomposite has improved the densification and the hardness of CaP with 2.90g/cm^3 and 4.71GPa respectively. The presence of SA in CaP affects the crystallite size, morphology as well as the grain size of the CaP sample. Further characterization such as in vitro analysis is required to validate the biocompatibility of CaP/SA biocomposite as one of potential materials for bone implant application.

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