Engineering Transactions, **71**(2): 185–195, 2023, doi: 10.24423/EngTrans.3070.20230328
Institute of Fundamental Technological Research Polish Academy of Sciences (IPPT PAN)
Université de Lorraine • Poznan University of Technology

Research Paper

Improvement of the Mechanical Properties of Biphasic Calcium Phosphate Ceramic Composite Using Silicene

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In light of recent events in the replacement and generation of human tissues, it is becoming extremely difficult to ignore the existence of bioceramics. Although hydroxyapatite and beta-tricalcium phosphate materials are frequently employed individually, they both lack certain qualities. As a result, combining hydroxyapatite and beta-tricalcium phosphate may result in the combination of their respective qualities. The current study aims to investigate the effect of using a novel nanostructure called silicene (silicon nanosheet-SiNS) on the mechanical properties of the composite ceramic (biphasic calcium p hosphate) at various ratios of hydroxyapatite and beta-tricalcium phosphate. The silicene has been synthesized and added at different weight percentages of 1, 3, and 5%. The results reveal that the compressive strength improved due to increasing the content of silicene. The average of increasing was between 58.6% and 142% because of the strong hexagonal structure of silicene. At the same time, the hardness of the biphasic calcium phosphate composite was enhanced by increasing the weight percentage of silicene. However, the hardness decreased when the content of silicene was more than 3% due to the presence of small cavities on the surface of the samples.

Keywords: silicene; silicon nanosheet; ceramic composite; calcium phosphates; hydroxyapatite; beta-tricalcium phosphate.

1. Introduction

Calcium phosphates ceramics are one of the most widely used groups of biomaterials and have been extensively used to replace and generate human tissues. Ceramic materials play an important role in medical fields that have direct contact with human life, and therefore, greatly influence the development of this field. This is due to their unique properties, such as excellent bioactivity, biocompatibility, and corrosion resistance [1, 2]. One of the most common calcium phosphate ceramics considered high-strength and non-resorbable material is hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA), which is used in various medical applications such as scaffolds and filling [3, 4]. Another type of calcium phosphate is beta-tricalcium phosphate ($Ca_3(PO_4)_2$, β-TCP), which has a bioresorbable ability [5].

Although HA and β-TCP materials are widely used individually, these materials suffer from some drawbacks, such as the lack of bioresorbable HA in body fluid, which is unfavorable, while the use of β-TCP alone causes too fast resorption uncontrollably [6]. However, combining HA and β-TCP can lead to merging their properties to produce beneficial outcomes. HA/β-TCP composite is called biphasic calcium phosphate (BCP) and consists of a mixture of HA and β-TCP. Based on scientific understanding, calcium phosphate ceramics have been used in different applications such as bone cement, antibacterial factors, and filters [7]. Furthermore, this biomaterial composite has been used successfully as a basic material in endodontics and bone grafts [8, 9].

Nanomaterial fillers have emerged as powerful platforms for enhancing the mechanical properties of materials in general because of their superior properties that are significantly different from those of large-grained counterparts [10, 11]. Nanomaterials have many shapes, and they are categorized into zero dimensions (0D), one-dimensional (1D), and two-dimensional (2D). Various nanomaterials fillers, including 0D, 1D, and 2D scales, have been used to improve the mechanical properties of bioceramics, such as HA and TCP [12]. More recently, research has emerged that presents the study of improving the mechanical properties of bioceramics by using 2D nanofillers such as graphene [13]. Among them, silicon nanosheets 2D (silicene) have attracted increasing attention, and are considered the next generation of graphene. Similar to graphene, silicon nanosheet or silicene (SiNS) does not exist naturally. SiNS presents good mechanical and electrical properties, making it a promising material for various applications due to its buckled honeycomb structure [14, 15]. One of these applications is biomedical [16].

Given all that has been mentioned so far, bioceramics materials still require more studies to improve their mechanical properties by using novel nanostructured fillers. Therefore, the present research aims to investigate HA/β-TCP (BCP) composite's mechanical properties at various ratios using silicene nanofillers (SiNS).

2. Materials and methods

2.1. Synthesis of BCP composites

Five types of BCP composites were produced based on the weight percentage of HA and β-TCP ceramics, as shown in Table 1. Sigma-Aldrich Co. provided HA and β-TCP ceramics with CAS No.: 1306-06-5 and 7758-87-4, respectively,

Table 1. Various ratios of BCP composites.

Sample	Composition of HA [wt%]	Composition of β-TCP [wt%]
1	100	0
2	75	25
3	50	50
4	25	75
5	0	100

with purity ≥99%. The powders were mixed at 25% humidity and ambient temperature using a mixer-type NQM-0.4 model planetary ball mill at 850 rpm for 1 h to ensure homogeneous mixing and overcome agglomeration. Ethanol was added as a liquid suspended to the powder to increase the homogeneity of the mixture. After that, the mixture was taken out and dried in the oven at a temperature of 80°C for 24 hours. This mixing process complies with previous studies [1, 17].

The mixture was then pressed into a circular-bore steel mold with a diameter of 13 mm. The inner wall of the mold was lubricated with paraffin to reduce the friction between the material and the wall of the mold and to facilitate the removal of the sample from the mold after the pressing process. The produced samples were sintered inside the oven, which was operated at a rate of 5°C/min to a temperature of 1200°C and stayed for two hours, then cooled down at the same rate to room temperature.

2.2. Synthesis of silicon nanosheets/silicene (SiNS)

Several materials were used in the production of silicene. The current process depends on using montmorillonite clay (MMT) (Sigma-Aldrich, St Louis, MO, USA), sodium chloride, and magnesium powder in proportions (1:3:0.7), respectively. The mixture was put in a stainless-steel reactor, and the reactor was placed inside a tube furnace in an inert atmosphere of argon to avoid oxidation at high temperatures. Then, the furnace was operated for five hours at a temperature of 650°C. After cooling, the mixture was placed in a magnetic stirrer for 3 h to remove NaCl. Next, 1 ml of hydrochloric acid was added to remove magnesium, and eventually, silicene was extracted in 0.2% HF with drying for 12 hours at a temperature of 80°C. The product was stored in a dry, inert and opaque container because the silicene is affected by moisture and light.

2.3. BCP/SiNS preparation

After completing the preparation of the BCP composites and silicene, the mixture of BCP/SiNS composites was prepared by adding silicene to each BCP composite shown previously in Table 1. Three weight percentages of silicene had been used: 1, 3, and 5 wt%. Firstly, the dry powders were mixed by using a ball milling mixer (type: NOM-0.4 Model Planetary Ball Mill) at 850 rpm for 1 h. Then, a binder was added, which is methylcellulose (MC), at a dosage of 10% to each mixture. Finally, the mixture was pressed and sintered using the same technique explained in Subsec. 2.1. Figure 1 shows the BCP/SiNS composites before and after the pressing process.

a) b) c)

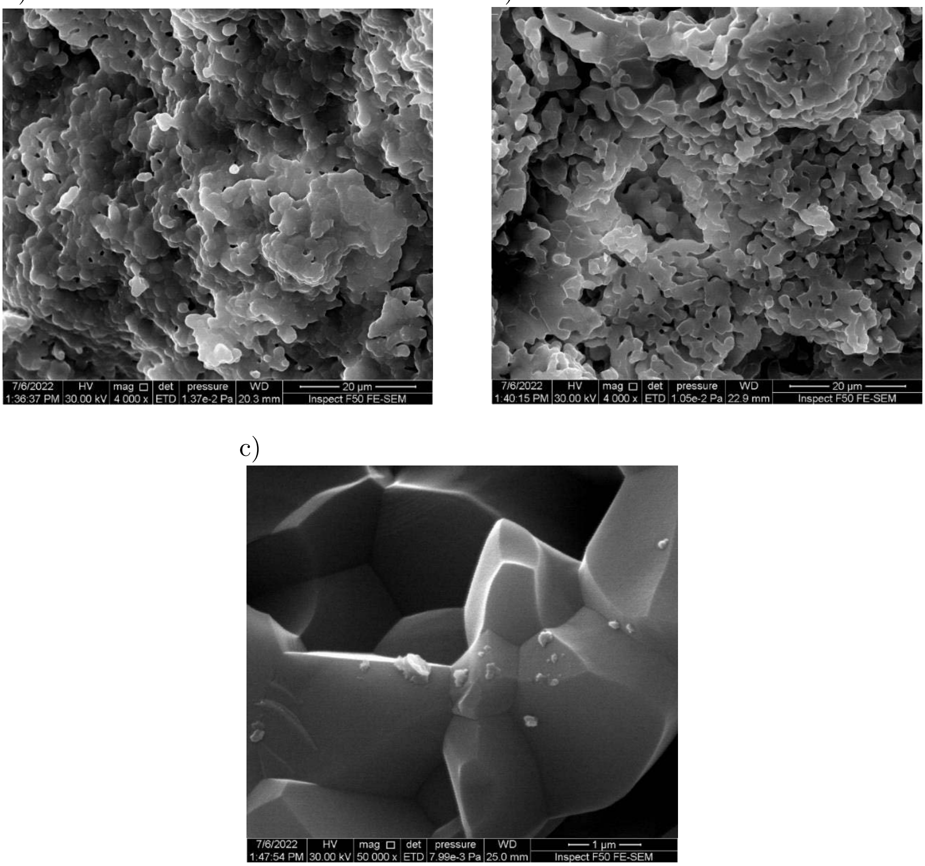

Fig. 1. The microstructure of: a) HA ceramics, b) β-TCP ceramics, c) BCP/ SiNS composite.

3. Mechanical tests

3.1. Compression test

A uniaxial compression test was conducted to measure the compressive strength of the BCP composites at various weight percentages of HA and TCP.

Besides, the influence of SiNS reinforcement on the compressive strength of the BCP composites was studied. The compression test was carried out at ambient temperature with a crosshead speed of 1 mm/min. Universal Testing Machine (Model UE34300) was used to carry out the compression test of the produced samples. Each test was repeated three times to ensure the findings.

3.2. Microhardness test

One of the necessary mechanical properties is hardness, which enables the resistance to plastic deformation by stopping penetration. Hence, the Vickers hardness test (HV) was used to investigate the effect of varying weight percentages of HA and TCP ceramics, and adding SiNS to the BCP composites. The hardness test was performed following the standard ASTM C1327. The universal hardness tester HBRVS-187.5 was employed to carry out hardness test. Each test was repeated three times to ensure the findings.

4. Results and discussion

4.1. Compression test

Figure 2 shows the relationship between the average compressive strength and the weight percentage of the filler SiNS for the BCP composite samples at various weight ratios between HA and TCP ceramics.

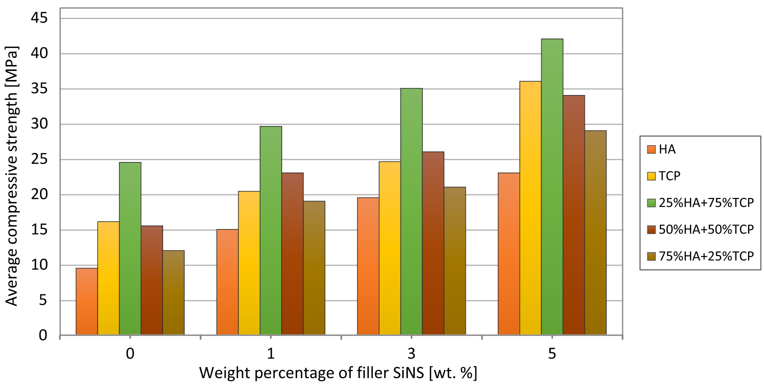

Fig. 2. The relationship between the average compressive strength and the weight percentage of the filler SiNS for the BCP composite.

Figure 2 reveals that there has been a gradual increase in the compressive strength of the BCP composite with an increase in the percentage of SiNS weight. Furthermore, the BCP composite made from 25% HA + 75% TCP has the highest compressive strength compared with other weight ratios through all percentages of adding SiNS. The maximum achieved compressive strength was 42 ± 1.2 MPa at 25% HA + 75% TCP and 5% of SiNS. Table 2 shows all results of the compression test.

Table 2. All results of the compression test.

Percentage of SiNS [wt.%]	The compressive strength [MPa]				
	HA (±1.15 MPa)	TCP (±1.96 MPa)	25% HA +75% TCP (±1.2 MPa)	50% HA +50% TCP (±3.15 MPa)	75% HA +25% TCP (±3.3 MPa)
0	9.50	16.11	24.50	15.51	12.00
1	15	20.40	29.60	23.00	19.00
3	19.50	24.60	35.00	26.00	21.00
5	23	36	42.00	34.00	29.00

The observed correlation between the compressive strength and the weight percentage of adding SiNS might be related to the granular distribution of HA and TCP molecules and their merging with (SiNS) grains. These grains are characterized as hexagonal nanosheets similar to graphene sheets but different from them in terms of the zigzag hexagonal shape towards the z-axis [18], as shown in Fig. 3.

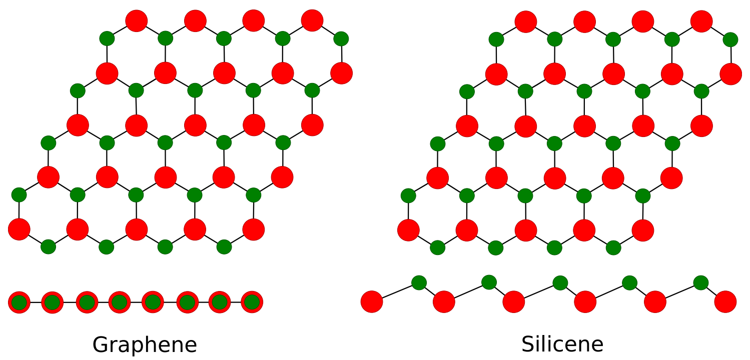

Fig. 3. The structure difference between graphene and silicene (SiNS).

The configuration of the SiNS (silicene) structure is called buckled structure, a more stable type of structure [19]. This gives the silicon nanosheets (silicene) a larger surface area, contact points, and a larger contact surface. It also enhances the structural and mechanical behaviors of the produced composite. Further, there is an increase in the bonding bridges between molecules, as well as having less energy than the flat structure, which leads to being more stable [20]. Figure 4 illustrates the silicene (SiNS) structure used in this research. Although the ceramic composite BCP was produced at 1200°C (sintering process), an

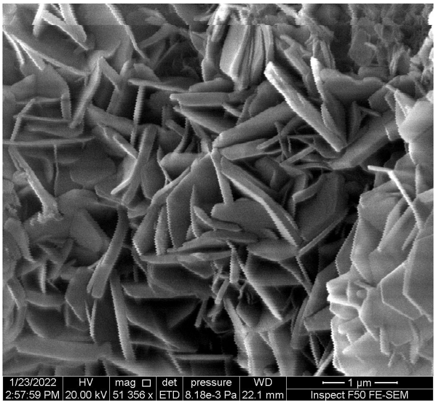

FIG. 4. The silicene (SiNS) structure.

X-ray diffraction (XRD) examination of the BCP composite was carried out to ensure no changes occurred in the structure with the SiNS. Figure 5 shows the XRD examination of the BCP/SiNS composite.

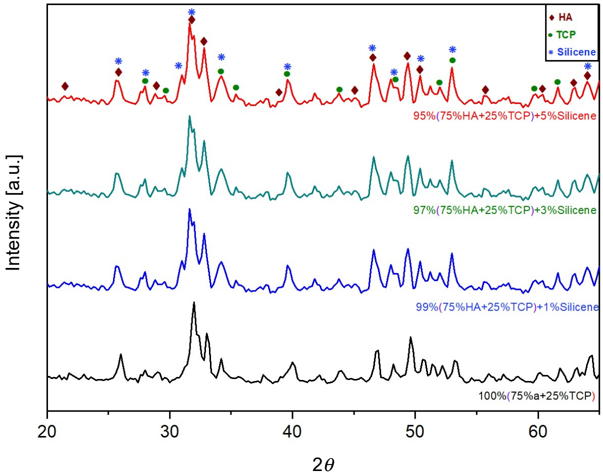

FIG. 5. The XRD examination of the BCP/SiNS composite.

4.2. Microhardness test

A highly significant characteristic to be improved in materials is hardness. Adequate hardness prevents penetration and makes it possible to resist plastic deformation. The results obtained from the preliminary analysis of the microhardness test are presented in Fig. 6. While Table 3 shows all results of the microhardness test.

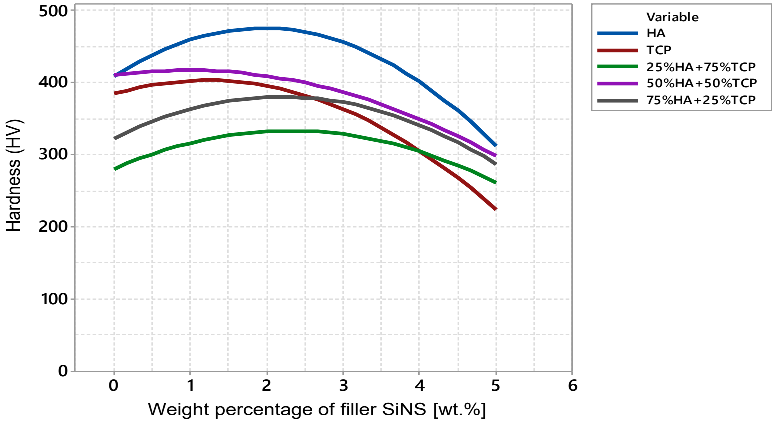

FIG. 6. The relationship between the microhardness and the weight percentage of the filler SiNS for the BCP composite.

Table 3. Microhardness test results.

Percentage of SiNS [wt.%]	Microhardness (HV)				
	HA (±13.13)	TCP (±10.57)	25% HA +75% TCP (±18.15)	50% HA +50% TCP (±9.98)	75% HA +25% TCP (±22)
0	414.00	389.00	288.00	407.00	332.00
1	450.00	395.00	303.00	425.00	347.00
3	463.00	369.00	338.00	382.00	384.00
5	310.00	222.00	259.00	300.00	284.00

From the data in Fig. 6 and Table 3, it is apparent that the microhardness values of the BCP composite at various weight ratios between HA and TCP have increased due to using silicene (SiNS). However, when the increase in the weight percentage of filler SiNS was excessive, above 3%, the hardness of the ceramic composite was decreased.

This is because the cohesion factor influences both the stiffness and the compressive coefficient. It is obvious that adding up to 3% of the SiNS filler produced the highest level of hardness. An excessive increase of filler causes more pores and microcracks. This is due to the different thermal expansion coefficients of these two materials. The bulk density has a significant impact on a ceramic material's hardness since a ceramic material's inability to deform plastically would prevent it from absorbing any energy applied to it. Due to the absence of plastic deformation, once a crack starts to progress, it will keep doing so until the material fractures. The creation of holes with increased SiNS content on the surface of the BCP composites can also be responsible for the decrease in hardness [21]. Figure 7 shows the effect of SiNS content on the apparent density. The percentage of increasing true porosity increased when the SiNS was added to reach up to 45% at 5% of the SiNS [22].

FIG. 7. Optical images for BCP composite (50% HA + 50% TCP), with: a) 1% SiNS, b) 3% SiNS, and c) 5% SiNS.

5. Conclusion

The objective of this research was to evaluate the BCP composite's mechanical characteristics. One of the study's more important conclusions is that the addition of silicene (SiNS) reinforcement improves the mechanical properties of the BCP composites. This study's findings contribute several new ideas to the existing body of knowledge.

According to the findings, the compressive strength of the BCP composites at various weight ratios between HA and TCB ceramics enhanced between 58.6% and 142% when the weight percentage of SiNS was 5%. This is related to the strong structure of SiNS, which is a hexagonal buckled structure with high resistance against the compression force.

Regarding the hardness property, the microhardness of the BCP composites increased up to 17% when the SiNS content in the ceramic composite reached 3%. After that, the BCP's hardness decreased with the excessive increasing the content of SiNS. This is due to producing some small holes on the surface of the samples which leads to a decrease in the hardness at the higher content of SiNS.

Based on these findings, it can be concluded that silicene (SiNS) has a significant effect on the mechanical properties of the bioceramics materials and their composites.

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Received November 17, 2022; accepted version January 23, 2023.