Deposition of Hydroxyapatite on Silica Made from Rice Husk Ash to Produce the Powder Component of Calcium Phosphate Cement

Tri Windarti1,2*, Widjijono3, and Nuryono2**

1Department of Chemistry, Faculty of Science and Mathematics, Universitas Diponegoro, Jl. Prof. Soedharto SH, Tembalang, Semarang 50275, Indonesia
2Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia
3Department of Dental Biomaterials, Faculty of Dentistry, Universitas Gadjah Mada, Jl. Denta 1, Sekip Utara, Yogyakarta 55281, Indonesia

*Corresponding author:
email: tri.windarti@lecturer.undip.ac.id; nuryono_mipa@ugm.ac.id**

Received: July 16, 2020
Accepted: September 10, 2020
DOI: 10.22146/ijc.57900

Abstract: Hydroxyapatite (HA) has been deposited on silica (SiO₂) particles to produce HA-SiO₂ composite that will be used as the powder component of calcium phosphate cement. HA was expected to be on the composite surface to maintain its bioactivity. SiO₂ was made by the sol-gel method, in which silicate solution was extracted from rice husk ash with NaOH solution. Deposition of HA on SiO₂ was carried out by wet chemical deposition method at various Ca/Si molar ratio (in a range of 5–25) followed by calcination at 600 °C for 2 h. Results showed that HA was successfully deposited on SiO₂ particles. The cell parameters of the HA crystals were slightly distorted by the presence of SiO₂ and HA in the composite had a bigger cell volume than pure HA. The crystallite size of HA in the composites increased with the increase of the Ca/Si ratio but the values were smaller than pure HA. SiO₂ acted as a morphology directing agent. At low Ca/Si ratio, the HA-SiO₂ particles were in a form of short rod-like particles with sizes of < 50 nm, while at high Ca/Si ratio, a mixture of short and long rod-like particles with the size of < 100 nm was obtained. The zeta potential of composites was almost similar to pure HA. These properties indicated that HA-SiO₂ composites support the bioactivity of injectable calcium phosphate cement.

Keywords: hydroxyapatite; silica; rice husk ash; calcium phosphate cement

INTRODUCTION

Calcium phosphate cement (CPC) has been widely developed due to its ability to induce bone formation and vascularization. Injectable CPC consists of powder and liquid components. Calcium phosphate and its mixture are common materials used as the powder component and an aqueous solution of calcium or phosphate ion is used as the liquid component. The mixture of the two components produces a paste that can be injected into a damaged bone. Inside the body, the paste may harden to result in a temporary bone substitute [1-3]. Additives are often added to improve the property of CPC. One of the most studied additives with a strong influence on the property of CPC is siliceous solids like silica (SiO₂) and calcium silicate (CaSiO₃) [4-9]. For instance, the addition of 5% fibrous CaSiO₃ into CPC increased the compressive strength of the resulting cement by 250% (from 14.5 MPa to 50.4 MPa) [10]. The setting reaction of CPC with silica precursor produced a porous composite with pore diameters in the range of 1–10 nm [11]. Moreover, CPC-silica composite was found to have an ability to improve cell adhesion and proliferation as well as stimulating osteogenic differentiation [12-14].

To adjust the contribution of silica additives to the improvement of CPC’s properties, modification of the powder component, typically calcium phosphate in the form of hydroxyapatite [HA, (Ca₁₀(PO₄)₆(OH)₂], has
been intensively studied. Synthetic HA is known as a good bone substitute due to its properties such as being osteoconductive, biocompatible, and bioactive [15-18]. Normally, modification of HA with SiO$_2$ that is performed under alkaline conditions, produce composites in which silica covers the HA particles [19]. Moreover, under high Ca/P reactant ratios, which are usually used to produce HA, CaO is formed as a secondary product. The presence of CaO decreases the composite surface area. This is undesirable for the powder component of CPC because the presence of silica on the composite surface and the reduced surface area of the composite reduce the bioactivity of HA. On the other hand, a study about HA–SiO$_2$ morphology showed that the composite was built in such a way that silica interacted with the $a$-plane of HA and then HA crystals grew along the c-axis and produced needle-like particles [20]. However, the formation of such shaped particles should be avoided for injectable CPC, because it reduces the injectability of the paste material.

Silica is silicon dioxide (SiO$_2$), which forms a three-dimensional framework through siloxane (Si–O–Si) bonds to build an amorphous and porous structure. Silica material has important properties such as soluble in water, chemically inert, thermally stable, and compatible for biomedical applications [21-23]. One of the sources of silica in nature is rice husk ash, in which rice is a very abundant and renewable commodity. Simple extraction of rice husk ash with NaOH produces silica with the same chemical and physical properties as commercial silica [24]. Silica from rice husk ash has a high purity and is a nano-sized material, and has also been applied for several industries such as pharmaceuticals and cosmetics [22].

In this study, the modification of HA with silica was conducted by depositing HA on SiO$_2$ to produce nano-sized HA-SiO$_2$ composites. Owing to such structure, it is expected that HA in the composite directly interacts with living bone tissue when the composite is used as CPC. In addition, composite particles are expected to have a shape that is suitable to improve the cement’s injectability. This study was based on a previous work regarding in situ synthesis of mesoporous silica MCM-41/HA composite [23]. The research found that the arrangement of HA and SiO$_2$ in the composite depended on the aging time. At shorter aging times, SiO$_2$ was found on the composite surface while at longer aging times, the composite was covered by HA. It can be concluded that, thermodynamically, during the synthesis process, SiO$_2$ and HA particles tried to get the lowest free energy. At first, silica was well dispersed in the reactant solution and the HA crystal was built on the silica surface by silanol-Ca interaction. The HA particles tended to interact with each other, which resulted in HA being inside of the composite and SiO$_2$ on the surface. With the increase of aging time, SiO$_2$ was then covered with HA that was built next from the reactant solution. That is why the position of SiO$_2$ and HA in the composite surface is seen to have changed during aging time. In the current work, these phenomena are predicted to occur when synthesis of the HA-SiO$_2$ composite is conducted at various Ca/Si reactant ratio. The silica was synthesized from rice husk ash by the sol-gel method and the formation of HA-SiO$_2$ composite was done by the wet chemical deposition method. The chemical structure, surface properties, and zeta potential of the HA-SiO$_2$ composite were studied according to the properties needed for the powder component of CPC.

### EXPERIMENTAL SECTION

#### Materials

Rice husk as the silica source was collected from a rice mill in Karanganyar, Central Java, Indonesia. Chemicals including NaOH (Merck), HCl (Merck), and deionized water were used in the silica preparation. For the synthesis of the HA-SiO$_2$ composite, Ca(NO$_3$)$_2$·4H$_2$O (Merck) and KH$_2$PO$_4$ (Merck) were used as Ca and P precursors, respectively. Double distilled water (Ikapharmindo Putramas) and NH$_4$OH 32% (Merck) were used as solvent and for pH adjustment, respectively. All chemicals were in analytical grade and used without further purification.

#### Instrumentation

The functional groups of the samples were analyzed with Fourier Transform Infrared (FTIR) spectrophotometer (Shimadzu) through a KBr pellet
method at a wavenumber range of 400–4000 cm\(^{-1}\) (Scan step wavenumber of 7.715264 cm\(^{-1}\)). The crystal structure was characterized by X-Ray Diffraction (XRD) (Rigaku type Miniflex600) that was equipped with monochromatic Cu Kα radiation, operated at 40kW (\(\lambda = 1.54 \text{ Å}\) ) and scanned for \(2^\circ \leq 2\theta \leq 90^\circ\) at a scan step degree of 0.02°. XRD data was fitted by using the Origin software. Cell parameters were calculated with mathematic equations based on hexagonal structure and Bragg’s law. Crystallite size was calculated by Scherrer equation. Surface morphology, element distribution, shape and size of particles on surfaces were observed using Scanning Electron Microscope -Energy Dispersive Spectroscopy (SEM-EDS) (Hitachi type SU3500) and Hitachi MC1000 sputter ion for sample coating with gold in a thickness of 1 nm. The shape and size of the particles were observed with Tunneling Electron Microscope (TEM) (JEOL type JEM-1400) by using ethanol as the dispersant. Zetaziser Nano form Malvern was used to record zeta potential value. The measurement was conducted at room temperature at pH 7 for samples that were dispersed in water and 1% (v/v) Tween 80.

**Procedure**

**Preparation of silica**

Rice husk was burned in fire to produce charcoal. The charcoal was then calcined at 700 °C for 4 h to obtain rice husk ash (RHA). The RHA sample was crushed and sieved with a 200 mesh sieve to obtain RHA powder. Afterwards, about 10 g of RHA powder was mixed with 60 mL of 2 M NaOH solution. The mixture was heated at 65 °C and stirred for 1 h to obtain a suspension. The suspension was then filtered, and the residue was mixed again for the second time with 30 mL of 2M NaOH solution. The obtained filtrate was added with HCl 25% dropwise to reach pH 7.0 or until a white gel was formed. The obtained gel was washed with deionized water by sonication for 1 h to get a white residue and then the white residue was heated at 400 °C for 4 h. The product was later crushed and sieved with a 200 mesh sieve and the obtained powders were considered as silica.

**Deposition of hydroxyapatite on silica**

A certain weight of Ca(NO\(_3\))\(_2\)·4H\(_2\)O and silica were mixed with double distilled water to produce 50 mL of solution I. Fifty mL of solution II was prepared by dissolving a certain weight of KH\(_2\)PO\(_4\) in double-distilled water. Solution II was then slowly added to solution I with gentle stirring. Afterwards, about 15 mL of NH\(_4\)OH 32% was added into the mixture to reach pH > 9. The stirring process was continued for 1 h and then the mixture was kept at room temperature for 24 h. The formed precipitate was washed with 2 L of double distilled water and dried in an electric oven at 50 °C for 48 h to obtain a white powder. The product was called as-precipitate powder. The as-precipitate powder was calcined in an electric furnace at 600 °C for 2 h at air atmosphere to obtain the HA-SiO\(_2\) composite (calcined powder). The composition of the precursors and the sample codes are presented in Table 1.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Ca(NO(_3))(_2)·4H(_2)O (g)</th>
<th>KH(_2)PO(_4) (g)</th>
<th>Ca/Si(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>19.719</td>
<td>6.804</td>
<td>-</td>
</tr>
<tr>
<td>A1</td>
<td>4.912</td>
<td>1.699</td>
<td>5</td>
</tr>
<tr>
<td>A2</td>
<td>9.824</td>
<td>3.397</td>
<td>10</td>
</tr>
<tr>
<td>A3</td>
<td>14.736</td>
<td>5.095</td>
<td>15</td>
</tr>
<tr>
<td>A4</td>
<td>19.647</td>
<td>6.793</td>
<td>20</td>
</tr>
<tr>
<td>A5</td>
<td>24.560</td>
<td>8.491</td>
<td>25</td>
</tr>
</tbody>
</table>

\(^1\)Ca/P ratio and SiO\(_2\) content were kept constant at 1.67 and 0.25 g

**RESULTS AND DISCUSSION**

The transformation of the chemical and crystal structure of the products at various Ca/Si reactant molar ratio (Ca/Si\(_{\text{R}}\)) were studied for the as-precipitate and calcined powder. Meanwhile, the surface properties and zeta potential were studied for the calcined powder.

**FTIR Analysis**

Fig. 1 shows the FTIR spectra of SiO\(_2\) and the HA-SiO\(_2\) composite. For the SiO\(_2\) spectrum, characteristic peaks of SiO\(_2\) appeared at 1100, 805 and 466 cm\(^{-1}\) that are attributed to the antisymmetric stretching vibration of Si–O–Si, symmetric vibration of Si–O–Si and bending vibration of Si–O–Si, respectively. A broad peak around 3500 cm\(^{-1}\) is attributed to the vibration of the silanol group. For the as-precipitate powder, the antisymmetric
Fig 1. FTIR spectra of SiO₂ and HA-SiO₂ composites

stretching vibration of Si–O–Si overlapped with the peak of the asymmetric stretching vibration of PO₄³⁻ at 1088 cm⁻¹. The peak of the bending vibration of Si–O–Si at around 466 cm⁻¹ decreased significantly and the peak of the symmetric vibration of Si–O–Si at 805 cm⁻¹ disappeared. This phenomenon has been explained by a literature, which stated that introducing Ca²⁺ ions into a SiO₂ network may damage some Si–O–Si bonds to form Si–O–Ca–O–Si groups [25].

During the deposition process, the silanol groups in SiO₂ released H⁺ due to the alkaline condition produced by the Si–O– site. The Si–O– site then interacted with Ca²⁺ to form Si–O–Ca⁺ which interacted further with PO₄³⁻ and another Ca²⁺ until HA crystal seeds were formed. The crystal seed grew continuously on the SiO₂ surface in 3 dimensions. The tetrahedral symmetry of the PO₄³⁻ group such as the asymmetric stretching (ν₃) appeared as sharp peaks at 1088 and 1043 cm⁻¹ and the asymmetric deformation (ν₄) appeared at 568 and 604 cm⁻¹ [26-27]. A wide peak around 3500 cm⁻¹ indicated the presence of stretching O–H groups with hydrogen bonds of HA or absorbed H₂O. The presence of absorbed H₂O is proven by a peak at 1637 cm⁻¹. CO₃²⁻ groups that substitute PO₄³⁻ site appeared at 1489 cm⁻¹ [28-29]. The spectra of calcined powder A₀–A₅ looks similar to the as-precipitate spectra but with sharper peaks. Calcination of the as-precipitate powder at 600 °C for 2 h caused molecules arrangement and the release of small molecules such as CO₂ and H₂O, causing the CO₃²⁻ peak to disappear, and the H₂O peak became shorter.

**XRD Analysis**

Crystal analysis based on XRD patterns is shown in Fig. 2. The characteristic peak of SiO₂ appeared as a broad peak at 2θ = 22°. This peak disappeared when SiO₂ was composited with HA, due to the strong interaction of silica – HA [30]. For all as-precipitate powder, HA with low crystallinity was formed in the composites. The intensity of the peaks and sharpness increased with the increase of the Ca/Si molar ratio of the reactants (Ca/Siᵣ). The peaks of the calcined powder were sharper than the as-precipitate powder. These peak patterns confirmed that the composites contained HA in hexagonal crystal lattice according to JCPDS card no 090432. The crystal cell parameters of the standard were a = b = 0.9418 nm c = 0.6884 nm, α = β = 90° γ = 120° and cell volume = 1.586 nm³. Broad peaks of HA that appeared at 2θ of around 25, 31, 32, 33, 34, 40, 47 and 49° are attributed to the crystal plane of (002), (211), (112), (300), (202), (212), (222), and (213), respectively. The low crystallinity of HA is desirable for biomaterial because it produces high bioactivity [31]. The effect of the Ca/Siᵣ molar ratio to the HA crystal formation can be seen from the increase of peak intensity and the sharpening of the
peak shape as the Ca/Si$_{(R)}$ ratio increases (Fig 2. inset). At high Ca/Si$_{(R)}$ molar ratio, the effect of silica on the formation of HA was not significant.

From the diffraction data that were fitted with Origin, the 2θ position and FWHM of every single peaks was able to be determined. The d-spacing that was calculated using Brag’s law and the information of miller indices from JCPDS data was used to determine the a and c parameters of HA crystal in A0–A5 samples. Also, the Scherrer equation was used to calculate the crystallite size. The cell parameters and crystallite size of HA in A0–A5 samples are shown in Table 2. The a value for all samples was almost the same. Meanwhile, the c value, as well as the cell volume of HA in the composites, were larger than pure HA but those values were fluctuated to Ca/Si$_{(R)}$. The formation of HA crystal was slightly distorted by the presence of SiO$_2$. The crystallite size of HA in A1–A5 samples was in the range of 7.557 ± 0.164–9.581 ± 0.144 nm which was lower than pure HA (12.788 ± 0.450 nm). The crystallite size increased with the increase of Ca/Si$_{(R)}$. The HA-SiO$_2$ composite is predicted to have a higher bioactivity than pure HA due to its higher volume and lower crystallite size. All parameters of the HA cell products were lower than the HA standard in JCPDS card no 090432. It is well known that HA cell parameters are dependent on the synthesis method used [31].

**SEM, EDS and TEM Analysis**

SEM images of sample A1–A5 showed different morphologies for each Ca/Si$_{(R)}$ molar ratio (Fig. 3). For

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>V (nm$^3$)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>0.935 ± 6. 10$^{-4}$</td>
<td>0.683 ± 3. 10$^{-4}$</td>
<td>1.549 ± 1.2. 10$^{-3}$</td>
<td>12.788 ± 0.450</td>
</tr>
<tr>
<td>A1</td>
<td>0.933 ± 5. 10$^{-4}$</td>
<td>0.687 ± 3. 10$^{-4}$</td>
<td>1.554 ± 1.0. 10$^{-3}$</td>
<td>7.557 ± 0.164</td>
</tr>
<tr>
<td>A2</td>
<td>0.935 ± 5. 10$^{-4}$</td>
<td>0.688 ± 3. 10$^{-4}$</td>
<td>1.561 ± 0.9. 10$^{-3}$</td>
<td>7.783 ± 0.230</td>
</tr>
<tr>
<td>A3</td>
<td>0.935 ± 4. 10$^{-4}$</td>
<td>0.688 ± 2. 10$^{-4}$</td>
<td>1.562 ± 0.8. 10$^{-3}$</td>
<td>8.413 ± 0.126</td>
</tr>
<tr>
<td>A4</td>
<td>0.937 ± 4. 10$^{-4}$</td>
<td>0.689 ± 2. 10$^{-4}$</td>
<td>1.572 ± 0.8. 10$^{-3}$</td>
<td>8.971 ± 0.152</td>
</tr>
<tr>
<td>A5</td>
<td>0.935 ± 4. 10$^{-4}$</td>
<td>0.686 ± 2. 10$^{-4}$</td>
<td>1.559 ± 0.8. 10$^{-3}$</td>
<td>9.581 ± 0.144</td>
</tr>
</tbody>
</table>
Ca/Si\(_{[R]}\) = 5 (A1), the image showed a rough surface that compose of regular shape particles with size < 100 nm. For Ca/Si\(_{[R]}\) = 10 (A2), the surface morphology was flat with more tightly arranged particles. A different image was shown for Ca/Si\(_{[R]}\) = 15 (A3), where the particles were larger than A1 and A2, and agglomerated without a pattern. For Ca/Si\(_{[R]}\) = 20 (A4) and 25 (A5), the images were nearly the same as A2, in which the particles have a regular shape with size < 100 nm.

TEM images of samples A0, A1, and A5 showed that particles of pure HA were different in shape and size compared to HA-SiO\(_2\) composite particles (Fig. 4). Pure HA particles were in the form of long rod-like shapes with particle size < 100 nm. Particles of the HA-SiO\(_2\) composite in sample A1 were regular-shaped in the form of rod-like particles but in smaller sizes (< 50 nm). A different phenomenon occurred to sample A5, in which its shape and size were a combination of A0 and A1 samples. Short rod-like particles with particle sizes of < 50 nm were mixed with long rod-like particles with particle sizes of < 100 nm. These images as well as the crystallite size data confirmed that SiO\(_2\) acted as a morphology directing agent. Through silanol – Ca interactions, the Ca\(_9\)(PO\(_4\))\(_6\) clusters were formed on the SiO\(_2\) surface, and then these intermediate states grew in 3 dimensions to build HA crystallite on the silica surface [30]. The other HA-SiO\(_2\) clusters inhibited further growth of HA so that HA-SiO\(_2\) composite with lower Ca/Si ratio had smaller particles, hence suitable to be used as the powder component of CPC. The particles can produce a paste
with high viscosity due to the low particle-particle and particle-syringe wall friction.

Table 3 shows the elemental composition of the surface of the HA-SiO2 composites. By increasing the Ca/Si(R) molar ratio, the Si content decreased from 2.72 to 0.54%, while the P content tended to be stable at 11.81–13.68%. The O content increased from 61.92 to 68.98%, while the Ca content fluctuated around 18.67–23.32%. The Ca/Si(p) ratio of the composites tended to increase linearly with Ca/Si(R), except for sample A3. Meanwhile, Ca/P(p) or Ca/P ratio of the composites tended to decrease by the increase of Ca/Si(R), except for sample A4. This can happen due to the tendency of HA and SiO2 particles to agglomerate [23]. For all Ca/Si(R) ratios except for Ca/Si(R) = 15 (A3), the Ca/Si(p) was higher than Ca/Si(R) (Table 1). This data confirmed that SiO2 tended to be in the inside of the HA-SiO2 composite while HA covered the composite surface.

The formation of HA-SiO2 composites with HA deposited on the SiO2 surface was confirmed with EDS element mapping (Fig. 5). Mapping was done for Ca, P, Si, and O on the sample surface area of 750 μm2. For Ca/Si(R) of 5 (A1), the mapping of Ca and P showed that both elements were evenly distributed on the sample surface with the same color intensity. Both images showed dark holes in the same position. Si element mapping confirmed that the dark holes were Si aggregates and there were at least five Si aggregates. The absence of black holes in the element mapping of O indicated that the composite surface was filled with oxygen. The image for element O showed that the composite surface was rough. For Ca/Si(R) of 25 (A5), the element mapping of Ca and P was not as intense as for the A1 sample. The images showed two dark holes in the same position. Image mapping of Si confirmed that only 1 of the holes was Si aggregate and from image mapping of O, the second hole indicated that the composite surface was rough. Besides appearing as an agglomerate, Si was also distributed evenly on the composite surface. At high Ca/Si ratios, Si had a low tendency to form aggregates. The surface phenomenon of sample A5 was related to the element composition in Table 3. The value of Ca/P(p) and Ca/Si(p) indicated that HA covered the composite surface. For CPC application, the presence of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca (%)</th>
<th>P (%)</th>
<th>Si (%)</th>
<th>O (%)</th>
<th>Ca/P(p) Ratio</th>
<th>Ca/Si(p) Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>22.48</td>
<td>12.88</td>
<td>2.72</td>
<td>61.92</td>
<td>1.75</td>
<td>8.26</td>
</tr>
<tr>
<td>A2</td>
<td>22.59</td>
<td>13.68</td>
<td>1.33</td>
<td>62.40</td>
<td>1.65</td>
<td>16.98</td>
</tr>
<tr>
<td>A3</td>
<td>20.50</td>
<td>12.65</td>
<td>1.47</td>
<td>65.37</td>
<td>1.62</td>
<td>13.95</td>
</tr>
<tr>
<td>A4</td>
<td>23.32</td>
<td>12.22</td>
<td>0.76</td>
<td>63.70</td>
<td>1.91</td>
<td>30.68</td>
</tr>
<tr>
<td>A5</td>
<td>18.67</td>
<td>11.81</td>
<td>0.54</td>
<td>68.98</td>
<td>1.58</td>
<td>34.57</td>
</tr>
</tbody>
</table>

Fig 5. Surface element mapping of A1 (a) and A5 (b) sample
Table 4. The zeta potential of SiO₂ and A0–A5 samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>-43.895 ± 0.061</td>
</tr>
<tr>
<td>A0</td>
<td>-1.623 ± 0.025</td>
</tr>
<tr>
<td>A1</td>
<td>-1.759 ± 0.028</td>
</tr>
<tr>
<td>A2</td>
<td>-0.259 ± 0.027</td>
</tr>
<tr>
<td>A3</td>
<td>-1.481 ± 0.027</td>
</tr>
<tr>
<td>A4</td>
<td>-1.411 ± 0.057</td>
</tr>
<tr>
<td>A5</td>
<td>-2.935 ± 0.030</td>
</tr>
</tbody>
</table>

HA on the composite surface is highly expected due to the HA ability to interact with living bone tissues [1-3]. In addition, the rough surface of the composite will support the attachment of CPC on the bone tissue surface [31].

Measurement of Zeta Potential

Table 4 shows the zeta potential of SiO₂ and A0–A5 samples in water. The zeta potential value of SiO₂ was -43.895 ± 0.061 mV, which indicated that the SiO₂ dispersion in water was stable. In contrast, a previous study found that silica nanoparticles made from Bambusa vulgaris leaves had a zeta potential value of -0.29 mV [32]. Sample A1 that contained pure HA had a zeta potential of -1.623 ± 0.025 mV, which indicated that HA dispersion in water was unstable and had a great tendency to form aggregates quickly. The same condition occurred to samples A1–A5. The zeta potential of HA-SiO₂ composites was about -0.259 ± 0.027 to -2.935 ± 0.030 mV. The stability of SiO₂ dispersion changed due to the deposition of HA. HA that was deposited on the SiO₂ surface decreased the repulsion energy of the particles in water. The negative zeta potential value of the HA-SiO₂ composite will be beneficial to CPC because it will drive Ca²⁺ ions in the body liquid to attach to the CPC surface. Furthermore, a negative zeta potential value is required in bone cell adhesion [26]. Therefore, the composite is predicted to have good bioactivity [33].

CONCLUSION

The obtained HA-SiO₂ composite had excellent properties such as being covered by HA, resulting in greater lattice volume and smaller crystallite size compared to pure HA. The shape of the HA-SiO₂ particles was similar to pure HA but smaller in size. The composites surface was rough with zeta potential values almost the same as pure HA. These properties make HA-SiO₂ composite a promising material to be used as a powder component of injectable calcium phosphate cement.


