

Physics and chemistry of producing silicon-hydroxylapatite-titanium composite materials

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Abstract. In the research, Si-HA powders have been synthesized using SBF solution with different content of silicon. It was found that all the samples synthesized from the model solution of extracellular fluid under varying concentration of silicate ions are single-phase and represent hydroxyapatite. The nature of the reagent containing SiO_4^{4-} ions does not affect the hydroxyapatite structure. In the study of the surface and morphological characteristics of the phosphate coatings modified by silicon ions, it was found that as the degree of phosphate calcium substitution by SiO_4^{4-} ions increases, the surface wettability on the titanium substrates deteriorates and cohesive energy decreases. It is shown that the titanium coating is formed in three stages. After irradiation of titanium substrates coated with Si-HA, the crystals can keep growing and the surface can keep regenerating.

Keywords: Calcium phosphates; Apatite nanocomposite synthesis; Crystallization; Modifying; Bioavailability; Biological fluids titanium coating.

1. Introduction

Development of calcium phosphate biomaterials is one of the important areas of modern material science which is at the interface of chemistry, medicine and physics. Synthetic hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HA) is a widespread material used in medicine for treatment of damaged bone tissue due to its chemical and phase similarity to the inorganic component of the bone tissue [1–9].

The bioactivity of materials is considered to be determined by their chemical composition, morphology of the crystals, and surface properties [9–14]. The main techniques to modify these characteristics are chemical modification of calcium orthophosphates and variation of the synthesis conditions. Since silicon is vital in the physiological processes of growth and remodeling of the bone and cartilaginous tissue, research in the properties of silicon-substituted hydroxyapatite (Si-HA) synthesized under conditions close to physiological ones is a promising and relevant physical and chemical problem.

The literature review shows that synthesis of thermally stable silicon-containing hydroxyapatite-based ceramic materials is currently of great interest since silanol (Si-OH) groups on the material surface contribute to splicing of the implant with the bone [10–14], which indicates their high practical significance to make progress in orthopedics and implantology.

It can be argued that silicon has a beneficial effect and improves the characteristics of non-substituted hydroxyapatite, and after annealing, the properties of Si-HA samples are similar to those of



a normal human bone. This fact indicates that silicon-substituted hydroxyapatite samples may be used in medicine as a ceramic coating on titanium implants.

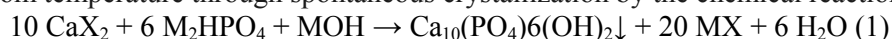
Most bioactive materials, when applying them to bioinert (titanium) substrate, lose their characteristics, therefore, it is important to produce materials which exhibit high stability, and retain their bioactive properties.

In biomimetic synthesis, it is essential to find optimal conditions to produce powders of a highly dispersed phase, with high resorption and biocompatibility with the human body. When depositing these calcium phosphates on a titanium substrate, it is necessary to find a stepwise mechanism of Si-HA deposition to use these samples in practice, to observe in vitro the processes occurring, possible destruction or degradation of the prepared ceramics. Therefore, research in this area is considered to be of current importance in modern implantology [15–17].

Thus, the aim of the research is to study the possibility of producing coatings on the titanium substrate by applying the modified silicate ions of calcium phosphates prepared via deposition from a model solution of extracellular fluid (SBF).

2. Experimental techniques

Synthesis of the substituted calcium phosphate crystals is carried out by deposition from aqueous solution at room temperature through spontaneous crystallization by the chemical reaction:



The main compounds for silicate groups were Na_2SiO_3 and tetraethoxysilane (TEX) as the most frequently used compounds. The weight content of silicon in the starting solution was 0.5, 2.5 and 5.0 %. The chosen ratio $\text{Ca/P} = 1.67$ corresponded to that for preparing stoichiometric hydroxyapatite [10]. The PH value was 7.40, pH characteristic of the extracellular fluid, and it remained constant.

The duration of the synthesis was 48 hours. Upon completion of the solid-phase crystallization, pH and concentration of Ca^{2+} ions were measured in the supernatant fluid by potentiometric method. The colorimeter CPC-2 was used to measure the residual concentration of phosphate-ions [RD 52.24.382-2006], silicate-ions (RD 52.24.433-2005) in the solution. The solid phase was filtered, dried and analyzed with FT-IR spectroscopy and X-ray diffraction analysis (XRD). IR spectra were recorded with FT-801 spectrometer (samples made in the form of pellets with KBr). XRD was performed with the Bruker D8 Advance X-ray diffractometer (Germany) under monochromatic $\text{Cu-K}\alpha$ radiation.

Statistical data processing was carried with StatSoft Statistica 6.0.

To deposit hydroxyapatite on the surface of VT1-0 titanium the titanium plates with a size of 15 mm * 15 mm * 1.2 mm were pretreated: polished; etched (we chose the pickling mixture HNO_3 : HF 1: 1 to enlarge the surface of the titanium substrates); exposed to powerful ionization beam (the setup "Temp" was used for irradiation); subjected to laser ablation; perforated (etched, not subjected to mechanical impact and chemical aggression, subjected to laser ablation), and plates which were not subjected to mechanical impact and chemical aggression.

After that, the plates were immersed into the prototype of the model solution of human interstitial fluid [18]. The system was kept for 3, 6 and 12 days (SBF base solution being changed and being not changed). After that, the plates were removed from the test solution, dried at room temperature and analyzed using optical microscopy.

3. Result and discussion

The X-ray analysis showed that all the samples synthesized in the medium of the model solution of extracellular fluid under varying concentration of silicate ions are single-phase and represent hydroxyapatite. In the diffraction pattern, the HA reflexes are found at $25.8^\circ(002)$, $31.7^\circ(211)$, $32.2^\circ(112)$, and $32.9^\circ(300)$ (Figure 1). It should be noted that the diffraction patterns corresponding to the solid phases with different sources materials for Na_2SiO_3 /TEL silicate groups are found to be similar. Thus, the nature of the reagent containing SiO_4^{4-} ions does not affect the hydroxyapatite structure.

The size of the prepared unmodified HA crystallite was 6.3 nm, and the size of Si-HA was $6.0 \div 7.1$ nm, which indicates the formation of nanocrystalline compounds. The parameters of the crystal lattice of the formed solid phase grew larger as compared to the unmodified hydroxyapatite. This confirms the possible substitution of the orthophosphate-ion by the silicate-ion of different size (distance Si-O = 1.66 Å, P-O = 1.55 Å [18]).

In the IR spectra of the samples formed in the presence of the silicate ions, the absorption bands characteristic of hydroxyapatite can be observed (Figure 2). The HA structure is defined by the following bands: the bands at 1040–1080 (ν_3), 960, 840 (ν_2), 602, 574 (ν_4) and 473 (ν_2) cm^{-1} corresponding to the vibrations of the phosphate groups, the broad band at 3440–3570 cm^{-1} which corresponds to deformation vibrations of OH⁻-groups and valence vibrations of the adsorbed water. High intensity of this peak in the modified HA is related to the fact that SiO_4^{4-} ions have high affinity for water molecules which results in hydration. Since HA is synthesized in air, during its formation carbon dioxide is adsorbed from atmospheric air, and carbonate ions are localized in the lattice in the position of the phosphate ion, and in the IR spectra, the bands absorbing deformation vibrations of C-O bonds of the CO_3^{2-} ion at 875 cm^{-1} and valence vibrations at 1422–1457 cm^{-1} correspond to these ions.

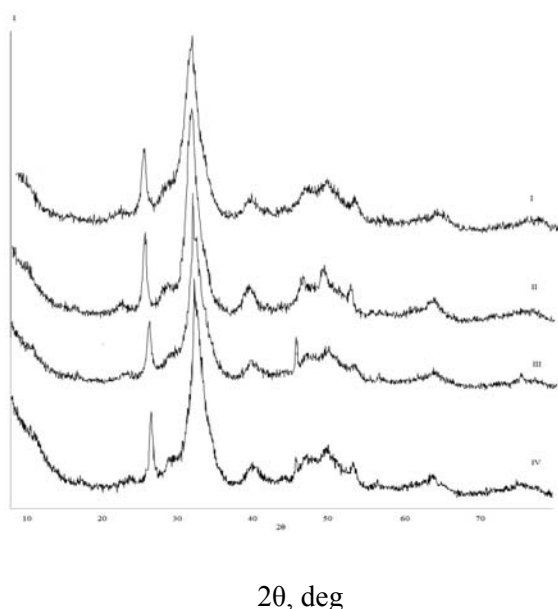


Figure 1. The diffraction patterns for hydroxyapatite samples modified by Na_2SiO_3 : *I* is C Si init. 0.5%; *II* is C Si init. 2.5%; TEX: *III* is C init. 0.5%; *IV* is C Si Si init. 2.5%.

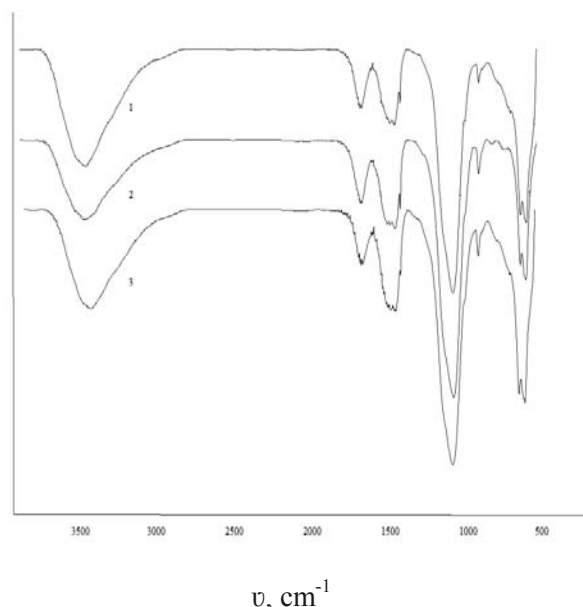


Figure 2. IR spectra for hydroxyapatite samples modified by: *1* is Na_2SiO_3 C Si init. 0.5%; *2* and *3* are TEX C Si init. 0.5 and 2.5%.

It has been observed that IR spectra contain a low intensity band of absorption of the silicate group bond vibrations at 511 cm^{-1} due to the deformation vibrations of SiO bonds. The absorption band of the Si–O bond vibration at 945 cm^{-1} is overlapped with the absorption band which corresponds to P–O bond vibrations at 960 cm^{-1} . Occurrence of these signals in the spectrum indicates the substitution of PO_4^{3-} by SiO_4^{4-} in the HA structure. This leads to distortion of the PO_4^{3-} tetrahedra, and as a result, the parameters of the cell change. Thus, the data obtained by FT-IR spectroscopy are in agreement with that obtained by XRD.

An essential problem in the production of calcium phosphate coatings is their long-time resistance to resorption which depends on the adhesive strength of the phase composition and the degree of the structure crystallinity. Hydroxyapatite synthesized from the SBF (Simulated Body Fluid) solution was used as adhesive material.

The values obtained in measuring the limiting wetting angle and the surface tension of the prepared suspensions on titanium substrates were used in the Young-Dupre equation [19] to calculate the adhesion energy of the calcium phosphate suspension applied to the solid surface of the titanium samples (Table 1).

Table 1. Adhesive characteristics of the titanium-based calcium phosphate suspension

| Additive Si | Composition | $\sigma_{01}, \text{MJ/m}^2$ | $\cos\Theta$ | $W_a, \text{MJ/m}^2$ | $W_k, \text{MJ/m}^2$ | W_a/W_k |
|---------------------------|-------------|------------------------------|--------------|----------------------|----------------------|-----------|
| Na_2SiO_3 | 1.00 % | 85.12 | 0.73 | 147.26 | 170.24 | 0.87 |
| | 2.50 % | 76.16 | 0.26 | 115.76 | 152.32 | 0.76 |
| | 5.00% | 76.82 | 0.44 | 110.62 | 153.34 | 0.72 |
| TEX | 1.00 % | 66.04 | -1 | 0 | 132.08 | 0 |
| | 2.50 % | 64.57 | 0.26 | 81.36 | 129.14 | 0.63 |
| | 5.00% | 66.67 | -0.76 | 16.00 | 133.34 | 0.12 |

It was found that as the concentration of silicate ions increases in the samples synthesized with inorganic ion carrier SiO_4^{4-} , the surface tension and limiting wetting angle decrease. This may be caused by partial dissolution of the resulting calcium phosphate and formation of inorganic surface-inactive substances in the solution. For samples with TEX as a SiO_4^{4-} ion, change in the concentration of silicon in the suspension leads to ambiguous results which require further research. The adhesion-cohesion energy ratio is an important characteristic of the produced coatings (Table 1). The calculated data allow the conclusion that the suspension containing 1.00 wt% of the silicate ion in the form of SiO_4^{4-} exhibits good adhesive interaction between silicon-containing hydroxyapatite and titanium samples.

In the study of the surface and morphological characteristics of the phosphate coatings modified by silicon, it was found that more complete deposition of Si-HA on the titanium substrate surface occurs in the etched samples (Figure 3). This technique of surface treatment provides uniform, dense, and finely-dispersed coating, and HA crystals are found to grow in the form of dendrites. The crystal growth becomes more structured. Increase in the time of keeping the titanium sample in the model solution results in discontinuous columnar crystal growth which indicates the start of Si-HA surface structuring. At this stage, the height of the formed aggregates is found to be different (Figure 3b). Further increase in the time of keeping the sample in the model solution for 6 days causes formation of non-uniform coating. The crystals are found to grow in the form of dendrites. The start of the crystal growth in the form of cylindrical columns can be observed, that characterizes the beginning of Si-HA structuring on the substrate surface (Figure 3 c). For longer period of keeping the sample in the solution without changing the model solution, the crystals are found to accumulate in the form of aggregates, and the crystal growth goes beyond the substrate (Figure 3 d).

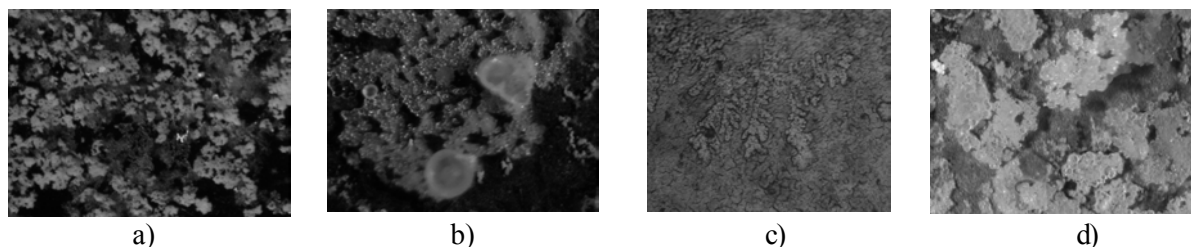


Figure 3. Deposition of Si-HA on titanium substrates (etched surface). Duration a) 3 days; b) 3+3 days, the model solution being changed; c) 6 days, the model solution being not changed; d) 3+3+6 days, the model solution being changed.

Different techniques are used to produce biocoatings on titanium implants, for example, plasma, and magnetron or laser deposition of the bioactive material. High temperature and high-energy action, which are typical of these techniques, cause partial degradation of the bioactive material and decrease its efficiency. Development of new methods for microcrystalline hydroxyapatite synthesis, low-cost and technological techniques to form bioactive titanium coatings from composites is considered to be of current relevancy and in great demand.

Coatings made on titanium substrates subjected to laser ablation (Figure 4a) are a non-uniformly distribution of the deposited phase. The deposition occurs in the craters formed under the exposure and in the near-crater areas. The crystals grow upwards, and columnar structures characteristic of the Si-HA phases are formed. Increase in the number of pulses results in a more uniform coating over the entire surface (Figure 4b). The deposition is dense and the thickness of the coating is significantly different. In some areas, thick coating is found to be with typical cracking. The deposition occurs in craters (more dense deposition), and in the near-crater areas. Further increase in the number of pulses causes deposition in the near-crater areas. Virtually no crystal growth can be observed in craters which may be due to hindered diffusion of the electrolyte components.

Another technique to treat the titanium substrate surface is to expose to a powerful ion beam (PIB). After this treatment, the surface coating is uniform, the deposition is dense and finely-dispersed (Figure 4a).

At the next stage, after synthesis of the Si-HA layer on the titanium substrates, the samples were exposed to PIB with $j = 0 \text{ A/cm}^2$ (Figure 4c-d). As a result, coating was observed to be uniform, dense, with melted edges. Dendritic crystals were found to grow on the substrates, and this enhanced further growth and renewal of the surface under physiological conditions.

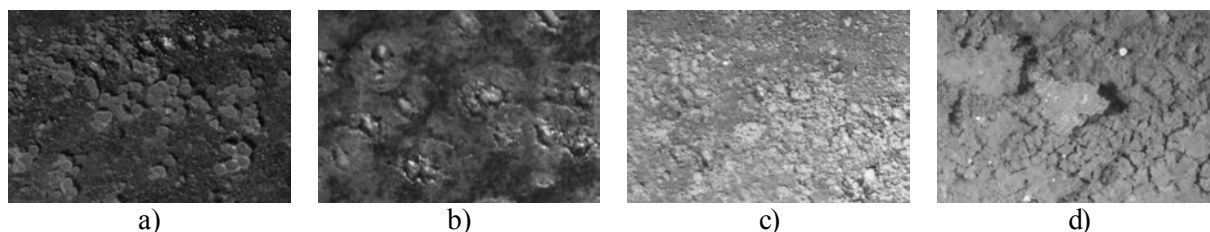


Figure 4. Deposition of Si-HA on titanium substrates after subjecting to laser ablation, deposition time is 3 days: a) the number of pulses is 1; b) the number of pulses is 3; c) the number of pulses is 5; d) the number of pulses is 3, the deposition time is 3 + 6 days, the model solution being changed.

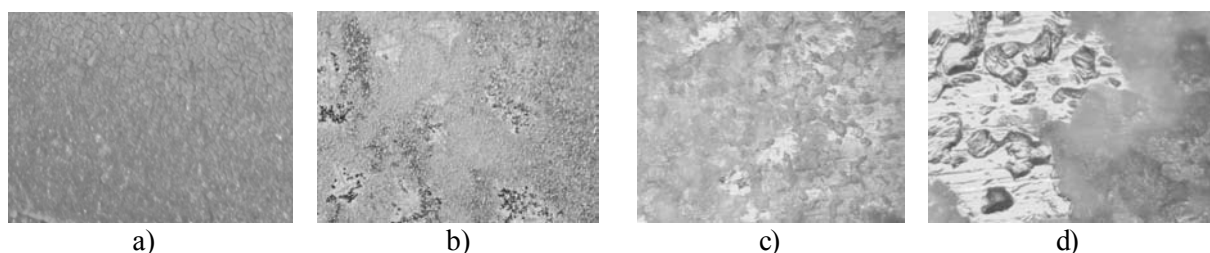


Figure 5. The morphology of the hydroxyapatite crystal surface grown on the titanium surface 1-0: a) surface treatment by exposure to PIB before deposition; b–d) after irradiation by PIB with $j = 50 \text{ A/cm}^2$.

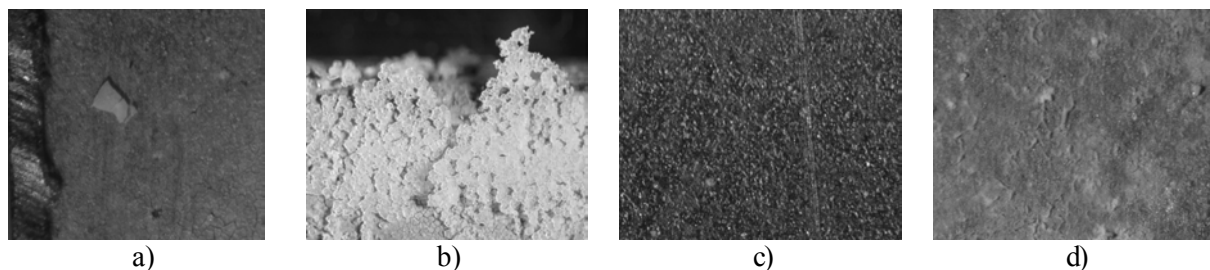
When measuring the coated area (Table 2), it was found that the highest percentage of deposition onto the substrate occurs within the first three days. This is attributed to the fact that three days are the basic time for Si-HA dissolution. After that, Si-HA dissolution stops. To attain better characteristics for the coated area the suspension is to be changed. As a result, the coated area of the substrate is not only larger, but the coating is more uniform both in size and in homogeneity of the crystals.

Table 2. The area of the coated surface depending on the technique of titanium substrate treating

| Treatment | $S_{\text{coating}}, \%$ | | | | |
|-------------------------------|--------------------------|--------|----------|----------|------------|
| | 3 days | 6 days | 3+3 days | 3+6 days | 3+3+6 days |
| Etching | 72 | 75 | 79 | - | 85 |
| Not treated | 60 | 67 | 70 | - | 78 |
| Perforation etching | 30 | - | - | 73 | - |
| Perforation without treatment | 25 | - | - | 79 | - |
| PIB | - | 60 | - | - | - |
| Laser n=1 | 20 | - | - | 30 | - |
| Laser n=2 | 23 | - | - | 35 | - |
| Laser n=3 | 25 | - | - | 40 | - |
| Laser n=5 | 27 | - | - | 44 | - |
| Laser perforation laser n=1 | 19 | - | - | 26 | - |

The analysis of the data from Table 2 shows satisfactory coating of the Si-HA surface for non-treated titanium samples. This confirms that titanium substrates are highly biocompatible, non-toxic, resistant to corrosion, and their characteristics are similar to the mechanical properties of the bone tissue [8]. The coating appears to be uniform, dense, with characteristic cracking, which indicates sufficient thickness of the coating; large and small Si-HA aggregates occur (Figure 6 a–d). As the time of keeping the sample in the model solution increases, discontinuous columnar growth of crystals can be observed and this indicates the start of Si-HA surface structuring.

No significant difference is found in the height of the newly grown crystals (Figure 6 b). The crystal growth does not go beyond the substrate surface, and the Si-HA lower layer takes the form of the titanium crystal lattice. In long-time keeping the titanium substrates in the SBF model, the coating appears to be uniform over the entire surface, dense, no Si-HA agglomerates can be detected (Figure 6 c, d).

**Figure 6.** Deposition of Si-HA on titanium substrates without surface treatment: a) 3; b) 3+3 days, the model solution being changed; c) 6; d) 3+3+6 days, the model solution being changed.

In addition to the above techniques of the substrate surface treatment, we used perforation of the titanium samples. The Si-HA coating on these substrates is not uniform; virtually no deposition occurs (Figure 7a). Repeated treatment of the surface (etching, laser ablation) results in partial depositing of Si-HA crystals in laser craters and on creater cuts (Figure 7b). As the time of keeping the titanium samples in the model solution increases, with the solution being changed, glassy aggregates are formed in the process of perforation hole closing with the following growing of crystals upwards in the shape of cylinders. In the near-perforation areas, the crystals grow in the form of dendrites (Figure 7 a–d).

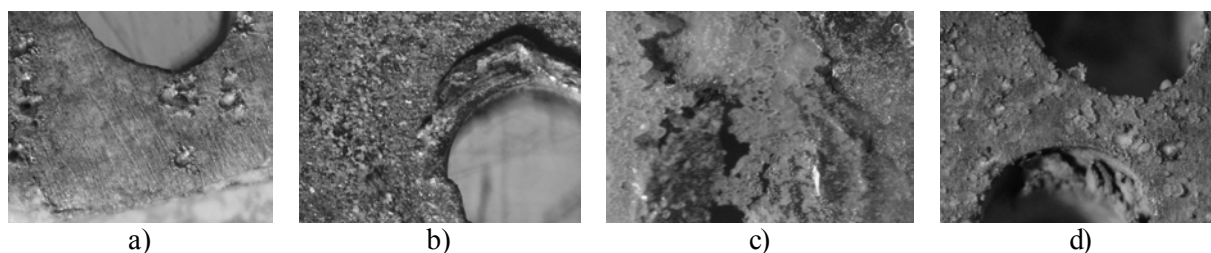


Figure 7. Deposition of Si-HA on perforated titanium substrates a) laser-treated $n = 1, 3$ days; b) etched, 3 days; c) unetched 3+6 days; d) laser-treated $n = 1$ 3+6 days.

4. Conclusions

Si-HA powders have been synthesized from SBF solution with the silicon content of 0.50; 1.00; 1.50; 2.50; 5.00 wt.%. It was found that all the samples synthesized in the model solution of extracellular fluid under varying concentration of silicate ions are single-phase and represents hydroxyapatite. The nature of the reagent containing SiO_4^{4-} ions does not affect the hydroxyapatite structure.

In the study of the surface and morphological characteristics of the produced phosphate coatings modified with silicon ions, it was found:

As the degree of the substitution of calcium phosphate by SiO_4^{4-} ions increases (inorganic silicate ions promoter was used in the synthesis) the surface wettability, limiting wetting angle and cohesion energy are found to deteriorate. The samples with organic silicon ion dopants are mainly characterized by nonwettability of the surface and low cohesive energy.

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