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Comparison of Ca/P mineralization on the surfaces of poly (ε-caprolactone) composites filled with silane-modified nano-apatite

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Abstract This study aims to comparatively investigate the Ca/P mineralization on the surfaces of poly (ε-caprolactone) (PCL) composites with apatite nano-fillers, which were modified with silane coupling agents. Three kinds of silane coupling agents like 3-Methylacryoxypropyltrimethoxy silane (KH560), γ-Methacryloxypropyltrimethoxy silane (KH570), and N-(β-aminoethyl)-γ-aminopropyltrimethoxy silane (KH792) were firstly employed to modify the surfaces of nano-apatite particles, and then silane-modified nano-apatite/PCL composites were prepared by combining solvent dispersion and melting co-blending with hot-pressing methods. The Ca/P mineralization of the modified PCL-Matrix composites was evaluated by soaking in 2-time simulated body fluid (2SBF) at 36.5 °C and pH 7.40 after 21 days. These results showed that the Ca/P mineralization on the surface of the silane-modified composite was same as not modified composite. Apatite obtained on the surface of the modified composite film was of lower crystallinity, 1.62 Ca/P ratio and carbonate ceramic, similar to inorganic composition of bone in biological body, and not notably different from one of not modified PCL composite. This discussion revealed that as-fabricated silane-modified composite could achieve Ca/P mineralization and exhibited the ability of obtaining like-bone apatite on own surface like other bioactive materials.

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Introduction

Emphasis on the development of biomaterial has been converted from monoliths to the bioactive composite for recent decade years [1–3]. To endue poly (ε-caprolactone) (PCL) biodegradable polymer with bioactive characteristics, nano-apatite (n-HA) particles were filled in this polymer and an n-HA/PCL composite biomaterial was developed by various techniques [4, 5]. Nowadays, improving mechanical properties of this composite is still one of research focus, through progress in enhancing mechanical properties of the n-HA/PCL composites has been achieved by many researches [6, 7]. Agglomeration of the n-HA particles in PCL-Matrix materials is still one of current main challenges to lessen mechanical properties of these nano-composites. Accordingly, it is very necessary to modify the surfaces of n-HA particles as the fillers, weak agglomeration and improve the interface structure between the filler and matrix of the composite, so that these PCL composites meet mechanical requirements as the repair materials. We employed three kinds of the silane couple agents to fabricate the silane-modified n-HA/PCL composites, and our experimental results showed that these silane-modified composites displayed higher mechanical properties than reported by other researchers [4, 8]. However, silane modification changed the surface microstructure of n-HA particle as a bioactive phase of this composite, and this suggested it was possible to change or affect the bioactive property of this material. It is known that bioactivity of a biomaterial is an important property and this property is bound to effect quality and life time of a repair material in biological environment. What is more, up to day, we have not found any report about bioactivity property of the silane-modified n-HA/PCL composite. Therefore, we do not know whether the silane-modified n-HA/PCL composite can induce Ca/P mineralization as not modified composite can. Further, if can, whether Ca/P crystallites deposited on the surfaces of these modified composites are like-bone apatite, and same as not modified PCL composite does.

Therefore, in this study, the Ca/P mineralization on the surface of PCL-Matrix composite with n-HA fillers modified by three kinds of the silane coupling agents is contrastively investigated with not modified PCL composite and in vitro bioactivity of the modified composites is evaluated.

Materials and methods

Surface modification of HA nano-particles

Ethanol aqueous solution was prepared by mixing 90 mL analytical ethanol with 10 mL distilled water, and then averagely divided into three parts. Three kinds of the silane coupling agents including 3-Methylacryloxypropyltrimethoxy silane (KH560), γ-Methacryloxypropyltrimethoxy silane (KH570), and N-(β-amino ethyl)-γ-aminopropyltrimethoxy silane (KH792) were added into three parts of ethanol aqueous solution and intensively stirred for 1 h, respectively. Following this, 200 nm HA particles (ST20G, Nanjing Haitai Nano-materials Co. Ltd., China) were charged to the mixed ethanol solutions with silane coupling agents, dispersed in ultrasonic apparatus (KH300B type, China) for 15 min and blended by intensive stirring. Finally, three kinds of the silane-modified n-HA ethanol solutions were dried at 80 °C, milled and then continued to be dried at 110 °C, respectively.

Preparation of the n-HA/PCL composites

First, PCL (Mw: 50,000, China) powders were added to an analytical N,N-Dimethylacetamide (DMAc) solvent, mechanically mixed for 2 h, then heated by the hot water at 60 °C. Simultaneously, three kinds of the silane-modified

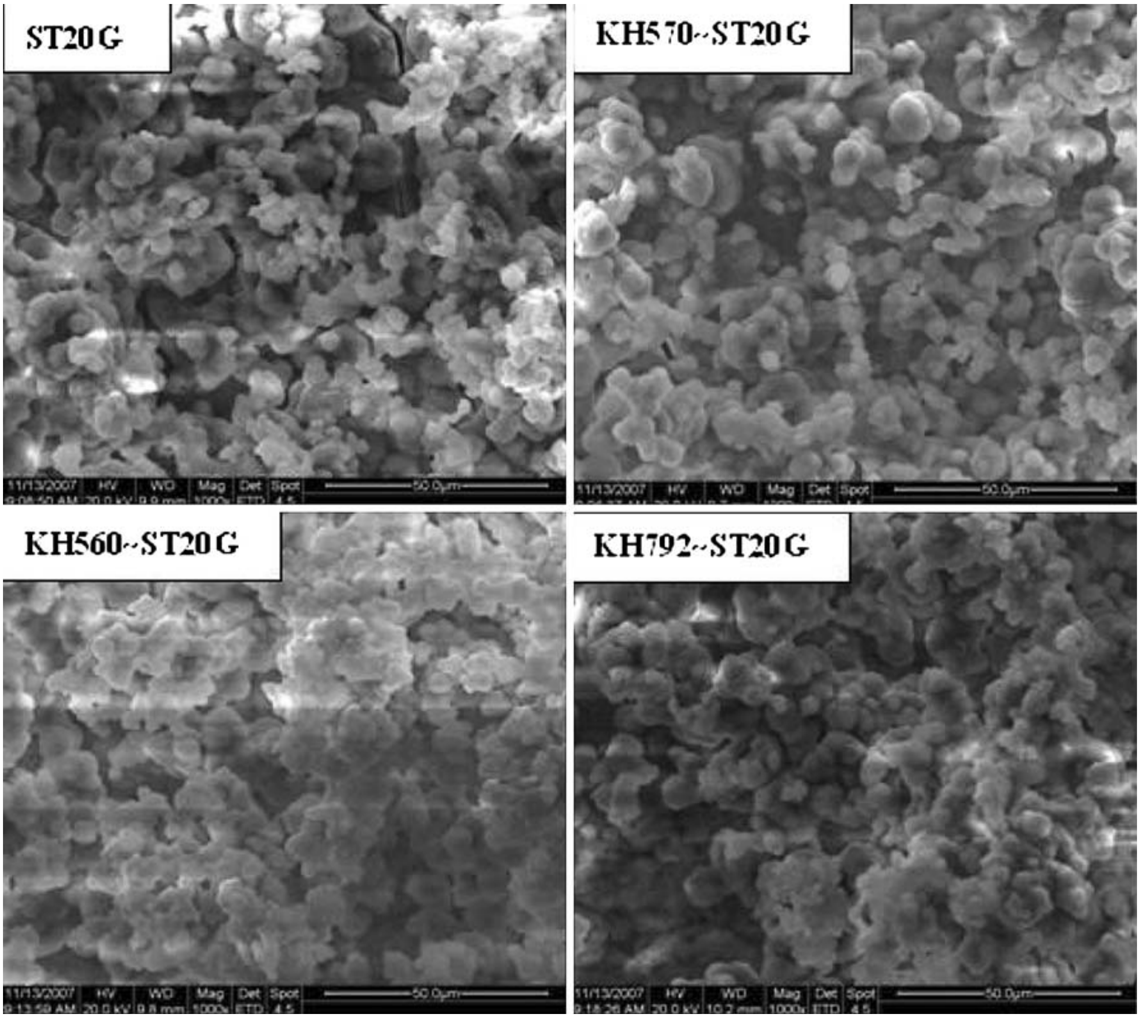

Fig. 1 SEM photograph of crystals deposited on the surfaces of not modified and the modified ST20G composites immersed in 2SBF at 36.5 °C and pH 7.40 after 21 days

n-HA particles obtained above were mixed with another three same DMAc solvents and then drastically stirred for 24 h, respectively. Second, PCL powders and the silane-modified n-HA synchronously dispersed by the DMAc solvents were blended together and continued to be mechanically dispersed using a magnetic stirrer for another 24 h, DMAc solvents were tardily vaporized by intensive stirring at 50 °C from the mixed solutions including the silane-modified n-HA, PCL, and DMAc. The resulting hybrids were repeatedly washed by ethanol to further eliminate the DMAc solvent. After this, the mixed materials were further dried by vacuum at 60 °C for 24 h. Third, three kinds of these hybrids were sent into torque rheometer (Plasti-corder type, German), mixed at 120 °C at the running velocity of 30 r/min for 20 min, taken away from the rheometer, washed by ethanol time and again and then dried by vacuum at 60 °C. Finally, three kinds of the co-blended composites such as KH560-HA/PCL, KH570-HA/PCL and KH792-HA/PCL were crushed into smaller pieces by disintegrator (Fritsh, German), put into mould and then compacted by hot-pressing machine (Carver, USA) under 6 MPa pressure at 105 °C for 15 min. Finally, three kinds of the composite films were obtained.

Likewise, not modified composite was prepared to form a compacted solid film as a control group.

Soaking in simulated body fluid

Four groups of PCL-Matrix composite samples were placed in beakers containing 2-time simulated body fluid (2SBF) buffered at pH 7.40 and 36.5 °C [9, 10]. The beakers charged by samples and 2SBF were synchronously maintained at 36.5 °C in the cultivated bin for 21 days, respectively, to ensure these composites to display Ca/P mineralization. The soaking fluids were refreshed at intervals of 2 days. After the soaking periods, the samples were taken out from beakers, and gently rinsed twice with distilled water to remove 2SBF, followed by drying in vacuum overnight at 60 °C.

Characterization

The phases of Ca/P mineralization on the surface of the film of n-HA/PCL composite immersed in 2SBF were characterized by X-ray Diffraction (XRD, X'Pert Pro MPD, USA). Morphologies of Ca/P mineralization deposited were observed using Scanning Electron Microscopy (SEM, S-450, Japan). Compositions of the phases of Ca/P mineralization were evaluated by Fourier Transformation Infrared Spectra (FT-IR). Molar ratio of Ca and P elements was determined by Energy Disperse Spectroscopy (EDX, S-450, Japan).

Results and discussion

Surface morphologies of films of the modified and not modified ST20G composites immersed in 2-time SBF at 36.5 °C and pH 7.4 after 21 days were observed as showed in Fig. 1. It is evident that small spherical crystals appear on the surfaces of all materials, whether the modified PCL composites or not modified materials, and the whole contours of all specimens cannot be clearly seen. This suggests that the silane-modified PCL composites have ability to deposit spherical crystals as not modified HA/PCL material has. Compared with crystals deposited on the surface of not modified ST20G composite film, those on the surfaces of the silane-modified composites are not markedly different in shape and size. Besides, distinct difference between crystals deposited on the surfaces of three kinds of the silane-modified ST20G composites cannot also be found in shape and size.

From Fig. 2, no obvious changes of the diffraction peaks of crystals deposited were observed for not modified and the modified ST20G composite films soaked in 2SBF after 21 days (Fig 2(1), (2), (3), (4)), indicating that spherical crystals of the deposited layers on the surfaces of the materials display the same phases with the almost same crystallinities. Compared with the diffraction peaks of n-HA sintered at 1200 °C (Fig. 2(5)), broader peaks of crystals deposited on the surfaces of not modified and modified ST20G composites, between 31° and 33°, mainly the (112), (211)and (300) reflections, indicate that the spherical crystals of the deposited layers formed in 2SBF

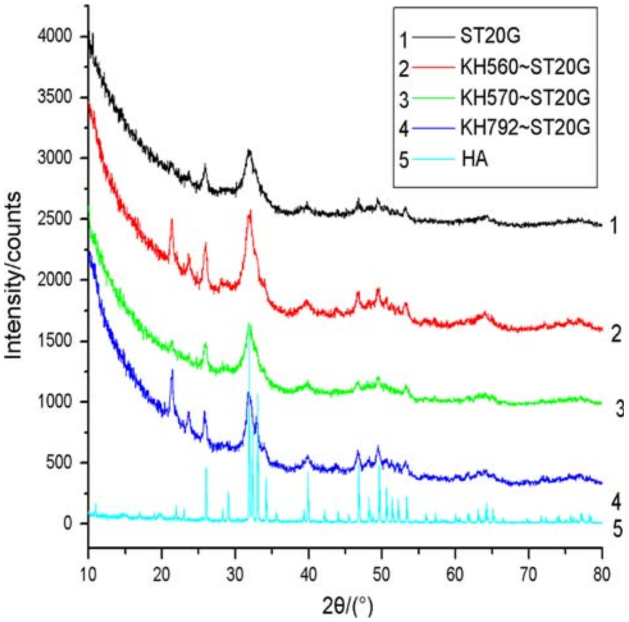

Fig. 2 XRD curves of crystals deposited on the surfaces of not modified ST20G, the modified ST20G composites immersed in 2SBF at 36.5 °C, pH 7.40 after 21 days and and ST20G sintered at 1200 °C

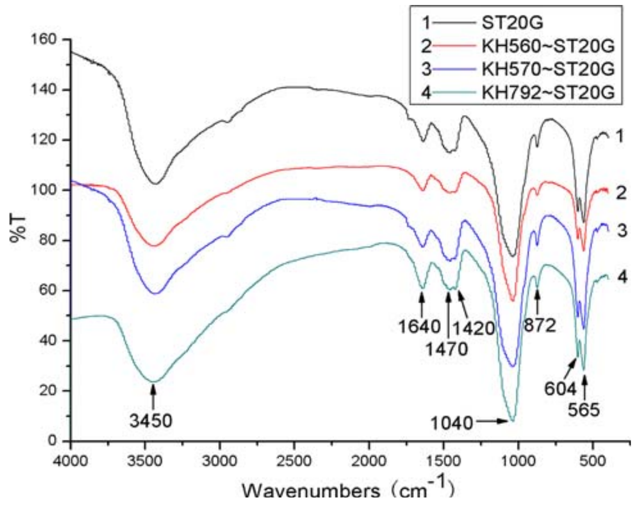

Fig. 3 FT-IR spectra of crystals deposited on the surfaces of not modified and silane-modified ST20G composites immersed in 2SBF at 36.5 °C, pH 7.40 after 21 days

are of lower crystallinity [11]. Besides, from Fig. 2, we can find that two characteristic peaks at 26° and 31.8° (2θ) illuminating that main phase of the crystals deposited on the surfaces of these composites is apatite with main composition hydroxyapatite.

Results of Fig. 3 further prove that the crystals deposited on the surface of composite films are apatite with main composition of hydroxyapatite. It was found that –OH vibration absorptive peak in 3550–3200 cm^{-1} presented in the curve of Fig. 3, and $-\mathrm{CO}_3^{2-}$ absorptive peaks in 1420 and 1470 cm^{-1} also showed up, suggesting that the deposited apatite contained CO_3^{2-} ion, and it was marker of CO_3^{2-} ion entering in crystal lattice of apatite [12].

Figure 4 gives spectra of energy dispersive X-ray detector (EDX) of crystals deposited on the surfaces of not modified and modified ST20G composite films, which were immersed in SBF at 36.5 °C, pH 7.4 after 21 days. After four groups of composite films were soaked for

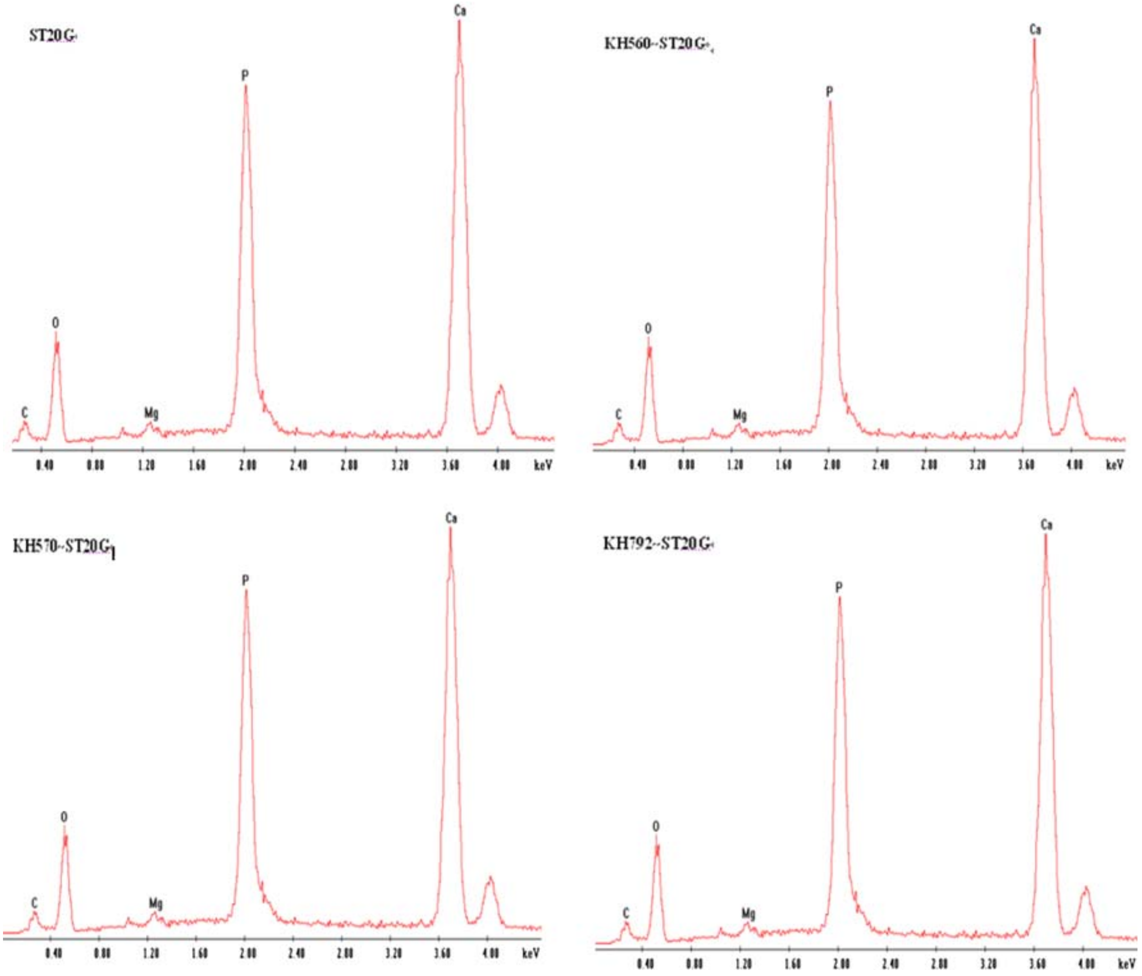

Fig. 4 EDX spectra of crystal deposited on the surfaces of not modified and the modified ST20G composites immersed in 2SBF at 36.5 °C, pH 7.40 after 21 days

21 days, apatite was apparent to appear. From Fig. 4, it is clear that molar ratio of Ca and P elements of formed apatite is 1.62, which belongs to calcium-deficient or non-stoichiometric apatite and close to Ca/P ratio of apatite in biological bone, which suggests that apatite mineralized on surfaces of not modified and modified ST20G composite films are similar to animal bone in main inorganic composition. This hints that crystals mineralized on the surfaces of all composites are bone-like apatite.

Conclusion

The Ca/P mineralization on the surface of the PCL-Matrix composite with HA nano-fillers modified with silane coupling agent was compared with one of not modified HA/PCL composite. Apatite obtained on the surfaces of the modified composite is the same as one of not modified composite in phase composition, shape and size, and crystallinity. The Ca/P phases mineralized on the surfaces of all the composites are of lower crystallinity, 1.62 Ca/P ratios and carbonate apatite, similar to inorganic of bone in biological body. The surfaces of three kinds of as-fabricated silane-modifying composites can achieve Ca/P mineralization and exhibit ability to induce growth of like-bone apatite as other bioactive materials.

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