

Preparation and mechanical property of poly(ϵ -caprolactone)–matrix composites containing nano-apatite fillers modified by silane coupling agents

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Abstract This study aims to improve the tensile strength and elastic modulus of nano-apatite/poly(ϵ -caprolactone) composites by silane-modification of the nano-apatite fillers. Three silane coupling agents were used to modify the surfaces of nano-apatite particles and composites of silanized apatite and PCL were prepared by a technique incorporating solvent dispersion, melting-blend and hot-pressing. The results showed that the silane coupling agents successfully modified the surfaces of nano-apatite fillers, and the crystallization temperatures of the silanized apatite/PCL composites were the higher than that of the non-silanized control material, although the melting temperature of the composites remained almost unaffected by silanization. The ultimate tensile strength and elastic modulus of the silanized composites reached 22.60 MPa and 1.76 GPa, as a result of the improved interfacial bonding and uniform dispersion of nano-apatite fillers. This study shows that the processing technique and silanization of nano-apatite particles can effectively improve the tensile strength and elastic modulus of nano-apatite/PCL composites.

1 Introduction

Nano-apatite is used in clinic due to its similarity to bone mineral in composition, structure and biocompatibility with human tissues [1, 2]. However, its application is limited by disadvantages such as brittleness, low strength, fatigue resistance [3] and slow degradation [4]. It is therefore necessary to develop techniques to toughen and strengthen nano-apatite to further its clinical application. Composites of nano-apatite and biodegradable polymers such as poly ϵ -caprolactone (PCL), poly-lactide, poly-glycolic acid and so on have gained attention because of their osteo-conductivity, osteo-inductivity and biodegradability [5–8]. Recent studies showed that these composites, particularly nano-apatite/PCL, have excellent biological and mechanical properties [9, 10]. Causa et al. prepared apatite/PCL composite by phase inversion and casting; they reported that the elastic modulus of this composite increased from 8.25 MPa to 27.90 MPa, and the ultimate tensile strength reached 2.19 MPa [11]. Chen et al. reinforced PCL of different molecular weight distribution with apatite of different particle sizes; the tensile strength and elastic modulus of this apatite/PCL composite was 17.2 MPa and 1.56 GPa, respectively [12]. These results indicated that the mechanical properties of HA/PCL composites approached those of cortical bone, thus making these composites potential bone substitutes in load-bearing application.

Although many studies have reported improved mechanical properties of nano-apatite/PCL composites [13, 14], agglomeration of nano-apatite fillers in the PCL-matrix remain a major challenge. This agglomeration adversely affects the mechanical properties of the nano-composite biomaterials, because it changes the actual size of the filler phase in PCL from nanometer to micrometer. Therefore, techniques to de-agglomerate or weaken the

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agglomeration of nano-apatite particles, such as melting co-blend and solvent dispersion, are important for the development of nano-apatite/PCL composite with desirable mechanical properties. In addition, surface modification technique can decrease the surface bonding energy of nano-apatite particles, weaken their agglomeration and improve the interfacial strength between these fillers and the matrix. Among various surface modification techniques, many studies focused on the use of silane coupling agents in the surface modification of nano-apatite particles [15].

In this study, three silane coupling agents including glycidoxypopyl trimethoxy silane (KH560), γ -methacryloxypropyltrimethoxy silane (KH570) and *N*-(β -aminoethyl)- γ -aminopropyltrimethoxy silane (KH792) were employed to modify the surface of nano-apatite particles, and then composite films of silane-modified nano-apatite/PCL were prepared by incorporating solvent dispersion and melting-blend with hot-pressing method. The ultimate tensile strength and elastic modulus of these nano-composite films were carefully studied to evaluate their mechanical properties.

2 Materials and methods

2.1 Surface modification of nano-apatite particles

Ninety milliliters of ethanol was mixed with 10 ml of distilled water to prepare an ethanol aqueous solution, which was then equally divided into three parts. Each of three silane coupling agents (KH560, KH570, and KH792) with the weight of 1.25 g were added to one part of this ethanol

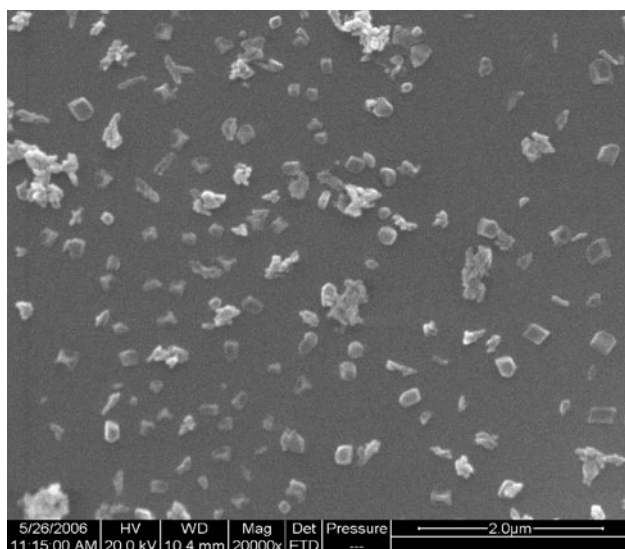


Fig. 1 A SEM micrograph showing the morphology and size of nano-apatite particles

aqueous solution and intensively stirred for 1 h. Apatite (Nanjing Haitai Nanomaterials Co. Ltd., China) particles (mean size: 200 nm, Fig. 1) with the weight of 23.75 g were added to these silane-containing ethanol solutions, dispersed by sonication (KH300B type, China) for 15 min, and blended by intensively stirring. These slurries were dried at 80°C, milled and dried again at 110°C.

2.2 Preparation of the silanized nano-apatite/PCL composites

PCL (Mw: 50,000, Japan) was added to *N,N*-Dimethylacetamide (DMAc), stirred for 2 h, and then placed in a 60°C water bath. Three silanized nano-apatite particles were mixed with three parts of DMAc in same volume and intensively stirred for 24 h. The PCL solution and the silanized nano-apatite suspension were blended and further dispersed by stirring for 24 h. DMAc was slowly evaporated by intensively stirring at 50°C. Then the remaining materials were repeatedly washed with ethanol to remove any residual DMAc and vacuum dried at 60°C for 24 h. The dried materials were fed into a torque rheometer (Plasti-corder type, German), mixed at 120°C and a running velocity of 30 rpm for 20 min, removed, rinsed with ethanol and then vacuum dried at 60°C. The resulting co-blended composites of KH560, KH570 and KH792-apatite/PCL were crushed into small pieces by a disintegrator (Fritsh, German), transferred into a mold, and pressed (6 MPa, 105°C, 15 min, Carver hot presser, USA) into thin films. Composite of non-silanized apatite/PCL with the filler weight of 20% was prepared by the same procedure and used as the control group.

2.3 Testing of mechanical properties

Dumbbell-shaped tensile specimens with an effective dimension of $110 \times 5 \times 1 \text{ mm}^3$ were prepared from each type of composite thin films, including the control group. Specimens were tested with an instron 5567 system at a cross-head speed of 5 mm/min. At least five specimens were tested for each type of composite.

2.4 Structural and morphological characterization

Material composition was analyzed with Fourier transform infrared spectrometry (Nicolet SXFYIRI 70 type, Perkin Elmer). The influence of nano-apatite surface silanization on the crystallinity and melting temperature of composite was studied by differential scanning calorimetry (Netsch, German). The fractography of tensile-tested apatite/PCL composite specimens and the dispersion of nano-apatite fillers in PCL-matrix were studied by scanning electron microscopy (SEM, Hitachi, Japan).

3 Results

3.1 FT-IR

The as-prepared KH560-modified nano-apatite particles showed (Fig. 2a, c) a peak attributed to –OH vibration at 3570 cm^{-1} and a peak attributed to P–O vibration at 962 cm^{-1} , both characteristic of apatite structure. In addition, the KH560-modified particles (Fig. 2c) showed a clear -OH vibration peak at $3550\text{--}3200\text{ cm}^{-1}$ attributed to the alcoholic product of hydrolyzation of KH560 molecule [16]. These FT-IR features confirmed that nano-apatite particles were successfully linked by KH560 polymer.

Similarly, the KH570-modified apatite particles also showed (Fig. 3c) a -OH vibration peak at $3550\text{--}3200\text{ cm}^{-1}$,

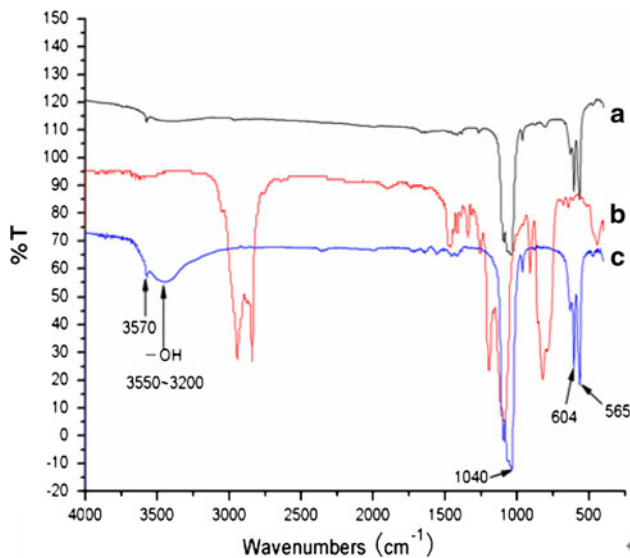


Fig. 2 FT-IR spectra of (a) apatite (b) KH560 and (c) KH560-apatite

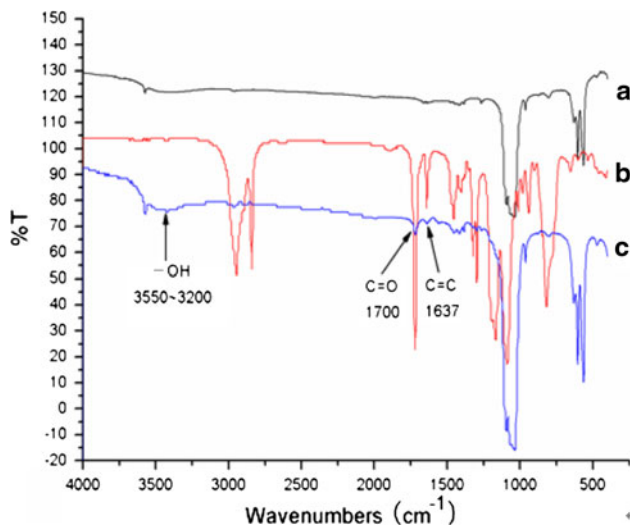


Fig. 3 FT-IR spectra of (a) apatite (b) KH570 and (c) KH570-apatite

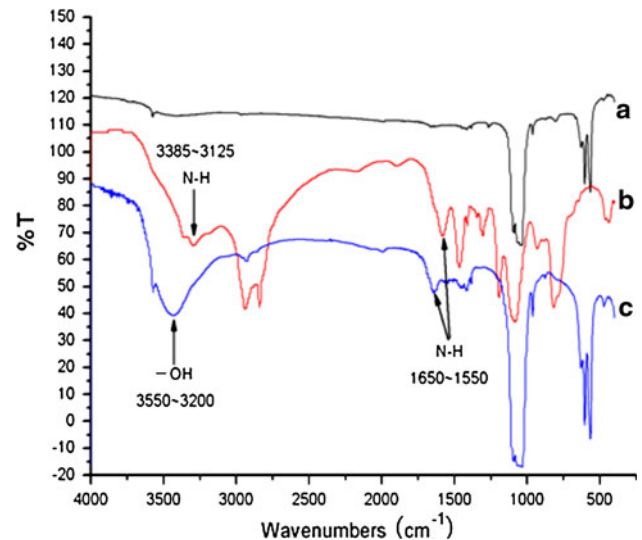


Fig. 4 FT-IR spectra of (a) apatite, (b) KH792 and (c) KH792-apatite

along with two peaks at 1700 cm^{-1} and 1637 cm^{-1} , which were attributed to the vibrations of C=O and C=C structures in KH570 molecule. The results suggested that nano-apatite particles were also successfully linked by KH570 polymer.

KH792-modified apatite also showed (Fig. 4c) a –OH vibration peak at $3550\text{--}3200\text{ cm}^{-1}$ and two peaks characterizing the presence of KH792 molecule (Fig. 4c), including a N–H peak at $1650\text{--}1550\text{ cm}^{-1}$. Clearly, KH792 molecule was also linked with the nano-apatite particle.

3.2 Effects of surface modification on crystallization and melting temperatures

The crystallization temperature and melting temperatures of the composites were listed in Table 1. The crystallization temperatures increased from 31.4°C in the control sample to 36.0°C in KH560-apatite/PCL, to 35.7°C in KH570-apatite/PCL and further to 35.6°C in KH792-apatite/PCL. In comparison, the melting temperatures of PCL composites remained almost unchanged among all samples. These results indicated that silanization of nano-apatite particles affected the crystallization temperature of the PCL–matrix composites. According to the theory of crystallization [17], during temperature decrease, the

Table 1 The melting and crystallization temperatures of non-silanized and silanized composites

Temperature	Control	KH560-modified	KH570-modified	KH792-modified
T_m	58.8 ± 0.1	58.8 ± 0.1	59.0 ± 0.1	59.1 ± 0.1
T_c	31.4 ± 0.1	36.0 ± 0.1	35.7 ± 0.1	35.6 ± 0.1

PCL–matrix composites require a higher crystallization temperature to maintain formation of crystallites, because the silane coupling agents reduced the density of nucleation sites on the surfaces of nano-apatite particles, or equivalently elevated the activation energy required for nucleation of crystallites. The explanation suggested that silanization changed the surface condition of these nano-apatite particles and this confirmed that silane coupling agents tailored the surface of nano-apatite particles in PCL composites.

3.3 Mechanical properties

The ultimate tensile strength (Fig. 5) of the silanized composite was higher than that of the non-silanized material, suggesting that the silanization of nano-apatite particles improved the ultimate tensile strength of the PCL–matrix composite. In addition, the ultimate tensile strength of KH792-apatite/PCL composite reached the highest value (22.60 MPa) among all types of samples studied, suggesting that a positive effect of KH792 on the strength of the nano-composite.

The elastic modulus (Fig. 6) of KH560-apatite/PCL and KH570-apatite/PCL was lower than the control material, suggesting a negative effect of KH560 and KH570 modification of apatite nano-particle on the elastic modulus of the composite with PCL. The KH792-apatite/PCL composite showed the highest elastic modulus among the four composites, suggesting a positive effect of KH792 on the elastic modulus of PCL composites.

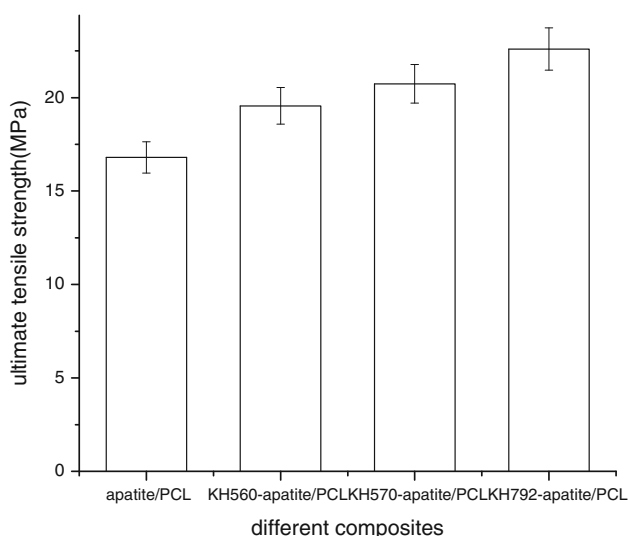


Fig. 5 Ultimate tensile strengths of different composites

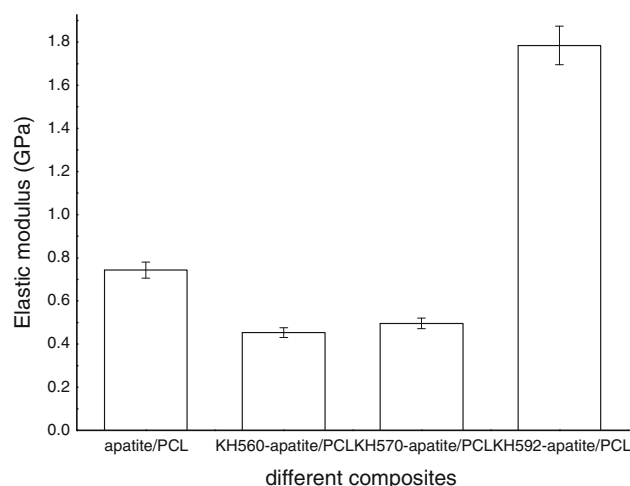


Fig. 6 Elastic modulus of different composites

3.4 Distribution of nano-apatite particles in PCL–matrix composites

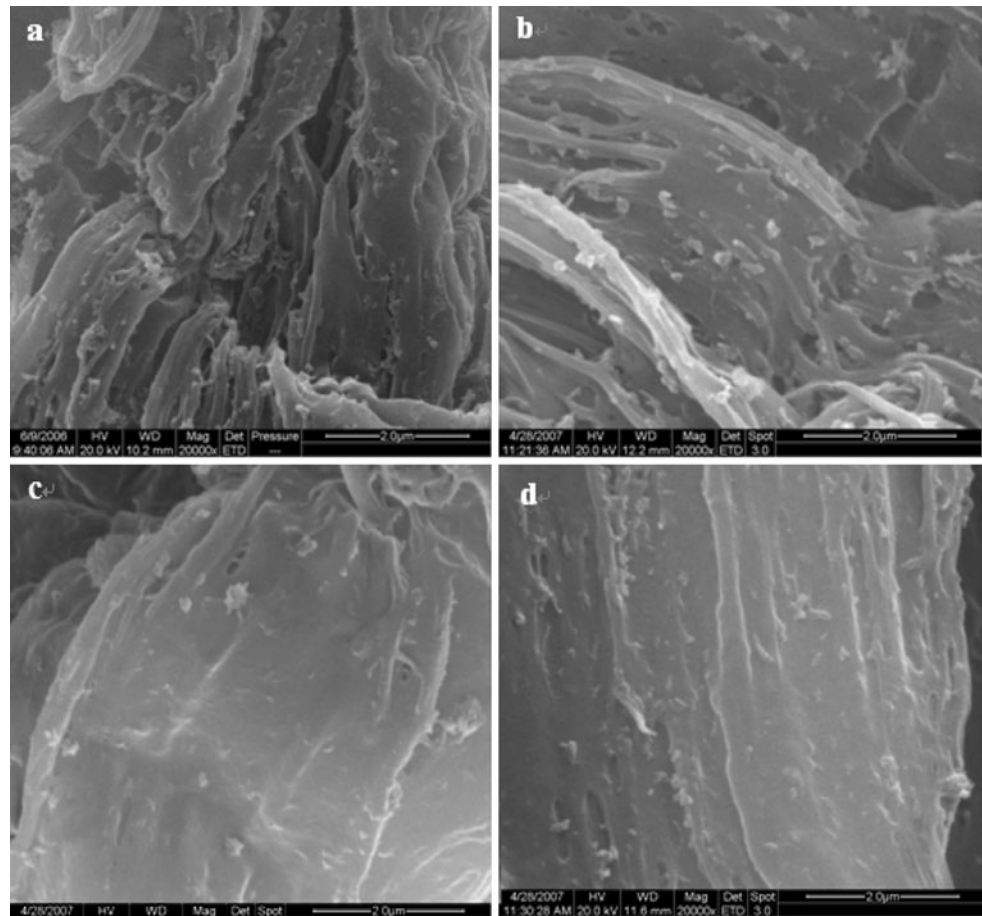
SEM (Fig. 7) showed there was generally no distinct agglomeration in any composite, regardless whether the nano-apatite particles were silanized or not. In four types of composite films, nano-apatite particles were distributed in a well-proportioned manner in the whole fracture surface. This implied that nano-apatite particles were effectively dispersed by our processing technique, which combined solvent dispersion and melting-blend with hot-pressing method.

Furthermore, the silanized nano-apatite particles appeared in the interior of fracture surface and encapsulated by PCL polymer; the contours of these modified particles were blurry, especially for KH570 or KH792-apatite (Fig. 7c, d). These observations suggested that the silanized nano-apatite particles had good compatibility with PCL and improved interfacial microstructure, and thus produced a stronger bonding with the PCL matrix. These analyzes also suggested that silane coupling agents tailored the surface of nano-apatite particle.

4 Discussion

Mechanical properties of composite materials are crucially affected by two important factors in microstructure. The first one is the interfacial bonding between fillers and matrix [18]. Because the ceramic filler and the polymer matrix are completely different, a weaker interfacial bonding is usually formed between apatite nano-particle and PCL polymer. It is thus necessary to introduce a third component to improve the interfacial bonding. In this study, we introduced silane coupling agents (KH560,

Fig. 7 SEM micrographs showing the fractography of **a** nano-apatite/PCL, **b** KH560-nano-apatite/PCL, **c** KH570-nano-apatite/PCL, and **d** KH792-nano-apatite/PCL



KH570 and KH792) for this purpose. Our findings (Figs. 2–4, 7, Table 1) showed that these silane coupling agents were successfully linked to the surfaces of nano-apatite particles, and these tailored surfaces exhibited a higher bonding with PCL matrix (Figs. 5, 6), especially for KH792-silanization. The improved interfacial bonding between the apatite fillers and the PCL matrix translated into improved mechanical properties such as ultimate tensile strengths and elastic modulus of PCL–matrix composites.

The other factor is the agglomeration of nano-apatite particles as the fillers [19]. Large-scale agglomeration can adversely affect the microstructure of polymer-matrix composites, and de-agglomeration and uniform distribution is an essential requirement for the achievement of excellent mechanical properties. In this study, the nano-apatite particles showed a well-proportioned distribution in whole fractured surface without large-scale agglomeration. These favorable microstructures were achieved because the surface modification of nano-apatite particles decreased their surface energy and thus weakened their agglomeration. In addition, we combined multiple preparation methods including solvent dispersion and melting-blend with hot-pressing technique in the processing of PCL–matrix

composites to ensure fully blend and effective de-agglomeration of the nano-apatite particles. As a result of these two aspects, the composites prepared by us exhibited the well-proportioned and ultra-fine dispersion of nano-apatite particles in the PCL matrix.

These two factors discussed above also contribute to the increased mechanical properties of the composites, especially KH792-apatite/PCL. Compared with the best results (16 MPa) in other studies [12, 20], the tensile strength of 22.60 MPa obtained in this study is substantially higher. In addition, the elastic modulus of 1.76 GPa of the silanized apatite/PCL composite reported here is also higher than the previously reported value of 1.55 GPa [12]. In summary, this study shows that the processing technique and silanization of nano-apatite particles can effectively improve the tensile strength and elastic modulus of nano-apatite/PCL composites.

5 Conclusion

Composites of poly(ϵ -caprolactone)-matrix and apatite nano-filler modified by silane coupling agents (KH560, KH570 and KH792) were developed by a processing

technique combining solvent dispersion, melting-blend with hot-pressing method. The silane coupling agents linked and tailored the surfaces of the nano-apatite particles. The silanized apatite particles showed well-proportioned and ultra-fine dispersion in the fractured surfaces of PCL–matrix composites. These composites exhibited unique physics characteristic including increased crystallization temperature compared with that of the control material. In particular, the KH792-apatite/PCL composite showed excellent mechanical properties such as a higher ultimate tensile strength and elastic modulus.

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