

Effects of *In Situ* Biomineralization on Microstructural and Mechanical Properties of Hydroxyapatite/Polyethylene Composites

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Received 3 July 2005; accepted 16 November 2005

DOI 10.1002/app.23866

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To improve the mechanical properties of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HAP)/High-density polyethylene (HDPE) composites, the process of *in situ* biomineralization was used, and its effect on the microstructure and mechanical properties of HAP/HDPE composite was investigated by means of Fourier transform infrared spectroscopy, energy dispersive X-ray analysis, scanning electron microscope, Instron testing machine, and Ceast Impact tester at room temperature. Results show that: (1) the HAP/HDPE composite prepared by *in situ* biomineralization has the better mechanical properties. The impact strength and the tensile strength reach 712 J/m and 96 MPa, respectively, which were more than three times higher than those of composites prepared by blending directly. (2) The biomin-

eralized HAP crystals grew onto the HDPE with chemical bond and dispersed in HDPE polymer on the level of nanometer dimension, which provided a greater surface area for bonding with the polymer, accordingly enhancing the interfacial bonding strength. On the other hand, the higher interfacial bonding strength will produce interfacial stress from the contraction of matrix, which can strain-induce the crystallization of matrix to form the extended-chain crystal structure in the area surrounding the filler. As a result, the mechanical properties of composite improved greatly. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1842–1847, 2006

Key words: biomaterials; mechanical property; polyethylene; composites; biomineralization

INTRODUCTION

Hydroxyapatite/high-density polyethylene (HAP/HDPE) composite, with modulus value approaching that of cortical bone, is promising in solving the problems of bone resorption occurring to implants of conventional materials which have much higher modulus value than bone.¹ However, the significant difference in the surface chemical properties between HAP and polyethylene leads to the poor interfacial bonding strength between HAP and polyethylene and to the aggregation of HAP particles in the matrix, which results in the limitation of its application in the bearing position in human body. Mechanical properties of an implant that do not match those of bone during physiological loading conditions will cause unwanted bone resorting around the implant, leading to bioma-

terials loosening, and provide eventual clinical complications that may require surgical removal of such failed implants.^{2,3} Therefore, it is crucial to find methods to improve the biomechanical properties of implant materials.

To produce HAP/HDPE composite with high mechanical properties, smaller particle size, sufficient bonding strength, and complete distribution of HAP particles in the matrix with nanometer dimension are necessary to support physiological loading conditions and to ensure overall implant efficacy. To enhance the mechanical properties of HAP/HDPE composite, researchers had done many studies to resolve the problem of interfacial strength between HAP and HDPE.^{4–10} Adding coupling agent and using high level of shear extruder to break down the agglomerates of HAP particle were considered as the efficient methods. However, their effects were not as satisfactory as anticipated.

Biomineralization is a deposition process of precise array of inorganic crystals in organisms, which involves controlled nucleation and growth of crystal at interface between the crystals and substrate macromolecules.^{11,12} Composites formed by biomineralization, such as bone, teeth, and shell, have precise microstructures with high mechanical properties.¹¹ So, the process of biomineralization is a promising one to

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Contract grant sponsor: High Technology Development Plan of China; contract grant number: 2003AA302210.

Contract grant sponsor: Nature Science Foundation of Hunan, People's Republic of China; contract grant number: 05JJ20014.

Contract grant sponsor: Central South University, People's Republic of China; contract grant number: 030615.

apply in many industrial processes, including the direct biotechnological exploitation of biogenic materials, the design of novel composite materials by *in situ* precipitation, and the mimicking of biological processes in an inorganic context.

Natural bone is a kind of biomineralized composite with good biomechanical properties, in which the biomineralized HAP crystals adhere to collagen with chemical bonds, and distribute well in the collagen matrix with the level of nanometer dimension. If we really mimic the microstructure of bone and simulate the process of bone formation, it is possible to manufacture the biomaterials with high biomechanical properties. On the basis of this idea, the method of *in situ* biomineralization was introduced to prepare HAP/HDPE composite, and its effect on the mechanical properties is discussed in this paper.

EXPERIMENTAL

Materials

HDPE was provided by the Second Beijing Agent Company, Beijing, People's Republic of China. HAP was prepared through hydrotherm method by our group, properties of which were described in detail in Ref. 13. Acetone, acrylic acid, and benzyl peroxide were purchased from the Tianjin Agent Company, Tianjin, People's Republic of China.

HDPE surface modification

HDPE was milled in Retsch Centrifugal mill (type 2MI) using liquid nitrogen as the coolant for 4 h to decrease the size of HDPE particles. Then the milled HDPE was immersed in the oxidation solution to carry out surface modification. The oxidation solution was made up of analysis-grade acetone, acrylic acid, and benzyl peroxide. After 3 h, the HDPE was filtered and washed by the distilled water, then dried in the oven for 3 days at 70°C.

Preparation of the HAP/HDPE composites

The modified HDPE was divided into two groups. One group was blended directly with HAP nanoparticles. The average particle size of HAP particle was about 100–500 nm. Then the HAP/HDPE mixed powder was fed into the hopper of a one-screw extruder at 170°C to compound and to extrude in the form of streams through a rectangular hole and die into a distilled water bath at room temperature to prevent oxidation of the polymer, and the samples were cut to shape and then polished using 8- μ m silicon carbide paper. This HAP/HDPE composite made by blending directly was named as composite A.

TABLE I
Ionic Concentration of Simulated Body Fluid

Ion	mmol/L
Na ⁺	6.5
Cl ⁻	5
H ₂ PO ₄ ⁻	2.994
Ca ²⁺	5
HCO ₃ ⁻	1.5

The other group of modified HDPE was prepared by *in situ* biomineralization. The modified HDPE was immersed into the simulated body fluid (SBF) at 37 \pm 0.1°C with magnetic stirring. SBF was prepared as in Ref. 14. The concentration of ions is shown in Table I. During biomineralization, the concentration of Ca and P was maintained with the molar ratio Ca/P = 1.67, and the pH value of the solution was regulated by HCl and NH₄NO₃ at pH = 7.4 \pm 0.1. After 3 days, the HDPE coated with calcium phosphate crystals was filtered and washed by distilled water and then dried in the oven for 3 days at 70°C. Then the HAP/HDPE composite powder was fed into the hopper of a one-screw extruder at 170°C and extruded in the form of streams through a rectangular hole die into a distilled water bath at room temperature to prevent oxidation of the polymer, and the samples were cut to shape and then polished using 8- μ m silicon carbide paper. These HAP/HDPE composite made by *in situ* biomineralization was named as composite B.

Characterization

Tensile tests and fracture testing were conducted on an Instron Go25 testing machine at a crosshead speed of 5 mm/min and at an ambient temperature. At least five specimens of each series of composite were tested. And the values of tensile and fracture strengths were obtained by averaging the sum of five data.

The surface chemical properties of HDPE before and after surface modification were investigated on the IFS60v Fourier transform infrared spectroscopy (FTIR), and the crystal structure and crystal morphology grown on HDPE were measured on the D98X XRD and the JSM-5600LV SEM, respectively. The dispersion and distribution of HAP particles in the HDPE matrix were determined using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX); the specimen preparation procedure included sectioning, mounting, grinding, polishing, and ultrasonic bath cleaning and gold coating.

RESULTS AND DISCUSSION

Studies on the mechanism of biomineralization suggest that the crystallization of inorganic molecules was

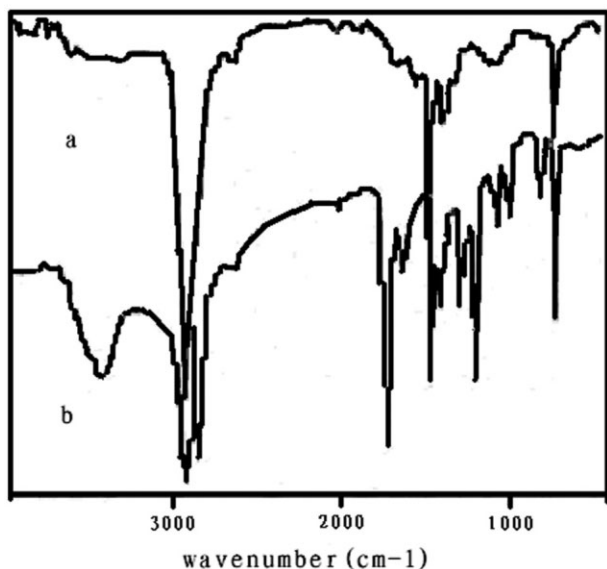


Figure 1 The FTIR spectra of HDPE before modification (a) and after modification (b).

controlled by the functional groups on the organic macromolecules through the “molecular recognition” effect, namely during the process of biomineralization, the functional groups, acting as the active seats, can induce the inorganic crystal growing from the solution with chemical bonds.^{15,16} And experiments have suggested that the —COOH group can induce HAP crystal growth from the SBF.¹⁷ Therefore, the key to produce the HAP/HDPE composite by *in situ* biomineralization is to graft —COOH functional groups onto HDPE. Figure 1 shows the infrared spectra of HDPE before and after surface modification by the oxidation solution. The presence of bands for the —COOH group (1720 cm^{-1}), —C=O group (1601.26 cm^{-1}), and —OH group (3439.97 cm^{-1}) indicates that the acrylic acid has been grafted onto the surface of HDPE [as shown in Fig. 1(b)].

Figure 2 shows the XRD spectra and the SEM photographs of HAP/HDPE composite powder prepared by *in situ* biomineralization. Results show that the resultant is the composite of HAP and HDPE. HAP crystals grew on the surface of HDPE with the size in the range of 100–500 nm. These indicate that those functional groups grafted on the modified HDPE polymer, through the effect of “interfacial molecular recognition,” can induce the nucleation and growth of nanometer level HAP crystals with chemical bonds, which will contribute to enhance the interface bonding strength between HAP and HDPE.

The SEM examinations and EDX of polished composite surface are shown in Figure 3. It can be seen that composite A exhibits a greater degree of HAP particle agglomeration [as shown in Figs. 3(a) and 3(b)]. These results are different from those obtained

by *in situ* biomineralization, which exhibits a homogeneous distribution of HAP particles in HDPE with the dimension of nanometer size [as shown in Figs. 3(c) and 3(d)]. Examination of longitudinal sections of composite and elemental X-ray mapping of distribution of element Ca also reveal such a difference.

As is well known, a smaller particle size provides a greater surface area for bonding with the polymer. And the interfacial surface area available per unit volume of the samples increased as the particle size decreased. Namely the smaller the particle size, the higher the bonding energy of composite. Compared with those of composite A, the HAP particles of composite B have smaller particle size (on the level of nanometer dimension) and better distribution in the HDPE matrix, which provide a greater surface area for bonding with the polymer, accordingly the interface bonding energy was higher. On the other hand, the HAP crystal of composite B adhered onto the polymer

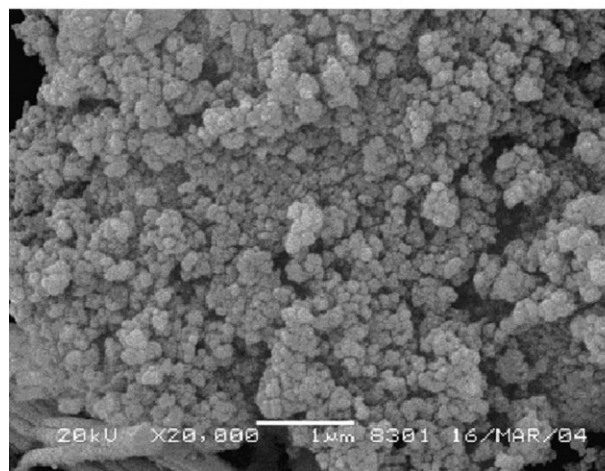
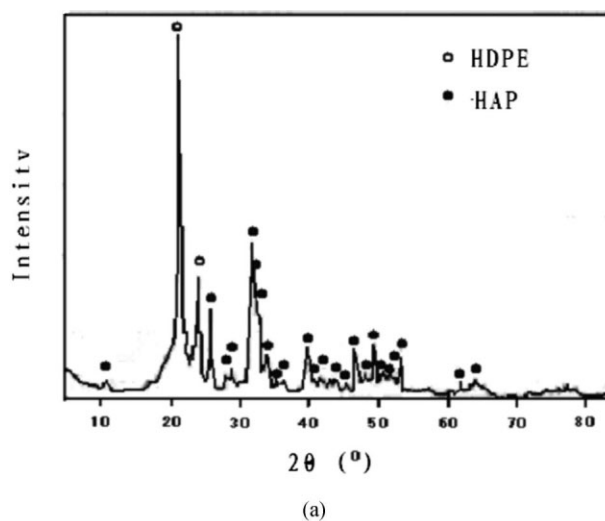


Figure 2 The XRD (a) and SEM (b) of HAP/HDPE composite powder prepared by *in situ* biomineralization.

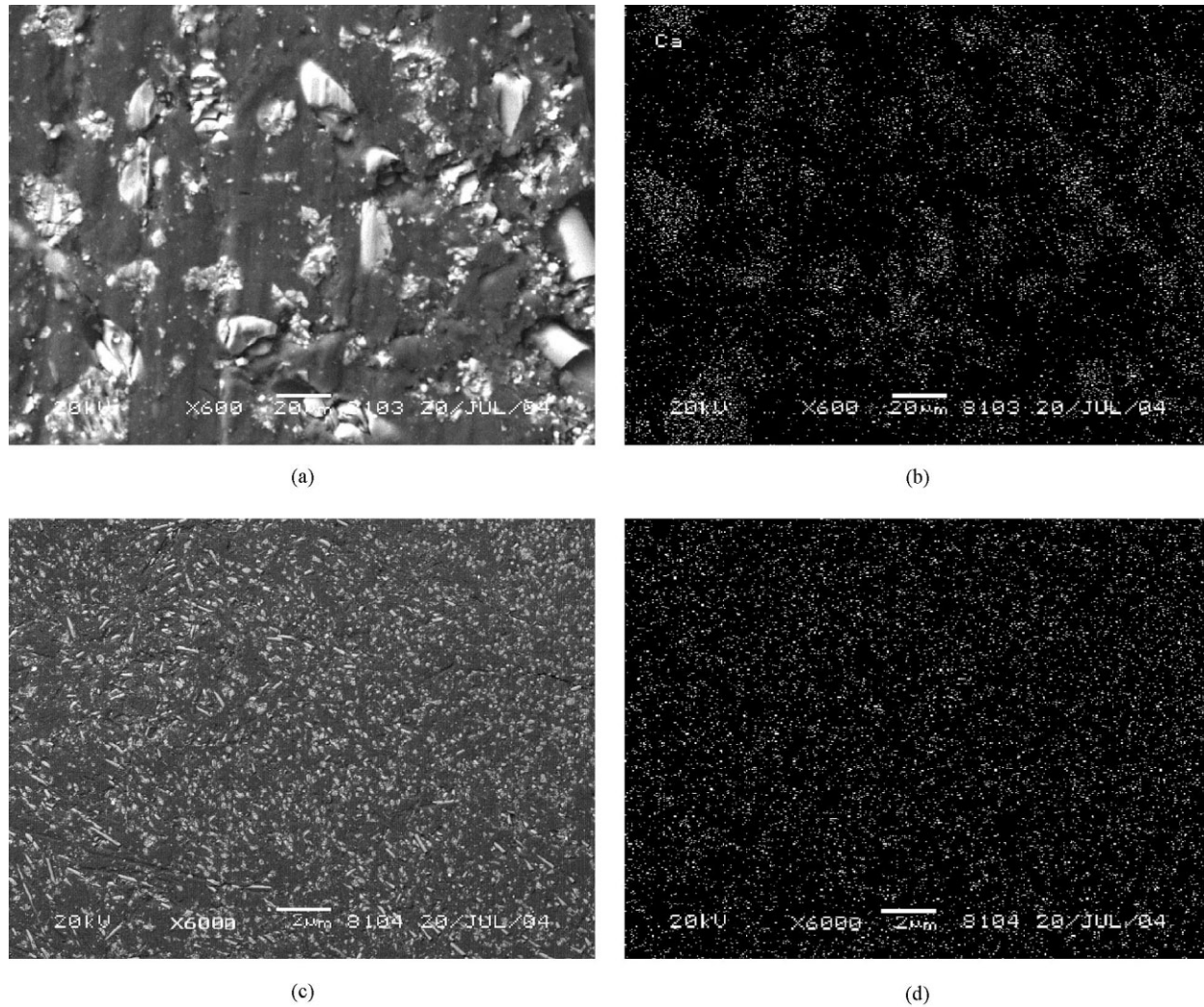


Figure 3 The SEM and EDX of polished composite (a) and (b) are SEM of composite prepared by melting blend; (c) and (d) are EDX of composite prepared by *in situ* biomineralization.

by chemical bonds. As a result, the adhesion and interaction between the filler and the matrix were improved, which contributes to enhance the interface bonding strength.

Tensile and impact testing results for the HAP/HDPE composites are tabulated in Table II, which shows the effect of *in situ* biomineralization on the behavior and properties of HAP/HDPE composites. Although the impact strength of composite A in-

creases a little, its tensile strength decreases. Compared with composite A, the mechanical properties of composite B are significantly improved. The impact strength reaches 712 J/m and the tensile strength reaches 96 MPa, which are more than three times higher than those of composites A.

SEM micrographs of tensile-fracture surface for composites are shown in Figure 4, which reveal the effect of *in situ* biomineralization on the interfacial

TABLE II
Mechanical Properties of Composite

Samples	Composite type	HAP content (vol %)	Tensile strength (MPa)	Impact strength (J/m)
Pure HDPE	—	0	22.4 ± 0.5	148.6 ± 0.6
Composite A	Blending directly	20	20.1 ± 0.3	220 ± 0.4
Composite B	<i>In situ</i> composite of mineralization	20	96 ± 0.4	712 ± 0.2

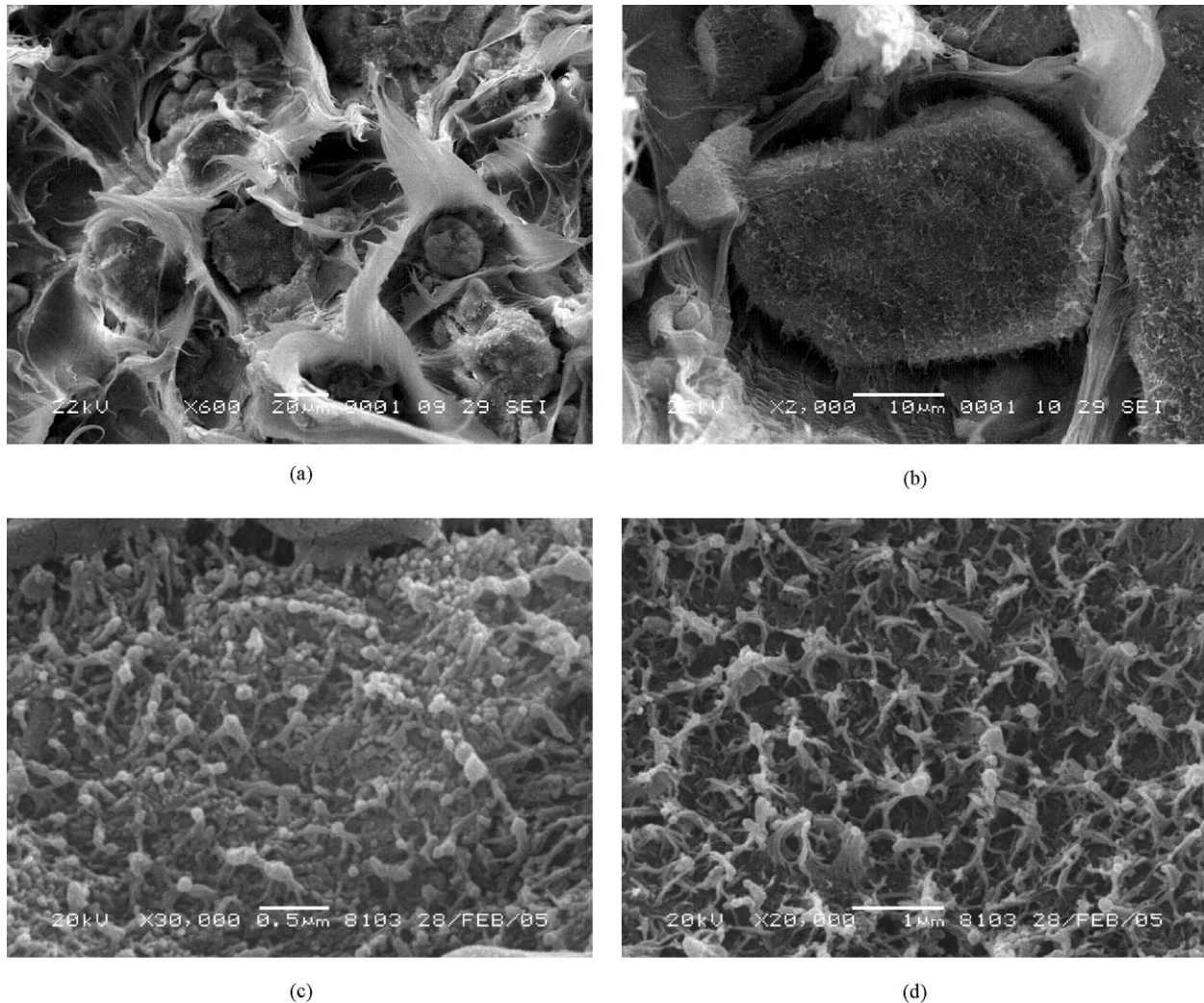


Figure 4 The fracture morphology of HAP/HDPE composite. (a), (b) Composite prepared by melting blend; (c), (d) composite prepared by *in situ* biomimeralization.

bonding strength between HAP and HDPE and on the size and microstructure of HDPE. For both series of HAP/HDPE composites, the polymer matrix undergoes extensive deformation in composites with 20% of HAP. From Figures 4(a) and 4(b), it can be seen that many mesh structures were formed on the surface because of pulling out of HDPE spherulites' crystal from the matrix, and the aggregated HAP particles existed in the hole of the mesh structure. The magnified photograph shows that a large gap, formed due to the contraction of HDPE matrix during cooling, was around the interface between HAP and HDPE. Results indicated that the interfacial bonding strength of composite A was very low, which plays no role in the crystallization of HDPE matrix. Therefore, the HDPE grows into spherulite crystals with large size, and the HAP particles accumulate on the interface of spherulites, and as a result, the mechanical properties of composite A were low.

Figures 4(c) and 4(d) show the tensile fracture surface of composite B. From them, it can be seen that

HDPE matrix is attached to the HAP particles closely. The HDPE crystallized with the extended-chain crystal structure in the area surrounding the HAP particles, and HDPE crystal size was very small, which indicated that the interfacial bonding strength of composite B was high, and that in this higher interfacial bonding strength condition, the produced interfacial stress from the contraction of matrix can strain-induce the crystallization of matrix to form the extended-chain crystal structure in the area surrounding the filler. As a result, the mechanical properties of composite B were improved greatly.

CONCLUSIONS

Application of *in situ* biomimeralization greatly improved the mechanical properties of resulting HAP/HDPE composites. The tensile strength and the impact strength of the biomimeralized composite were 96 MPa and 712 J/m, which were more than three times higher

than those of the composite prepared by blending. Tensile fracture analysis and EDX results indicated that HAP crystal induced by *in situ* biomineralization grew onto the HDPE with chemical bond and dispersed in the HDPE matrix on the level of nanometer dimension, which contributes to enhance the interface bonding strength and to strain-induce the crystallization of matrix to form the extended-chain crystal structure in the area surrounding the filler. As a result, the mechanical properties of composite were improved to a great extent, which illustrates that *in situ* biomineralization was an efficient method to improve the mechanical properties of ceramic/polymer composites.

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