TRIAL OF HYBRID INTERFACE CONTROL IN HAP/PLA COMPOSITES

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Abstract

The biocompatible materials composed of hydroxyapatite (HAp) particles and poly-lactic acid (PLA) are one of the most promising candidates as scaffold materials for bone regeneration. In this study, we proposed the "hybrid" interface control using both pectin and chitosan, in order to improve the efficiency of the interface control, for HAp/PLA composite materials. As results, the improvement of interfacial bonding by the hybrid interface control induced the remarkable increase in the tensile fracture properties of HAp/PLA composite.

1 Introduction

In the traditional bone filling surgery, biocompatible substitute materials are implanted into bone defects. In this case, the re-implantation of substitute materials is inevitable owing to the age-related deterioration. In addition, surrounding bone is sometimes absorbed owing to the stress-shielding phenomenon induced by the extremely high stiffness of substitute materials in comparison with surrounding bone [1]. Therefore, the development of the bone regeneration technique is expected utilizing porous scaffold materials as bone substitutes and cellular bone formation activities [2-4]. Here, the complete bone regeneration will be achieved by the hydrolytic resorption of scaffold materials and the replacement into newly formed bone. The main requirements for scaffold materials are biocompatibility, bone-conductivity, biodegradability, and comparable stiffness and strength to healthy bone. Therefore, the biocompatible materials composed of hydroxyapatite (HAp) particles and poly-lactic acid (PLA) are one of the most promising candidates as scaffold materials, owing to the bone-conductivity of HAp and the biodegradability of PLA. However [5-8], the poor fracture properties, mainly caused by the weak interface, are one of the factors limiting their practical application [6,8].

Recently, we have studied the effect of the microstructural control on the mechanical properties, hydrolytic behavior and fracture mechanisms of HAp/PLA composite materials [9-11]. In particular, we tried the interface control by the surface treatment of HAp particles using natural-derived biocompatible polymers, in order to improve the bonding strength of interface between HAps and PLA and consequently the mechanical properties of HAp/PLA composite materials [9,10]. Here, pectin and chitosan were selected as the surface treatment polymers in consideration with the biological affinity. As results, the interface control using pectin or chitosan improved the interfacial bonding strength and the deformation/fracture properties of HAp/PLA composite materials. In addition, the better interfacial bonding suppressed the selective and local hydrolysis at the interface and the consequent deterioration of the fracture properties of HAp/PLA composites, as shown in Figure 1 [10]. However, since we utilized the effects of hydrophobic and electrostatic interactions between HAps and natural-derived biocompatible polymers (pectin: acidic polymer, chitosan: basic polymer), the interfacial defects still existed by using these polymers separately. It had been expected that the increase in the efficiency of the interface control potentially would improve the elastic modulus and strength of HAp/PLA composite materials.

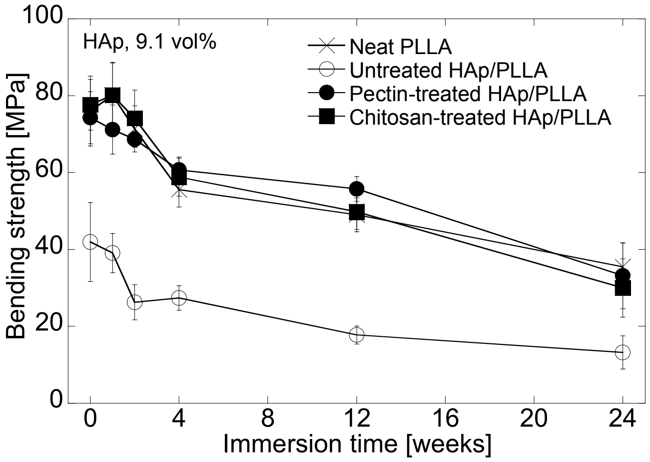

Figure 1. Change in bending strength of neat PLLA and HAp/PLLAs with hydrolysis [10].

In this study, we tried the "hybrid" interface control in HAp/PLA composite materials using both pectin and chitosan. Here, photo-dissociable protective groups, which can be eliminated from the protection site by the irradiation of ultraviolet rays, were applied into carboxyl groups of pectin, in order to avoid the direct chemical reaction between pectin and chitosan. The molecular structure of hybrid-interface-controlled HAps was analyzed using a Fourier transform infrared spectrophotometer. Tensile tests for the hybrid-interface-controlled HAp/PLA composite materials were carried out using a servohydraulic testing machine, followed by the fracture surface observation using a field emission scanning electron microscope. Finally, the effect of the hybrid interface control on the fracture behavior of HAp/PLA composite materials was discussed from the viewpoint of the interfacial mesoscopic structures.

2 Preparation of hybrid-interface-controlled HAps

2.1 Approach of hybrid interface control

In this study, we aimed to achieve the chemical modification of HAps using both pectin and chitosan, as the "hybrid" interface control. Here, pectin is acidic polymer, and chitosan is basic polymer. Thus, it is suggested that the direct chemical reaction between pectin and chitosan possibly disturbs the hybrid interface control.

Therefore, we considered that the chemical modification of HAps using both pectin and chitosan could be achieved by utilizing photo-dissociable protective groups, which can be eliminated from the protection site by the irradiation of ultraviolet rays. In this study, the photo-dissociable protective groups, which react to carboxyl groups of pectin, were selected. It was expected that the chemical modification of the whole surface of HAps would be enabled by the introduction of photo-dissociable protective groups to carboxyl groups of pectin on pectin-modified HAps, and the consequent chemical modification of protected pectin-modified HAps using chitosan. Finally, the hybrid interface control can be completed by the deprotection of photo-dissociable protective groups by the irradiation of ultraviolet rays.

2.2 Hybrid-interface-control method of HAp surface

HAp particles (Ube Materials Industries, Ltd., ϕ: about 0.2 μm, aspect ratio: 10 - 20) were used in this study. As surface treatment polymers, pectin (Kanto Chemical Co., Inc.) and chitosan (Kanto Chemical Co., Inc.) were selected in consideration with the biological affinity. As photo-dissociable protective groups, o-nitrobenzyl alcohol (Wako Pure Chemical Industries, Ltd.) was used after grinding in a mortar.

First, HAp particles were dissolved into the pectin solution (solute: pectin (1 wt% against HAp), solvent: distilled water), followed by stirring at 30 °C, standing at room temperature and drying of the obtained precipitation (pectin-modified HAps). Pectin-modified HAps and o-nitrobenzyl alcohol (3 wt% against HAp) were dissolved into dichloromethane (Kanto Chemical Co., Inc., purity: 99.5 %) at room temperature, followed by stirring, standing and drying of the obtained precipitation (protected pectin-modified HAps). Protected pectin-modified HAps were dissolved into the chitosan solution (solute: chitosan (1 wt% against HAp), solvent: acetic acid (Kanto Chemical Co., Inc.)), followed by stirring at 30 °C, standing at room temperature and drying of the obtained precipitation (protected pectin&chitosan-modified HAps). Finally, hybrid-interface-controlled HAps were prepared by the deprotection of the photo-dissociable protective groups. The deprotection of photo-dissociable protective groups was conducted by the irradiation of ultraviolet rays (wave length: 365×10^{-9} m, irradiation time: 1800 s) for protected pectin&chitosan-modified HAps dissoloved into dichloromethane.

The spectrum of prepared hybrid-interface-controlled HAps was measured by the KBr method, using a Fourier transform infrared spectrophotometer (Horiba, Ltd., FT-720). As a result, spectral peaks were observed at wave number of 1700 m^{-1} (amino group in chitosan) and 1600 m^{-1} (carboxyl group in pectin). Thus, it is considered that the modification of HAps using both chitosan and pectin was successfully achieved.

3 Effect of hybrid interface control on tensile fracture properties of HAp/PLA

3.1 Preparation of HAp/PLA composites

In this study, PLA (Toray Industries, Inc., initial viscosity average molecular weight: 2×10^5) was used as matrix of HAp/PLA composites. The hybrid-interface-controlled and uncontrolled HAp/PLA composites were prepared as follows. Here, HAp particles as supplied were used as fillers for the uncontrolled HAp/PLA composite as the reference material.

First, PLA was dissolved into dichloromethane suspension of HAps, followed by stirring and re-precipitation. Weight fraction of HAps was 20 wt% (9.1 vol%) against PLA. After the filtration and drying of the obtained re-precipitation, hot-pressing (Figure 2) was repeated twice under the conditions of 200 °C and 6 MPa using a hot-pressing device (TechnoSupply Co., Ltd., G-12), followed by the rapid cooling. Thickness of prepared HAp/PLA composite films was nominally 0.5 mm. As results of the crystallinity measurement using a differential scanning calorimetry (Rigaku Corporation, DSC8230), the crystallinity of PLA after preparation was 11.3 % and 13.8 % for hybrid-interface-controlled and uncontrolled HAp/PLA composites, respectively.

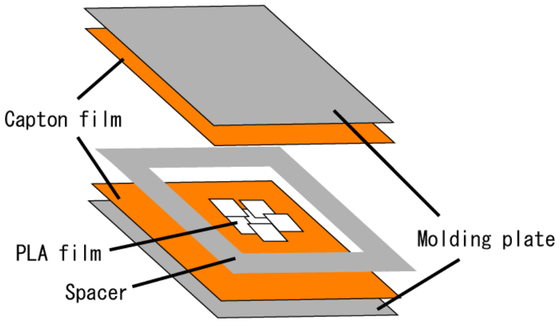

Figure 2. Hot-pressing set-up.

3.2 Tensile test method

For tensile test, specimens of 50 mm in length, 5 mm in width and 0.5 mm in nominal thickness were prepared from HAp/PLA composite films. The glass fiber reinforced plastic (GFRP) tabs of 10 mm in length, 10 mm in width and 0.8 mm in thickness were glued at both ends of specimens. Dimensions of specimens were shown in Figure 3. Tensile test was carried out using a compact tabletop universal tester (Shimadzu, EZ Test) with a load cell of 500 N in capacity. The crosshead speed was 1.0 mm/min. After testing, fracture surfaces were observed using a field emission scanning electron microscope (FE-SEM) (Hitachi, Ltd., S-4500).

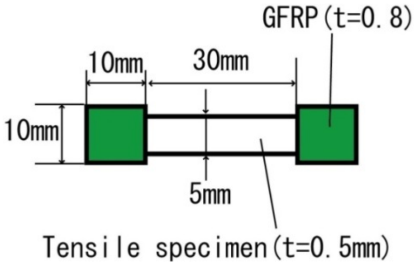

Figure 3. Dimensions of specimen. (Dimension are in mm.)

3.3 Results of tensile test

Typical stress-strain curves obtained by tensile tests were shown in Figure 4. Uncontrolled HAp/PLA composites fractured just after the maximum stress point. On the other hand, hybrid-interface-controlled HAp/PLA composites showed the large plastic deformation after the maximum stress point. Elastic modulus of hybrid-interface-controlled and uncontrolled HAp/PLA composites was 1.4 GPa and 1.2 GPa, respectively. Figures 5 and 6 shows tensile strength and fracture energy of HAp/PLA composites, respectively. Tensile strength of HAp/PLA increased by the proposed hybrid interface control. It is notable that fracture energy increased as more than 20 times by the proposed hybrid interface control as a result of the increase in fracture strain.

Figures 7 and 8 show typical fracture morphologies of uncontrolled and hybrid-interface-controlled HAp/PLA composites, respectively. In uncontrolled HAp/PLA composite, necking or whitening cannot be observed. On the other hand, necking and whitening can be observed over all in hybrid-interface-controlled HAp/PLA composite.

Figures 9 and 10 show typical fracture surfaces of uncontrolled and hybrid-interface-controlled HAp/PLA composites, respectively. In uncontrolled HAp/PLA composite, interfacial debonding and trace of debonded HAp particles were remarkably observed. On the other hand, interfacial debonding cannot be observed in hybrid-interface-controlled HAp/PLA composite. Thus, it is considered that the interface-control of whole surface of HAp particles could be almost perfectly achieved by the hybrid-interface-control proposed in this study.

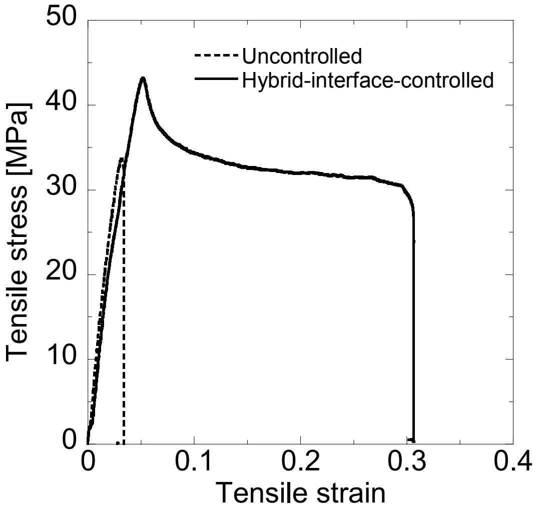

Figure 4. Typical stress-strain curves of HAp/PLA composites.

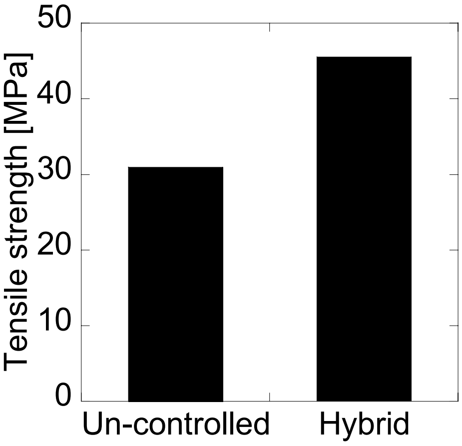

Figure 5. Tensile strength of HAp/PLA composites.

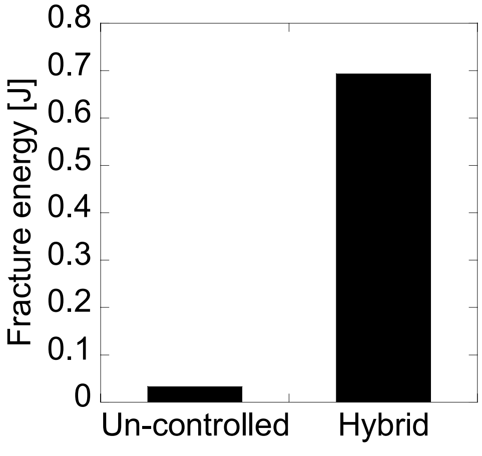

Figure 6. Fracture energy of HAp/PLA composites.

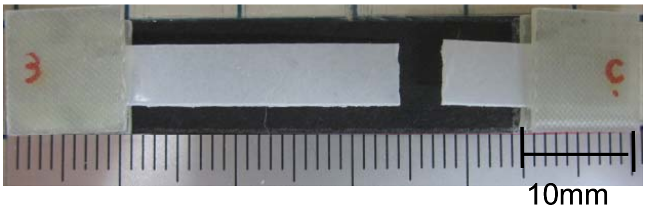

Figure 7. Typical fracture morphologies of uncontrolled HAp/PLA composites.

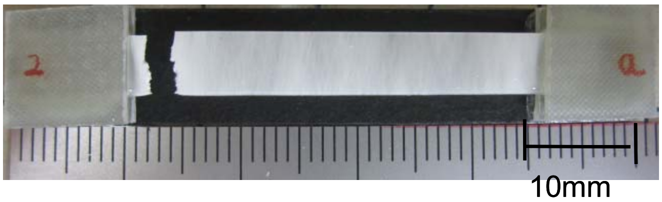

Figure 8. Typical fracture morphologies of hybrid-interface-controlled HAp/PLA composites.

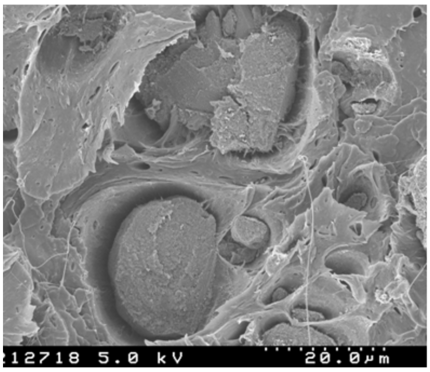

Figure 9. Typical fracture surfaces of uncontrolled HAp/PLA composites.

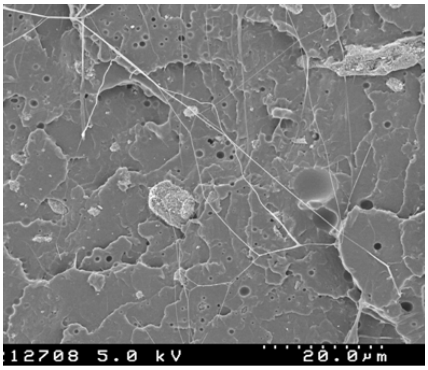

Figure 10. Typical fracture surfaces of hybrid-interface-controlled HAp/PLA composites.

3.4 Effect of hybrid interface control

As mentioned in the previous section, uncontrolled HAp/PLA composites fractured just after the maximum stress point. In addition, it is considered that the interface of uncontrolled HAp/PLA composites is quite weak, from the results of the fracture surface observation. Thus, it is suggested that the interfacial debonding before the large plastic deformation of PLA matrix brought the over all fracture of uncontrolled HAp/PLA composites.

On the other hand, it is considered that the interface of hybrid-interface-controlled HAp/PLA composites is well bonded from the results of the fracture surface observation. Thus, it is suggested that the increase in the stress transfer capacity between HAps and PLA matrix induced the increase in the elastic modulus of HAp/PLA by the proposed hybrid interface control. It is also suggested that the increase in the interfacial bonding strength prevented the interfacial debonding, resulting in the increase in the tensile strength and the large plastic deformation of PLA matrix in hybrid-interface-controlled HAp/PLA composite. In addition, necking and whitening could be observed over all in hybrid-interface-controlled HAp/PLA composite, as mentioned previously. It is suggested that the disturbance of the local damage progress by well-bonded HAp particles induced the over all necking and whitening, resulting in the increase in the fracture strain and the consequent remarkable increase in the fracture energy, in hybrid-interface-controlled HAp/PLA composite. Finally, we can conclude that the hybrid interface control proposed in this study is quite effective method to improve the interfacial bonding strength in HAp/PLA composite materials.

4 Conclusions

In this study, we tried the "hybrid" interface control in HAp/PLA composite materials using both pectin and chitosan. The effect of the hybrid interface control on the fracture properties of HAp/PLA composites was evaluated by tensile tests, and was discussed from the viewpoint of interfacial mesoscopic structures. As results, the modification of HAps using both chitosan and pectin was successfully achieved as the hybrid interface control for HAp/PLA composite. The improvement of interfacial bonding induced the increase in the tensile fracture properties of HAp/PLA composite. Particularly, the fracture energy of HAp/PLA composite increased as more than 20 times by the hybrid interface control. As the next step, it is desired that the effect of the hybrid interface control on the hydrolytic behavior in the pseudo biological environment is clarified for HAp/PLA composites.

Acknowledgements

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