

EFFECT OF HYDROLYSIS ON FRACTURE PROPERTIES OF HYBRID INTERFACE CONTROL IN HAP/PLA COMPOSITES

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Abstract

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, was applied into the carboxyl groups of pectin, in order to avoid the direct chemical reaction between pectin and chitosan. Tensile tests for neat PLA, uncontrolled HAp/PLA, pectin-modified HAp/PLA, chitosan-modified HAp/PLA and hybrid-interface-controlled HAp/PLA were carried out after hydrolysis in pseudo biological environment. As results, hybrid-interface-controlled HAp/PLA showed the smallest hydrolytic degradation in the tensile strength among HAp/PLA composites in the early stage of hydrolysis, whereas the largest in the later stage. Finally, the effect of hybrid interface control on hydrolysis behavior was evaluated and discussed from the viewpoint of interfacial structures.

1. Introduction

In recent years, biocompatible materials with fracture properties enough for substituting bone, stiffness equivalent to surrounding bone and biodegradability equivalent to bone formation speed had been developed as scaffold materials for bone regeneration surgery of bone defects [1-4]. Biocompatible materials composed of poly-lactic-acid (PLA) matrix and bio-ceramic particles, such as hydroxyapatite (HAp) particles, are one of the most promising candidates for this application [5-13]. However, mainly poor interfacial bonding between PLA and HAp caused low fracture properties of HAp/PLA composites, limiting their practical application [6, 8]. Thus, it is desired that the interfacial bonding strength would be improved using the method appropriate for material systems applied in living bodies.

Therefore, we have investigated the interface control for HAp/PLA composites by modifying the surface of HAp particles using natural-derived polymers (pectin: acidic polymer, chitosan: basic polymer), utilizing hydrophobic and electrostatic interactions [14-15]. As results, the employed interface control improved the interfacial 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. However, since we utilized the

effects of hydrophobic and electrostatic interactions between HAp and natural-derived polymers, 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 improves elastic moduli and strength of HAp/PLA composites. Then, we have proposed the "hybrid" interface control in HAp/PLA composite materials using both pectin and chitosan [16]. Here, photo-dissociable protective groups, which can be eliminated from the protection site by the irradiation of ultraviolet rays, was applied into the carboxyl groups of pectin, in order to avoid the direct chemical reaction between pectin and chitosan. As results, the modification of HAp using both chitosan and pectin was successfully achieved as the hybrid interface control for HAp/PLA composite, resulting in the notable increase in the initial fracture properties of HAp/PLA composite.

In this study, as the next step, the effect of hydrolysis on fracture properties of hybrid-interface-controlled HAp/PLA composite was evaluated by tensile tests using a servohydraulic testing machine. The effect of interface control on hydrolysis behavior was discussed from the viewpoint of interfacial structures. Finally, the possibility to control and optimize initial fracture properties and biodegradability for bone regeneration is discussed.

2. Methods

2.1. Hybrid-interface-control of HAp surface

HAp particles (Ube Materials Industries, Ltd., ϕ : about 0.2 μm , aspect ratio: 10 - 20) were used as fillers in this study. Pectin (Kanto Chemical Co., Inc., originated from citrus) and chitosan (Kanto Chemical Co., Inc., originated from shell of crab) were chosen as surface treatment polymers in consideration with the biological affinity. However, it is suggested that the direct chemical reaction between pectin (acidic polymer) and chitosan (basic polymer) possibly disturbs the hybrid interface control. Thus, we utilized photo-dissociable protective groups, which can be eliminated from the protection site by the irradiation of ultraviolet rays, and introduced them into carboxyl groups of pectin, in order to hinder the direct chemical reaction between pectin and chitosan and achieve the chemical modification of the whole surface of HAp. In this study, o-nitrobenzyl alcohol (Wako Pure Chemical Industries, Ltd.) was used as photo-dissociable protective groups after grinding in a mortar. A schematic drawing of the hybrid-interface-control method is shown in Figure 1.

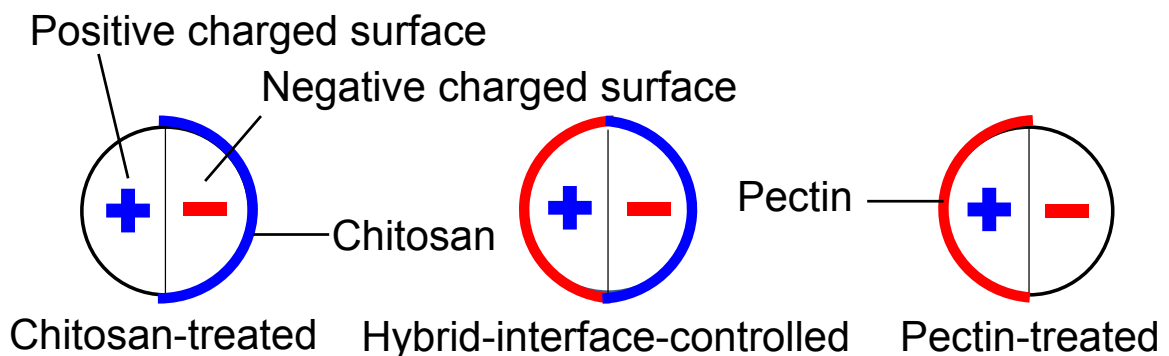


Figure 1. Schematic drawing of hybrid-interface-control for HAp surface.

First, HAp particles were dissolved into the pectin solution (solute: pectin (1 wt% against HAp), solvent: distilled water), followed by stirring at 30 °C and standing at room temperature. Pectin-modified HAPs were prepared by drying of the obtained precipitation. Secondary, 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 and standing. Protected pectin-modified HAPs were prepared by drying the obtained precipitation. Then, 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 and standing at room temperature. Protected hybrid-interface-controlled HAPs were prepared by drying the obtained precipitation. Finally, the photo-dissociable protective groups were deprotected by the irradiation of ultraviolet rays (wave length: 365×10^{-9} m, irradiation time: 1800 s) for protected hybrid-interface-controlled HAPs dissolved into dichloromethane.

2.2. Preparation of HAp/PLA composites

PLA (Toray Industries, Inc., initial viscosity average molecular weight: 2×10^5) was used as matrix of the hybrid-interface-controlled HAp/PLA composite. The uncontrolled, pectin-modified, and chitosan-modified HAp/PLA composites were prepared as well. Here, HAp particles as supplied were used as fillers for the uncontrolled HAp/PLA composite. Pectin-modified and chitosan-modified HAPs were prepared by dissolution into modification polymer solution, followed by stirring, standing at room temperature and drying.

First, HAPs (3.5 w/w%) were dissolved into dichloromethane, followed by stirring. Then, PLA was dissolved into dichloromethane suspension of HAPs, followed by stirring until PLA was completely dissolved. Weight fraction of HAPs was 25 wt% against PLA. Obtained solution was poured into ethanol, resulting in re-precipitation. Obtained precipitate was dried at room temperature for 24 h in a desiccator and then at 40 °C for 5 h in a thermostat oven, followed by cutting into small pieces. These pieces were melted at 180 °C for 15 min on a hot-pressing device (TechnoSupply Co., Ltd., G-12), as shown in Figure 2. Then, hot-pressing was conducted at 180 °C under pressure of 8 MPa for 3 min, followed by the rapid cooling. Thickness of prepared HAp/PLA composite films was nominally 0.5 mm. As the reference material, neat PLA was also prepared by the same hot-pressing process.

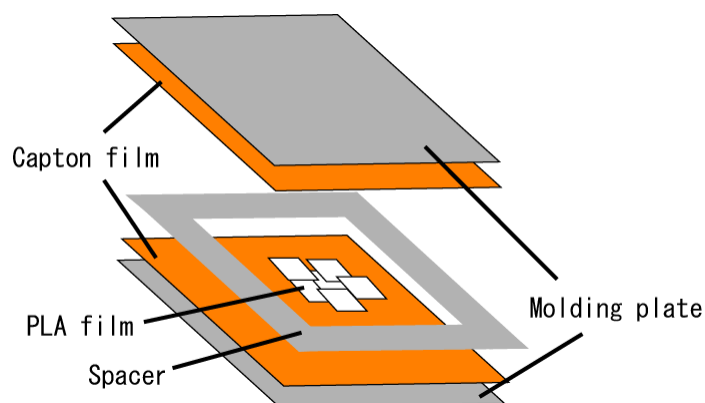


Figure 2. Hot-pressing set-up.

2.3. Test method

For tensile test, specimens of 50 mm in length and 5 mm in width were cut from prepared films and immersed into phosphate buffer solution (37 °C, pH = 7.4) as a pseudo biological environment. The water absorption was measured after immersion into pseudo biological environment. After hydrolysis, 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.

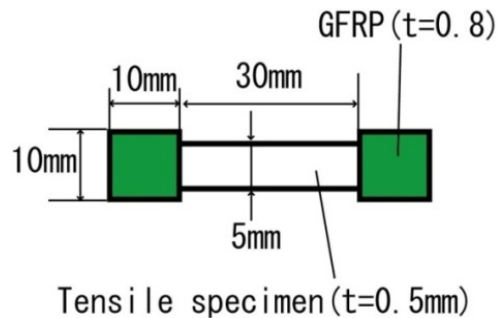


Figure 3. Dimensions of specimen. (Dimension are in mm.)

3. Results and discussion

Figure 4 shows typical stress-strain curves of neat PLA, uncontrolled HAp/PLA, chitosan-modified HAp/PLA, pectin-modified HAp/PLA and hybrid-interface-controlled HAp/PLA without immersion into pseudo biological environment. Neat PLA showed the large plastic deformation, characteristic in thermoplastics resins. On the other hand, uncontrolled, chitosan-modified and pectin-modified HAp/PLAs fractured without large plastic deformation. This indicates that uncontrolled, chitosan-modified and pectin-modified HAp/PLAs fractured before the deformation ability of PLA matrix. It is suggested that the interface between HAp and PLA was not well bonded in uncontrolled, chitosan-modified and pectin-modified HAp/PLAs. However, hybrid-interface-controlled showed larger plastic deformation than neat PLA. Thus, the modification of HAp 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.

Figure 5 shows the water absorption after immersion into pseudo biological environment. Neat PLA showed the smallest water absorption. This means that the interface between HAp and PLA was the location where the water molecules were captured. Among all HAp/PLA composites, the water absorption of hybrid-interface-controlled HAp/PLA was the smallest in the early stage whereas the largest in the later stage. This suggests that un-bonded interface existed although only slightly in hybrid-interface-controlled HAp/PLA and the remaining photo-dissociable protective groups might induce the penetration of protective groups in PLA molecular chain, producing space for water molecules.

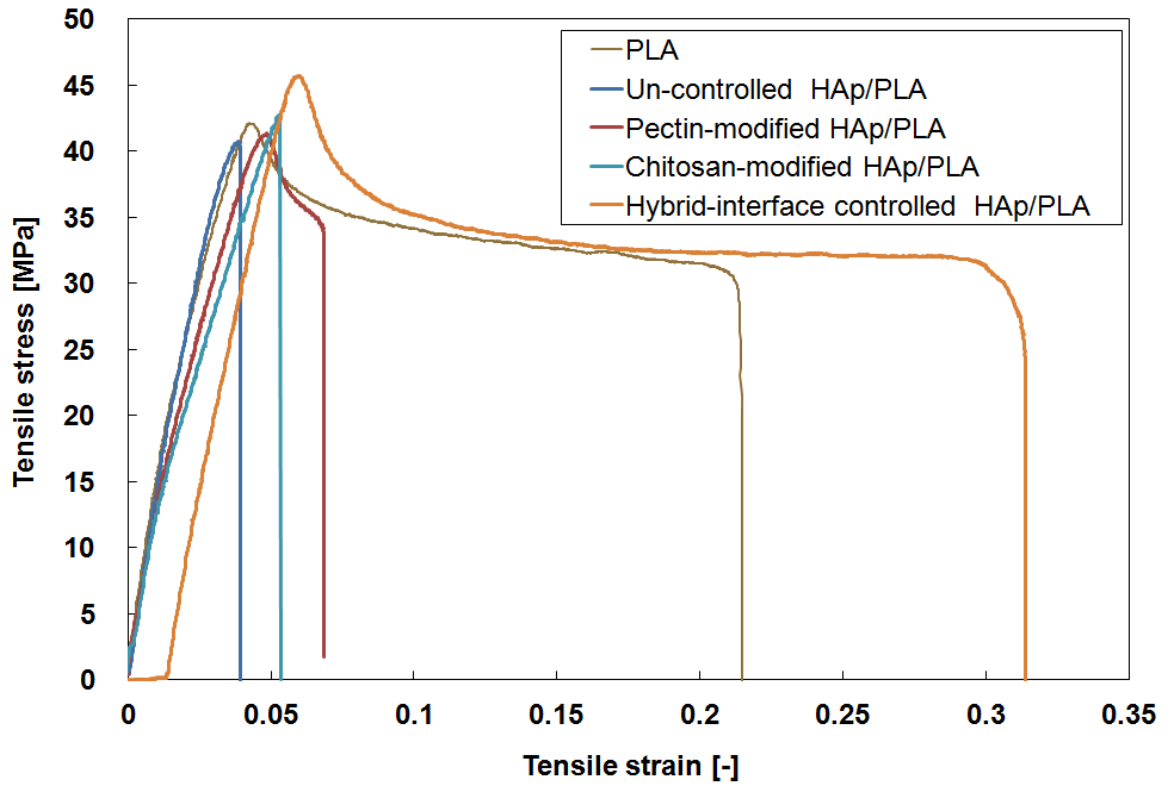


Figure 4. Typical stress-strain curves before hydrolysis.

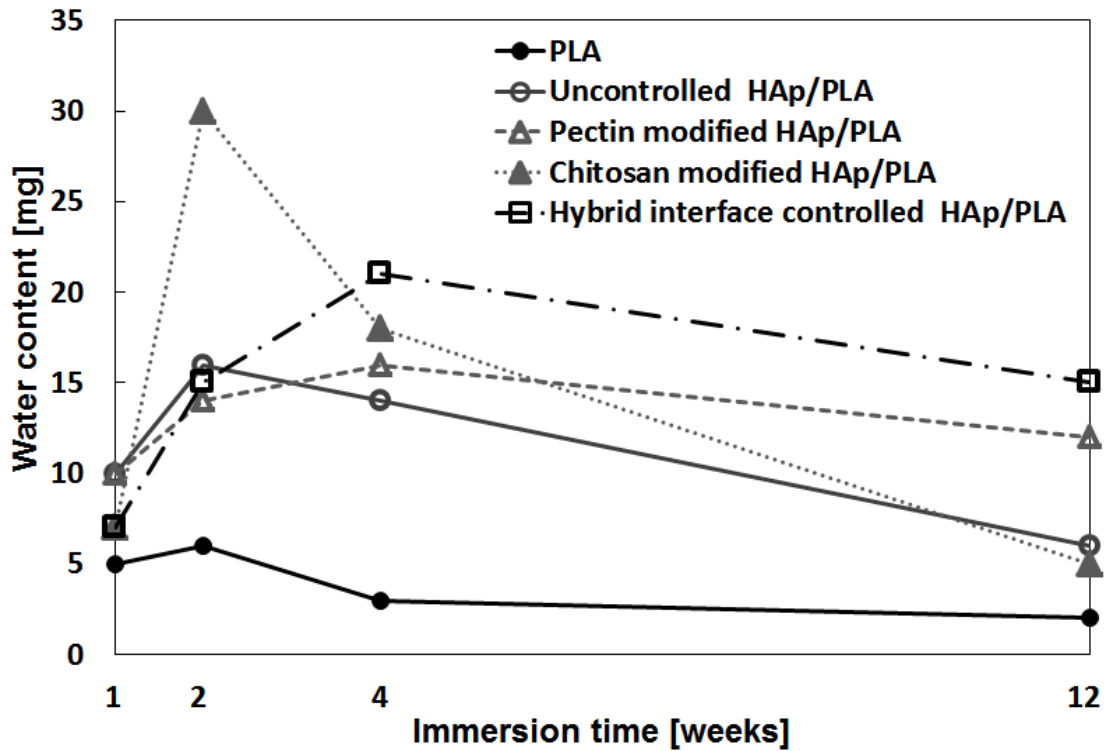


Figure 5. Water absorption after immersion into pseudo biological environment.

Figure 6 shows the effect of hydrolysis on the tensile strength of all prepared specimens. The hydrolytic degradation in the tensile strength of neat PLA was the smallest among those of prepared specimens. In the early stage, the hydrolytic degradation in the tensile strength of un-controlled HAp/PLA was the largest among those of HAp/PLA composites. This tendency could arise if water molecules diffused and localized at un-bonded interface, resulting in local acceleration of hydrolysis. Here, it is notable that still hybrid-interface-controlled HAp/PLA showed larger hydrolytic degradation in the tensile strength than neat PLA. It is suggested that un-bonded interface existed although only slightly in hybrid-interface-controlled HAp/PLA.

In the later stage, HAp/PLA composites still showed larger hydrolytic degradation in the tensile strength than neat PLA. However, hybrid-interface-controlled HAp/PLA showed the largest hydrolytic degradation in the tensile strength among all prepared specimens. It might be considered that PLA molecular chains were affected by remaining photo-dissociable protective groups. Hydrolyzation site might be formed in PLA molecular chain. Therefore, it is suggested that the optimum design/control of the interface-control efficiency and the introduction of the acceleration site in PLA molecular chain could realize the HAp/PLA composites with excellent fracture and hydrolysis properties.

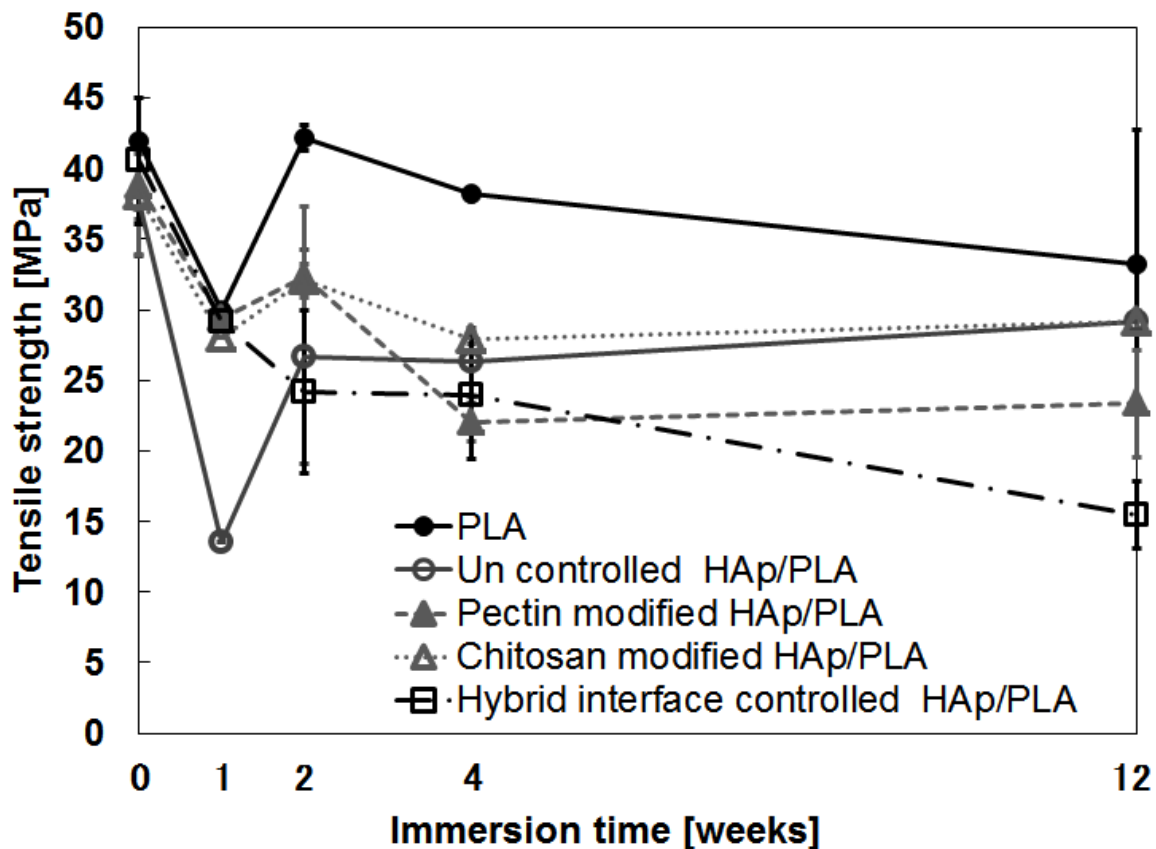


Figure 6. Effect of hydrolysis on tensile strength.

4. Conclusions

In this study, we tried the "hybrid" interface control in HAp/PLA composite materials using both pectin and chitosan. In addition, we evaluated the effect of hydrolysis on deformation and fracture properties in the hybrid-interface-controlled HAp/PLA. As results, hybrid-

interface-controlled HAp/PLA showed the smallest hydrolytic degradation in the tensile strength among HAp/PLA composites in the early stage of hydrolysis, whereas the largest in the later stage. It might be considered that PLA molecular chains were affected by remaining photo-dissociable protective groups. Finally, it is suggested that the optimum design/control of the interface-control efficiency and the introduction of the acceleration site in PLA molecular chain could realize the HAp/PLA composites with excellent fracture and hydrolysis properties. The hybrid-interface-control method proposed in this study has the possibility to control and optimize biodegradability for bone regeneration.

Acknowledgements

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