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Preparation of Anisotropic Hydroxyapatite / Poly-L-Lactic Acid Composites Using Hot-Pressing

WAKAMATSU NOBUKAZU, IIJIMA MAYUMI, KAMEMIZU HIDEO,
ADACHI MASANORI and DOI YUTAKA

The aim of this study was to prepare pore-free hydroxyapatite (HAP) -reinforced poly-L-lactic acid (PLA) composites with an anisotropic microstructure using hot-pressing. Two synthetic HAP powders (HAP 1, HAP 2) with different aspect ratios were prepared in aqueous medium. The morphology of HAP 1 crystals was a thin rectangular plate about 100nm in length and about 25nm in width, whereas that of HAP 2 crystals was a hexagonal column about 6μm in length and about 300nm in width. Each HAP powder was mixed with 30mass % of a commercial PLA powder. The powder compacts were uniaxially hot-pressed at the temperature from 55℃ to 180℃. It was found that the relationship between the bulk density of HAP 1/PLA composites and the linear shrinkage in the loading direction was linear. When the linear shrinkage was 86.3%, the bulk density of HAP 1/PLA composites reached 2.18g/cm^3, which corresponded to the relative density of 99.5%. It was found, therefore, that hot-pressing at 180℃ was effective to make pore-free HAP 1/PLA composites. Under this condition, however, anisotropic HAP 1/PLA composites were not obtained. When HAP 2/PLA composites were hot-pressed at 140℃ and then hot-pressed again at 55℃ under 10kN loading, the bulk density reached 2.14g/cm^3, which corresponded to 97.7% of the theoretical density. It was revealed that hot-pressed HAP 2/PLA composites were composed of glassy PLA matrix and HAP crystals aligned perpendicular to the loading direction near the surface by X-ray diffraction analysis and TEM observation. It was also revealed, however, that the randomness in the orientation of HAP 2 crystals increased toward the center of the composites.

Key words: hydroxyapatite, poly-L-lactic acid, composite, hot-pressing

INTRODUCTION

Since a polylactic acid polymer(PLA), a biodegradable polymer, is essentially non-toxic, and the lactic acid yield after hydrolysis is the normal intermediate of carbohydrate metabolism,[1] PLA polymers are interesting as biodegradable materials not only in dental and orthopaedic applications, but also in drug delivery systems and bone tissue engineering. The mechanical properties of PLA polymers such as Young's modulus, however, are lower than those of bones such as long bones.[2] One way of improving their mechanical properties is to incorporate a second phase such as bioactive hydroxyapatite(HAP).

In designing HAP-reinforced PLA composites, it is preferable that Young's modulus of the composites is matched with that of bone because the stress distribution with a high stress consentration will arise at the interface under loading conditions.[3] Up to the present, however, no HAP-reinforced PLA composite showing Young's modulus similar to that of long bones (longitudinal direction: about 20 GPa[4]) has been obtained, though various attempts[5-10] to prepare the composites have been made.

Bone can be considered a complex natural composite material with load-bearing constituents such as osteons and interstitial lamellae, and even the osteons and interstitial lamella are microstructurally inhomogeneous. They are made up of fibers of an organic constituent, collagen, and an inorganic constituent, hydroxyapatite epitaxially formed on collagen fibers.[11] In long bones, for example, the main constituents have a preferred orientation along the long axis of the bone, and the Young's modulus of the bone is a function of its orientation with respect to the long axis, which is a reflection of the anisotropic microstructure.[4] In order to match Young's modulus of HAP-reinforced PLA composites with that of the bone, therefore, it is necessary to prepare composites with an anisotropic microstructure.

Shown in Fig. 1 is a schematic illustration of hot-pressed anisotropic HAP-reinforced PLA composite, in which HAP

Department of Dental Materials Science, Division of Oral Functional Science and Rehabilitation
Asahi University School of Dentistry

1851 Hozumi, Mizuho, Gifu, 501-0296 Japan
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crystals exhibit a preferred orientation in a plane perpendicular to the pressing direction. As shown in Fig. 1, it is thought that preparation of the anisotropic composite becomes possible when the composite is uniaxially hot-pressed under appropriate conditions. The aim of this study, therefore, is to prepare pore-free HAP-reinforced PLA composites with an anisotropic microstructure by hot-pressing.

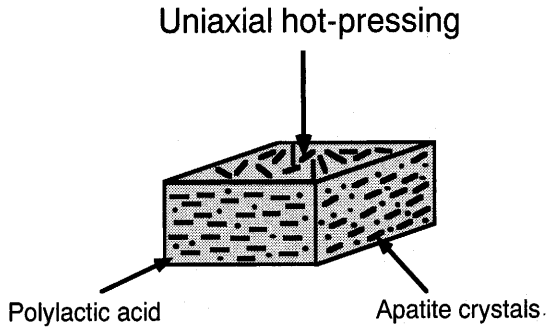

Fig. 1 Schematic illustration of hot-pressed anisotropic HAP-reinforced PLA composite, in which HAP crystals exhibit a preferred orientation in a plane perpendicular to the pressing direction.

MATERIALS AND METHODS

In this study, two kinds of synthetic HAP powders with different aspect ratios were prepared. The first, HAP1, was prepared by adding 4 *l* of 0.3 M phosphoric acid solution to 4 *l* of 0.5 M calcium hydroxide suspension at 100 ℃.[12] After mixing, the suspension was aged while stirring it for 2 weeks at 100 ℃. The suspension was filtered, washed with 4 *l* of distilled water three times, and dried at 80 ℃ for 24 hours. The second HAP powder, HAP2, was prepared by adding 1 *l* of 50 mM calcium acetate monohydrate solution and 1 *l* of 30 mM ammonium dihydrogen phosphate solution to 1 *l* of 1.3 M ammonium acetate solution at 80 ℃.[13] The pH of the solution mixed was maintained at 7.3 ± 0.1 with conc. ammonium hydroxide. After precipitation, the suspension was aged at pH 7.3 ± 0.1 and 25 ℃ for 24 hours, filtered, washed with distilled water three times and dried at 80 ℃ for 24 hours. TEM and SEM observations indicated that the morphology of the HAP1 crystals was a thin rectangular plate about 100 nm in length and about 25 nm in width. On the other hand, that of the HAP2 crystals was a hexagonal column about 6 μm in length and about 300 nm in width.

A commercial PLA powder (Nacali Tesque Inc.) with a molecular weight of 10,000 was used. Shown in Fig. 2 is the powder X-ray diffraction pattern of the PLA powder.

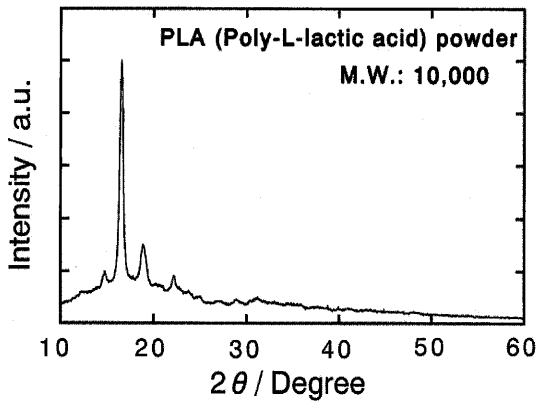

Fig. 2 Powder X-ray diffraction pattern of a commercial poly-L-lactic acid.

The diffraction pattern showed both crystalline and amorphous features. Differential thermal analysis of the PLA powder showed that the melting point of the crystalline phase and the glass transition temperature were 178 ℃ and 54 ℃, respectively.

In order to prepare pore-free HAP-reinforced PLA composites with an anisotropic microstructure, either HAP1 or HAP2 powder was mixed with 30 mass% PLA powder. The mixed powder were pressed uniaxially at 50 MPa into plates (10 mm×10 mm× 5 mm), and pressed isostatically at 600 MPa by using cold isostatic pressing. Shown in Fig. 3 is a schematic illustration of the hot-pressing equipment. For the HAP1/PLA composites, the powder compact was placed in a stainless steel mold, and then kept at 180 ℃ for 20 min before pressing in order to melt the crystalline phase

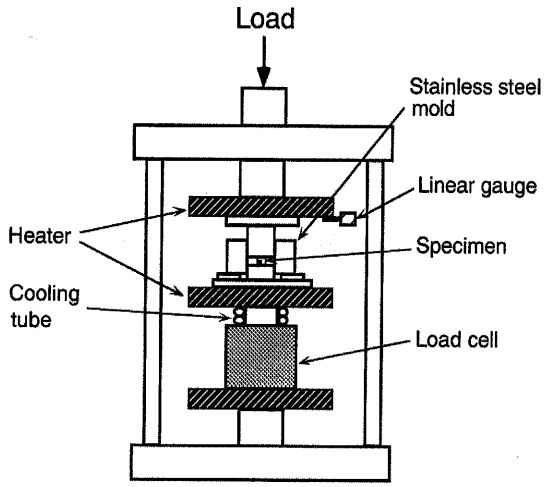

Fig. 3 Schematic illustration of the hot-pressing equipment. A powder compact of HAP/ PLA mixtures was placed in a stainless steel mold, and then kept at the desired temperature for 20 min before pressing. The load was applied by moving the upper plate down, and the linear shrinkage of specimens was measured with a linear gauge.

of the PLA. The load was applied by moving the upper plate down for about 2 min, and the load was maintained from 2 kN to 3 kN during hot-pressing. Linear shrinkage of the specimens was measured using a linear gauge (MLH-327, Mitutoyo Co. Ltd.). The output of a load cell attached to the equipment was amplified (AUTOGRAPH AG-5000 C, Shimadzu Co., Ltd.), sampled at 50 Hz by an analogue to digital converter (MP100, Monte System Co., Ltd.), and analyzed using a data analysis program (AcqKnowledge, Monte System Co., Ltd.). After the specimen was pressed, the temperature was kept at 180 ℃ for 30 min, and gradually cooled to room temperature. For the HAP2/PLA composites, firstly, the specimen was hot-pressed at 140 ℃ for 20 min, and hot-pressed again at 55 ℃, which corresponded to just above the glass transition temperature of the PLA, to align HAP2 crystals perpendicular to the pressing direction. The maximum load of either 5 kN or 10 kN was applied during hot-pressing at 55 ℃.

The bulk density of the hot-pressed HAP-reinforced PLA composites was measured by the fluid displacement method with distilled water, and the relative density was calculated assuming that the theoretical densities of HAP and PLA were 3.16 g/cm^3 and 1.27 g/cm^3, respectively. The orientation of the HAP crystals was estimated from the ratio of the height of reflection from the (002) plane to that of the (300) reflection of HAP crystals evaluated using X-ray diffraction (XD-3A, Shimadzu Co., Ltd.).

RESULTS AND DISCUSSION

Shown in Fig. 4 is the relationship between the bulk density and linear shrinkage in the pressing direction when HAP1 with 30 mass% PLA composites were hot-pressed at 180 ℃. The load from 2 kN to 3 kN was maintained during hot pressing, though the load decreased due to specimen shrinkage. The bulk density of the HAP1/PLA composites increased with the increase in the linear shrinkage. For a linear shrinkage of 86.3 %, the bulk density reached 2.18 g/cm^3, that corresponding to 99.5 % of the theoretical density of the composite. From the results, it was found that hot-pressing at 180 ℃ was effective for making pore-free HAP1/PLA composites. From X-ray diffraction analysis, however, it was found that there was no significant difference between the ratio (I_{002}/I_{300}) of the HAP1/PLA composites hot-pressed at 180 ℃ and that of HAP1 powder. That is, anisotropic HAP1/PLA composites were not obtained when composites were hot-pressed at 180 ℃, and HAP1 crystals exist randomly in three-dimensional directions.

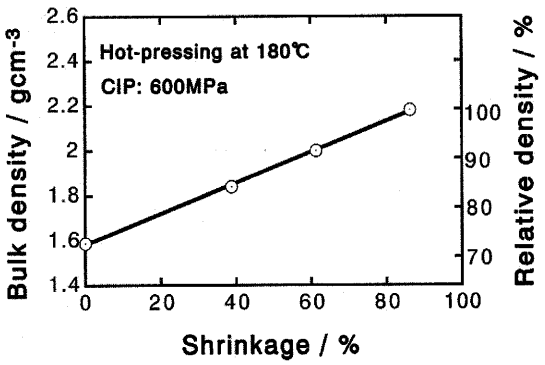

Fig. 4 The relationship between the bulk density and the linear shrinkage of HAP1/PLA composites hot-pressed at 180 ℃.

Shown in Fig. 5 is the bulk density and linear shrinkage of hot-pressed HAP2/PLA composites. Fig. 6 (A) and (B) show the X-ray diffraction patterns of HAP2 powder and the HAP2/PLA composite hot-pressed at 55 ℃, respectively. X-ray diffraction analysis revealed that HAP2/PLA composites hot-pressed at 55 ℃ were composed of glassy PLA, HAP and an other unidentified phase (asterisk shown in Fig. 6 (B)). The orientations of HAP2 crystals in the HAP2/PLA composites evaluated using X-ray diffraction are also summarized in Table 1. The bulk density of the HAP2/PLA composites increased up to 2.0 g/cm^3 (relative density : 91.3 %) when hot-pressed even at 140 ℃, which is considerably lower than the melting point of the PLA. It is thought that the densification of the composites hot-

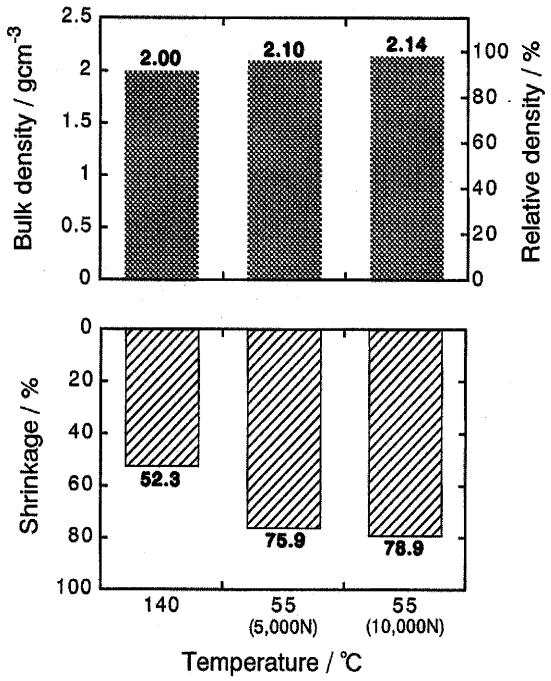

Fig. 5 The bulk density and linear shrinkage of HAP2/PLA composites.

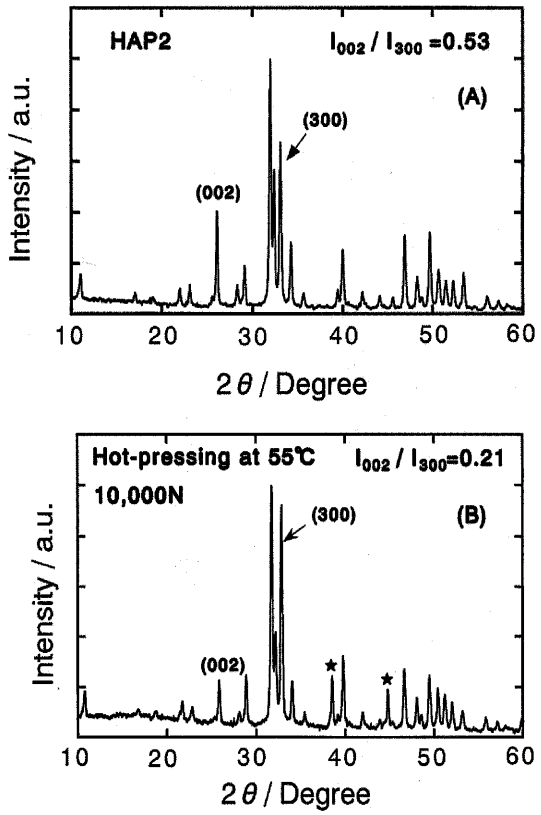

Fig. 6 X-ray diffraction patterns of HAP2 powder(A) and HAP2/PLA composite hot-pressed at 55 ℃ (B).

pressed at 140 ℃ probably happened due to viscous flow of the PLA matrix. As shown in Table 1, however, the ratio of the reflections (I_{002}/I_{300} : 0.45) had slightly decreased compared with that (I_{002}/I_{300} : 0.53) of HAP2 powder. The HAP2/PLA composites hot-pressed at 140 ℃ are thought to be almost isotropic materials, in which HAP2 crystals still exist randomly in three-dimensional directions. One reason why HAP2 crystals do not rotate in the normal direction of the pressing axis with the viscous flow of the PLA matrix might be the high fluidity of the PLA matrix. In order to align HAP2 crystals perpendicular to the pressing direction, therefore, the HAP2/PLA composites hot-pressed at 140 ℃ were hot-pressed again at 55 ℃.

Table 1 The ratio of the height of the (002) reflection to that of the (300) reflaction of the HAP crystals evaluated using X-ray diffraction.

Specimen	I_{002}/I_{300}
HAP2 powder	0.53
Composite hot-pressed at 140℃	0.45
Composite hot-pressed at 55℃ (5 kN)	0.27
Composite hot-pressed at 55℃ (10 kN)	0.21
Composite hot-pressed at 55℃ (10 kN) after polishing:120μm	0.32

As shown in Fig.5, the bulk density and linear shrinkage of composites hot-pressed at 55 ℃ increased with an increase of the applied load. For 10 kN loading, the bulk density reached 2.14 g/cm^3, corresponding to 97.7 % of the theoretical density. When the two X-ray diffraction patterns shown in Fig. 6 are compared, not only a decrease in the height of reflection from the (002) plane, but also an increase in that from the (300) plane of HAP2 crystals is clear. Therefore, it is thought that HAP2 crystals align as an a-axis of those perpendicular to the pressing direction because the aspect ratio of HAP2 crystals is large and the viscosity of the PLA matrix is probably high. Kasuga et al.[9] developed HAP fiber-reinforced PLA composites for artificial bone by hot-pressing. Although Young's modulus to 12 GPa was obtained when the composites were hot-pressed at 180 ℃ under a pressure of 40 MPa, the HAP fibers tended to be agglomerated in the PLA matrix, and the anisotropic microstructure, in which the HAP fibers aligned perpendicular to the pressing direction, was not obtained.

Shown in Fig. 7 is a TEM photograph of the HAP2/PLA composite hot-pressed at 55 ℃ under 10 kN loading. Many hexagonal HAP2 crystals, vertically aligned in the pressing direction, were observed in the subsurface region of the composite. It was found, however, that the ratio of I_{002}/I_{300} increased from 0.21 to 0.32 after polishing the sur-

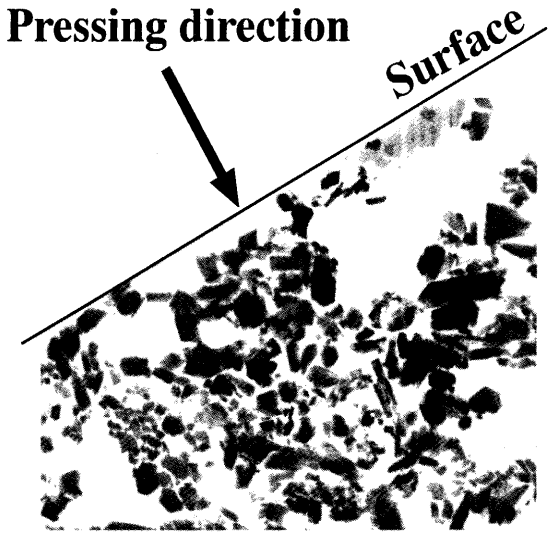

Fig. 7 TEM photograph of the HAP2/PLA composite hot-pressed at 55 ℃ under 10 kN loading. A thin section cut parallel to the pressing direction was observed by TEM.

face of the HAP2/PLA composites by 120 μm. This indicated that the randomness in the orientation of HAP2 crystals increased toward the center, though the crystals aligned perpendicular to the pressing direction only in the vicinity of the surface.

CONCLUSION

Within the limitations of this study, it is suggested as follows:

1) When the HAP1/PLA composites were hot-pressed at 180 ℃, the bulk density of the composites reached 2.18 g/cm³, corresponding to 99.5 % of the theoretical density. It was found, therefore, that hot-pressing at 180 ℃ was effective in making pore-free HAP/PLA composites. In this condition, however, anisotropic HAP1/PLA composites were not obtained.

2) When HAP2/PLA composites were hot-pressed at 140 ℃, and then hot-pressed again at 55 ℃ under 10 kN loading, the bulk density reached 2.14 g/cm³, corresponding to 97.7 % of the theoretical density. It was revealed that hot-pressed HAP2/PLA composites were composed of a glassy PLA matrix and HAP crystals aligned perpendicular to the loading direction in the vicinity of the surface by X-ray diffraction analysis and TEM observation. It was also revealed that the randomness in the orientation of HAP2 crystals increased toward the center of the composites.

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ホットプレスを用いた異方性を示すハイドロキシアパタイト／ポリ乳酸複合体の作製

若松宣一　飯島まゆみ　亀水秀男
足立正徳　土井　豊

抄録：本研究の目的はホットプレスを用いて緻密で異方性を示すハイドロキシアパタイト（HAP）/ポリ乳酸（PLA）複合体を作製することである．アスペクト比の異なる二種類のHAP粉末（HAP1とHAP2）を水溶液から合成した．HAP1は長さおよそ100nm，幅およそ25nmの薄い板状結晶であり，一方HAP2は長さおよそ6μm，幅およそ300nmの六角柱状結晶である．各HAP粉末は30mass%の市販PLA粉末と混合し，その圧粉体を55℃から180℃の温度範囲でホットプレスした．その結果，HAP1/PLA複合体では，加圧軸方向の線収縮率と複合体の嵩密度の間には直線関係が得られた．線収縮率が86.3%の場合，HAP1/PLA複合体の嵩密度は2.18g/cm³にまで増加し，これは相対密度99.5%に相当することが分かった．すなわち，180℃でホットプレスすることは，緻密なHAP1/PLA複合体を作製するには有効である．しかしながら，この条件では異方性を示すHAP1/PLA複合体は得られなかった．HAP2/PLA複合体を140℃でホットプレスし，さらに55℃で10kNの荷重下ホットプレスした場合，その嵩密度は2.14g/cm³まで増加し，それは理論密度の97.7%に相当する．X線回折およびTEM観察から，このHAP2/PLA複合体はガラス状のPLAマトリックスと表面近傍では加圧軸に対して垂直に配向したHAP2結晶からなることが分かった．しかし，このHAP2結晶の配列の不規則性は複合体の中心部に向かって増加することも明らかになった．

キーワード：ハイドロキシアパタイト，ポリ乳酸，複合体，ホットプレス

朝日大学歯学部口腔機能修復学講座歯科理工学分野
501-0296　岐阜県瑞穂市穂積1851