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Analysis of orientation behavior in extruded tricalcium phosphate/poly(lactic acid) composite billet using finite element method and chain network model

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Abstract

The poly(lactic acid) (PLA)–tricalcium phosphate (TCP) composite attracts much attention as a material for a bone fixation device because both have bioabsorbability. However, the applications of the composite bone fixation device are limited to low-loaded regions because of lower strengths. In this study, PLA and TCP/PLA composite cylindrical billets were extruded to improve their strengths, with the aim of clarifying the molecular orientation behavior of the PLA and TCP/PLA billets in extrusion. First, the effect of the orientation behavior in the PLA billets on the extrusion ratio (ER) was calculated. Next, the TCP/PLA billets were analyzed. The molecular orientation obtained by extrusion was investigated by a combination of the finite element method and the chain network model. Consequently, the orientation function of the extruded billet was found to increase with the ER. Furthermore, the orientation function of the TCP/PLA billet was higher than that of the PLA billet, which may be due to the change in the yield stress and n value of the billet by TCP addition. The orientation distribution in the radius direction of the extruded PLA billet showed that the orientation function at the surface region was larger than that at the center region. This orientation distribution might be because the movement distance of the surface region during extrusion was longer than that in the center region. The surface region in the billet was drawn by the difference of those movement distances and might be orientated. The workability of the PLA and TCP/PLA billets was also investigated using pressure during extrusion. The results showed that the extrusion pressure increased with the TCP content and ER. Therefore, extrusion workability decreased with the TCP content and the ER.

Keywords: Molecular orientation, Drawing, Poly(lactic acid), Tricalcium phosphate, Extrusion, Finite element method

1. Introduction

Poly(lactic acid) (PLA) has been investigated as a material for a bone fixation device because it is bioabsorbable and nontoxic (Bergsma et al., 1993; Partio et al., 1992; Yamamuro et al., 1994). However, the application of the PLA bone fixation device is limited because of low stiffness, osteoconductivity, and radiolucency. Therefore, the composites of PLA and bioactive ceramics have also been investigated. This study focuses on bioabsorbable tricalcium phosphate (TCP) as one of the various bioactive ceramics and investigates the TCP/PLA composite. The mechanical properties, particularly strength, of particle-filled composites, such as TCP/PLA, are decreased by the stress concentration around the filler particle. Therefore, the effect of the particle surface modification on the mechanical properties of the particle-filled composites is studied (Qiu et al., 2005; Cui et al., 2009; Kunze et al., 2003). Qiu et al. modified hydroxyapatite (HA) nanoparticles using an L-lactic acid oligomer (Qiu et al., 2005). As a result, the tensile strength,

modulus, and thermal stability of the surface-modified HA/poly (L-lactic acid) composites were improved. On the contrary, the strength of the surface-modified particle-filled composites did not significantly exceed that of the matrix polymer.

The drawing of a polymer, such as PLA, has been investigated to improve mechanical properties (Leenslag and Pennings, 1987; Eling et al., 1982; Droscher and Bandara, 1982; Li et al., 2020; Sakaguchi and Kobayashi, 2015). Leenslag and Pennings (1987) reported that the PLA fiber strength reached 2.1 GPa by dry spinning and subsequent hot drawing. Eling et al. drew the PLA fiber under various conditions. Consequently, the tensile strength of the drawn PLA fiber depended on the draw ratio, molecular weight, and drawing temperature (Eling et al., 1982). Recently, drawing using plasticity techniques for metal, such as pull-out, extrusion, and forging, has been applied to bulk polymers. Droscher and Bandara (1982) investigated the effect of drawing temperature, rate, and ratio on the extrusion pressure, degree of orientation, and mechanical and thermal properties of solid-state extruded copoly(ether ester)s. Li et al. investigated the effect of equal channel angular pressing (ECAP) on the mechanical and physical properties and *in vitro* degradation behaviors of the β -TCP/PLA composites. Their result showed that the bending strength of β -TCP/PLA increased to a maximum of 158 MPa through ECAP (Li et al., 2020). The shear strength of the PLA screw was increased to a maximum of 90 MPa by extrusion (Sakaguchi and Kobayashi, 2015). The mechanical properties of the drawn polymer depend on the molecular orientation that occurs by drawing. The orientation depends on the drawing condition. Complex orientation occurs in bulk polymer drawing.

Molecular orientation by drawing was analyzed to elucidate the orientation mechanism (Shang et al., 2015; Wong et al., 2008; Sakaguchi et al., 2019). Shang et al. (2015) simulated the uniaxial deformation of polyethylene using a molecular dynamics model. They found that in uniaxial deformation, sliding between macromolecules dominates after the chains are stretched and extended. Wong et al. (2008) applied two network models, namely, the affine and pseudo-affine models, to explain the orientation behavior of a tensile-drawn PLA film. Their result suggested that the orientation behavior of PLA appears to follow the pseudo-affine model at the macroscopic level. As described earlier, the orientation behavior of the drawn polymer was also analyzed. On the contrary, there are few examples of the orientation behavior analysis on the matrix in the drawn composite.

This study aims to clarify the molecular orientation behavior of the TCP/PLA billet during extrusion. The combined analysis of the finite element method (FEM) and the chain network model is used to simulate the molecular orientation of the extruded TCP/PLA billet. In a past study, this analysis simulated the molecular orientation of the extruded PLA billet (Sakaguchi et al., 2019). The present study uses the material properties under the drawn temperature for the FEM to investigate the deformation behavior of the extruded TCP/PLA billet.

2. Analytical Method

2.1 Compression Testing Under Drawing Temperature

A PLA pellet with a weight average molecular weight of approximately 155,000 and TCP powder with a particle size of approximately 5.32 μm were prepared for specimen molding. The PLA pellets were dried in a drying oven at 70°C for more than 7 h. The PLA pellets and the TCP powder were then dry-blended and kneaded using a twin-screw kneading extruder (Kurimoto, Ltd., S1 KRC kneader). The kneading conditions were as follows: TCP content, 15 mass%; kneading temperature, 200°C; and screw rotation number, 81 rpm. The kneaded compound was pulverized, and a cylindrical billet was molded by compression molding. In compression molding, the TCP/PLA compound was heated to 200°C and pressurized by cold pressing of a plunger at 40 MPa under room temperature. The diameter and length of the compression-molded TCP/PLA billet were approximately 6 and 10 mm, respectively.

The material properties of the TCP/PLA billet under drawing temperature were obtained in the compression test using a servopulser fatigue and endurance testing machine equipped with an electric furnace (Shimadzu, Servopulser EHF-FD1-4LA). This compression testing was conducted at a test speed of 0.5 mm/min under 130°C. Strain gauges were bonded in the axial and circumferential directions of the specimen to determine the Poisson's ratio.

Table 1 presents the material properties of the TCP/PLA billet obtained in this compression testing and the material properties of the PLA billet as a control.

Table 1 Material properties of the compression-molded billet under 130°C.

	PLA	TCP/PLA
TCP content [mass%]	0	15
Elastic modulus [MPa]	5.22	181.9
Poisson's ratio	0.156	0.344
Yield stress [MPa]	0.0964	4.57
n Value	0.487	0.282

2.2 Analysis of Deformation Behavior Using FEM

The plastic strain in the axial direction obtained during extrusion was calculated by the FEM using ANSYS Ver 19 as the solver software. Extrusion was a drawing method in which the cylindrical billet was heated to between the glass transition and melting points and then extruded by forward extrusion. This analysis was an elastic–plastic analysis assuming a static deformation. The Hollomon equation was used as the constitutive equation for the plastic region. The material properties in Table 1 were substituted in this analysis.

The analysis model constituted a metal mold of extrusion and the PLA billet (Figure 1). The model was a two-dimensional axisymmetric model. The extrusion ratio (ER) was determined as the ratio of the cross-sectional area of the pre-extruded billet and the postextruded rod. This ratio corresponds to the ratio of the length of the extruded rod to the original length when it can be assumed that no volume change happens during extrusion. The dimensions of the models and the billets for each ER were determined as shown in Table 2 such that the extruded rod length was the same. Extrusion was simulated by applying the same displacement as the billet length. The billet underwent a large deformation during extrusion. Therefore, the model shape of the PLA billet was rezoned during analysis, and the model mesh was reconstructed.

Billets of ERs of 1.3, 2, 4, and 8 were analyzed for the FEM. Since ER and dice angle were large in this study, deformation of billet might be dominant for pressure and strain generated during extrusion. Therefore, the friction between the mold and the PLA and /or the TCP/PLA billet was ignored. The mesh was a quadrangular free mesh of 0.3 mm with four nodes. The mechanical properties of the metal mold were markedly higher than those of heated PLA and TCP/PLA; hence, the metal mold was rigid. The von Mises yield criterion was used in the FEM.

Fig. 1 Geometry of the simulation model.

Table 2 Dimension of modeling for extrusion ratios of 1.3 to 8.

Extrusion Ratio	l mm	d_1 mm	d_2 mm	d_3 mm	R mm
1.3	30	7.5	7	6	0.5
2	21	9	8.5		
3	16	11	10.4		
4	13	13	12		
8	7	17.5	17		

2.3 Analysis of Orientation Behavior Using a Chain Network Model

The chain orientation behavior during uniaxial drawing can be described by two theoretical models: (i) affine model and (ii) pseudo-affine model (Wong et al., 2008). The pseudo-affine model agreed well with the experimental orientation function of the extruded PLA rods in past studies (Sakaguchi et al., 2019). Therefore, the pseudo-affine model was used herein. In the pseudo-affine model, the orientation function f in the tensile deformed polymeric material was obtained as follows (Kang et al., 2001):

$$f = \frac{1}{2} \left(\frac{2\lambda^3 + 1}{\lambda^3 - 1} - \frac{3\lambda^3 \cos^{-1} \lambda^{-3/2}}{(\lambda^3 - 1)^{3/2}} \right), \quad (1)$$

where λ is the ratio of the length of the extruded rod l to the original length l_0 . The ratio λ was calculated using the following equation from the true strain ε_t in each node obtained by the FEM:

$$\lambda = \frac{l}{l_0} = e^{\varepsilon_t}. \quad (2)$$

The three-dimensional true strain can be obtained from the FEM, while the experimental value of the orientation function was only obtained in axial direction. Therefore, the axial true strain was used as ε_t in this study to compare with experimental values.

3. Experimental Method

3.1 Extrusion of the PLA and TCP/PLA Billets

PLA and TCP/PLA billets prepared in Section 2.1 were drawn at ER 1, 2, 4 and 8 by the extrusion drawing. Those billets were set in a mold, and heated to 130°C for 10 minutes. Then, compressive loading was applied to the heated billet via a push component with a hot press system. The extruded rod was taken from the hot press system and cooled to 50°C or below. The billet and mold with same dimensions as in Table 1 were used for extrusion drawing at each ER. The length and diameter of billet at ER1 were respectively 40 mm and 6 mm. The billet at ER 1 was not extruded, although was heated to 130°C. Polyethylene glycol was sprayed as lubricant to decrease the friction between molds and billet. The length and diameter of the extruded rods were about 40 mm and 6 mm at all ER, respectively.

3.2 Characterization of Molecular Orientation

The molecular orientation of the extruded rod in the axis direction was characterized by determining the orientation function using polarized infrared (IR) spectroscopy. The specimen was buried in an epoxy matrix and cut in the axis direction. The cut cross-sectional surface was polished with emery paper and buffing. The IR spectra on this cross-sectional surface were recorded using a Fourier transform infrared spectrometer (IR Prestige-21, Shimadzu) equipped with a single reflection-type attenuated total reflection measuring device (MIRacle A, PIKE Technology) and a grid polarizer (GPR-8000, Shimadzu). The IR spectra were measured using a polarized infrared beam in parallel and perpendicular directions to the axis direction of the extruded rod (Figure 2). The resolution of this measurement was 4.0 cm⁻¹.

Oriented PLA consisting of α crystals exhibited an absorption peak at 923 cm⁻¹, which can be assigned to the CH₃ rocking mode showing a transition moment perpendicular to the chain axis (Kang et al., 2001). Therefore, the IR dichroic ratio R for the band in 923 cm⁻¹ was calculated as follows:

$$R = \frac{A_p}{A_s}, \quad (3)$$

where A_p and A_s are the absorbances of the polarized IR in the perpendicular and parallel directions to the axial direction, respectively. The crystalline chain orientation function f_c was calculated from R as follows:

$$f_c = \frac{R-1}{R+2} \frac{R_0+2}{R_0-1}, \quad (4)$$

where R_0 is $2\cot^2\phi$ and ϕ is the angle between the transition moment associated with the considered absorption and molecular axis, with ϕ being 90° (Sawai et al., 2003).

Fig. 2 Schematic view of the specimen embedded in epoxy resin and polarized direction of infrared light.

4. Results and Discussion

4.1. Effect of the TCP Content and Extrusion Condition on the Orientation Behavior

Figures 3 and 4 depict the contour views of the axial plastic strain on the extruded PLA and TCP/PLA billets. Figure 5 illustrates the plastic strain distributions in the axial center of each contour view. The axial center position in each contour view is indicated by the red broken lines in Figures 3 and 4. The orientation function distributions calculated from Figure 5 at each ER are shown in Figure 6. Figure 7 illustrates a comparison of the analysis and experimental values. The analysis values are the average of the orientation function distribution in Figure 6. The experimental values were plotted from ER1 as a control. The TCP/PLA billets of ER4 and 8 could not be extruded through. Hence, the experimental values could not be plotted in ER 4 and 8.

The orientation function of the extruded PLA and TCP/PLA rod increased with the ER (Figure 7) and saturated in ER 4 and above. The orientation functions of the TCP/PLA rod were higher than those of the PLA rod. These results suggested that the orientation function in the extruded rod increased with the ER and the TCP content. The mechanical properties of PLA at the drawn direction increased with the orientation function and/or degree of orientation (Droscher and Bandara, 1982; Sakaguchi and Kobayashi, 2015). Therefore, the mechanical properties of the extruded rod might increase with the ER and the TCP content.

The orientation function of the experimental value was lower than that of the analysis values (Figure 7). This might be due to the relaxation of orientation after extrusion. The same tendency was shown in a past study comparing the analytical and experimental values of the orientation function on the extruded PLA (Sakaguchi et al., 2019).

The distribution of the plastic strain and the orientation function in Figures 5 and 6 showed the same trend. Consequently, the orientation function increased with the plastic strain generated during extrusion. Therefore, we focused on the plastic strain to investigate the orientation behavior during extrusion. The comparison of the strain distributions in Figures 3 and 4 was almost homogeneous in the axial direction at ER 1.3 to 4. On the contrary, the comparison of the radial direction in Figures 5 showed that the plastic strain on the surface region of the extruded rod was larger than that on the center region. The surface and center regions were over and under 1 mm, respectively, from the center axis. This may be due to the difference in the movement distance of the material during extrusion. The movement distance was the shortest on the central axis and the longest on the surface in contact with the mold. Hence, the material in the surface region was stretched, and a strain larger than that in the central region was generated. This tendency was in agreement with the deformation behavior during the forward extrusion of the lead rod (Eisbein et al., 1931). Therefore, the molecular chain on the surface region in the extruded rod may orient compared to that of the center region. Hence, the bending strength of the extruded rod may improve compared to the tensile strength.

No significant difference was found between the strain distributions of the extruded PLA and TCP/PLA rods. By contrast, the extruded TCP/PLA rod was longer than the PLA rod, and the strain was larger. The difference between the PLA and TCP/PLA billets in this analysis is the material properties shown in Table 1. Therefore, the strain generated during extrusion may depend on the material properties. The yield stress and the elastic modulus of heated TCP/PLA billet were larger than that of PLA billet as shown Table 1. Therefore, the flow of the TCP/PLA billet during the extrusion might not be able to follow the shape of the mold. As a result, the extruded composites billet shrank in the radial direction as shown in Figure 4, in particular ER2. This radial shrinkage caused an axial elongation because the volume of the billet is not change in plastic deformation.

Fig. 3 Axial direction plastic strain of the extruded PLA rod.

Fig. 4 Axial direction plastic strain of the extruded TCP/PLA rod.

Fig. 5 Plastic strain distribution in the radial direction on the extruded PLA and TCP/PLA rods.

Fig. 6 Orientation function distribution in the radial direction of the extruded PLA and TCP/PLA rods.

Fig. 7 Comparison between the analytical and experimental orientation functions.

4.2. Effect of the TCP Content on Extrusion Workability

The pressure generated between the billet and the ram is called the extrusion pressure. Figure 8 was plotted the average of the extrusion pressure to investigate extrusion workability. Consequently, the extrusion pressure increased with the ER and contained TCP. The TCP content particularly increased the extrusion pressure of 1.36 MPa to 28.2

MPa at ER 8. The increase extrusion pressure with ER is due to increase deformation amount of billet. The stress increase with deformation amount, resulting in an increase in extrusion pressure. In addition, the increase extrusion pressure with contain of TCP might be due to change of the material properties. The yield stress of the heated TCP/PLA billet was about 47.4 times that of the PLA billet as shown in Table 1. Therefore, TCP content and increase of ER increase extrusion pressure, and decrease workability. On the other hand, TCP content and increase of ER increase deformation amount of billet, resulting in further orientation of the molecular chain. As a result, the mechanical properties of billet might increase.

Fig. 8 Relationship of the extrusion pressure and the ER during extrusion.

5. Conclusions

This study investigated the molecular orientation behavior of the TCP/PLA composite billet during extrusion by analysis using the combination of the FEM and a molecular network model. The results suggested that the orientation function of the extruded rod increases with the ER and TCP content. The plastic strain distribution simulated using the FEM showed that the strain of the extruded rod on the surface region was larger than that on the center region.

Extrusion workability was investigated using extrusion pressure. Consequently, extrusion pressure increased with the TCP content and the ER. Therefore, extrusion workability decreased with the TCP content and the ER.

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