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Research paper

Mechanical and biodegradable properties of porous titanium filled with poly-L-lactic acid by modified in situ polymerization technique

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ABSTRACT

Porous titanium (pTi) can possess a low Young's modulus equal to that of human bone, depending on its porosity. However, the mechanical strength of pTi deteriorates greatly with increasing porosity. On the other hand, certain medical polymers exhibit biofunctionalities, which are not possessed intrinsically by metallic materials. Therefore, a biodegradable medical polymer, poly-L-lactic acid (PLLA), was used to fill in the pTi pores using a modified in-situ polymerization technique. The mechanical and biodegradable properties of pTi filled with PLLA (pTi/PLLA) as fabricated by this technique and the effects of the PLLA filling were evaluated in this study.

The pTi pores are almost completely filled with PLLA by the developed process (i.e., technique). The tensile strength and tensile Young's modulus of pTi barely changes with the PLLA filling. However, the PLLA filling improves the compressive 0.2% proof stress of pTi having any porosity and increases the compressive Young's modulus of pTi having relatively high porosity. This difference between the tensile and compressive properties of pTi/PLLA is considered to be caused by the differing resistances of PLLA in the pores to tensile and compressive deformations. The PLLA filled into the pTi pores degrades during immersion in Hanks' solution at 310 K. The weight loss due to PLLA degradation increases with increasing immersion time. However, the rate of weight loss of pTi/PLLA during immersion decreases with increasing immersion time. Hydroxyapatite formation is observed on the surface of pTi/PLLA after immersion for ≥8 weeks. The decrease in the weight-loss rate may be caused by weight gain due to hydroxyapatite formation and/or the decrease in contact area with Hanks' solution caused by its formation on the surface of pTi/PLLA.

1. Introduction

For biomedical titanium alloys, a low Young's modulus similar to that of cortical bones (10–30 GPa) is an important property to prevent the stress shielding effect (Niinomi, 2008). Therefore, lowering the Young's modulus of titanium alloys was investigated; new β-type alloys with a bcc lattice and possessing Young's moduli of around 40–60 GPa have been developed in the past two decades (e.g., Ahmed et al., 1996;

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Hao et al., 2006; Kuroda et al., 1998; Matsumoto et al., 2005; Saito et al., 2003). These titanium alloys possessing low Young's moduli help mitigate the harmful effects of stress shielding on bone healing and remodeling, such as thinning and disappearance; however, these alloys do not completely solve this problem because their Young's moduli are still higher than those of cortical bones (Sumitomo et al., 2008). Therefore, it is essential to further lower the Young's modulus of titanium alloys such that it is equal to those of cortical bones.

One approach to obtain an even lower Young's modulus is to use porous metallic materials. For example, the Young's modulus of porous titanium (pTi) has been reported to be lower than that of solid titanium, and a Young's modulus equal to that of cortical bone has been achieved by controlling porosity (Erk et al., 2008; Esen and Bor, 2007; Murray and Dunand, 2006; Oh et al., 2002, 2003). However, the mechanical strength of pTi deteriorates drastically with the increase in porosity (Esen and Bor, 2007; Oh et al., 2002, 2003). In order to improve the deteriorated mechanical properties and to retain the low Young's modulus of pTi, Nakai et al. proposed using a medical polymer possessing a Young's modulus lower than those of cortical bones to fill in the pTi pores (Nakai et al., 2008a,b, 2010). To fabricate pTi filled with the medical polymer, a new polymer filling process that can yield a fairly high filling rate of the polymer in the pTi pores was developed previously using the corresponding monomer solution with low viscosity. This polymer filling improved the tensile strength of pTi while preventing the increase in its Young's modulus. However, polymethylmethacrylate (PMMA), which exhibits non-biofunctionality, was used as the medical polymer for filling in the pTi pores. If the polymer used to fill in the pTi pores possesses any biofunction that is not intrinsically present in metallic materials, its biofunction can be imparted to pTi in addition to the improvement in the mechanical strength; pores are an attractive space for imparting additional functions to metallic biomaterials. Therefore, poly-L-lactic acid (PLLA), which exhibits biodegradability, was employed as the medical polymer filling in this study. The pTi pores have been reported to play a role in enhancing bone ingrowth (osteoconductivity) when pTi is implanted in animals (Cameron et al., 1976; Kienapfel et al., 1999; Ryan et al., 2006). Osteoconductivity is supposed to disappear in the case that the pTi pores are filled with PMMA. However, when PLLA is employed as a filling material, the mechanical strength of pTi should be improved at an early stage of implantation, and its osteoconductivity should appear after biodegradation inside the pores.

Therefore, on the basis of the above-mentioned material design, pTi filled with PLLA (pTi/PLLA) was fabricated using the developed process, which was optimized for filling PLLA; its mechanical and biodegradable properties as well as the effects of the PLLA filling on these properties were evaluated in this study.

2. Experimental

2.1. *Preparation of porous titanium*

In order to evaluate the tensile properties of pTi/PLLA, seven kinds of pTi samples with porosities of 22%–50%—the same as the samples used in the previous study (Nakai et al., 2008b, 2010)—were used in this study for the tensile test; details of the preparation procedure have been reported elsewhere. The particle-diameter range and porosity of the pTi tensile samples are listed in Table 1. The names of the pTi tensile samples correspond to the maximum particle diameter of titanium powder and the porosity of pTi; for example, pTi45-22 represents a sample with the porosity of 22% produced using titanium powder with the maximum particle diameter of 45 μm. The porosity, or the volume fraction of pores in pTi, was calculated using the ratio of the apparent specific gravity to the absolute value of titanium. Fig. 1 shows a photo of a representative tensile sample (pTi150-38) prepared in this study. A tensile sample with a cross section of 3 mm × 2 mm and parallel-part length of 13 mm (gauge length of 10 mm) were cut from the sintered pTi disk with a diameter of 100 mm and thickness of 2 mm by water jet machining. The microstructures of pTi tensile samples with porosities of 22%–50% have already been reported (Nakai et al., 2008b, 2010). They were observed by optical microscopy and scanning electron microscopy (SEM). The sintering rate was dependent on both the sintering condition and the titanium particle diameter; sintering proceeded rapidly with increasing sintering temperature and time and with decreasing titanium particle diameter. Moreover, the constituent phase in the pTi tensile samples was identified by X-ray diffraction analysis (XRD). Each pTi tensile sample comprised a single α phase.

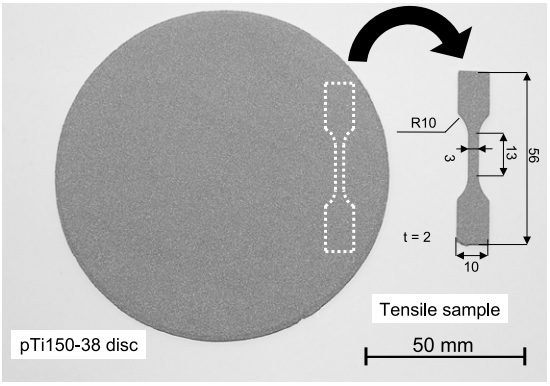

Fig. 1 – Photos of representative porous titanium (pTi150-38) disk of 2 mm thickness and the resultant tensile sample.

To evaluate the compressive properties of pTi/PLLA, pTi samples for use in the compressive test were prepared by partial sintering of titanium powder, which was also done for the tensile samples. Spherical titanium powder produced by a gas atomization technique (Ti: bal., O: ≤0.13 mass%) (Onishi et al., 2007; Shiraishi et al., 1995) was used as a starting material for the pTi compressive samples. This powder was sieved into three different particle diameters—less than 45 μm, 45 to 150 μm, and 150 to 250 μm—with average particle diameters of 24, 79, and 179 μm, respectively (Onishi et al., 2007). They were used to fill a cylindrical zirconia tap with a diameter of 100 mm and thickness of 50 mm. Fig. 2 shows a schematic drawing of the sintering conditions