Bioactivity Treatment to Polylactic Acid Fabric Cloth and Foam by Precipitation of Apatite Nuclei

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An aqueous solution with doubled ion concentration of simulated body fluid (2.0SBF) was prepared. In order to impart hydroxyapatite formation ability to polylactic acid (PLA) matrixes, the PLA fabric cloth and foam were immersed in 2.0SBF and the pH value was increased. By this treatment, apatite nuclei were precipitated on the PLA matrixes. By immersing in physiological SBF, hydroxyapatite layer was formed on the surface of the PLA matrixes and hydroxyapatite formation ability was successfully performed.

Key words: polylactic acid, hydroxyapatite formation ability, apatite nuclei.

1. INTRODUCTION

When either pH or temperature of simulated body fluid (SBF) with inorganic ion concentrations nearly equal to those of human blood plasma [1-4] is raised, fine particles of calcium phosphate are precipitated in the fluid. Recently, we found that the fine particles have high activity to induce hydroxyapatite (HA) formation in SBF and named this fine particle Apatite Nucleus (AN) [5,6].

Organic polymeric materials have advantages about its excellent flexibility and formability in comparison with metallic and ceramic materials. Among them, polylactic acid (PLA) has been widely applied as one of the most typical biodegradable biomaterials and already used as bone fixation devices and scaffolds. It is well known that most of bioactive materials spontaneously form HA layers on their surfaces and can bond to living bone through the layers [2,3]. If PLA acquire high HA formation ability, range of its clinical application will be largely extended.

In our previous study, we precipitated ANs in the pores of the porous polyethylene [7], sandblasted polyethylene terephthalate [8] and acid-treated polyetheretherketone [9,10] and imparted high HA formation ability to these polymers. These polymeric composites spontaneously formed HA layer in SBF and the HA layer showed high adhesive strength to the composites by mechanical interlocking effect because of their existence of pores.

In this study, we applied PLA foam and fabric cloth as porous matrixes and precipitated ANs on the surface of these PLA matrixes for imparting HA formation ability to biodegradable polymeric materials. HA formation ability was examined by immersing in SBF with physiological condition.

2. MATERIALS AND METHODS

2.1 Preparation of SBFs

SBF with ion composition shown in Table I was prepared by dissolving reagent-grade NaCl, NaHCO3, KCl, K2HPO4∙3H2O, MgCl2∙6H2O, CaCl2, and Na2SO4 in ultrapure water and its pH value was controlled at pH 7.40 at 36.5 °C by using tris-hydroxymethyl-aminomethane and 1 mol∙m-3 HCl.

2.0SBF, which is the aqueous solution with doubled ion concentration of that of SBF as shown in Table I, was prepared by dissolving the doubled amount of the above chemical reagents in ultrapure water and its pH value was controlled at pH 7.40 at 36.5 °C by using tris-hydroxymethyl-aminomethane and 1 mol∙m-3 HCl.

2.2 Precipitation of ANs on PLA matrixes

The PLA fabric cloth (Corefront, Tokyo, Japan) and its foam (Kasahara Industry, Fukushima, Japan) were immersed in 2.0SBF. Subsequently, the pH value of 2.0SBF was increased to 8.20 at 36.5 °C by dissolving tris-hydroxymethyl-aminomethane and kept at 36.5 °C for 1 day. By this treatment, ANs were precipitated on the surface of the PLA matrixes. After the immersion, the PLA matrixes were washed with distilled water and dried at room temperature. We denoted the obtained material as ‘bioactive PLA’ hereafter.
2.2 Examination of HA formation ability

HA formation ability of the bioactive PLA was examined by immersing in SBF at 36.5 °C for 14 days. After the immersion, the bioactive PLA was washed in distilled water and air-dried. The surface of the bioactive PLA was analyzed by thin film X-ray diffraction instrument (TF-XRD; Rint 2500, Rigaku, Tokyo, Japan), scanning electron microscope (SEM; ESEM-2700, Nikon, Tokyo, Japan) and energy dispersive X-ray analyzer (EDX; DX-4, EDAX, USA).

3. RESULTS AND DISCUSSION
3.1 Bioactive PLA fabric cloth

Fig.1 shows the XRD patterns of the surface of the untreated PLA fabric cloth, the bioactive PLA fabric cloth before immersing in SBF, and that after immersing in SBF. For the untreated fabric cloth and the bioactive fabric cloth before immersing, diffraction peaks of HA were not observed. After immersing in SBF, diffraction peaks of HA were slightly detected. This result indicates that HA formation was induced by ANs precipitated on the PLA fabric cloth.

Fig.2 shows the SEM images and the EDX spectrum of the surface of the bioactive PLA fabric cloth after the precipitation of ANs. In the EDX spectrum, peaks of Ca and P were observed on the surface of the PLA fabric cloth. This result suggests that ANs were formed on the surface of the PLA fabric cloth by immersing in 2.0SBF and subsequently increasing the pH value. By the SEM observation, however, the particles-like precipitates were not observed. This result suggests that the precipitated ANs were extremely minute and could not be detected by the SEM method similar to our previous study [8].

Fig.3 shows the SEM images and the EDX spectrum of the surface of the bioactive PLA fabric cloth before immersing in SBF. By the SEM observation, it was observed that the whole surface of the PLA fabric cloth was covered with coatings which characterize HA formed in SBF. In the EDX spectrum, peaks of Ca and P, constituents of HA, were strongly detected in comparison with those before immersing shown in Fig.1(c). This result indicates that HA formation was induced by ANs precipitated on the surface of the PLA fabric cloth and grew on the surface in the physiological SBF. From these results, it is considered that bioactivity treatment using ANs are applicable to biodegradable polymers.
3.2 Bioactive PLA foam

Fig. 4 shows the XRD patterns of the surface of the untreated PLA foam, the bioactive PLA foam before immersing in SBF, and that after immersing in SBF. For the untreated foam and the bioactive foam before immersing, diffraction peaks of HA were not observed. After immersing in SBF, diffraction peaks of HA were clearly observed. This result indicates that HA formation was induced by ANs precipitated on the PLA foam similar to the case of the fabric cloth described in 2.1.

Fig. 5 shows the SEM images and the EDX spectrum of the surface of the bioactive PLA foam after the precipitation of ANs. In the EDX spectrum, peaks of Ca and P, constituents of HA, were strongly detected in comparison with those before immersing shown in Fig. 5(c). This result indicates that bioactivity treatment using ANs are advantageous to not only material selectivity but also shape selectivity.

4. CONCLUSION

We precipitated ANs on the surface of the PLA fabric cloth and foam by immersing in 2.0SBF and subsequently increasing the pH value. By the SEM observation, however, the particles-like precipitates were not observed. This result suggests that the precipitated ANs were extremely minute and could not be detected by the SEM method similar to the case of the fabric cloth.

Fig. 6 shows the SEM images and the EDX spectrum of the surface of the bioactive PLA foam after immersing in SBF. By the SEM observation, it was observed that the whole surface of the PLA foam was covered with coatings which characterize HA formed in SBF. In the EDX spectrum, peaks of Ca and P, constituents of HA, were strongly detected in comparison with those before immersing shown in Fig. 5(c). This result indicates that HA formation was induced by ANs precipitated on the surface of the PLA foam and grew on the surface in the physiological SBF similar to the case of the fabric cloth. From these results, it is considered that bioactivity treatment using ANs are advantageous to not only material selectivity but also shape selectivity.
5. REFERENCES


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