Processing Technology and Characteristic Evaluation of Polylactic Acid/316L Stainless Steel Composite Braids with Hydroxylapatite Deposition

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Abstract.

Biodegradable polymer has been widely used in surgical suture, dressing, artificial bone and other bone-related applications. Studies have demonstrated that metals, such as titanium, titanium alloys or 316L stainless steel, can be widely used in dental and maxillofacial surgeries. The present study aimed to fabricate a scaffold with a blend of multilayer polylactic acid (PLA) ply yarns with 316L stainless steel (SS) braids, which was then immersed in simulated body fluid (SBF), forming the PLA/SS composite braid with hydroxylapatite deposition. After being immersed in SBF for 14 days, the PLA/SS composite braid was covered with precipitate which was confirmed to be apatite deposition according to surface observation and EDS evaluation.

Introduction

The commonly used materials for bone scaffolds could be mainly divided into three groups-metallic, ceramic, and polymer materials. Metallic biomaterials were developed and applied earlier than ceramic biomaterial and polymer biomaterials, giving it a mature technology, appropriate processing, and complete biocompatibility and clinical application. In late 1940s, the SS was firstly introduced to implant surgery [1]. In 1950s, Beder et al. future showed that pure titanium has good biocompatibility in their publication. At the same time, the polymer biomaterial such as a fiber type is also one of the most widely used and studied to explore its potential usage in implant surgery [2-12].

Materials and methods

Scaffolds made of multilayer PLA ply yarn and 316L stainless steel (SS) braids

The PLA ply yarns (75d/36f, UNITIKA Co., Japan) were alkali treated beforehand. 316L SS fibers (YUEN NENG Co., Taiwan) were braided with 2, 3, and 4 layers first and then received alkali treatment and heat treatment [13]. Then, the resulted SS braids were wrapped with PLA ply yarns with 8, 6, and 4 layers, forming the multilayer PLA/SS composite braids with the layer ratios of PLA to SS as 8:2, 6:3 and 4:4. Next, the optimum PLA/SS composite braid was immersed in a simulated body fluid (SBF) at 36.5 ℃ for 7, 14, 21 and 32 days. The SBF was composed of the chemicals of NaCl, $NaHCO_3$, KCl, K_2HPO_4-$3H_2O$, $MgCl_2$-$6H_2O$, Na_2SO_4, and $NH_2C(CCH_2OH)_3$ [13]. Chloride acid (1M) was added to adjust the pH of the initial SBF solution only. The final SBF pH value was controlled at 7.4. Before and after the immersion, the samples were then examined using a field emission scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) system to study the morphological and Ca/P ratio changes of the precipitates formed during aqueous reactions.

Result and discussion

Morphologies of 316L SS braids without and with the process of alkali and heat treating

The SEM figures (Figs. 1 and 2) clearly show the detailed topographies of the 316L SS braids after treatment. If the topography of the braids was changed through the treatment, the mechanical property would be declined and the surface energy will be raised. No topographical difference has been observed in the samples without and with alkali and heat treating. The results showed that treatment in the 316L SS braids by alkali and heat treating had no significant effects on the mechanical strengths.

Fig. 1 Surface morphology (x5.0k) of 316L SS braids not through alkali treating

Fig. 2 Surface morphology (x5.0k) of 316L SS braids through 5M NaOH alkali and 600℃ heat treating.

Effects of multilayer on ultimate tensile strength of scaffolds

In our previous study [14], the alkali treating process had no significant impact on PLA ply yarn's tensile strength. The alkali and heat treating process also made no significant contribution to the mechanical properties of 316L SS braids. Accordingly, this study used the fixed thickness of the braids and changed the multilayer's ratios of PLA ply yarns/ 316L SS braids to evaluate the mechanical strength. Actually, the strength of the scaffolds should match with the natural tissue in a human being as shown in Table 1 [15]. That could reduce the cost and prevent the occurrence of osteoporosis which is due to the effect of stress concentration after implantation. The tensile strength which human bone required ranged between 120 and 140 MPa. The major strength of the prepared PLA /SS composite braids for bone scaffolds was with a layer ratio of PLA to SS of 6:3, which was according used in all our immersed characterizations of *in vitro* properties in this study (Fig. 3).

Variation in immersed time and morphologies observation

With the above-mentioned as an experiment group, we studied samples were treated and immersed in SBF at 36.5 ℃ for different immersion days. The surface structure (obtained at specific immersion time) of the samples was examined using a SEM. SEM topography was performed on the scaffold that had been immersed in SBF for up to 7 days, there was a little amount of precipitate formed on the composite surfaces (Fig. 4a). A larger precipitation amount on the surface was showed at the 14 days immersion (Fig. 4b). After immersion for 21 days, the scaffold exhibited significant amounts of precipitation and the scaffold surfaces were covering with the particles (Fig. 4c). The precipitation was still wrapping the fibers of the scaffolds up to 28 days immersion (Fig. 4d).

Table 1. Mechanical properties of the natural tissues in a human being. [15]

Tissue	Direction of test	Tensile strength (MPa)
Leg bones Femur		
Femur	Longitudinal	121
Tibia	Longitudinal	140
Fibula	Longitudinal	146
Arm bones		
Humerus	Longitudinal	130
Radius	Longitudinal	149
Ulna	Longitudinal	148
Vertebrae		
Cervical	Longitudinal	3.1
Lumbar	Longitudinal	3.7

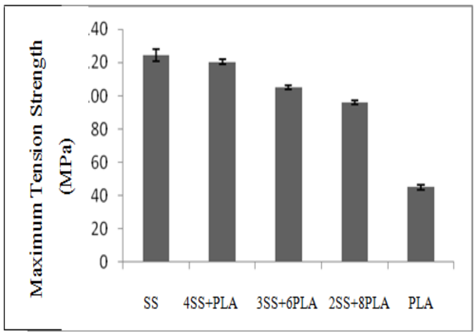

Fig. 3 Ultimate tensile strength of multilayer PLA /SS composite braids with related to different layer ratios of PLA to SS ranging from 8:2, 6:3, and 4:4. (SS: 316L stainless steel braids)

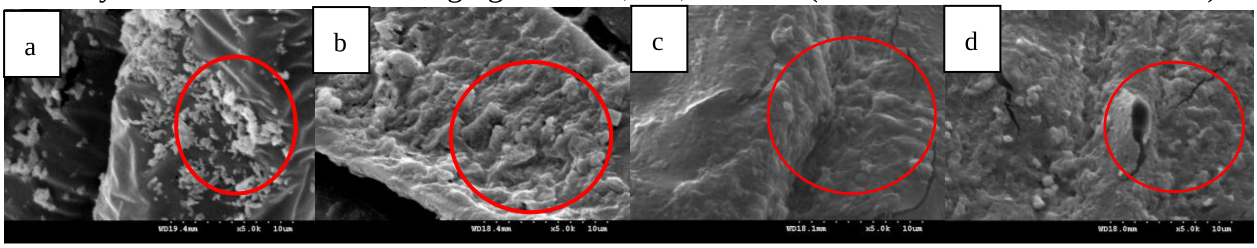

Fig. 4. Surface morphologies (x5.0k) of the precipitation by immersion the multilayer scaffold after 7 (a), 14 (b), 21 (c) and 28 (d) days in SBF.

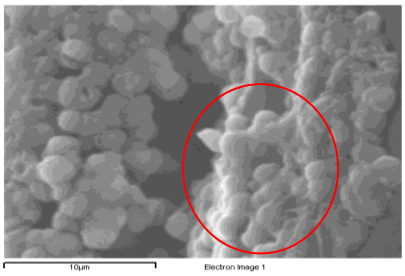

Fig. 5 Surface morphologies of the precipitation by immersion the multilayer scaffold after 21 days in SBF.

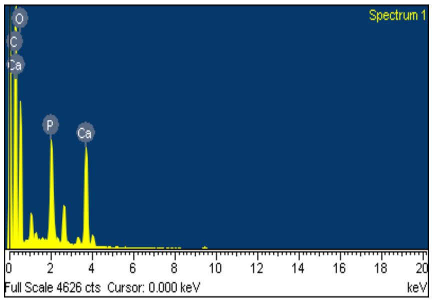

Fig. 6 EDS analysis of the elements and the area in red cycle in Figure 5.

Table 2. EDS analyses of the precipitate produced by immersion the scaffold after 21 days in SBF

Elements (Kα) *	Weight(%)	Atomic(%)
C	43.00	55.07
O	38.74	37.25
P	5.90	2.93
Ca	12.36	4.74
Totals	100.00	

*C: carbon, O: oxygen, P: phosphorus, Ca: calcium.

To measure the effects of varying the Ca/P ion-molar ratios on the precipitates (Fig. 5), the samples were evaluated with a detailed EDS analysis. The elements mapping of calcium (Ca) and phosphorus (P) were shown in Fig. 6. The majority of the precipitate was the Ca and P elements on the surfaces of multiplayer PLA /SS composite braids. The average Ca/P ratio of the precipitates at the time after 21 days was 1.61 and the phases should be composed of apatite. That value of Ca/P precipitate's ratio was closely to the stoichiometric HA, $Ca_5(PO_4)_3OH$, whose Ca/P ratio is 1.67. The formation of Hydroxylapatite *in vitro* was expected to induce the regeneration of bone cells to form osteoid *in vivo*.

Summary

The experimental results showed that the fracture tensile force of PLA ply yarns was strengthened by the incorporation of the 316L SS. When the layer ratio of PLA ply yarn to SS braid was 6:3, the PLA/SS composite braid exhibited the ultimate tensile strength, which was above 120 MPa, qualifying the PLA/SS composite braid a suitable bone scaffold. A uniform and large amount of hydroxylapatite could be found on the PLA/SS composite braids which were immersed in SBF for three weeks. Finally, the Ca/P ratio of hydroxylapatite of the PLA/SS composite braids was 1.61 which was close to that of human bone (Ca/P ratio: 1.61), thus this research successfully produce a bone scaffold with a certain tensile strength and with deposition of hydroxylapatite.

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