Enhanced adhesion of polymer coating on stainless steel surface by direct ring-opening polymerization of L-lactide

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Introduction: Bare metal stent (BMS) is very useful in patients of coronary artery disease (CAD) but often elicits inflammation, thrombosis, and even restenosis. To prevent this problem, a drug-eluting stent (DES) has been developed and found effective in reducing restenosis. However, DES on which polymer coated is a delamination of the sub-micrometer scale between polymeric layer and the metal surface, after a polymeric layer was coated onto metal surface by electrospraying. This separation interrupts interfacial adhesion between them, leading to unstable state in their adhesion. We introduced a new nanocoupling concept by the grafting method such as surface-initiated ring opening polymerization (SI-ROP). Poly(L-lactide) (PLLA) was grafted by direct SI-ROP from the hydroxyl group generated by oxygen-plasma discharge on stainless steel.
Materials and Methods: Stainless steel (SS) plate (10 × 10 mm^2) was obtained from HanKook Vacuum Metallurgy (Korea). Poly(lactide-co-glycolide) (PLGA; 50:50, MW: 40,000) was purchased from Boehringer Ingelheim (Germany). All the chemicals were used without further purification. Prior to the plasma treatment, SS specimens were cleaned in acetone, rinsed with ethanol, and dried by argon gas. After O_2 plasma treatment for 10 min, the samples were exposed to air for 30 min. They were then immersed in the rounded-bottom flasks, filled with the solution of L-lactide (10 wt%) and stannous octoate (100 μl) in toluene. After degassing and completely sealing, direct SI-ROP was carried out at 80 °C for 5 h under magnetic stirring. PLGA was coated on PLLA-nanocoupled SS plate by electrospray method. Nanocoupled SS substrate was characterized by ellpisometry, ATR-FTIR, and atomic force microscopy (AFM). The thickness of electrsprayed PLGA film was determined from the cross-sectional scanning electron microscopy (SEM) image. Scratch and 90° peel off tests were carried out at room temperature by scratch apparatus and Instron machine, respectively. Polymer degradation test was performed with samples immersed in phosphate-buffered saline (PBS, pH 7.4) in water bath at 37°C.
Results and Discussion: Plasma treatment easily generates many reactive species in the form of hydroxyl, peroxy, and carboxyl groups on the surface. PLLA was successfully grafted from the hydroxyl groups generated on SS substrate. The presence of nanocoupled PLLA was confirmed by ATR-FTIR (Fig. 1). The peaks at 1750, 2930, and 2960 cm^{-1} were attributed to carbonyl of ester groups and C-H stretching in PLLA. The thickness of nanocoupled PLLA layer was 4 ± 0.7 nm, as determined by ellipsometer. In addition, the surface roughness from AFM was 0.7 ± 0.3 nm. From both results, it was proved that PLLA was nanocoupled with extremely thin and very uniform layer on SS substrates by direct SI-ROP. Meanwhile, PLGA on nanocoupled SS substrate was electrosprayed with the thickness of 12 μm, as determined by SEM. In order to investigate the effect on interfacial adhesion between polymer layer and metal substrate by nanocoupling, peel off test was carried out. The average failure loads were 0.6 N for nanocoupled substrate and the adhesive force was much higher than the others. While PLGA coating of control SS-PLGA and plasma-treated SS-P-PLGA was easily delaminated from surface, nanocoupled SS-P-L-PLGA presented significant improvement of adhesive force. Therefore, these results demonstrate that nanocoupling can be effective in increasing the adhesive strength between polymer coating and metal substrate. The nanocoupling effect was confirmed from polymer degradation test as well. Fig. 2 shows the serial SEM images. It was commonly observed that PLGA electrosprayed on substrates became hydrated and swollen within 28 days. PLGA completely disappeared at control and plasma-treated surface, whereas nanocoupled SS was still left with some polymer matrix. It is postulated that a relatively strong adhesion by nanocoupling may be responsible for resisting the bulk erosion.

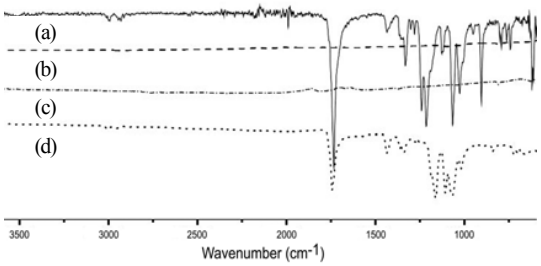

Fig. 1. ATR-FTIR spectra of (a) L-lactide, (b) control SS, (c) plasma-treated SS-P, and (d) nanocoupled SS-L.

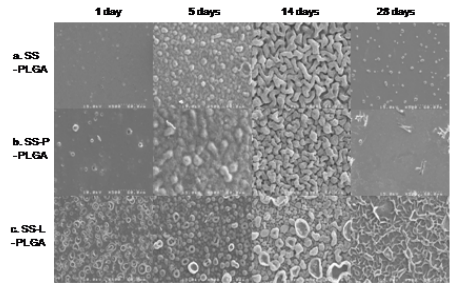

Fig. 2. SEM images of *in vitro* degradation behavior of PLGA matrix for 28 days.

Summary: PLLA was nanocoupled successfully by direct SI-ROP method on SS surface and it was confirmed to significant effect on the increase of interfacial adhesion of polymer coating for the application of various medical devices including stents.

References:

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