European Cells and Materials Vol. 10. Suppl. 2, 2005 (page 70) ISSN 1473-2262

Biomimetic Synthesis of Apatite on Polycaprolactone for Bone Tissue Engineering

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INTRODUCTION: Biodegradable polymers such as polycaprolactone (PCL) have been used for bone tissue engineering (TE) scaffolds. The material surface must be modified to support the cell attachment, proliferation and differentiation. It has been reported that nanocrystalline apatite can facilitate the osteo-inductivity and osteo-conductivity of the polymer scaffolds [1]. The objective of the work is to produce an apatite coating on PCL using a biomimetic method. To induce the apatite formation on PCL, a chemical treatment was carried out to functionalise the PCL surface with carboxyl ligands.

METHODS: PCL (CAPA®6500/6800 Solvay) with a MW of 120,000 was used as film substrates. They were surface treated with NaOH solutions of different concentrations (1M, 5M, and 10M) and subsequently dipped in 0.4M of Ca^{2+} and PO_4^{2-} solutions alternatively. After rinsing and drying, the samples were immersed in a stimulated body fluid (SBF) at 37°C. The SBF solution was prepared according to a newly improved procedure[2] to minimize the precipitation. Scanning electron microscopy (SEM) with an EDS attachment was used to characterize the morphology and chemical composition of apatite coatings. Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) was used to analyse the surface chemistry of PCL films before and after treatments.

RESULTS: Figure 1 shows the surface treated PCL samples after immersing in SBF for different time. After 14 days, apatite was formed on the PCL. EDS analysis showed that the Ca/P ratio of the apatite was 1.63, close to that of hydroxyapatite (1.67). When the immerse time was increased to 30 days, the Ca/P ratio was reduced to 1.44, which was between that of tricalcium phosphate (1.50) and octacalcium phosphate (1.33). Platelike morphology was observed at high magnification (Fig.2). FT-IR results (Figure 3) showed gradual changes when the PCL was immersed in SBF. P-O peaks around 1000 cm^{-1} were only detectable after 14 days, which is in agreement with the SEM observation.

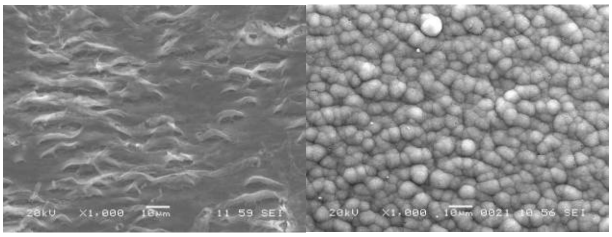

Fig. 1: 5M NaOH surface treated PCL films incubated in 1xSBF solution for different time: left-7days; right-14 days.

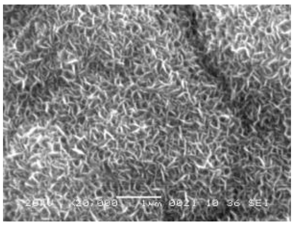

Fig. 2: SEM micrograph of the PCL film surface treated with 1M NaOH, showing platelike apatite formed after 30 days in SBF.

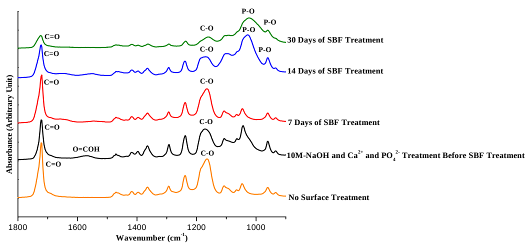

Fig. 3: FT-IR spectra for 10M NaOH treated PCL films at different stages.

DISCUSSION & CONCLUSIONS: NaOH surface treatment of PCL is crucial in inducing the apatite formation. The reason is mainly due to the PCL hydrolysis, resulting in chain scission of the polyester chains in PCL and formation of carboxylic acid ligands on the surface. FT-IR results clearly show a new peak around 1560 cm^{-1} which is representative of -COOH. This peak increases as the NaOH concentration increase. Carboxyl ligands have been reported to induce apatite formation through strong binding to positively charged Ca^{2+} ions to form nuclei and undergo subsequent growth to apatite.

REFERENCES: [1] Murphy WL and Mooney DJ. *J Am Chem Soc* 2002; 124: 1910-1917. [2]Takadama H, Hashimoto M, Mizuno M, Ishikawa K and Kokubo T. *Bioceramics* 2004; 16: 115-118