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The formation of hydroxyapatite on chemically-modified cellulose fibers

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A direct bond between cellulose and calcium phosphate does not form under physiological conditions. In this study, NaOH was used to modify the surface of cellulose fibers in an attempt to form a template for hydroxyapatite growth. Surface modification of cellulose fibers with NaOH was used to accelerate the biomimetic formation of bone-like apatite. After surface modification, NaCl was produced on the surface of cellulose fibers that were immersed in simulated body fluid before the formation of calcium phosphate could occur. However, calcium phosphate nucleated on the surface of the NaOH-treated cellulose fibers in a simulated body fluid solution without NaCl. After calcium phosphate had nucleated on the cellulose fibers in the NaCl-free simulated body fluid, the resulting cellulose fibers were immersed in a normal simulated body fluid solution. The result was an increase in the thickness of the calcium phosphate layer on the cellulose fibers immersed in SBF, followed by the formation of hydroxyapatite on the cellulose fibers.

Key words: Polymer, Cellulose, Hydroxyapatite, composite materials.

Introduction

Tissue engineering is an important tool for reconstructing or replacing diseased tissue. One possible approach to fabricating artificial tissue combines porous scaffolds, autogenous tissue-specific cells, and a bioreactor to cultivate tissue in vitro [1-4]. Because hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) has biochemical and mechanical properties that are similar to those of human teeth and bones, it is widely used in prosthetic implants, but its low mechanical strength limits its applications as a bone substitute material. One alternative is to use organic-inorganic composites, which might provide a versatile new group of biomaterials. One organic material that can be used in such composites is cellulose, since it can be formed into a wide variety of shapes and since the biocom-patibility of cellulose and its derivatives has been well established [5]. However, the potential of cellulose for use as artificial bone is limited because it does not bond directly to bone [6]. A number of studies have been carried out to address this problem [7-8]. The aim of this study was to develop a simple process for depositing a bioactive hydroxyapatite layer on the surface of cellulose fibers.

Experimental

Non-woven cellulose fibers (Lyocell, Lenzing, Austria) with a diameter of 10 mm were used. They were cut into 5-cm lengths and washed ultrasonically in double-distilled water for 20 minutes and then dried at 50 °C for 24 h. The cleaned fibers were immersed in 3-M NaOH for 1 minute to modify the surface characteristics of the cellulose fibers. A portion of the treated fibers were soaked in normal simulated body fluid (SBF) at 37 °C, while the remainder of the treated fibers were soaked in modified NaCl-free SBF for 24 h and then soaked in normal SBF. The fibers were exposed to the SBF solutions under static conditions in a biological thermostat at 36.5 °C for 12, 24, 48, 72, and 96 h. After soaking, the samples were washed with distilled water and dried at room temperature. Table 1 summarizes the composition of the normal SBF, the modified SBF without NaCl, and human blood plasma.

The changes in the cellulose fibers caused by the treatment were examined with FT-IR(Fourier Transform Infrared Spectroscopy), SEM (Scanning Electron Microscopy), EDS (Energy Dispersive X-ray Spectroscopy), XPS (X-ray Photoelectron Spectroscopy), and XRD (X-ray Diffraction) analysis.

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Results and Discussion

The NaOH solution promoted the formation of calcium phosphate nuclei on the surface of the cellulose fibers. The influence of the NaOH on the cellulose was confirmed by the FT-IR analysis. Fig. 1 compares the FT-IR spectra

Table 1 Ionic concentrations [mmol/l] of the normal SBF, modified NaCl-free SBF, and human blood plasma

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	HPO_4^{2-}
SBF	142.0	5.0	2.5	1.0	131.0	5.0	1.0	1.0
SBF (-NaCl)	21	5.0	2.5	1.0	4	5.0	1.0	1.0

from pure cellulose and the cellulose treated in NaOH. The broad band appears to peak at around 3000-3700 cm^{-1}, which corresponds to the stretching region of OH groups. The intense peaks that can be seen at 1030-1060 cm^{-1} correspond to C-OH stretching. The peak seen at 670 cm^{-1} can be interpreted as the out-of-plane mode of OH vibration. The OH stretching peak of the cellulose was broadened as the amount of NaOH treatment time increased. It was as though the NaOH treatment caused the OH stretching bands to widen, as shown by the broadening of the peak in the OH stretching region of spectra (Fig. 1b and c). Furthermore, the broadening can be attributed to the OH stretching band from OH groups that are chemically bonded to the cellulose structure. However, when the NaOH treatment time was increased to 10 minutes, exfoliation and shrinkage was observed on the surface of the cellulose fibers.

Fig. 2a show an SEM micrograph of the cellulose fibers treated in 3-M NaOH and immersed in normal SBF for 48 h. A new surface layer with cubic-shaped particles can be seen. EDS revealed sodium and chlorine to be the major components present on the surface of the fiber, which suggests that these crystals were NaCl. We observed small, spherical particles on the surface of the cellulose fibers that had been treated with 3-M NaOH and then immersed in the modified NaCl-free SBF for 24 h (Fig. 2b). EDS indicated the presence of calcium and phosphorus. We observed a dense calcium phosphate layer on the cellulose fibers that had been treated in 3-M NaOH, immersed in the modified NaCl-free SBF for 24 h and then soaked in normal SBF for 96 h (Fig. 2c). The thickness of the layer was approximately 20 μm.

Fig. 3 shows the XPS spectra of (a) the untreated cellulose fibers, (b) the cellulose fibers treated in 3-M NaOH, and (c) the cellulose fibers treated in 3-M NaOH and then soaked in the modified NaCl-free SBF. Prominent bands for sodium can clearly be seen on the surface of the cellulose fibers treated with 3-M NaOH (Fig. 3b). This suggests that Na ions adhered to the surface of the fibers during the 3-M NaOH treatment. However, the Na was replaced with Ca after soaking in the modified NaCl-free SBF (Fig. 3c).

Fig. 4a shows the XRD pattern of the precipitates that formed on the cellulose fibers treated with 3-M NaOH and then soaked in the normal SBF for 48 h. The XRD peaks at $2\theta = 27^{o}$, 32^{o}, 46^{o}, 56^{o}, and 75^{o} in Fig. 4a correspond to those of NaCl with very high crystallization. Therefore, the Na adsorbed after the 3-M NaOH

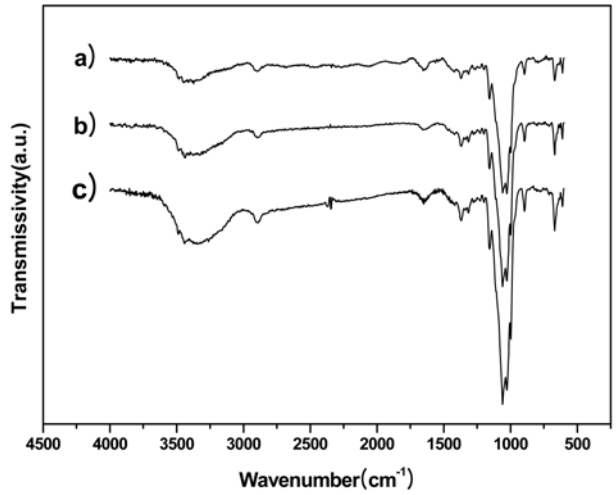

Fig. 1. FT-IR spectra of a) pure cellulose, and cellulose fibers treated in 3-M NaOH for b) 1 minute and c) 10 minutes.

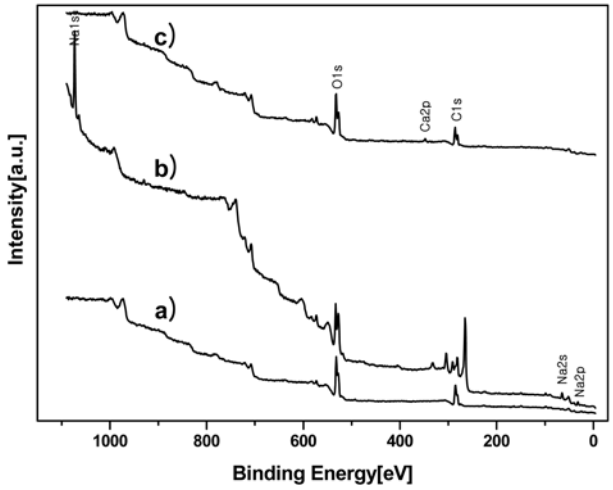

Fig. 3. XPS spectra of a) the cellulose fibers and b) NaOH-treated cellulose fibers.

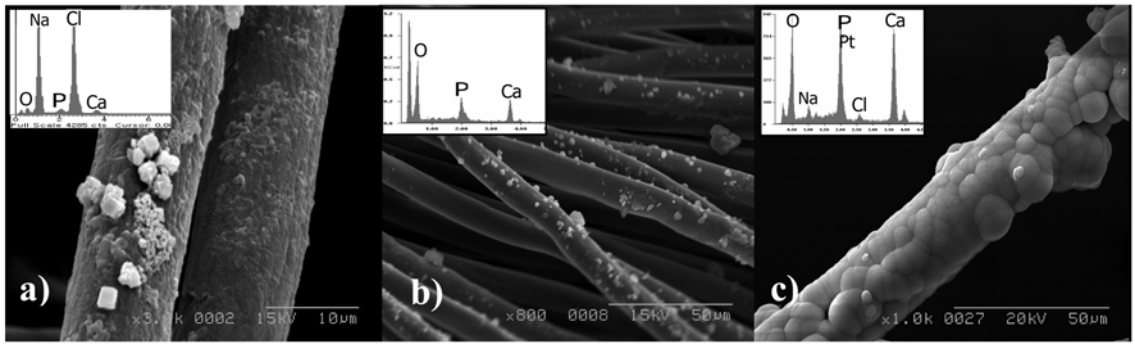

Fig. 2. Micrographs of the surface modifications to the cellulose fibers a) after soaking in SBF for 48 h, b) after soaking in NaCl-free SBF for 24 h, and c) after soaking in NaCl-free SBF for 24 h followed by immersion in SBF for 96 h.

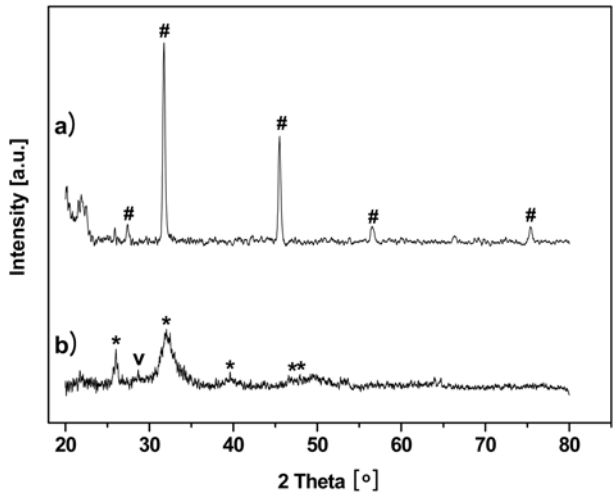

Fig. 4. XRD patterns of the precipitates formed on the NaOH-treated cellulose fibers in a) SBF and b) NaCl-free SBF after immersion in SBF(#: Sodium Chloride, *: Hydroxyapatite, v: Calcium pyrophosphate).

treatment is believed to leach from the surface while soaking in the normal SBF, resulting in the formation of NaCl because of the high Na concentration in the surrounding solution. However, Ca substitutes for Na after the fibers are soaked in the modified NaCl-free SBF. Hydroxyapatite and calcium phosphate are formed on the surface of the cellulose fibers during the subsequent treatment in normal SBF (Fig. 4b).

Conclusions

A pretreatment of cellulose fibers with 3-M NaOH can induce the formation of hydroxyapatite on the surface of the fibers if the fibers are soaked in modified NaCl-free SBF and then immersed in normal SBF. NaCl forms on the surface of the cellulose fibers when the cellulose fibers treated with 3-M NaOH are soaked in normal SBF. Then Ca substitutes for Na as the fibers were soaked in the modified NaCl-free SBF, and a dense hydroxyapatite layer forms on the surface during the subsequent treatment in normal SBF.

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