**Fabrication of Novel Calcium Phosphate-Reinforced Polylactic Acid Continuous-Yarn Composites**

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**Introduction:** Calcium phosphate (CaP)-reinforced polymer composites were originally envisioned as biomaterials for bone replacement on the basis of producing appropriate mechanical compatibility, as well as the required biocompatibility [1-3]. According to published reports [1-3], up to 50 wt% of the CaP was incorporated into the polymer matrix to achieve sufficiently high values of the elastic modulus. Unfortunately, the composites lacked sufficient toughness for use in different applications. In this study, a novel CaP-reinforced biodegradable polylactic acid (PLA) continuous-yarn composite was prepared that features a biomimetic coating on the yarns to gain a high modulus. The coated yarns were then assembled into a unidirectional composite using a poly(ε-caprolactone) matrix. The mechanical properties of the composite were determined.

**Methods:** Commercially available PLA yarn was treated using 1M NaOH for 1 min at the room temperature. CaP was deposited on these surface-saponified yarns using an alternating-soaking technique. The PLA yarns were initially soaked in a calcium nitrate solution for either 0.5 or 1 h, rinsed with de-ionized water, and subsequently soaked in a phosphate solution for the same period of time to complete one coating cycle. This process was repeated 6 times to maximize the amount of calcium phosphate deposited on the surface of the yarns. The yarns were washed with de-ionized water after each coating cycle. Finally, the CaP-coated yarns were dip-coated with poly(ε-caprolactone) solution in tetrahydrofuran (THF), dried, and compression molded at an elevated temperature to form rectangular bars. The amount of CaP deposited after each cycle was measured gravimetrically and characterized using X-ray diffraction. Scanning electron microscope (ESEM) images of the yarn were taken after each deposition cycle. Three-point bending test was done to measure both the flexural modulus and flexural strength at break of the fabricated composites.

**Results/Discussion:** Table 1 details the amount of CaP deposited on the yarn with increasing number of cycles and soaking time for each cycle. Even higher number of cycles resulted in the detachment of CaP from the yarn. Fig. 1 shows the ESEM images of the yarns before and after CaP coating. Homogenous PLA yarns with individual filaments of approximate diameter of 25 μm were used to prepare the composites (Fig. 1. a). While it was found that CaP particles were sparsely deposited on the surface of the PLA yarns after the first cycle of alternate-soaking, significantly large amount of CaP was deposited on the surface of the yarns after a few cycles of soaking (Fig. 1. b). These findings are in qualitative agreement with the gravimetric analysis of the deposit on the yarn.

Table 1. CaP deposition on PLA yarns with varying time and repetition cycles.

| Repetition cycles | wt% CaP deposition | | Flexural modulus, GPa | |
|---|---|---|---|---|
| | 0.5-h soak time | 1-h soak time | 0.5-h soak time | 1-h soak time |
| 1 | 7.8 | 9.45 | - | - |
| 2 | 12.4 | 17.4 | - | - |
| 3 | 16.5 | 23.7 | - | - |
| 4 | 19.2 | 29.4 | - | - |
| 5 | 22.4 | 33.6 | 3.94 | 4.66 |
| 6 | 23.3 | 35.1 | 6.45 | 7.89 |

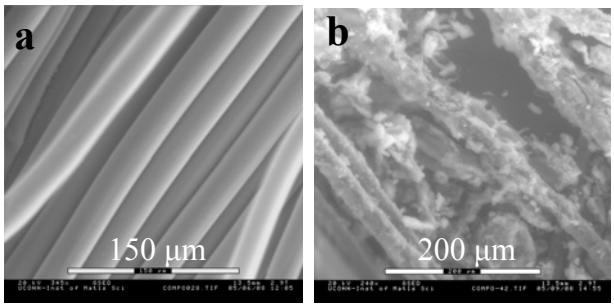


Fig. 1. ESEM images of PLA yarns (a) before deposition, (b) CaP deposition after four soaking cycles.

A consistent increase of modulus with increasing CaP content in the composites was observed (Table 1). A flexural modulus as high as 7.9 GPa was achieved for the composites prepared under the conditions of 1 h soaking at each step and after 6 soaking cycles. This value of modulus falls into the lower end of the elastic modulus of human cortical bone, 7-25 GPa. None of the composites broke in a brittle fashion during the bending test, indicating that the composites not only had a high modulus, but also superior toughness.

**Conclusions:** CaP was successfully deposited on the surface of PLA yarns using an alternating soaking biomimetic technique. The amount of CaP deposited depends on the operational parameters, such as the soaking time and coating cycles. A biodegradable composite with high modulus and excellent flexibility has been fabricated, which may be suitable to be used at medium to high load-bearing applications.

**References:**

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