The Effect of Surface-Modified Nano-Hydroxyapatite on Mechanical Properties and Biocompatibility of Hybrid Nanocomposites

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Statement of Purpose: Hydroxyapatite (HAp) nano-crystals have gained an expanding interest in the fabrication of artificial bone-like ceramic/polymer composites due to its similarity to bone minerals in size, crystallinity, and morphology. Of many factors determining the properties of composites, the affinity between inorganic HAp and organic polymer phases is significant in that the good interfacial adhesion can result in the enhanced mechanical properties of the composites. The colloidal stability of the nano-apatite in solutions as well as dispersibility in the nano-composites is another important factor for fabrication of composites with enhanced biocompatibility due to the high specific surface area. This work describes the effect of surface-modified HAp nano-crystals on mechanical properties and biocompatibility of a new-type nanocomposite based on poly(ε-caprolactone) (PCL) and surface-modified HAp with PCL. PCL-grafted HAp contributed much more to the improved tensile strength, toughness, and biocompatibility of the PCL-grafted HAp/PCL nano-composites, compared with unmodified HAp.

Methods: HAp containing PCL on its surface was prepared by grafting polymerization of CL. To control the grafted PCL amount, unmodified HAp (surface OH) and HAp modified with ethylene glycol (primary OH) were utilized for surface grafting polymerization. Each PCL-grafted HAp was denoted as C-HAp and EC-HAP, which have the grafted PCL amount of 8.4 and 24.6 wt %, respectively. For protein adsorption and cell adhesion/proliferation test on nanocomposite surfaces, nano-composite films containing various contents of HAp (10, 30 and 50 wt %) prepared. HAp, C-HAp, and EC-HAp were dispersed separately in CH_2Cl_2, and the PCL solution in CH_2Cl_2 was added to each HAp suspension. The solution was coated onto a siliconized cover-slide, and the solvent was removed by air-drying.

Results/Discussion: The nanocomposites of PCL and PCL-grafted HAp showed enhanced tensile strength and toughness, compared with that of unmodified HAp and PCL (Table 1). Increased interfacial interaction parameters ($B_{\sigma\gamma}$) for the composite of PCL and PCL-grafted HAp strongly supported the enhanced mechanical strength of the nanocomposites. HAp modified with a larger amount of PCL was much more effective in improving mechanical properties of the nanocomposites.

Table 1. Mechanical Properties of Nanocomposites

Specimen	Tensile modulus (MPa)	Tensile strength (MPa)	Ultimate elongation at break (%)	Interfacial interaction parameter ($B_{\sigma\gamma}$)
Pure PCL	2.6	20.3	213.7	-
HAp/PCL	3.2	22.1	136.5	5.77
C-HAp/PCL	3.6	25.0	237.9	7.96
EC-HAp/PCL	5.5	28.2	269.6	9.54

Time-dependent phase monitoring indicated that PCL-grafted HAp could be more uniformly dispersed in the CH_2Cl_2 solution of PCL than unmodified HAp. Particularly, EC-HAp with the highest grafting amount of PCL showed the excellent colloidal stability as shown Figure 1. This ensures the homogeneous dispersion of HAp at nano-level in nanocomposites.

Figure 1. Time-dependent phase behavior of the mixture of PCL and PCL-grafted HAp nano-crystals

The protein adhesion and cell experiments showed that the presence of PCL-grafted HAp nano-crystals in nanocomposites gives a positive effect on biocompatibility of nanocomposites. Uniformly distributed EC-HAp in nanocomposites provided more favorable environments for protein adsorption, compare with unmodified HAp and C-HAp (Figure 2). Figure 3 shows that EC-HAp in the composite facilitated adhesion and proliferation of NIH 3T3 fibroblast cells on nanocomposite surfaces. Besides, both protein adsorption and cell attachment/proliferation dramatically improved as the amount of EC-HAp increased.

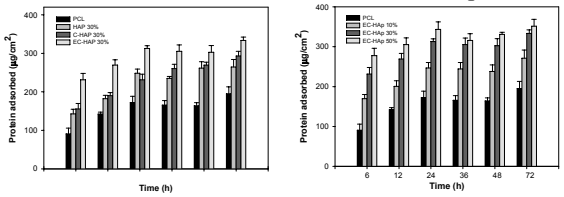

Figure 2. Protein adsorption on various classes of substrates

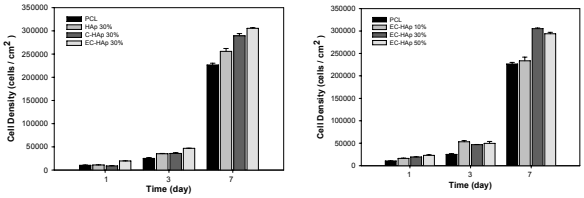

Figure 3. Cell proliferation on various classes of substrates

Conclusions: The hybrid nanocomposites containing PCL-grafted HAp nano-crystals provided many benefits as bone regeneration materials due to the improved mechanical strength and the favorable environments for cell proliferations. The approach described in this study may allow us to systemically design useful porous 3D-scaffolds for hard tissue regeneration.

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