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Micro-structural evolution and biomineralization behavior of carbon nanofiber/bioactive glass composites induced by precursor aging time

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ABSTRACT

Bioactive glass (BG)—containing carbon nanofibers (CNFs) are promising orthopaedic biomaterials. Herein, CNF composites were produced from electrospinning of polyacrylonitrile (PAN)/BG sol–gel precursor solution, followed by carbonization. Choosing 58S-type BG (mol%: 58.0% SiO_2-26.3% CaO-15.7% P_2O_5) as the model, micro-structural evolution of CNF/BG composites was systematically evaluated in relating to aging times of BG precursor solution. With aging time prolonging, BG precursors underwent morphological changes from small sol clusters with loosely and randomly branched structure to highly crosslinked Si-network structure, showing continuous increase in solution viscosity. BG precursor solution with low viscosity could mix well with PAN solution, resulting in CNF composite with homogeneously distributed BG component. Whereas, BG precursor gel with densely crosslinked Si-network structure led to uneven distribution of BG component along final CNFs due to its significant phase separation from PAN component. Meanwhile, BG nanoparticles in CNFs demonstrated micro-structural evolution that they transited from weak to strong crystal state along with longer aging time. Biomineralization in simulated body fluid and in vitro osteoblasts proliferation were then applied to determine the bioactivity of CNF/BG composites. CNF/BG composites prepared from shorter aging time could induce both faster apatite deposition and cell proliferation rate. It was suggested weakly crystallized BG nanoparticles along CNFs dissolved fast and was able to provide numerous nucleation sites for apatite deposition, which also favored the proliferation of osteoblasts cells. Aging time could thus be a useful tool to regulate the biological features of CNF/BG composites.

1. Introduction

Ceramic nanoparticle-containing carbon nanofibers (CNFs) are promising orthopaedic biomaterials [1–3]. They could be used directly for cell culture or as reinforcements for polymeric biomaterials. On one hand, CNFs possess advantages of light weight and high mechanical properties, and are close in size to the triple helical collagen fibrils. They were shown to support attachment and proliferation of osteoblastic cells [4–6]. On the other hand, ceramics such as calcium phosphate (CaP) and bioactive glass (BG) are osteoinductive for bone regeneration [7–12]. In comparison with pure CNFs, combinations of CNFs with ceramic nanoparticles would result in CNF composites with enhanced bioactivity and biodegradability owing to the dissolution of ceramic components [7–9]. To produce ceramic nanoparticle—containing CNFs, an efficient approach was the electrospinning of polyacrylonitrile (PAN) solution with incorporation of sol–gel solutions of ceramic precursors, followed by carbonization [1,10–12]. The process showed advantages of catalyst-free preparation and strong flexibility in tailoring the bioactivity of CNFs by choosing proper ceramic components. In both our previous studies [2–4,13] and literatures [1,14,15], CNFs containing ceramic nanoparticles, including different types of BG and beta-tricalcium phosphate, have been well documented in having good biocompatibility and cell affinity, and strong ability in inducing biomineralization. The features of ceramic nanoparticles depended significantly on their chemical compositions, the sol–gel

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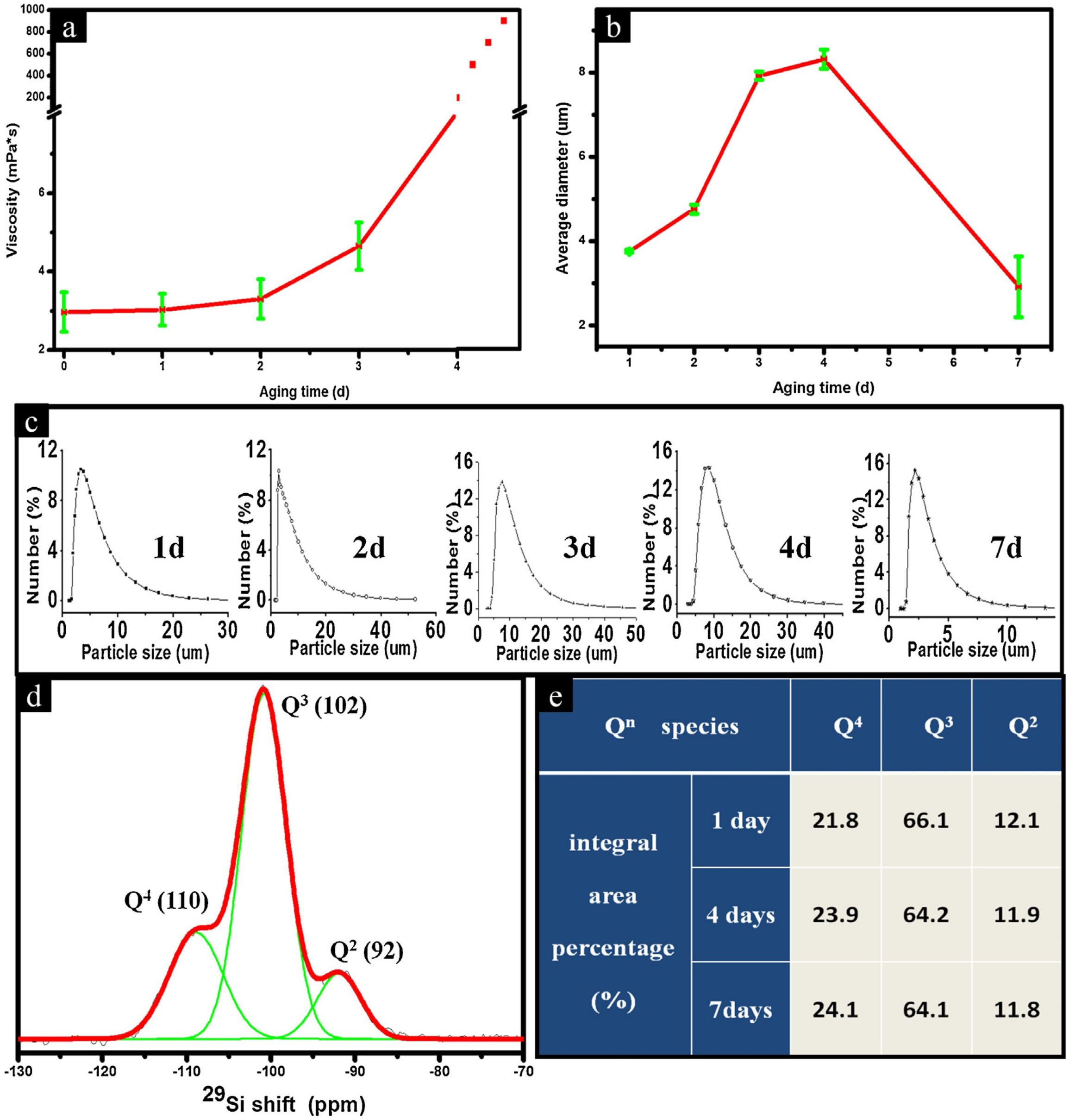

Fig. 1. Effect of aging time in sol–gel transformation on (a) the viscosity of BG sol–gel precursor solution, (b) the average size and (c) size distribution of precursor particles, and (d) ^{29}Si NMR spectrum of precursor solution with aging time of 4 days and (e) characteristic parameters of ^{29}Si NMR spectra for precursor solutions with various aging times.

formation and the carbonization, etc. Up to now, the published data mainly concerned the effects of chemical compositions on cell biological behaviors. Sparse study could be found in relating the sol–gel formation of ceramic precursors with the micro-structural evolution of ceramic nanoparticles during the carbonization of PAN.

In literatures [16–18], the aging parameters such as time, temperature and pH, etc., have long been recognized as critical factors influencing the subsequent micro-structural evolution of sol–gel derived solids. Liu et al. [16] studied the aging effect of precursor solution on the phase evolution of water-based sol–gel hydroxyapatite. They exposed that critical aging time was required to complete reaction between Ca and P precursors to form a desired intermediate complex, which permitted a further transformation to apatite phase under appropriate thermal treatment. Hosseini et al. [17] reported the aging time and temperature of precursor solution would significantly affect the impurity phases in preparing the sol–gel-derived hydroxyapatite. Smith et al. [18] found both aging time and temperature showing similar effect on the evolution of bulk density, surface area and pore volume of silica aerogels due to the time-temperature equivalence principle. These data made us be aware that the aging time of sol–gel precursor would definitely affect the micro-structural evolution of ceramic nanoparticles in CNF composites. Therefore, it was worth looking into the effect of aging time of sol–gel precursor on the morphological and micro-structural evolution of ceramic nanoparticle-containing CNF composites, as well as on their bioactivity thereof.

Herein, BG—containing CNF composites (CNF/BG) were prepared for the purpose. BG was used for its excellent binding ability to both bone and soft connective tissues [7,19,20]. It can induce the formation of mineralized layer along with the chemical degradation of BG by releasing calcium and silicium ions [4–6]. In our previous work [2,4], CNF/BG composites containing 58S type BG (mol%: 58.0% SiO_2-26.3% CaO-15.7% P_2O_5) had shown high solubility, strong apatite formation ability from simulated body fluid (SBF) and good osteocompatibility. Therefore, in the present study, CNF composites containing 58S type BG were produced from