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Improving interfacial adhesion with epoxy matrix using hybridized carbon nanofibers containing calcium phosphate nanoparticles for bone repairing

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ABSTRACT

Hybridized carbon nanofibers containing calcium phosphate nanoparticles (CNF/CaP) were investigated as osteocompatible nanofillers for epoxy resin. The CNF/CaP was produced by electrospinning mixture solution of polyacrylonitrile and CaP precursor sol–gel, followed by preoxidation and carbonization. The continuous and long CNF/CaP was ultrasonically chopped, mixed into epoxy resin and thermo-cured. Compared to pure CNFs with similar ultrasonication treatment, the shortened CNF/CaP reinforced composites demonstrated significant enhancement in flexural properties of epoxy composites, benefiting from the improved interfacial adhesion between CNF/CaP and resin matrix. The resulting composites also displayed good biocompatibility and sustained calcium ion release, which categorized them as promising materials for bone repairing.

1. Introduction

In orthopedic surgery, a major problem is mismatch of the stiffness between the prosthesis and host bone, a phenomenon known as "stress shielding" will weaken the bones [1]. A composite bone repairing material could have similar modulus to cortical bones and reduce contact stresses significantly in comparison with metal materials, which categorized polymeric composites good orthopedic prostheses for effective bone healing [2,3]. To develop composite materials with satisfactory mechanical and biological properties, reinforcements are surely the key issues in improving the composite properties [4].

Carbon nanofibers (CNFs) have received intensive attention as composite fillers due to their immense specific surface area, superior strength and high conductivity for electricity and heat [5,6]. Nanocomposites such as epoxy/CNF have found applications in various areas like energy storage, biosensor and bone fixing [3,7–10]. In most of these applications, vapor-grown CNFs were studied and used. The concerns of non-uniform dispersion of CNFs in polymeric matrices and the poor interfacial adhesion between CNFs and the matrix are ameliorated by chemical functionalization of CNFs [11–13]. For bone fixing, however, biocompatibility and osteocompatibility are also important issues in designing repairing materials in addition to the mechanical properties [14]. The vapor-grown CNFs thus can have potential cytotoxicity issue because of the possible residues of metallic catalysts like Co/Ni in the CNFs.

Different from vapor-grown CNFs, electrospun CNFs from polyacrylonitrile (PAN) and carbonization demonstrate advantages of catalyst-free preparation and ability in tailoring the strength and elastic modulus of CNFs by regulating the carbonization temperature and alignment degree [15,16]. More importantly, the solution electrospinning provides strong flexibility in modulating the features of CNFs by introducing functional ingredients [17,18]. Calcium phosphates (CaP) such as hydroxyapatite (HA) and β-tricalcium phosphate (β-TCP) are well known osteoconductive or osteoinductive materials [19]. Ceramic nanofibers including CaP nanofibers had been widely fabricated by the combination of electrospinning and sol–gel [20]. By mixing sol–gel solutions of CaP precursors into PAN solution, then hybridized CNFs containing CaP nanoparticles (CNF/CaP) were readily fabricated via electrospinning and carbonization, displaying good cell affinity to osteoblasts [21,22]. In comparison with those cases of introducing CaP nanoparticles into PAN solution directly and electrospinning, the electrospinning/sol–gel technique produced hybridized CNF/CaP conquered the disadvantage of serious aggregation of nanoparticles in the solution and in the resulting CNFs. In comparison with vapor-grown CNFs, this hybridized CNF/CaP is envisioned as an osteocompatible nanofiller for epoxy composites targeted for bone repairing applications.

Herein, sol–gel solution of calcium nitrate (CN) and triethyl phosphate (TEP) was made and added into the PAN solution in N, N-dimethyl formamide (DMF), and the mixture was submitted to electrospinning, preoxidation and carbonization in this study. To facilitate the even dispersion of CNF/CaP in epoxy resin at low content, the as-produced long and continuous CNF/CaP was ultrasonically broken down. The shortened CNF/CaP was mechanically mixed into epoxy

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resin at different ratios, followed by thermo-curing. The resulting composites were tested flexural properties and fracture morphology using pure CNF reinforced epoxy composites as control. The biocompatibility and calcium ion release behavior of CNF/CaP reinforced epoxy composites were also evaluated.

2. Materials and methods

2.1. Materials

PAN (10^5 g/mol) used for the electrospinning was purchased from Courtaulds Co. (UK), being composed of 93.0 wt.% acrylonitrile, 5.3 wt.% methylacrylate and 1.7 wt.% itaconic acid. Calcium precursor CN and phosphorus precursor TEP required for preparing sol–gel solution were both purchased from Aldrich and used directly. The epoxy resin (E-51) was from Shell, and other components for making the epoxy mixture including hexahydrophthalic anhydride and 2,4,6-tri(dimethylaminomethyl)phenol (DMP-30) were from Sigma-Aldrich. Solvents and other chemicals involved in this study were of analytically pure grade and obtained from Beijing Chemical Plant (China).

2.2. Preparation of hybridized CNF/CaP

Hybridized CNF/CaP was prepared referring to our previous work [21], and briefly described as follows: (1) TEP was added into mixed DI water and absolute alcohol (1/1, *v*/*v*) containing nitric acid (0.5 wt.%), and stirred at 80 °C for 24 h to obtain a hydrolyzed TEP solution. To the solution, CN dissolved in ethanol (3 mol/L) was added at a Ca/P ratio of 1.3. After aged for 7 days at R.T., a sol–gel solution of Ca–P complexes was obtained. (2) The sol–gel solution was added into PAN solution in DMF (10 wt.%), and electrospun using a rolling rod as the collector under parameters as 20 kV (voltage), 0.1 mL/h (flow rate) and 15 cm (receiving distance). (3) The as-spun nanofibers were stabilized at 280 °C in air atmosphere for 0.5 h, and subsequently carbonized at 900 °C for 1 h in nitrogen atmosphere. (4) The obtained CNF/CaP was suspended in acetone and ultrasonically (500 W) treated for 0–40 min (JY92-II, Ningbo, China). Transmittance of the suspensions was monitored by a UV–Vis spectrophotometer (Unico UV-6100SPC, USA) under the wavelength of 200 nm. Shortened CNF/CaP was retrieved from the suspension and dried naturally. Shortened pure CNFs were prepared in a similar way except the addition of sol–gel solution of CaP precursors.

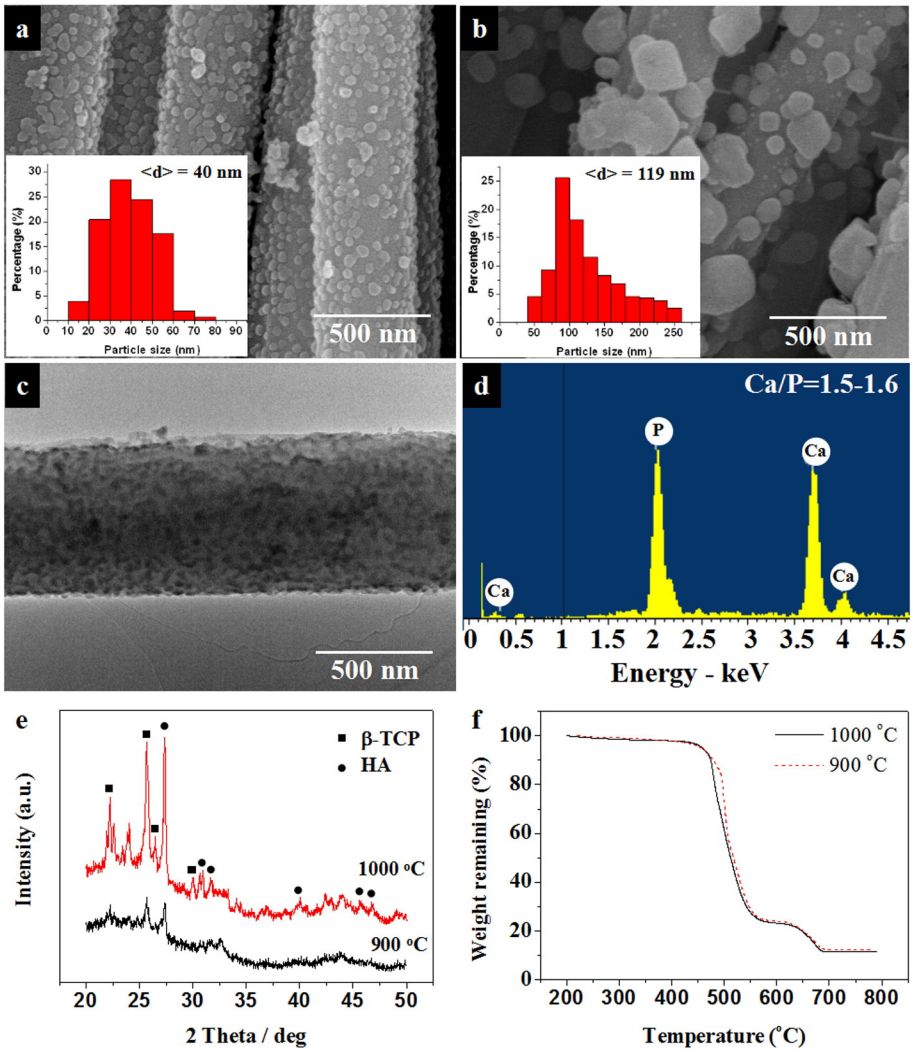

Fig. 1. CNF/CaP prepared by electrospinning and carbonization at 900 °C (a, c, d) or 1000 °C (b), and corresponding characterizations of morphological observation by SEM (a, b) and TEM (c), chemical composition (d), crystalline structure (e) and loading content of CaP in hybridized CNF/CaP (f). The insets in (a) and (b) are the particle size and size distribution of CaP nanoparticles in corresponding CNF/CaP.