

Biomimetic three-dimensional carbon fiber reinforced polymer hydroxyapatite nanocomposite for major load bearing orthopedic application

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Abstract

We report a novel biomimetic three-dimensional carbon fiber reinforced polymer hydroxyapatite nanocomposite having mechanical compressive strength (~116 MPa) and elastic modulus (~1.9 GPa) for load bearing orthopedic application. The synthetic route is very simple cost effective biomimetic process. It does not require any binder/porogen for the synthesis of mechanically strong porous nanocomposite. Physicochemical properties of synthesized nanocomposite are systematically characterized by XRD, FT-IR, SEM and Universal Testing Machine. It revealed that only small fraction of carbon fiber increased the compressive strength (~116 MPa) and elastic modulus (~1.9 GPa) by 11-12 folds from unreinforced polymer hydroxyapatite nanocomposite (compressive strength~ 12MPa, Elastic modulus~ 0.33 GPa). Copyright © 2018 VBRI Press.

Keywords: Carbon fiber; hydroxyapatite; biomimetic; nanocomposite; bone graft.

Introduction

Human bone defects occur due to trauma, cancer, infection and congenital abnormality and cause affect millions of people worldwide each year [1]. Currently, autografts and allografts are the most common approaches for the repairing of bone defects. Nevertheless, the scarce amount of bone that can be safely harvested and the risk of donor site morbidity limit the applicability of this approach [2]. Consequently, an alternative approach for bone grafting has been taken up in the form of synthetic materials. The synthetic materials, polymer-hydroxyapatite composites have been studied extensively for the reconstruction of bone defects [3-6]. However, low mechanical strength of the composites limited their usage in application of high load bearing implants. To enhance the mechanical properties Prof. Bonnfield developed polymer-HA composite with high mechanical strength using nondegradable polymer, poly-methyl methacrylate [7]. But he could not induce bioactivity in the nanocomposite system. In our previous report, we demonstrated biomimetic osteoconductive three dimensional load bearing polymer-hydroxyapatite nanocomposites having mechanical strength and modulus in the range of 2-12 MPa and 157-330 MPa respectively, porosity 60-80% as a synthetic bone grafts analogous to human cancellous bone [8]. Developed synthetic route controlled the size of HA particle and also assisted to the formation of mechanically strong 3D structure due to physical cross linking of HA with CMC matrix. In order to improve the mechanical properties of composites, many reinforcements, metal long fibers, partially stabilized zirconia, whiskers and

nanoparticles etc. have been used [9-12]. Considering the bioactivity and mechanical properties of composites, we have selected functionalized C-fibers as a reinforcement to reinforce polymer-HA nanocomposite system. The functionalized C-fibers are highly bioactive. In our present study, we developed a new biomimetic route for the synthesis of three-dimensional C-fibers reinforced polymer hydroxyapatite nanocomposite as bone graft and characterized systematically by different instrumental techniques. It revealed that the nanocomposite achieved high mechanical compressive strength of 116 MPa and elastic modulus 1.9 GPa respectively with three dimensional nanocrystalline structure.

Experimental

Materials

Analytical grade of di-ammonium hydrogen phosphate $[(\text{NH}_4)_2\text{HPO}_4]$, calcium nitrate tetra hydrate $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$, liquid ammonia were purchased from Merck, India. Sodium salt of carboxymethyl cellulose (CMC) polymer (degree of substitution 0.9) was purchased from Merck, India. PAN precursor carbon fiber (diameter~7-10 μm , tensile strength~ 3.5 GPa, density~ 1.77 g cm⁻³) was procured from Nickunj Group, Mumbai, India. In all experiment, deionized (DI) water was used.

Synthesis of 3D C-fibers reinforced polymer-HA nanocomposite

The nanocomposite was synthesized in two steps. In first step, C-fibers were functionalized. C-fibers were chopped

into 1-2 mm size and immersed into aqueous solution of 37 % Ortho-phosphoric acid for 2 h. After incubation, C-fibers were filtered and rinsed with DI water. In the second step, the nanocomposite was synthesized by the addition of functionalized C-fibers. 12.0 g CMC was dissolved in 900 ml DI water and stirred continuously for 5 h. 70.8 g Calcium nitrate tetra hydrate (0.6 M) was dissolved in 500 ml DI water, then added functionalized C-fiber and stirred well for 15 min. The mixture is slowly added to polymer solution and stirred continuously till the fibers are completely dispersed in polymer matrix. It was made alkaline by adding aqueous ammonia solution and kept for aging for 24 h at $30 \pm 2^\circ\text{C}$. 22.0 g Di-ammonium hydrogen phosphate (0.8M) was dissolved in 200 ml DI water. It is slowly added to pre-prepared fiber containing calcium polymeric gel. Milky white coloration was observed instantaneously, and the total volume of the slurry made up to 2100 ml which was allowed to age for a week at a temperature of $30 \pm 2^\circ\text{C}$. After a week the slurry was washed with DI water to neutralize and dried in an oven at $60 \pm 2^\circ\text{C}$ for 72 h to obtain 30 g of three dimensional C-fibers reinforced polymer-HA nanocomposite.

Characterizations

The crystalline inorganic phase of nanocomposite was crystallographically characterized using X-ray diffractometry (XRD) (Bruker, D₈ Discover, Cu K α radiation with $\lambda = 0.154$ nm, 40 kV, 40 mA). Morphological characterization was performed using scanning electron microscopy (SEM). The physicochemical characterization of nanocomposite was carried out using FTIR (JASCO-FTIR, Model 410) and infrared spectrum was recorded in the range of 4000-400 cm^{-1} at resolution of 4 cm^{-1} . The compressive mechanical properties of nanocomposite of dimension 20 mm x 18 mm x 10 mm was tested using a Hounsfield Universal Testing machine-UTM, QMAT 3.75, ASTDM 695.

Results and discussion

Structural and morphological analyses

Fig. 1 shows the XRD pattern of the nanocomposite. The diffraction peaks could be indexed as (0 0 2), (2 1 1), (3 1 0), (2 2 2), and (2 1 3) which are characteristic peaks of hexagonal HA peaks as per the JCPDS file (card no. - 9-432). The average crystallite size of HA (considering four prominent peaks) was calculated by Debye Scherer formula as 14 nm [13].

Fig.2 shows the FT-IR spectra of functionalized carbon fiber, as received carbon fiber and nanocomposite and the assigned functional groups for the observed absorption bands are given in Table 1. The absorption bands at 1610 cm^{-1} , 1425 cm^{-1} , 1289 cm^{-1} and 919 cm^{-1} appeared in functionalized C-fiber indicating the presence of COO⁻, C-H, OH, P=O and C-O-P groups respectively. Bands at 3450 cm^{-1} and 3132 cm^{-1} indicate the presence of hydroxyl group and aromatic -CH stretching. These results confirm the formation of functionalized C-fiber. The absorption

bands appeared in the nanocomposite indicating the presence of polymer CMC as well as functionalized C-fibers. The absorption bands at 1100- 1034 cm^{-1} , 605-600 cm^{-1} and 560-565 cm^{-1} of nanocomposite correspond to phosphate group of hydroxyapatites. The absorption band at 3432 cm^{-1} corresponds to hydroxyl group of polymer and hydroxyapatite confirming the presence of H-bonding between HA and CMC, functionalized C-fibers. A shift in the absorption bands (1614 cm^{-1} and 1421 cm^{-1} corresponding to COO⁻ and C-H groups) is observed for nanocomposite. These results confirmed the ionic interaction between Ca⁺² of HA and COO⁻ of polymer as well as functionalized C-fiber. The developed biomimetic process involved *in situ* mineralization of HA nanoparticles in the matrix of polymer and functionalized C-fibers through hydrogen bonding and ionic interactions with the formation of three dimensional structures. These interactions are the key factor in the nucleation and growth of HA nanoparticles. *In situ* synthesis of HA nanoparticles in polymer and functionalized C-fiber is schematically presented in **Fig. 3**.

SEM image of C-fibers reinforced polymer hydroxyapatite nanocomposite (**Fig. 4**) showed the presence of carbon fibers in well distributed and partially aligned in a particular direction. The mineralization of HA nanoparticles in the matrix of C-fibers and polymer is also observed.

Mechanical properties

Mechanical properties of nanocomposite is evaluated by measuring compressive strength (116 MPa) and elastic modulus (1.9 GPa) respectively. Stress vs. strain curve of nanocomposite is shown in **Fig. 5**. It revealed that the nanocomposite followed elastic and plastic deformation process with higher elastic modulus and less plastic region. These results confirmed the formation of biomimetic three dimensional mechanically strong C-fibers reinforced polymer-HA nanocomposites. More detailed study will be published elsewhere.

Conclusion

We have synthesized novel three dimensional mechanically strong C-fibers reinforced polymer hydroxyapatite nanocomposite following a simple cost effective biomimetic route. Compressive strength and elastic modulus of nanocomposite has been increased by 11-12 folds with the incorporation of small quantity of C-fibers which is comparable to human bone (compressive strength: 2-190 MPa, elastic modulus: 0.01-20 GPa). The nanocomposite has great potential as major load bearing orthopedic application.

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Author's contributions

Conceived the plan: Subhadra Garai; Performed the experiments: Chandrani Sarkar; Data analysis: Chandrani Sarkar, Subhadra Garai; Wrote the paper: Chandrani Sarkar, Subhadra Garai.

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