



Chitosan–nanohydroxyapatite composites: Mechanical, thermal and bio-compatibility studies



Pratik Roy, R.R.N. Sailaja*

The Energy and Resources Institute (TERI), SRC, Bangalore 560071, India

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ABSTRACT

Bionanocomposites of chitosan were prepared with nanohydroxyapatite (nHA) using 2-hydroxyethyl methacrylate (HEMA) as coupling agent. The tensile and flexural properties for 8% nHA loading showed optimal values. Compressive modulus also considerably increased from 525.16 MPa (0% nHA) to 1326.5 MPa with 10% nHA. Surface functionalization of fillers along with the addition of HEMA as coupling agent led to enhanced mechanical properties similar to human bone. The mechanical properties were further analyzed using micromechanical theories which indicated good interfacial adhesion between the matrix and fillers. The composites showed cytocompatibility. Multiple layers of apatite formation have been observed when the nanocomposites were soaked in simulated body fluid (SBF). Hence, these composites showed potential for bone substitute applications.

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1. Introduction

The need for a benign bone substitute is becoming a major need especially for elderly population with various bone defects. This requirement needs: (a) material matching in chemical composition with natural bone; (b) biocompatibility and mechanical strength similar to human bone. Extensive studies on hydroxyapatite are being carried out as it is a well-known material for biocompatibility and osteoconductivity with a chemical structure and composition matching the human bone and hence can mimic the same [1]. However, hydroxyapatite alone has certain shortcomings such as poor load bearing properties, difficulty to cast into the desired shape and its tendency to migrate from the implanted sites [2,3]. Hence, another biocompatible, natural and abundant biopolymer such as chitosan has been combined along with hydroxyapatite to develop bone substitute composites. Chitosan is a linear polysaccharide derived from partial deacetylation of chitin [4,5]. The ability of chitosan to support cell attachment and proliferation is attributed to its chemical properties. The polysaccharide backbone of chitosan is structurally similar to glycosaminoglycans, the major component of the extracellular matrix of bone and cartilage [6]. Chitosan is considered as an appropriate functional material for biomedical applications because of high biocompatibility, biodegradability, non-antigenicity and adsorption properties [7,8]. Further, anti-inflammatory or allergic reactions have not been

observed in human subjects following topical application, implantation, injection and ingestion [7,8]. An updated review article by Pighinelli et al. [9] suggested the need and importance of natural biopolymer such as chitosan–hydroxyapatite composites which can play a vital role in skeletal reconstruction. However, natural biopolymers such as chitosan have poor load bearing characteristics with rapid degradability. Mechanical properties especially compressive strength is important to tolerate the internal stress till tissue regeneration takes place. Han et al. [10] suggested that alginate–chitosan–hydroxyapatite composite exhibited enhanced mechanical strength due to strong ionic interactions. Further efforts to enhance mechanical strength using biocompatible materials like titania was carried out by Kavitha et al. [11]. It was found that the nanocomposites thus developed showed large surface area with good antibacterial activity. An improvement in compressive strength and Young's modulus was observed by adding a small amount of citric acid due to salting out effect [12]. It has also been envisaged that enhanced chemical bonding with the inorganic material such as nHA will restrict its migration and also reduce tissue damage. Thus, nHA has been blended with chitosan and gelatin to improve mechanical properties [13]. A drastic reduction in mechanical properties was observed for chitosan/hydroxyapatite composites as nHA loading increased [14]. Chitosan is a brittle material and hydroxyapatite is also brittle, thus a combination of the two further reduces the mechanical properties. Ai et al. [15] studied the effect of micro and nanosized hydroxyapatite particles in chitosan–starch composites. The composites loaded with nanosized particles showed increased modulus values.

* Corresponding author. Tel.: +91 80 25356590.

E-mail address: sailaja.bhattacharya@gmail.com (R.R.N. Sailaja).

In the present study, an attempt to enhance the mechanical properties of chitosan–starch composite reinforced with nHA and very small amount of nano carbon fiber (NCF) has been carried out. Biocompatible material i.e. HEMA has been added as a coupling agent to enhance interfacial bonding. Enhanced interfacial adhesion due to addition of HEMA will lead to better interaction between aminosilane functionalized nHA and chitosan, thereby leading to better mechanical strength. The bio-nanocomposites thus developed have been characterized for mechanical, thermal, water absorption and in vitro biocompatibility and osteogenicity properties.

2. Experimental

2.1. Materials

Chitosan powder used in this study was obtained from Marine Chemicals, Cochin (India) with 85% deacetylation. nHA was procured from J.K. Impex, Mumbai (India). Tapioca starch used in this study was purchased from Natsyn Catalysts, Bangalore (India). HEMA monomer was purchased from M/s. Tech Dry India Pvt Ltd., Bangalore, India. NCF and 3-aminopropyl triethoxy silane (APTS) was purchased from Global Nanotech, Mumbai (India). All other chemicals were purchased from S.d.Fine Chem, Bangalore (India) and were used as received.

2.2. Silane treatment of nHA and NCF

10 g of nHA powder along with 300 ml of DMF were introduced into a two necked round bottom flask. The mixture was stirred at reflux temperature (153 °C) under nitrogen atmosphere for 45 min, followed by drop wise addition of 5 ml of APTS. The reaction was carried out in a locally fabricated microwave reactor at 80 °C (Enerzi Microwave Systems, India) for 1 h under reflux. After reaction, the modified nHA was separated by centrifugation (8000 rpm, 5 min) and washed with chloroform and absolute alcohol. The resulting modified nHA powder was dried in a vacuum oven at 60 °C for at least 24 h before use. Similar silane surface treatment was given to NCF to enhance dispersion and compatibility with the other components of the nanocomposites.

2.3. Preparation of crosslinked thermoplastic starch

In order to improve starch processability, it has been plasticized and crosslinked using glycerol and glutaraldehyde, respectively. Thermoplastic tapioca starch was prepared following the method described by Sailaja and Chanda [16]. In this method, 48% of starch, 33% of glycerol and 19% of water were initially mixed for 15 min and left it to stand for 1 h in order to allow starch to swell. Further, blending of starch mixture was carried out using a high speed mechanical mixer with a hydro foil blade impeller at 1500 rpm by heating the mixture at 70 °C for 30 min followed by slow addition of 25% (w/w) glutaraldehyde crosslinking agent. The crosslinking reaction was allowed to continue for 30 min with constant stirring. The crosslinked thermoplastic starch (CTS) thus obtained was cut into small pieces, oven dried and ground into fine powders.

2.4. Blend preparation

A mixture of chitosan (47.5%), CTS (47.5%) and HEMA (5%) were taken for the preparation of composites. The loading of NCF was 0.1% and the loading of nHA was varied from 0 to 15% (w/w of chitosan, CTS and HEMA mixture). The mixture was mixed in a kitchen mixer for 10 min and then sonicated using Ultra Sonicator (Branson, 2510E/DTH) for 30 min. The nanocomposite powders

thus prepared were kept in zip-locked plastic packets and labeled for further processing.

2.5. Compression molding

The nanocomposites were prepared by using compression molding machine (Compression Molding Press, Santec, India). Thoroughly mixed nanocomposites powder were placed in mold covered with polished stainless steel plates and then compression molded at 200 °C under the pressure of 18 MPa. The heating time was kept at 10 min and the curing time at 5 min. After curing, the molds were cooled to room temperature before releasing the pressure for demolding. Sheets of dimensions 15 cm × 15 cm × 0.4 cm were obtained.

3. Characterization

3.1. Fourier transform infrared spectroscopy (FTIR)

The Fourier transform infrared spectroscopy (FTIR) spectra of nanocomposites were recorded between 600 and 4000 cm^{-1} using Bruker ALPHA FT-IR spectrometer. The samples were coated on a potassium bromide (KBr) plate and dried in a vacuum oven at 120 °C before it was tested.

3.2. X-ray diffraction (XRD)

X-ray diffraction measurements (XRD) for the composites have been performed using advanced diffractometer [PANalytical, XPERT-PRO] equipped with Cu-K α radiation source ($\lambda = 0.154 \text{ nm}$). The diffraction data were collected in the range of $2\theta = 2\text{--}60^\circ$ using a fixed time mode with a step interval of 0.05° .

3.3. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy [SEM] (JEOL, JSM-840A microscope) has been used to study the morphology of the fractured specimens. To study the surface morphology of the nanocomposites the specimens were soaked in hot water for 1 h. These specimens were then dried and gold sputtered prior to microscopy (JEOL, SM-1100E).

3.4. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) for nanocomposites has been performed using a JEOL, Model 782, operating at 200 kV. TEM specimens were prepared by dispersing the composite powders in methanol by ultrasonication. A drop of the suspension was put on a TEM support grid (300 mesh copper grid coated with carbon). After drying in air, the composite powder remained attached to the grid and was viewed under the transmission electron microscope.

4. Mechanical properties

4.1. Compression properties

The compressive properties of the nanocomposites were performed as per ASTM: D 695 by using Zwick UTM (Zwick Roell, ZHU, 2.5) with a pre load of 4.5 kN and a test speed of 5 mm/min. The samples were having a length of 5 cm, width of 1.5 cm and a thickness of 0.4 cm. A minimum of five specimens were tested for each variation in composition of the blend and results were averaged.

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