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ScienceDirect

Ceramics International 41 (2015) 12717–12727

CERAMICS INTERNATIONAL

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Preparation and characterization of carboxyl functionalized multiwall carbon nanotubes–hydroxyapatite composites

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Received 11 May 2015; received in revised form 16 June 2015; accepted 20 June 2015
Available online 29 June 2015

Abstract

In this article the experiments are described concerning the preparation conditions and the properties of multiwall –COOH functionalized carbon nanotube (fMWCNT)/hydroxyapatite and silica substituted hydroxyapatite composites. During the experiments the products were compared from several synthesis methods and the one with the highest homogeneity was established. The optimal fMWCNT content of the composites was also determined by analyzing the specific surface area and the particle size. The specific characteristics of the composites were defined by crystallinity, thermal stability, morphology and in vitro behavior studies, in order to correlate the preparation parameters to the possible applications.

Keywords: Composite materials; Co-precipitation method; Silica substitution; Multiwall carbon nanotube

1. Introduction

Hydroxyapatite (HAP) has received increasing attention as a bone implant material promoting the ability of bonding chemically with living bone tissues owing to its similar chemical composition and crystal structure to apatite in the human skeletal system [1,2]. However, the intrinsic brittleness and poor strength of the synthetized HAP restrict its clinical applications under load-bearing conditions [3]. HAP is a multisubstituted calcium–phosphate apatite and is able to replace the Ca^{2+} and the PO_4^{3-} ions with different types and amounts of ions. The bioactivity of the material can be enhanced by SiO_2 substitution [4–6]. Unfortunately neither the substituted HAPSi, nor HAP has good mechanical properties but this deficiency can be improved by adding carbon nanotubes (CNTs). Carbon nanotubes have aroused increasing interest due to their remarkable tensile strength, high mechanical strength, flexibility brilliant electrical and physicochemical properties and other unique structural, mechanical characteristics [7–10. Attempts have been made to create advanced engineering materials with new or better properties through the incorporation of CNT in the selected matrices such as polymers, metals and ceramics [11]. It is expected that by including CNT in a ceramic matrix will be produced composites with high stiffness and

Abbreviations: HAP, Hydroxyapatite; HAPSi, Silica substituted hydroxyapatite; fMWCNT–HAP, Hydroxyapatite with –COOH functionalized multiwall carbon nanotube; fMWCNT–HAPSi, Silica substituted hydroxyapatite with –COOH functionalized multiwall carbon nanotube

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http://dx.doi.org/10.1016/j.ceramint.2015.06.104
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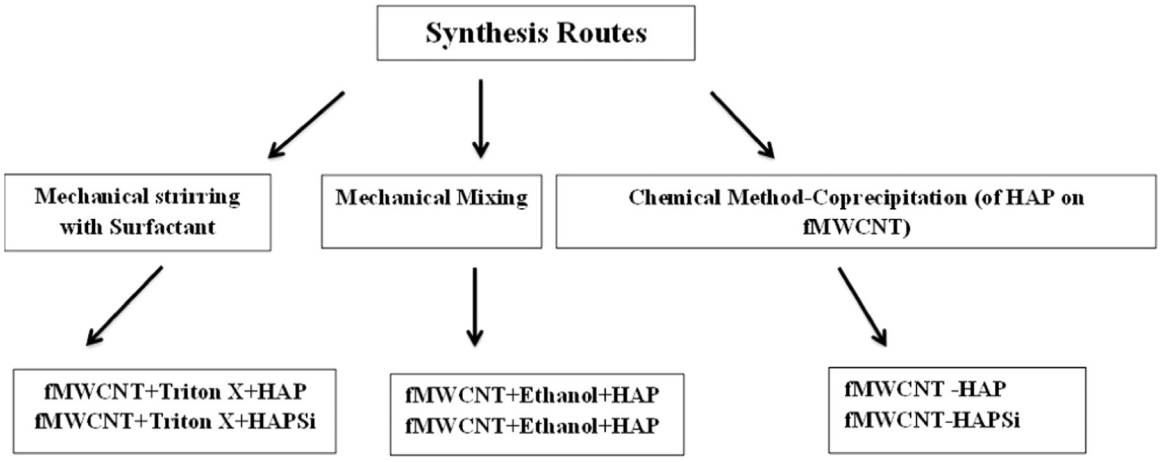

Fig. 1. Preparation methods.

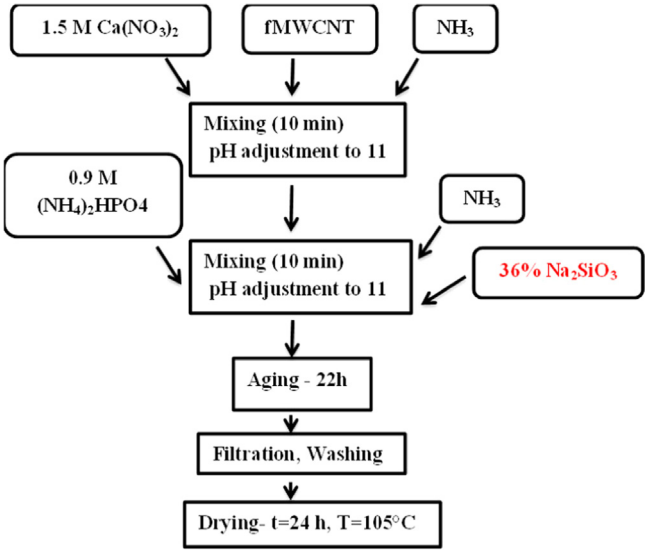

Fig. 2. The preparation schemes of MWCNT and MWCNT

better mechanical properties compared to the single phase ceramic material [7].

On the other hand, CNTs have also been supposed to be toxic [12–14] to human health [15–17]. It has been proved that the toxicity of CNTs can be reduced through chemical functionalization or by coating them with substances like polymers, hydroxyapatite or collagen [1,2]. In this way functionalized CNTs are soluble in many organic solvents because the hydrophobic nature of CNTs is turned into hydrophilic nature due to the attachment of polar groups [18]. The dispersion capacity of CNT is poor [19], but functionalization with oxidation promotes dispersion and at the same time surface activation is also achieved [20]. During the oxidation process, the defects on the CNTs, whether original or newly created, play an important role in the "decoration" of the functional groups (OH and COOH) on the CNT walls [21]. CNTs functionalized with groups such as carboxylates have negative charges, which make the CNTs repel each other and keep the solution dispersed [22]. These functional groups not only promote chemical reactivity of the CNTs but they also serve as the first step for subsequent surface treatment to make the CNTs easier to manipulate. Functionalization of the CNTs with organic chains or functional groups will not only advance their dispersion but will also reinforce the interactions between the CNTs and the hydroxyapatite [23].

Several methods are described in the literature for the preparation of hydroxyapatite and multiwall carbon nanotube composites (fMWCNT–HAP), e.g. mechanical-, chemical- and other mixing methods [23].

The aim of this work was to prepare fMWCNT–HAP and fMWCNT–HAPSi composites with different methods and different fMWCNT contents and to characterize the materials by several methods (XRD, BET, TEM, SEM, in vitro bioactivity, etc.). Thermal stability measurements and in vitro testing in form of pellets are important for the future application of the composites.

2. Materials and methods

2.1. Preparation of the materials

2.1.1. Synthesis of HAP and HAPSi

HAP and HAPSi were prepared by the co-precipitation method [24]. $Ca(NO_3)_2$ (Merck, Germany), $(NH_4)_2HPO_4$ (Merck, Germany), NH_3 (Merck, Germany) and Na_2SiO_3 (Lach:ner, Czech Republic) were used as precursors. In case of HAP the reaction time was 22 h and in case of HAPSi only 8 h. At the end of the reaction time the products were filtered and washed to eliminate excess ammonium nitrate and were dried for 24 h at 105 °C.

2.1.2. Preparation and functionalization of multiwall carbon nanotube (fMWCNT)

The multiwall carbon nanotubes (MWCNTs) were synthesized by a Chemical Vapour Deposition technique (CVD) and were purified by chemical treatment [25]. The MWCNT powder was first treated with NaOH and HCl solutions to remove the alumina support and the metallic catalyst particles. MWCNTs with oxygen containing functional groups (fMWCNT) were formed