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Enhanced magnetic behaviour and cell proliferation of gamma irradiated dual metal ions co-doped hydroxyapatite – poly(methyl methacrylate) composite films

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ABSTRACT

The poly (methyl methacrylate) (PMMA)/Iron-Zinc co-doped nanosized hydroxyapatite (Fe−Zn nHAp) composite films have been prepared by solvent evaporation method. The as prepared composite films were subjected to gamma irradiation at various dosages. Physico-chemical and biological characterization of the composite film were carried out. The XRD, FTIR and SEM analysis confirmed the presence of hydroxyapatite in the PMMA matrix. Irradiated composite films revealed reduced saturation magnetization (42%) and retentivity (66%) due to the defects created on irradiation. The gamma irradiated composite films showed strong antimicrobial activity on gram negative bacteria (*E. coli*) which may be due to the action of leakage of zinc ions on the surface that block the transport channels of the cell leading to the cell death. Moreover, substantial modification was seen in the hydrophobicity and surface roughness. The irradiations also tend to turn the samples semi conductive. The biocompatibility studies of the gamma irradiated composite films showed enhanced cell viability to NIH 3T3 fibroblast cells. Hence, the gamma irradiated samples showed excellent multifunctional properties that could be used in tissue engineering, bio-sensing and wound healing applications.

1. Introduction

A vertebral compressive fracture occurs when an individual spine bone was compressed due to trauma. Such fractures of bone are permitted to heal naturally. In vertebroplasty, the bone cement is injected into the injured or damaged vertebra to strengthen and prevent other micro-fractures [1]. Very few bone cement injections are available to treat vertebral fractures [2]. An ideal bone cement must possess appropriate inject ability, good stiffness, highly bioactive, rapid setting time and low setting temperature. Among the various bone cements, poly (methyl methacrylate) commonly known as PMMA and its derivatives are successfully used in various orthopaedic surgeries. PMMA is also used as dentures and space-filler. It is easy to make dentures and fillings quickly according to the requirement that is closer to size and color of the original teeth. Apart from this, PMMA is used to make contact lens and intraocular lens. The conventional PMMA have been employed in orthopaedic surgeries for more than two decades. Its weak mechanical properties compared to that of the cortical bones [3], monomer toxicity, non-bioactivity [4], and extreme exothermic reactions during polymerization limited the usage of PMMA in spinal surgeries [5].

Apart from PMMA, the other commercially available bone cements are glass polyalkenoate cements (GPCs) and calcium phosphate cements (CPCs) which are used in various orthopaedic and dental applications. The CPCs are biocompatible and bioactive in nature and are used only in the maxilla-facial and cranial surgeries. The mechanical strength of the cement is very low. Silver doped brushite CPCs showed an excellent antimicrobial property and exhibited an increase in the compressive

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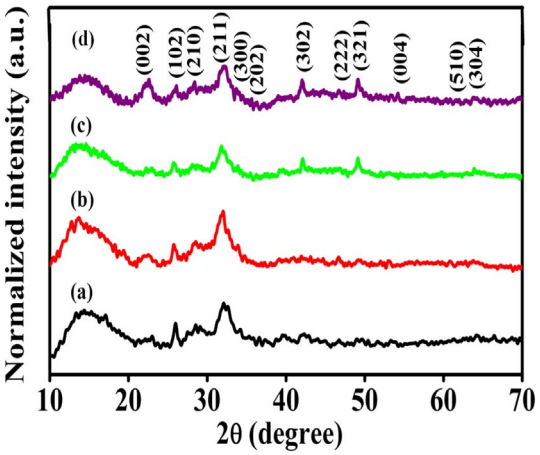

Fig. 1. XRD patterns of the samples (a) PFZH, (b) PFZH-25, (c) PFZH-50 and (d) PFZH-100.

Table 1
Lattice parameters of PFZH and gamma irradiated composite films.

S. No	Samples	Lattice parameters (Å)	
		a = b (± 0.01)	c (± 0.03)
1.	PFZH	9.49	6.54
2.	PFZH-25	9.63	6.95
3.	PFZH-50	9.65	7.01
4.	PFZH-100	9.73	6.79

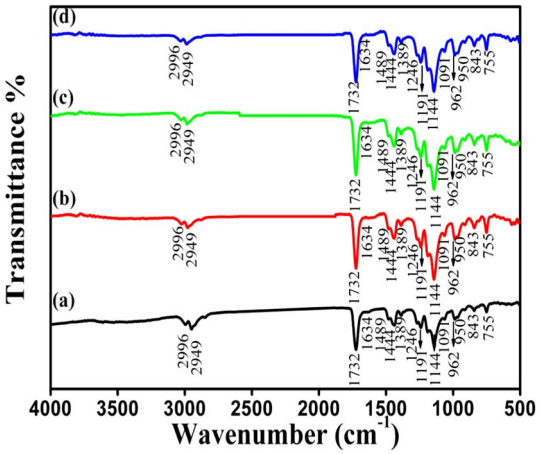

Fig. 2. FTIR spectra of (a) PFZH, (b) PFZH-25, (c) PFZH-50 and (d) PFZH-100.

modulus [6]. Despite of various bone cements available in the market, researchers continue in developing novel materials to reduce the adverse effects of the PMMA [7]. The U.S. Food and Drug Administration (FDA) approved the bone cement for knee and hip prosthetic fixation in 1970 [8]. Aghyarian et al. developed the promising new composite bone cements viz., PMMA-HAp and PMMA-brushite cements which served well than the usual PMMA cement [9]. Antibiotic such as levofloxacin based calcium phosphate-PMMA bone cement composites were synthesized to control the bone and joint infections [10]. Silver nanoparticles were added to PMMA as the silver nanoparticles showed high-antimicrobial activity and could serve an effective and promising material [11]. Zirconia and barium sulphate particles introduced in PMMA matrix showed a greater osteoblast density after 24 h compared to the other unmodified PMMA [12]. Chitosan-loaded PMMA, gentamicin-loaded PMMA and PMMA without antibiotic were compared in which the chitosan-loaded PMMA showed better results [13].

The motivation of this present investigation is to study the physicochemical and biological properties of PMMA-Fe-Zn-HAp composite films subjected to gamma irradiation with various dosages such as 25, 50 and 100 kGy. Here we report this composite material for the first time.

2. Experimental methods

2.1. Material preparation

The nano-sized hydroxyapatite and Iron (Fe^{3+})-Zinc (Zn^{2+}) co-doped hydroxyapatite powders were synthesized by wet chemical precipitation route. The precursors used for the synthesis were diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, Merck), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$, Merck), zinc chloride ($ZnCl_2$, Merck), ferric chloride ($FeCl_3$, Qualigens) and ammonia solution (analytical grade).

Diammonium hydrogen phosphate of 0.6 M concentrations was prepared using triple-distilled water. Calcium nitrate of 1 M concentration was mixed with different molar concentrations of $FeCl_3$ and $ZnCl_2$ (0.01 M, 0.05 M and 0.1 M) respectively. The calcium, iron and zinc mixture were added drop by drop to the diammonium phosphate solution in 1:1 volume ratio with vigorous stirring, using a magnetic stirrer for 3 h. The solution was maintained with the pH of 10 using aqueous ammonia. Further, the slurry was subjected to ultrasonication for 1 h with Sonics-Vibra-Cell VCX 750 (750 W) probe ultrasonicator. The resultant mixture was washed 8 times with triple distilled water and dried at 80 °C in a hot air oven. The Iron/Zinc co-doped HAp of particle size 50–70 nm was obtained [14].

2.2. Preparation of PMMA-nFZHAp composites films

The PMMA–Fe-Zn-nHAp composite films were prepared by solvent evaporation technique. PMMA powder of 10 wt% was dissolved in acetone. The Fe-Zn-nHAp (1 M) of 1 wt% was added to the polymer solution slowly in the ratio 10:1 (PMMA:Fe-Zn-nHAp). Once the polymer was blended well with the HAp, the solution was casted in a glass petriplate and kept in 20 °C atmosphere. The solvent evaporated slowly and the resultant composite films of PMMA-Fe-Zn-nHAp were named as PFZH.

2.3. Gamma irradiation

The composite films were subjected to gamma irradiation at different doses (25 kGy, 50 kGy and 100 kGy). Hereafter, the gamma irradiated PFZH composites films of 25 kGy, 50 kGy and 100 kGy doses were denoted as PFZH-25, PFZH-50 and PFZH-100 respectively.

2.4. Characterization

The phase confirmation and crystallinity of the synthesized samples were analysed with a PANalyticalX'Pert Powder XRD System of Cu K_α radiation (0.154 nm) with step size 0.02° in the 2θ range of 10° to 80° in a continuous scan mode. The functional groups of the pristine and gamma irradiated samples were studied by Fourier Transform Infrared Spectrometer. The Carl Zeiss MA 15/EVO 18 scanning electron microscope (SEM) was used to study the morphology of the samples. The Lakeshore VSM 7410 vibrating sample magnetometer instrument was used to measure the magnetic fields of the sample with an applied magnetic field of ± 2 T between − 17,500 to + 17,500 G. The atomic force microscope (AFM) images were recorded using Dimension Edge-Bruker instrument by non-contact mode. Diffuse reflectance spectra (DRS) were measured using Jasco UV–vis-NIR spectrometer model V670 in the range of 300–700 nm. The Tauc plot of the samples were drawn to estimate the optical band gap (E_g) using the expression $(\alpha h\nu)^{1/n} = 0$, where α is the absorption coefficient and hν is the photon energy. The absorption coefficient of the samples can be calculated