

Synthesis and characterization of acrylic bone cement reinforced with calcium carbonate-bioceramic

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Acrylic bone cement reinforced with bioceramic was synthesized by mixing beads of PMMA (produced by suspension polymerization), methylmethacrylate (MMA) as monomer, benzoyl peroxide (BPO) as free radical initiator and calcium carbonate (CaCO_3) powder as bioceramic. The structure of PMMA, the structure of calcium carbonate and that of the acrylic bone cement reinforced or not with bioceramic were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Bioactivation of the PMMA bone cement by adding CaCO_3 powder acting as bioceramic can be an advantageous solution for problems of bone filling as well as bone regeneration.

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1. Introduction

For nearly five decades, poly(methyl methacrylate) (PMMA) bone cement is one of the most important primary synthetic biomaterials used in orthopaedics to anchor artificial joints [1, 2, 3]. The PMMA bone cement fills the free space between the implant and the bone and constitutes a crucial interface. It acts as a grout, adapting the surface irregularities of the surrounding bone tissue to the surface of the inserted implants [2, 4]. However, poor integration with bone, local tissue damage due to chemical reactions during polymerization, monomer toxicity, the high shrinkage of the cement after polymerization, the stiffness mismatch between the bone and the cement are some drawbacks associated with PMMA-based bone cements [3, 5]. Therefore, the development of new formulations namely bioactive bone cements is highly desirable, in order to promote bone growth and the formation of a strong chemical bond between the implant and the bone tissue. The incorporation of a bioactive component in combination with the acrylic polymer seems to be the main route to improve the interfacial strength of cement to the bone [6, 7]. In this sense, a wide variety of PMMA bone cements based on corn starch/cellulose acetate blends filled with hydroxyapatite (HA) or Bioglass, cements composed of chitosan and natural bone powder, cements containing microspheres of chitosan/ β -TCP or calcium phosphate cements have been used to improve the properties [6, 7].

Bioactive bioceramics include: bioactive glass, calcium carbonate (natural coral), calcium sulfate and

calcium phosphates of biologic (derived from bovine bone, coral and marine algae) or synthetic origin [8, 9].

Calcium carbonate (CaCO_3) is one of the most abundant minerals in nature and has three polymorphs known as calcite, aragonite and vaterite [10, 11]. The most thermodynamically stable phase is calcite followed by aragonite and vaterite [12, 13]. The industrial importance of calcium carbonate is well recognized as a filler in composition materials such as plastics, textiles, rubbers, paints, pigments, paper, coating, tooth paste cosmetics, sealants and in the food industry [14, 15].

Calcium carbonate is also considered one of the most significant building materials of natural hard tissues such as bones and teeth [16].

Recent applications as a bioceramic material for implantation purposes have been proposed due to its potential in biomineralization, biocompatibility and bioresorbability properties [15, 17]. Furthermore, calcium carbonate could be an interesting candidate to prepare cement with improved biodegradation rates due to its higher solubility compared to apatite [12]. Ohgushi et al. [18] showed that the bone forming response of CaCO_3 was comparable to that of the well-known bioactive hydroxyapatite.

In this work, an acrylic bone cement reinforced with bioceramic was prepared by mixing beads of PMMA (produced by suspension polymerization), methylmethacrylate (MMA) monomer, benzoyl peroxide (BPO) as free radical initiator and calcium carbonate powder acting as bioceramic.

2. Experimental

2.1. Preparation of the calcium carbonate

A 4.24 g quantity of sodium carbonate (Na_2CO_3) (Sigma Aldrich) and 5.33 g of calcium chloride (CaCl_2) (Sigma Aldrich) were each dissolved in 200 ml of deionized water. The Na_2CO_3 solution was added slowly drop wise to the CaCl_2 solution under magnetic stirring, yielding a milky suspension, which was then stirred for 1.5 h at room temperature. The products (calcium carbonate) were filtered, washed with deionized water and dried in an electrical air oven at 60°C for 48 h. The procedure was similar to that of Guo et al. [19].

The structure of the calcium carbonate (CaCO_3) was investigated by FTIR, XRD and SEM.

2.2. Preparation of PMMA beads

PMMA beads were prepared by free radical suspension polymerization [20, 21]. The raw materials: water, suspending agent (CMC) (Fluka), monomer (MMA)(Fluka) and initiator (BPO)(Merck) were added in a 1L three-necked reactor equipped with a reflux condenser, a mechanical stirrer and a temperature control system. The polymer was received as beads and after sieving its portion less than $250\ \mu\text{m}$ was used.

The produced PMMA was characterized by FTIR, XRD and scanning electron microscopy (SEM).

2.3. Preparation of the acrylic bone cement reinforced or not with bioceramic (calcium carbonate powder).

The acrylic bone cement reinforced with bioceramic was prepared by mixing beads of PMMA (produced by suspension polymerization), methylmethacrylate (MMA) as monomer, benzoyl peroxide as free radical initiator and calcium carbonate powder as bioceramic. Bioceramic powder (calcium carbonate powder in 13 % w/w of mixture components) was added to a solution of PMMA beads (2 g) in MMA (1.42 ml) with benzoyl peroxide as free radical initiator (0.5 % w/v of MMA). The components of the acrylic bone cement reinforced or not with bioceramic were hand-mixed for ca. 5 min until the mixture became a paste with high viscosity. Then, the paste was placed into small parallelepiped moulds and polymerized at 60°C for 24 hours to give acrylic bone cement or acrylic bone cement reinforced with bioceramic.

The structure of the acrylic bone cement reinforced or not with bioceramic (calcium carbonate powder) was investigated by FTIR, XRD and SEM.

2.4 Characterization of the materials by FTIR, XRD, SEM/EDS

FTIR spectra were recorded using a Perkin Elmer Spectrum 2000, on discs prepared by mixing of the sample powder and KBr.

XRD measurements were performed with a Siemens D5000 X-Ray Diffractometer by using sample of the material as powder.

The SEM studies were carried out in a FEI Quanta 200 Scanning Electron Microscope (SEM). The material was examined as specimen with dimensions of $10\times 8\times 4\text{mm}$.

3. Results and discussion

3.1 FTIR

Fig. 1 shows the FTIR spectra of PMMA beads, calcium carbonate (CaCO_3) after drying at 60°C for 48 h and acrylic bone cement reinforced with bioceramic (CaCO_3 powder in 13% w/w).

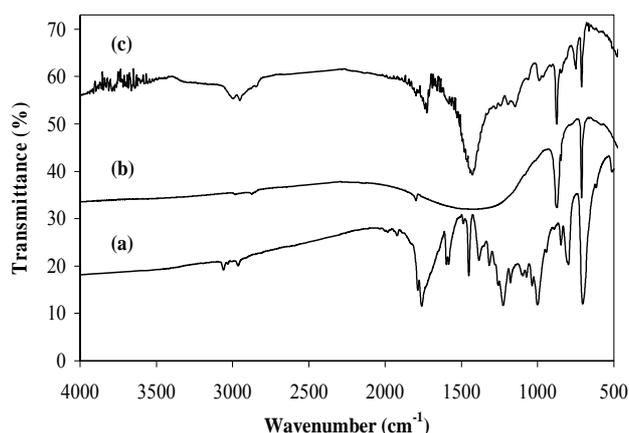


Fig. 1. FTIR spectra of (a) PMMA, (b) calcium carbonate (CaCO_3) after drying at 60°C for 48 h and (c) acrylic bone cement reinforced with bioceramic (CaCO_3 powder in 13% w/w).

According to Fig. 1(a), the characteristic vibration bands of PMMA appear at $1757\ \text{cm}^{-1}$ $\nu(\text{C}=\text{O})$ and $1451\ \text{cm}^{-1}$ $\nu(\text{C}-\text{O})$. The bands at 3054 and $2959\ \text{cm}^{-1}$ correspond to the C-H stretching of the methyl group (CH_3) and the bands at 1315 and $1451\ \text{cm}^{-1}$ are associated with C-H symmetric and asymmetric stretching modes, respectively. The $1244\ \text{cm}^{-1}$ band is assigned to torsion of the methylene group (CH_2) and the $1176\ \text{cm}^{-1}$ band corresponds to vibration of the ester group C-O, while C-C stretching bands are at 997 and $845\ \text{cm}^{-1}$ [22, 23, 24].

All the characteristic vibration bands of calcium carbonate (CaCO_3) are presented in Fig. 1 (b). The bands at $1799\ \text{cm}^{-1}$, $1469\ \text{cm}^{-1}$, $1091\ \text{cm}^{-1}$, $877\ \text{cm}^{-1}$ and $711\ \text{cm}^{-1}$ are assigned to the carbonate group (CO_3^{2-}) and according to literature [19] are bands characteristic of calcite structure.

According to *Fig. 1 (c)*, the presence of calcium carbonate (CaCO_3) powder in the acrylic bone cements is indicated by the additional vibration bands at 1799 cm^{-1} , 1444 cm^{-1} , 877 cm^{-1} and 711 cm^{-1} attributed to the carbonate group (CO_3^{2-}) [19].

3.2 XRD

Fig. 2 shows the XRD results of PMMA beads, calcium carbonate (CaCO_3) after drying at 60°C for 48 h, acrylic bone cement not reinforced with bioceramic (CaCO_3) and acrylic bone cement reinforced with bioceramic (CaCO_3 powder in 13% w/w).

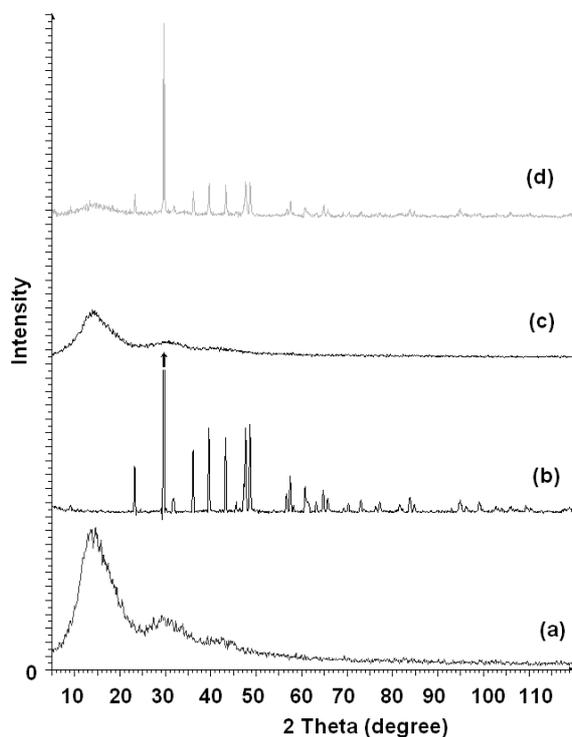


Fig. 2. XRD diffractograms of (a) PMMA beads, (b) calcium carbonate (CaCO_3) after drying at 60°C for 48 h, (c) acrylic bone cement not reinforced with bioceramic (CaCO_3) and (d) acrylic bone cement reinforced with bioceramic (CaCO_3 powder in 13% w/w).

The XRD diffractogram of PMMA beads is shown in *Fig. 2(a)*.

PMMA is known to be an amorphous polymer and shows three broad peaks at 2Θ values of 11.62° , 30.67° and 31.96° (d spacing approx. 7.61 , 2.91 and 2.79 \AA correspondingly) with decreasing intensity. According to literature, the shape of the first most intense peak reflects the ordered packing of polymer chains while the second peak denotes the ordering inside the main chains [22].

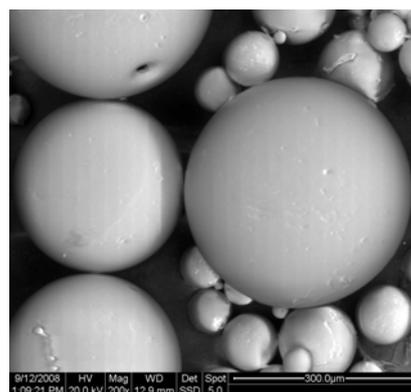
According to the diffraction peaks shown in *Fig. 2(b)*, the corresponding d spacings (\AA) were determined: $d=3.85$ ($2\Theta=23.08^\circ$), $d=3.02$ ($2\Theta=29.4^\circ$), $d=2.83$

($2\Theta=31.5^\circ$), $d=2.49$ ($2\Theta=36.0^\circ$), $d=2.15$ ($2\Theta=41.9^\circ$), $d=2.08$ ($2\Theta=43.2^\circ$), $d=1.96$ ($2\Theta=46.2^\circ$), $d=1.92$ ($2\Theta=47.2^\circ$), $d=1.87$ ($2\Theta=48.5^\circ$), $d=1.60$ ($2\Theta=57.4^\circ$), $d=1.58$ ($2\Theta=58.2^\circ$), $d=1.43$ ($2\Theta=64.7^\circ$), $d=1.41$ ($2\Theta=65.7^\circ$), $d=1.35$ ($2\Theta=69.2^\circ$), $d=1.33$ ($2\Theta=70.3^\circ$), [25, 26]. The corresponding d (lattice spacing) of the 2Θ ($^\circ$) peaks are similar to those determined in the literature [25, 26] for the crystalline calcite phase of calcium carbonate.

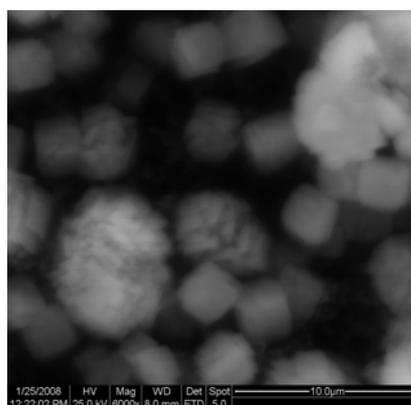
The XRD diffractogram of the acrylic bone cement without bioceramic (calcium carbonate powder in 13% w/w) presented in *Fig. 2 (c)* indicate amorphous structure. The acrylic bone cement has similar peaks to those of PMMA.

The XRD diffractogram of the acrylic bone cement reinforced with bioceramic (calcium carbonate powder in 13% w/w) presented in *Fig. 2(d)* shows the characteristic peaks of calcite with the peaks of the amorphous PMMA, mainly its first peak [25, 26].

3.3 SEM

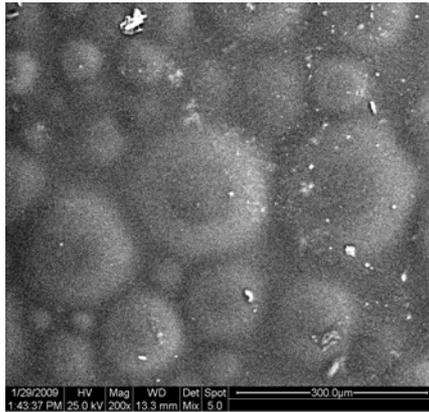


(a)

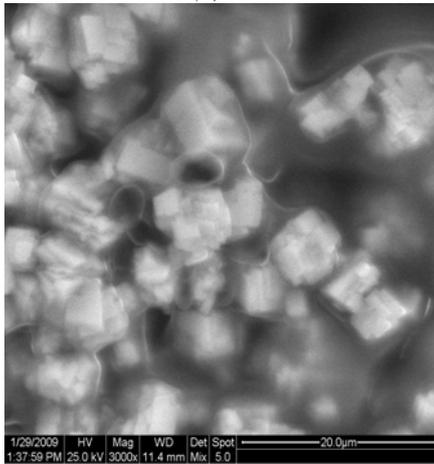


(b)

Fig.3. SEM image of the (a) PMMA beads and of the (b) calcium carbonate (CaCO_3).



(a)



(b)

Fig.4. SEM images of (a) acrylic bone cement without bioceramic and (b) reinforced with bioceramic (CaCO_3 powder in 13 % w/w).

Fig. 3 (a) shows the SEM image of PMMA beads. As clearly seen, the PMMA beads have a spherical form. The diameter of the most beads is approx. 250 μm .

Fig. 3 (b) shows the SEM images of calcium carbonate crystals (CaCO_3). It can be seen that rhombohedral calcite crystals (CaCO_3) with an average diameter around 4 μm were obtained.

According to SEM image presented in Fig. 4 (a), the PMMA beads are distinguished in the acrylic bone cement, with the polymerized MMA connecting the beads.

According to Fig. 4 (b), the acrylic bone cement is a multiphase composite material. The PMMA beads are surrounded by the polymerized MMA monomer acting as binding agent. The small white particles are calcium carbonate powder used as bioceramic.

4. Conclusions

It can be concluded that a suitable acrylic bone cement reinforced with bioceramic (calcium carbonate powder) has been synthesized which can be used as

biomaterial candidate. Bioactivation of the PMMA bone cement by adding CaCO_3 powder acting as bioceramic can be an advantageous solution for problems of bone filling as well as bone regeneration.

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