



Towards optimization of the silanization process of hydroxyapatite for its use in bone cement formulations



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ABSTRACT

The aim of this work was to provide some fundamental information for optimization of silanization of hydroxyapatite intended for bone cement formulations. The effect of 3-(trimethoxysilyl) propyl methacrylate (MPS) concentration and solvent system (acetone/water or methanol/water mixtures) during HA silanization was monitored by X-ray diffraction (XRD), FTIR spectroscopy and EDX analysis. The effect of silanized HA on the mechanical properties of acrylic bone cements is also reported. It was found that the silanization process rendered hydroxyapatite with lower crystallinity compared to untreated HA. Through EDX, it was observed that the silicon concentration in the HA particles was higher for acetone–water than that obtained for methanol–water system, although the mechanical performance of cements prepared with these particles exhibited the opposite behavior. Taking all these results together, it is concluded that methanol–water system containing MPS at 3 wt.% provides the better results during silanization process of HA.

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1. Introduction

It is well known that the incorporation of hydroxyapatite (HA) to bone cement formulations enhances the biocompatibility and bioactivity of these materials but generally reduces their mechanical properties [1–4]. This is related not only to the lack of interfacial bonding between polymeric matrix and the inorganic filler but also due to hydroxyapatite agglomeration (i.e. hydrophilic inorganic particles are not easily dispersed in a hydrophobic matrix) that acts as stress concentrators [5,6]. In order to overcome this drawback, coupling agents such as titanates, zirconates and silanes have been used to modify the surface properties of the HA particles and thereby improve the interfacial compatibility between inorganic particles and organic matrix [7].

According to a literature review, silanes are the most common coupling agents used to modify the surface characteristics of the HA [3,8–14]. During the surface modification process, many factors such as type and concentration of coupling agent, nature of solvent(s), pH, etc., may influence the way in which the silane molecules are absorbed, condensed or interacted with the substrate thus affecting the coupling efficiency [14]. In this regard, the most popular silane coupling agent for dental materials and bone cement formulations is the 3-

(trimethoxysilyl) propyl methacrylate (also called 3-methacryloyloxy propyl trimethoxysilane) as its organofunctional group matches the chemical structure and reactivity of the monomer/polymer systems involved in these applications. In contrast, a variety of different solvents have been used during silanization process with MPS including cyclohexane [11], acetone [15], acetone/water mixture [3,4,6,8], methanol/water mixture [9,11,12], ethanol/water [13] among others.

Another factor that has been varied extensively during surface treatment of the HA particles is the concentration of silane coupling agent. For example, Dagiilar and Erkan [10] used 0.2 wt.%; Harper et al. [8] and Ho and Marcolongo [15] used 5 wt.%; Tham et al. [9] used 2, 4, 6 and 8 wt.%; Santos et al. [11] and Domingo et al. [12] used 10 wt.%; and Deb et al. [4] and Roether and Deb [3] used 12.5 wt.%. On the other hand, manufacturers of coupling agents indicate that the typical fillers, with average particle sizes of 1 to 5 μm, often give the best results when these are treated with about 1% silane, although the optimal level of silane treatment should be determined experimentally [16]. It has also been reported that too much silane within formulation can lead to a detrimental effect of the properties measured [17,18] as oligomers (siloxanes) can be formed.

Taking into account the abovementioned considerations, in this work we attempt to provide information that may lead to the optimization of silanization process of the hydroxyapatite for its use in bone cement formulations. Some attempts to optimize the silane deposition onto surface hydroxyapatite have been performed but these studies

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were focused either on the type of silane coupling agent [13] involving vinyl, methacryloxy, primary and secondary amine functionalities, or silane concentrations of 2, 4, 6 and 8 wt.% [9].

From all the potentially useful solvents in the silanization process, acetone/water and methanol/water mixtures were selected not only because they are the most reported in the literature review but also because they contain some amount of water, which at acid pH facilitates the hydrolysis of the alkoxy groups [19]. Different amounts of 3-(trimethoxysilyl) propyl methacrylate (silane A-174) were tested for each solvent system and the influence of these factors (silane concentration and solvent system) on the mechanical properties of acrylic bone cements was studied.

2. Materials and methods

The synthetic hydroxyapatite particles used in this work were prepared in our laboratories by means of an aqueous precipitation reaction between calcium hydroxide suspension and an aqueous solution of phosphoric acid at 90 °C. The wet powders were filtered and calcined at 800 °C for 2 h to produce HA particles.

Acetone and methanol, analytical (reagent) grade, from Baker ACS and acetic acid from Fisher Scientific were used for the different surface treatments; 3-methacryloyloxy propyl trimethoxysilane (silane A-174) from Aldrich was used as coupling agent.

Methyl methacrylate (MMA), N,N-dimethyl-p-toluidine (DMPT) and benzoyl peroxide (BPO) were also purchased from Aldrich and used as received. PMMA beads (60 µm) were supplied by Manufacturera Dental Continental and used as the solid component in bone cement formulations.

2.1. Silanization of hydroxyapatite particles

Solvent mixtures for silanization processes were based on ratios reported previously in the literature. Roether and Deb [3], Deb et al. [4] and Harper et al. [8] reported a ratio of acetone to water of 70:30 whereas Santos et al. [11] and Domingo and Fraile [12] used a ratio of methanol to water of 95:5.

2.1.1. Acetone–water system

Hydroxyapatite (HA) particles were dispersed in a 70:30 acetone–water mixture at room temperature. The pH of the solution was adjusted to 3.5 with acetic acid and it was stirred continuously during 1 min. Then, the silane coupling agent at 1, 2 or 3 wt.% (all weight percentages of silane were estimated with respect to the weight of the HA particles) was added to the solution and left under agitation for 1 h. The mixture was then heated at 100 °C to evaporate the excess of water and acetone and the powder was left in a vacuum oven at 70 °C for 24 h; no further washing was carried out. Finally, the treated particles were stored in a desiccator until its use.

2.1.2. Methanol–water system

HA particles were dispersed in a 95:5 methanol–water mixture at room temperature. The pH of the solution was adjusted to 3.5 with acetic acid and it was stirred continuously during 1 min. Then, the silane coupling agent at 1, 2 or 3 wt.% was added to the solution and left under agitation for 1 h. Suspension was then decanted and the remaining slurry was heated in a vacuum oven at 70 °C for 24 h; no further washing was carried out. The treated particles were stored in a desiccator until its use.

2.2. Characterization of the silanized hydroxyapatite

2.2.1. X-ray diffraction (XRD)

XRD patterns were obtained using a D-5000 Siemens diffractometer with Cu K α = 1.5418 Å radiation generated at a voltage of 35 kV and a current of 24 mA. Data were collected in the 2 θ range of 5–50°, with a

step count of 3 s and step size of 0.02°. XRD was also used to determine the crystallinity of hydroxyapatite according to the methodology reported by Landi et al. [20] using the following equation:

$$X_c(\%) = \frac{I_{300} - V_{112/300}}{I_{300}} * 100$$

where I_{300} is the intensity of (300) diffraction peak and $V_{112/300}$ is the intensity of the hollow between (112) and (300) diffraction peaks of the hydroxyapatite.

2.2.2. Fourier transform infrared spectroscopy (FTIR)

Infrared analysis was performed using a Nicolet Protegé 460 FTIR spectrometer. Spectra were obtained from either KBr pellets or by means of diffuse reflectance (DRIFT) accessory, in a spectral range from 4000 to 400 cm⁻¹, averaging 100 scans and 4 cm⁻¹ of resolution.

2.2.3. Energy dispersive X-ray microanalysis (EDX)

Elemental composition of the HA particles was studied by means of energy dispersive X-ray microanalysis (EDX) using an Oxford Inca Energy 200 energy dispersive spectrometry (EDS) system coupled to scanning electron microscope (SEM) JEOL JSM 6360 LV.

2.3. Preparation of bone cements

The experimental bone cements were formulated by adding the liquid component to the powder component at room temperature (25 °C). The powder component consisted of PMMA beads, BPO (1 wt.%) and HA at 10 wt.% (HA10) or 20 wt.% (HA20), whereas the liquid component consisted of MMA (97.5 v/v) and DMPT (2.5 v/v).

A weight ratio of powder to liquid of 2 was kept in all cases and the cements were prepared by hand mixing without vacuum. Cements containing untreated HA were prepared for comparison purposes as control.

In order to study the effect of silanization process of the HA on the mechanical properties of bone cements, the silane coupling agent was added at 1, 2 or 3 wt.% with respect to the weight of the HA (1MPS, 2MPS, 3MPS) and radiopaque agent was not added to bone cement formulations.

2.4. Mechanical properties

Mechanical properties were evaluated according to ISO 5833 (Annex C) using a Shimadzu Autograph AG-I Universal Testing Machine. Specimens were tested after storing them for one week in air at 25 °C. Compression tests were performed on cylindrical specimens (6 mm diameter, 12 mm height) at a cross-head speed of 20 mm/min with a load-cell of 5 kN; compressive strength and modulus were recorded. Rectangular bar specimens of dimension (length = 75 mm, width = 10 mm and thickness = 3 mm) were prepared for determination of flexural strength and modulus. Four-point bending experiments were carried out using a crosshead of 5 mm/min and a load-cell of 500 N. At least six specimens were tested per condition and a one-way analysis of variance was performed for the analysis of results (Tukey, $P < 0.05$).

Fracture surfaces of bone cement specimens were observed by SEM after bending experiments. Samples were gold-coated and observed with a JEOL JSM 5900-LV at an accelerating voltage of 20 keV.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the X-ray diffraction (XRD) patterns of the HA particles without treatment and those treated with silane A-174 using the acetone–water (Fig. 1(a)) and methanol–water (Fig. 1(b)) systems. As noted, all samples exhibited the characteristic peaks of HA reported in

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