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Influence of magnesium and silver ions on rheological properties of hydroxyapatite/chitosan/calcium sulphate based bone cements

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ABSTRACT

Rheology of bioceramic bone cements is usually described as properties of ceramic slurries, neglecting the self-setting character of these materials. In our studies calcium sulphate based bone cements with Ag^+ , Mg^{2+} and $\text{Mg}^{2+}/\text{CO}_3^{2-}$ modified hydroxyapatite were investigated. Despite of expectations, it has been proven that the presence of magnesium ions significantly influence the rheological properties of cement pastes. Changes in rheological properties were connected with (I) chemical interactions between Mg^{2+} and sulphate ions (II) chemical interaction between Mg^{2+} and chitosan. These effects were not observed for silver additive. Most of the developed calcium sulphate based pastes, except material containing MgHA and chitosan, have been categorized as thick pastes applicable with the spatula. It has been found that the chitosan present around and at the calcium sulphate grains acted as a lubricant and prolong the period of quasi-constant viscosity of the pastes.

1. Introduction

Bioceramic bone cements are believed to be a promising alternative for the traditional sintered bioceramics in the restoration of bone defects. Bone cement formulations consist of powder and liquid phase, which when mixed together create shapeable, self-setting paste. Application of injectable, self-setting formulations offers significant advantages in comparison to conventional, pre-shaped bone substitutes. Delivery of the cement through a needle or cannula will make it more useful in clinical applications. Bone cements can be introduced directly into the defect, where conforms to its shape. This offers enhanced contact to the host tissue. Calcium phosphate bone cements (CPCs) are the largest and most intensively studied group of bioceramic bone cements. On the other hand biomaterials on the basis of calcium sulphate and polymers are nowadays of great interest [1–6]. Calcium sulphate (CS) possesses a long history of clinical use and is known to be a well-tolerated, rapidly and completely bioresorbable material [7–10]. In addition to its space-filling and barrier functions, CS has been investigated as a local delivery vehicle for therapeutic agents, such as antibiotics or growth factors [11,12]. So far calcium sulphate based bone substitutes are believed to resorb too fast to provide appropriate mechanical support for new forming bone tissue. That is why composites on the basis of calcium sulphate and other inorganic or organic additives such as hydroxyapatite, chondroitin sulphate, hyaluronic acid or chitosan have been recently intensively explored [10,13–17]. The incorporation of some metal ions such as Ag^+ , Cu^{2+} , Mg^{2+} into

hydroxyapatite is a popular strategy to influence its biological properties [18].

Due to the great variety of bioceramic bone cement compositions, there is still a lot to be done to reach a better understanding and creating of their physical, chemical and biological properties. Some of the fundamental properties of these chemically bonded materials such as rheology are still poorly known and rarely investigated. Rheology is applicable to all materials, from gases to solids and may be defined as the study of flow and deformation of materials under applied forces. Many biomaterials exhibit very complex rheological properties. Their viscosity and viscoelasticity can vary depending upon the external conditions applied, such as stress, strain, timescale and temperature, but also the internal properties of the material [19,20]. Furthermore, the rheology of organic-inorganic composites is usually dominated by the rheological properties of the polymer matrix. As rheology is one of the key features to describe setting behaviour and injectability of cements various rheological parameters were extensively studied [21–23].

Rheology of bioceramic bone cements is usually described as properties of ceramic slurries, neglecting the self-setting character of these materials. So far rheological properties of some calcium phosphate bone cements have been successfully investigated [19,20,24,25], whereas only a few manuscripts on calcium sulphate based bone cements are accessible [2,26]. Bohner et al. [27] and Qi et al. [28] showed that improvement of rheological properties can be obtained by adjusting material parameters, such as: phase composition, liquid to

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powder ratio or the powder particle size distribution and particle shape. To obtain injectable materials also modification of injection system parameters (e.g. length of the diameter of syringe cannula or injection rate) can be applied. Relevant shear rates for the injection process can be assumed between $10\text{--}1000\text{ s}^{-1}$ [29]. A compromise between rheological properties of the cement and the injection system need to be found. Kumar et al. [30] investigated rheology of chitin hydrogel with addition of calcium sulphate hemihydrate and nanofibrin. Obtained biomaterials possessed good mouldability as well as high potential for osteoregeneration via enhanced angiogenesis. Developed hydrogels with containing calcium sulphate were found to be injectable but the ejected gel showed rough margins with intermittent breaks. Kumar et al. suggested that the addition of CSH particles to chitin gel, resulted in the formation of dihydrate crystals which might interrupt the uniformity of polymeric chains and impart brittleness to the gel. For medical application alpha form of calcium sulphate hemihydrate is believed to be more appropriate, however beta calcium sulphate has also been investigated. Liu et al. [2] examined the potential of the β -calcium sulphate hemihydrate (β -CSH) as an injectable material. He demonstrated that β -CSH can be injected into the bone defect, exhibits promising capability of repairing in vivo bone fracture and shows a degradation speed similar to that of commercial α -CSH based material.

The objective of this work was to study the influence of the chitosan and hydroxyapatite modified via magnesium, silver and/or carbonate ions on the rheological behaviour of the cements on the basis of calcium sulphate hemihydrate (CSH), during the early stages of setting.

2. Materials and methods

2.1. Initial powders preparation

The wet chemical method was applied to synthesize non-modified hydroxyapatite (HA) as well as hydroxyapatite doped with silver (AgHA), magnesium (MgHA), and $\text{Mg}^{2+}/\text{CO}_3^{2-}$ ions (MgCHA). The conditions and reagents applied during the synthesis of non-modified and modified hydroxyapatite initial powders were summarize in Table 1.

Materials doped with 0.3 wt% of magnesium and 12.0 wt% of carbonate ions (MgCHA), 0.3 wt% of Mg^{2+} (MgHA) and 1.0 wt% of silver (AgHA) were obtained. During synthesis, the pH value of the reaction environment was stabilized at ~ 11 using ammonium hydroxide solution. The suspensions were aged for 24 h at room temperature, decanted and dried. The obtained powders were heat treated and ground into a grain size less than 0.063 mm. Alpha form of calcium sulphate hemihydrate (α -CSH) was purchase from Acros Organics.

Specific surface area of the initial powders was measured using BET (Brunauer-Emmett-Teller) method for nitrogen adsorption at liquid nitrogen temperature (ASAP 2010, Micromeritics) (Table 1).

2.2. Cement pastes preparation

To obtain initial powder batches the modified hydroxyapatite powders and calcium sulphate hemihydrate were mixed together in the

Table 1

The conditions and reagents applied during the synthesis of initial powders.

Synthesised powder	Symbol	Initial reagents	Sintering temperature [°C]	SSA [m ² /g]
Non-modified hydroxyapatite	HA	CaO (POCH, Poland) 85 wt% H ₃ PO ₄ (POCH, Poland).	800	5.87 ± 0.11
Magnesium doped carbonate hydroxyapatite	MgCHA	Ca(OH) ₂ (Merck, Poland), (NH ₄) ₂ HPO ₄ (POCH, Poland), (CH ₃ COO) ₂ Mg (POCH, Poland) NH ₄ HCO ₃ (POCH, Poland)	400	74.30 ± 0.20
Magnesium doped hydroxyapatite	MgHA	Ca(OH) ₂ (Merck, Poland), (NH ₄) ₂ HPO ₄ (POCH, Poland), (CH ₃ COO) ₂ Mg (POCH, Poland)	800	20.10 ± 0.01
Silver doped hydroxyapatite	AgHA		800	25.20 ± 0.02

Table 2
The initial composition of cements.

Symbol	Powder phase (P)	Liquid phase (L)	L/P [g/g]
A-1	HA: CSH	Distilled water	
A-2	2:3	1.0 wt% chitosan solution in 0.3 wt% acetic acid solution	0.9
B-1	MgHA: CSH	Distilled water	
B-2	2:3	1.0 wt% chitosan solution in 0.3 wt% acetic acid solution	0.9
C-1	MgCHA: CSH	Distilled water	
C-2	2:3	1.0 wt% chitosan solution in 0.3 wt% acetic acid solution	0.9
D-1	AgHA: CSH	Distilled water	
D-2	2:3	1.0 wt% chitosan solution in 0.3 wt% acetic acid solution	0.9

2:3 weight ratio (Table 2). The cement batches were prepared in the mixer ball mill MM200 (Retsh). Homogenization was performed by introducing 5 g of powder mixture to each jar and mixing them for 5 min (8 Hz, 5 zirconium oxide balls per jar). Distilled water and chitosan solution in 0.3% acetic acid were used as liquid phases. For preparation of liquid solution medium molecular weight chitosan (100,000 kDa, degree of deacetylation: 75–85%, Sigma Aldrich) was applied.

2.3. The setting time measurements

The setting times of the cement pastes (initial and final) were determined using Gilmore Apparatus according to the ASTM C266-08 standard [31]. The cement samples (8 × 10 × 5 mm) were prepared by mixing powder batches with the liquid phases at fixed L/P ratio equal 0.9. All experiments were performed at room temperature (23 ± 2°C). Each measurement was repeated 6 times and an average value was calculated.

2.4. Phase composition

The crystalline phases of the initial powders and set cement pastes were analyzed by powder X-ray diffraction with CuK α radiation (D2 Phaser, Bruker) in the 2 θ range of 10°–60° at a scanning speed of 1°/min. The experimental X-ray diffractograms were compared to the standards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS): HA (JCPDS 01–070–0798), calcium sulphate dihydrate (JCPDS 00–006–0047). Each measurement was repeated 3 times. Phase quantification was calculated using the Rietveld method. A pseudo-Voigt peak shape model was used for refinements.

2.5. SEM observations

Microstructure of the samples was investigated using scanning electron microscopy (SEM, JEOL 5400) equipped with the EDS attachment for elemental analyses in microareas. Before examination, the

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