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THE EFFECT OF DISPERSANT CONCENTRATION ON PROPERTIES OF BIOCERAMIC PARTICLES

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This work reports the use of PAA/PEG polymer as a dispersing medium for slurry compaction of HAp powders. Poly(acrylic acid) (PAA) modified with poly(ethylene glycol) (PEG) was used as dispersant in preparation of hydroxyapatite aqueous suspensions. HAp was natural origin, obtained from bone sludge via two-step procedure. The effect of dispersant structure on particle stabilization were investigated through physicochemical properties of suspensions. A novel HAp dispersions were characterized using pH, viscosity, rheology and sedimentation measurements.

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1. Introduction

In the colloidal processing of ceramic powders it is essential that the powder particles are completely dispersed so do not form aggregates. These aggregates increase flaws in the final sintered product causing reduction in strength and reliability [1-3]. Aggregates are formed in sub micron powders due to the ubiquitous attractive van der Waals forces. Traditionally, in colloidal processing this attractive force can be countered by a greater repulsive force separating particles from each other. This can be achieved in two ways; either by the addition of charge to the particles so that they repel one another-termed electrostatic stabilisation achieved by altering the pH value; alternatively by the addition of a polymeric molecule, which when adsorbed onto the powder surface prevents the particles physically coming close enough for the attractive force to cause flocculation - this is termed steric stabilisation. A combination of these two effects is termed electrosteric stabilisation and is the probable stabilisation mechanism when polyelectrolytes are adsorbed onto the particles [4-6].

Polymers are widely used in colloidal processing of ceramic powders to improve characteristics of suspensions such as powder concentration homogeneity, rheology and state of dispersion [7, 8]. These characteristics are necessary to obtain high density green parts with a homogeneous microstructure. Polyelectrolytes are widely used as dispersants in aqueous processing of calcium phosphate family. The polymers dissociate in the media and adsorb onto the particle surface shielding particles from each others. As a result, the particles are separated and stabilized in the suspension via the electrosteric mechanism [9-11].

From a number of factors, efficiency of a polyelectrolyte as a dispersant is mainly dictated by its molecular structure and pH value of the suspension. Both parameters strongly influence dissociation degree of polyelectrolytes, polimer chain conformation and adsorption behavior of the

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polymeric chains on particle surface. Although many research groups have extensively investigated aqueous ceramic processing in the past decade, there were a few profound studies on the effects of pH value and dispersant structure which compared various dispersants in a systematic way [12-14].

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is among of the few materials that are classified as bioactive, meaning that it will support bone ingrowth and osseointegration when used in orthopaedic, dental and maxillofacial applications [15–17]. Coatings of hydroxyapatite are often applied in metallic implants, especially stainless steels and titanium alloys to improve the surface properties. Hydroxyapatite may be employed in forms such as powders, porous blocks and hybrid composites to fill bone defects or voids. These may arise when large sections of bone have had to be removed or when bone augmentations are required (e.g. dental applications). HAp can be produced from coral, seashell, eggshell and also from body fluids [17-23].

2. Experimental

2.1 Materials and methods

Acrylic acid (AA), ammonium persulphate (APS), potassium hydroxide KOH were obtained from POCh Gliwice, Poland. Poly(ethylene glycol) (PEG) and polyethylene glycol diacrylate (NMBA) were acquired from Sigma Aldrich. All chemicals were of analytical grade and used without further purification. Hydroxyapatite (HAp) applied in our research was natural origin (obtained in 3-step process from pork bones – acid hydrolysis and double calcination) [24].

2.2. Dispersions preparation

As dispersant polymer matrix (SAP) was applied, which was received on the base of poly(acrylic acid) (PAA) modified with 15% poly(ethylene glycol) (PEG) in the field of the microwave irradiation [25-28].

2.3. Hydroxyapatite HAp

Hydroxyapatite (HAp) applied in our research was animal origin and was received in the calcining process of bone sludge in two stages. In the first stage the material was calcined at a temperature of 600°C in a chamber kiln with electric heating in air atmosphere within 180 minutes. In the next stage the unified material from the first stage was calcined at 850°C while kept at maximum temperature within 150 minutes in the chamber kiln [29]. The particle diameter of HAp was in the range of under 0.10 mm.

2.4. Preparation of HAp aqueous suspensions

The preparation of dispersant solution was performed as follows: acrylic polymers were added at various amounts of 0.05%, 1%, 2%, 3%, 4%, 5% by weight and HAp was added at amount of 1 wt.% based on 100ml dispersion weight.

2.5. Stability of the dispersion measurement

Investigation of the stability was carried out for the dispersion on the base of the pH measurement in time of 10 days. Measurements were conducted for suspension with the different concentration of SAP which contained the constant HAp amount.

2.6. Rheology measurement

The viscosity of the HAp dispersions were measured at room temperature using a Anton Paar DV-2 P viscometer with mandrel R2. The results of viscosity versus dispersant concentration, i.e. the deflocculation curves, suggested the optimum concentrations of each dispersant at the point where the viscosity reached the minimum.

2.7. Sedimentation behavior

Particle stabilization in the suspensions was studied by means of sedimentation experiment. The suspensions were filled in sealed graduate test tubes and initial suspension heights (h_0) were measured. Sedimentation heights (h) and characteristics of the supernatant were investigated after 1 and 24 hours. The h/h_0 ratios were reported as a function of dispersant concentrations.

3. Results and discussion

As one of the important parameters in aqueous processing, the effects of pH value must be considered. The pH affects the net particle surface charges, the degrees of dissociation of carboxylic groups and polymer chain conformation, causing the variation in the adsorption behaviors of the polymer on particles. As a result, particle stabilization and suspension properties are altered with pH value of the suspension. In this section, the effects of acrylic polymers concentration on the properties of HAp aqueous suspension were studied (Fig. 1).

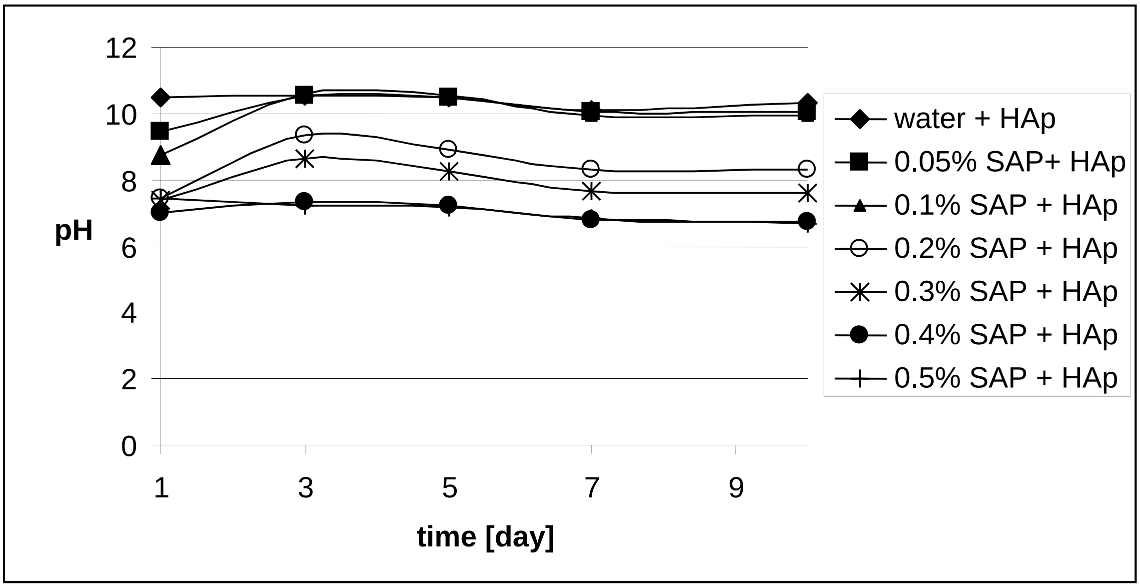

Fig. 1. Changes in the pH value of dispersions

The change of viscosity as a function of dispersant concentrated was illustrated in the Fig. 2. The viscosity of suspensions decreased with decreasing SAP concentration. For minor concentration of solid phase in suspension the range between molecules is large what increases mobility of particles. The increase of concentration decreases the range between molecules what effects in greater friction between particles improving the viscosity. Molecules of protective colloids adsorb onto solid phase particles what prevents agglomeration. That is why diffused phase particles are well separated and settle slower. Therefore such colloids are used for particles settlement regulation through dispersion viscosity change. According to Stokes law the higher viscosity of diffusing phase the lower rate of solid particles settlement. However, the suspension viscosity can not be to high because of application problems.

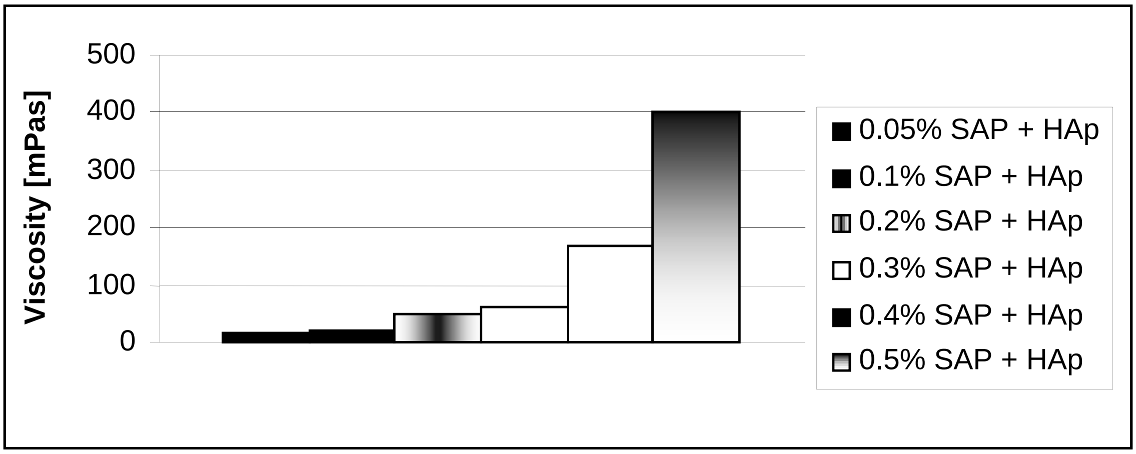

Fig.2. Viscosity of dispersions

The results of sedimentation measurements (Fig. 3) indicates that the lower SAP concentration the lower dispersion rate and sediment density. Whereas higher polymer concentration increases dispersion rate of ceramic particles. In stable dispersion, including polymer, HAp particles settle slowly. In the first stage big particles are falling down, while small ones are still suspended. In the fig. 4 a stable dispersion is shown. The upper part of suspension is turbid because of small particles. Higher SAP concentration increases sediment volume. This is the effect of lower pH value of suspension causing formation of porous structure of the sediment during sedimentation process. Such residue characterizes many free spaces between agglomerates and higher volume. The ionic force slightly influences sedimentation process. High ionic force stretch polymer macromolecules and HAp particles are weakly repelled because of electrostatic interactions screening. The polymer used in this research is a polyelectrolyte with anionic groups which can be screened by other inorganic ions influencing interactions.

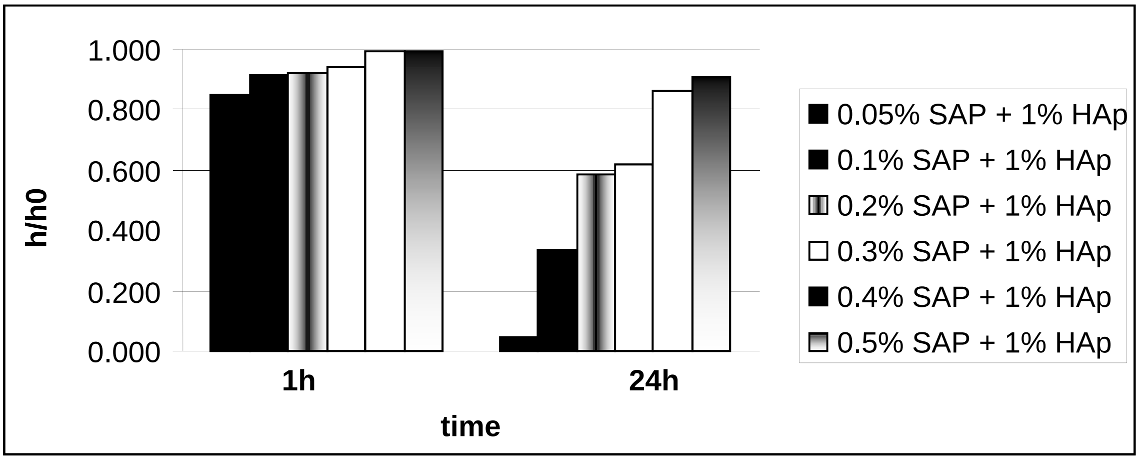

Fig.3. The ratios of sedimentation height (h) to the initial suspension height (h_0) of the suspensions

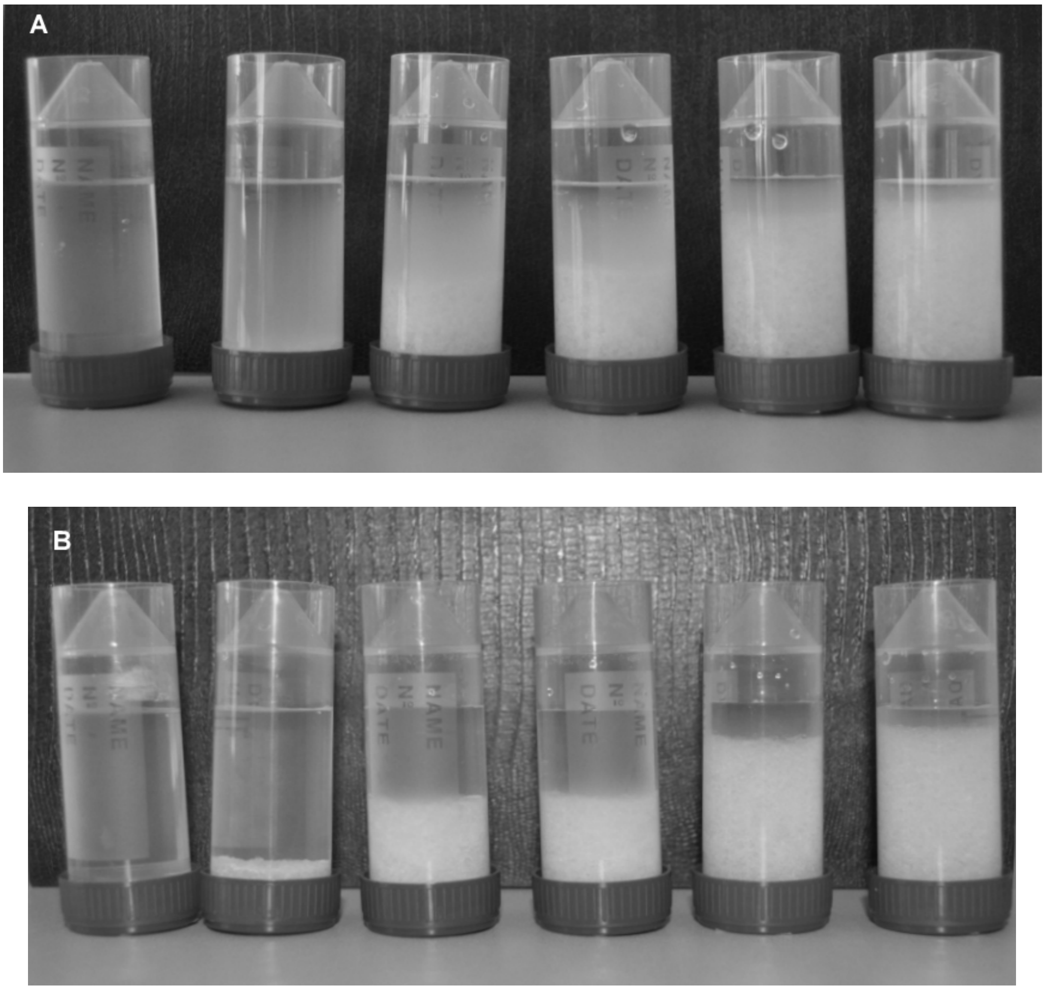

Fig. 4. Sedimentation behavior after (a) 1 h and (b) 24 h

4. Conclusions

Various polymers were evaluated for their potential application as biocompatible dispersants in the synthesis of biomimetic composites with a dispersed mineral phase. HAp dispersions were prepared by using SAP as dispersants. It was found that SAP enhanced dispergation and stability of the dispersion. The measurements of dispersions viscosity as a function of SAP concentration indicated that the decreased with decreasing SAP concentration. The results of sedimentation measurements indicates that the higher SAP concentration the higher dispersion rate and sediment density. Consequently, aggregation and sedimentation of mineral phase was reduced considerably.

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