Dispersion and stability of tricalcium phosphate powders in polyacrylate dispersions

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Biomaterials is a term used to indicate materials that constitute parts of medical implants, extracorporeal devices, and disposables that have been utilised in medicine, surgery, dentistry and veterinary medicine as well as in every aspect of patient health care. Ceramics biomaterials are used as components of hip implants, dental implants, middle ear implants and heart valves. Porous or particulate calcium phosphate ceramic materials such as tricalcium phosphate (TCP) have proved successful for resorbable hard tissue replacements when low loads are applied to the material. The aim of the present work was to evaluate the biological characteristics of the biomaterial developed. Interactions of TCP with polyacrylate polymers in aqueous dispersions were characterised using X-ray diffraction, Fourier transform infrared spectroscopy, pH determination and viscosity measurements.

1. Introduction: Nowadays bioceramics are used in numerous medical and dental applications including repairing bone fractures, attaching bone plates and other prostheses. Granulated products are commonly used as bone substitute materials in dental and orthopedic applications. Recently, a growing interest has been observed in calcium-based biomaterials such as hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) and tricalcium phosphate (TCP, $(Ca_3(PO_4)_2$). They are biocompatible, non-toxic, resorbable, and non-inflammatory, cause no immunological, foreign-body or irritating response and have excellent osteoconductive ability. β-TCP has a hexagonal crystal lattice and is more soluble than hydroxyapatite. It is currently used in several clinical applications in dentistry, maxillofacial surgery and orthopedics, that is as a component of several commercial mono- or biphasic bioceramics and composites [1—17].

Ceramic technology is a very important colloidal processing technique and provides well-dispersed suspension. Polyelectrolytes are widely used as dispersants because they improve the properties of suspensions such as powder concentration homogeneity, rheology and state of dispersion. The polymers dissociate in the media and the dissociation degree strongly depends on the molecular structure and pH of the suspension. The stabilisation and separation of particles is possible because of electrostatic interactions associated with carboxyl groups (—COOH), which are derived from poly(acrylic acid) (PAA) [18, 19].

Additive metal particles to the colloidal system, such as silver nanoparticles (AgNPs), improve its properties. AgNPs with their unique chemical and physical properties are proving an alternative for the development of new antibacterial agents. AgNPs have also found diverse applications in the form of wound dressing, coatings for medical devices, AgNPs impregnated textile fabrics etc. [20—23].

The antimicrobial property of silver is related to the amount of silver and the rate of silver released. Silver in its metallic state is inert but it reacts with the moisture in the skin and the fluid of the wound and gets ionised. The ionised silver is highly reactive, as it binds to tissue proteins and brings structural changes in the bacterial cell wall and nuclear membrane leading to cell distortion and death. Silver also binds to bacterial DNA and RNA by denaturing and inhibits bacterial replication [23—26].

The aim of this work is to obtain and characterise TCP/polymer dispersions as a potential material useful in biomedical applications.

2. Experimental procedure

2.1. Methods: The phase of phosphorus ceramic was determined with the use of the X-ray method on a Philips X'Pert diffractometer equipped with a PW 1752/00 graphite monochromator, Cu Kα 1.54 nm, and an Ni filter (40 kV, 30 mA).

Nanosilver particle size distribution was analysed by a dynamic light scattering (DLS) measurement technique. Dynamic light-scattering measurements were performed in a Malvern Zetasizer Nano ZS apparatus (Malvern Instruments) at 25°C and started 2 min after the cuvette was placed in the DLS apparatus to allow the temperature to equilibrate. Measurements were carried out 24 h after the preparation of the suspension.

A SEM image was obtained using JEOL JSM 7500F with a back scattered electrons (BSE) detector. A drop of the sample solution was left to dry on a copper holder coated with chromium film.

For all obtained suspensions, which contain a constant concentration of polymer solution (1 wt%) and different amounts of TCP (1—5%), pH measurements were conducted. They were determined for 10 days.

The viscosity of obtained suspensions was measured at room temperature with the use of an Anton Paar DV-2 P viscometer with an R2 spindle.

Particle stabilisation in suspensions was studied by means of sedimentation experiments. The colloidal solutions were placed in test tubes and sedimentation behaviour was observed after 1 and 24 h.

The phase composition of TCP was determined with the use of the X-ray method on a Philips X'Pert diffractometer equipped with a PW 1752/00 graphite monochromator, Cu Kα 1.54 nm, and an Ni filter (40 kV, 30 mA).

2.2. Materials: Acrylic acid (AA), ammonium persulphate (APS), and potassium hydroxide (KOH) were obtained from POCh Gliwice, Poland. The silver nitrate (99.9% $AgNO_3$) and sodium borohydride (98% $NaBH_4$) were purchased from the POCh Chemical Company whereas polyvinylpyrrolidone (PVP) M.W. 8000 and TCP were obtained from Acros Organics. Poly(ethylene glycol) (PEG) M.W. 8000 and N,N′-methylenebisacrylamide (NMBA) were acquired from Sigma Aldrich. All chemicals were of analytical grade and used without further purification.

2.2.1 AgNPs: AgNPs were prepared by the chemical reduction process, that is by the reduction of silver nitrate with sodium borohydrate in the presence of PVP [27]. Concentration of silver amounted 750 ppm.

2.2.2 Dispersions preparation: In conducted investigations, the polymer system was used consisting of PAA modified with PEG (10%) and nanosilver (Ag) (5% solution). The PAA/PEG/Ag system (SAP) was obtained under microwave irradiation [28—30].

2.2.3 Preparation of TCP aqueous suspensions: In the first research step 1 wt% of PAA/PEG/Ag was dissolved in deionised water and as result prepared a colloidal system. Next, this solution was poured to 100 ml containers and mixed with 1, 2, 3, 4 and 5 g of TCP. The obtained suspensions were investigated with the use of X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The viscosity measurement, sedimentation behaviour and pH determination indicated that the addition of dispersants improved particle stabilisation.

3. Results and discussion

3.1. Characterisation of AgNPs: The reduction of $AgNO_3$ by $NaBH_4$ and PVP as an excellent stabiliser could take place in 'aqueous' solutions. The molar ratio of $AgNO_3/NaBH_4$ amounted to 10/1. The content of stabilisation in nanoparticles suspension amounted to 3%.

The SEM images of the sample solution show that nanosized metal silver particulates were formed. Fig. 1 graphically expresses the detailed particle size distributions of samples; it can be observed that silver from a dry drop of the sample solution was agglomerated.

Dynamic light-scattering graphs (Fig. 1) indicate that the size of the nanosilver changed from 0.51 to 1.23 nm. It is known that nanosilver in a smaller size has higher surface energy, and thus the reactivity is higher.

3.2. Characterisation of dispersion

3.2.1 Dispersion stability system: Stabilisation of ceramics with polymeric dispersants is generally because of two basic mechanisms, charge or electrostatic stabilisation and steric stabilisation. Electrostatic stabilisation in an aqueous system involves adsorbed ionic polymers building up a charged layer around the pigment, preventing aggregation. The efficiency of ionic polymers, usually anionic, to provide electrostatic stabilisation is well known, however the stabilising charge can be readily reduced by the presence of external influences such as surface or ionic solution impurities, or with the addition of other pigments with different surface charge properties [31, 32]. The results of pH measurements for all obtained suspensions, which contain a constant concentration of solution of the polymer system (1 wt%) and different amounts of additional TCP (1—5 g), are illustrated in Fig. 2. The data indicate that all suspensions have very similar pH values (about 6—7). Probably this situation results from the presence of AgNPs, which contribute to improvements of dispersion stability. It is because of the more easy interactions of carboxylic groups (—COOH) with TCP particles. The pH measurements were determined for 10 days, allowing us to conclude that all suspensions are very stable systems.

3.2.2 Viscosity measurement: Steric stabilisation is generally considered to arise from two factors: a volume restriction component and a mixing or osmotic component, involving compression of the adsorbed layer causing an increase in polymer concentration. It is also important to assess the interparticle forces that may be present in concentrated suspensions. Rheological investigations are often used for this purpose and commonly yielded stress is measured. Knowledge of the effect of polymer adsorption on the electrochemical and rheological properties of mineral suspensions is of great industrial importance [33—36].

The changes of viscosity measurements for all suspensions are presented in Fig. 3. The obtained results show that progressive addition of TCP caused decrease of viscosity values. This dependence is directly related to the pH of all suspensions and the different dissociation degree of carboxylic groups from PAA. The suspension containing 1% of TCP exhibits the highest viscosity value (about

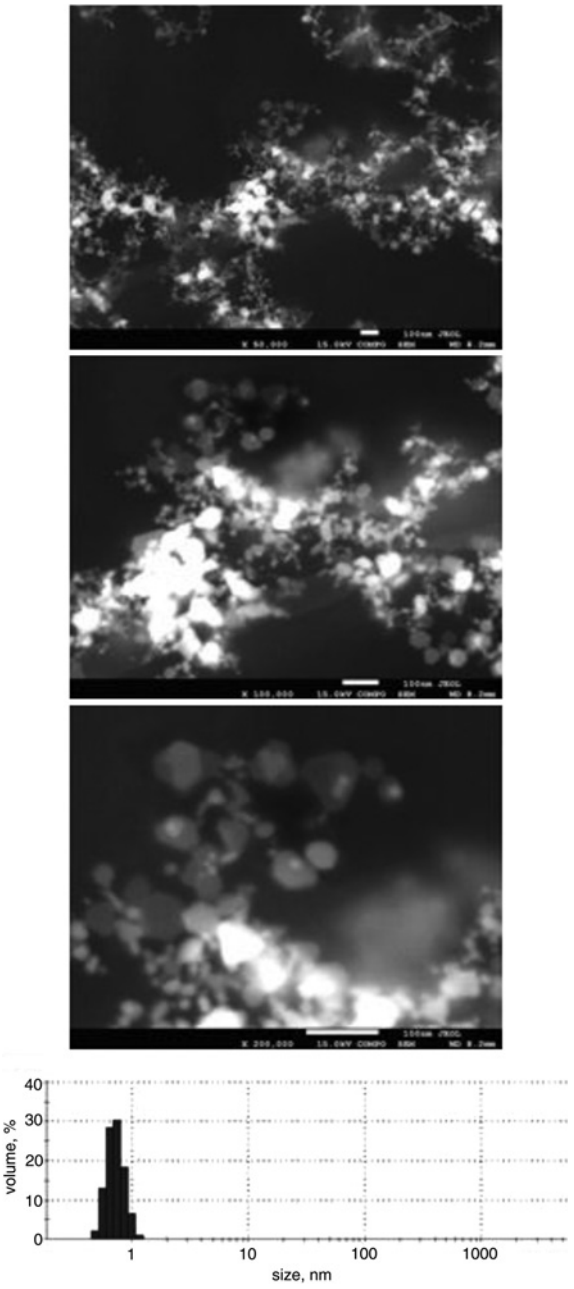

Figure 1 *SEM-BSE pictures of AgNPs with different magnifications, size distribution of AgNPs*

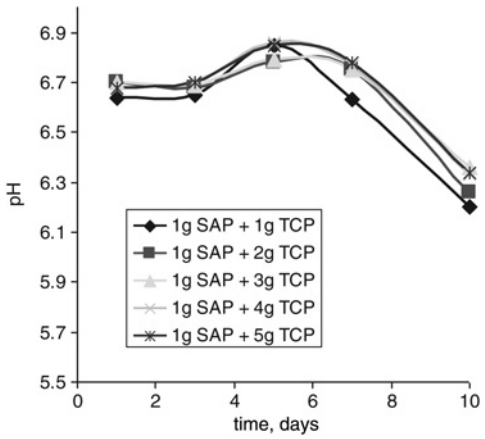

Figure 2 *Changes of dispersants pH during 10 days*

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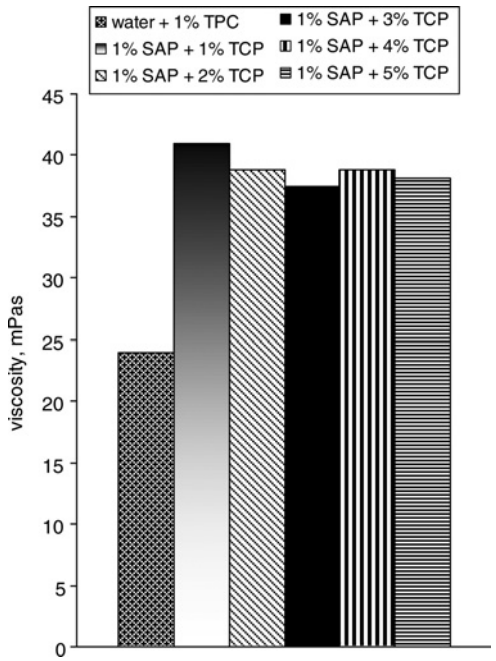

Figure 3 *Results of viscosity measurement*

40 mPa). However, in other cases, changes to this value are very similar (about 39—37 mPa), which results from presence of AgNPs improving the dispersion stability. It is possible because of the different structure of the polymer system PAA/PEG/Ag (SAP), because SAP contains short chains and inside the colloidal system appears additional electrostatic interactions.

3.2.3 Sedimentation behaviour: Sedimentation experiments demonstrate significant improvement of dispersion system stability after the addition of the polymer matrix, which is a result of electrostatic interactions between macromolecules and HAp particles.

In Fig. 4, a considerable difference between the sedimentation coefficient of the reference sample and obtained dispersions can be observed. There is no significant difference between samples in the gravitational fall of particles after 1 h, nevertheless after 24 h such little difference can be observed. The stability of sedimentation behaviour is caused by the properties of polymer dispersant, that is, charge or electrostatic stabilisation and steric stabilisation.

Sedimentation coefficient for each sample can be calculated from received results

$$S = h/h_0$$

where h is the height of a liquid column after time t (1 h, 24 h), and h_0 is the initial height of a liquid column.

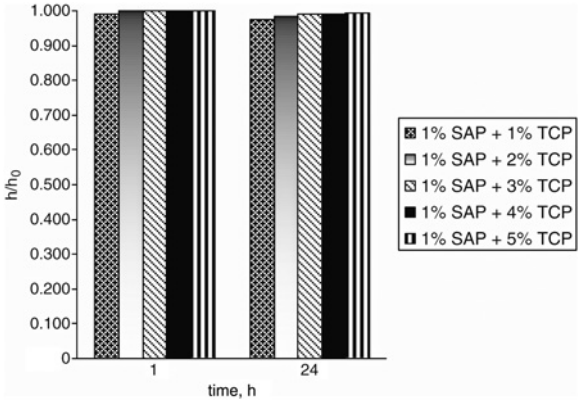

Figure 4 *Results of sedimentation behaviour after 1 and 24 h*

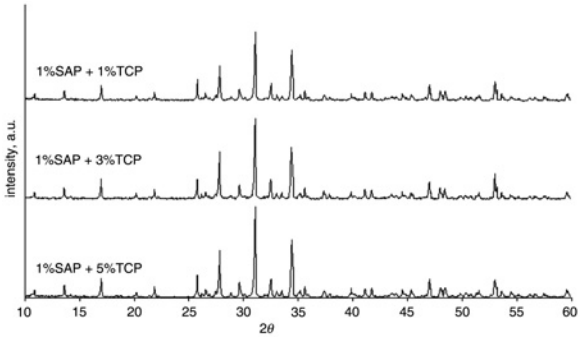

Figure 5 *X-ray diagram of TCP immersed in PAA/PEG/Ag dispersions*

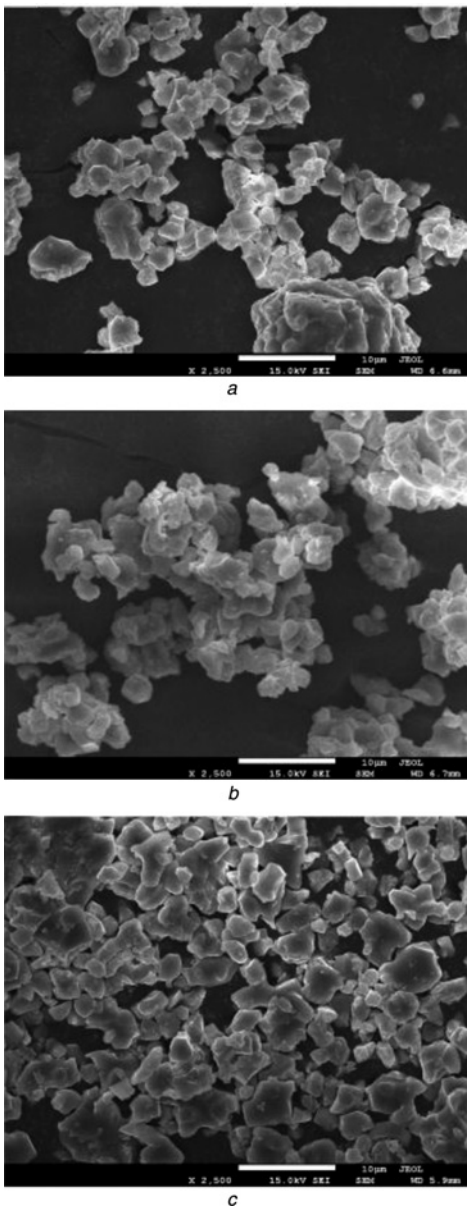

Figure 6 *SEM investigation of dry TCP/PAA/PEG/Ag dispersion film*
a 1% TCP
b 3% TCP
c 5% TCP

3.2.4 XRD investigation: The X-ray analyses confirmed that β-TCP was the only phase indicated in all the samples immersed in the polymer solution environments. All the powders have similar diffraction profiles, Fig. 5.

3.2.5 SEM investigations: The efficiency of dispersants was studied by SEM analysis of the dried drop of dispersion. Figs. 6*a* and *b* show the powder agglomerates of ceramics. By using the PAA/PEG/Ag system with a concentration of 5 wt% TCP, these agglomerates completely disappear, as illustrated in Fig. 6*c*. During drying dispersant was worked like glue and caused the TCP agglomeration; however this effect was not observed for higher concentration TCP and the same bigger specific surface of ceramic powder.

4. Conclusions: TCP is a very important ceramic material currently used worldwide and it is being used widely in clinical applications such as dentistry, maxillofacial surgery and orthopaedics because of its outstanding physicochemical properties. TCP suspension properties are very important for consumer industries; if aggregates are present, the endurance of properties including gloss, opacity and storage stability will be highly affected. Dispersion properties can be greatly improved by the addition of a polymeric dispersant.

It is therefore very important to understand the interaction between the ceramic particles and polymeric dispersants. Polymeric dispersant functional groups will not only impact on adsorption properties but also potentially affect TPC dispersion behaviour, once it is adsorbed. Anionic polymeric dispersants PAA/PEG/Ag presented in this Letter provide electrostatic and steric ceramic stabilisation. Consequently, aggregation and sedimentation of TCP were reduced considerably. On the basis of the investigation results, it could be inferred that suspensions TCP/PAA/PEG/Ag have great potential to be used as biomaterial for medical applications.

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