JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **13** (2002) 639–643

Rheological behavior of aqueous suspensions of hydroxyapatite (HAP)

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The aim of this study is to characterize the influence of organic dispersants on the stability of hydroxyapatite (HAP) dispersions, using viscosity measurements, electrokinetic sonic amplitude (ESA) measurements and adsorption isotherms.

Colloidal stability of aqueous suspensions of HAP as a function of solids loading and of the type and concentration of deflocculant has been studied. The interaction between particles and dispersant molecules was characterized. Adsorption measurements of the amount of dispersants on the particles surface, viscosity and electrophoretic measurements as a function of the dispersant concentration are correlated.

Suspension parameters have been adjusted in order to obtain a high solids loading slurry with a plastic viscosity which will allow its use in colloidal processing.

1. Introduction

Colloidal processing of ceramic powders requires control of the homogeneity, rheology and dispersion of the suspensions. Particle dispersion is often the limiting factor, affecting both rheology and homogeneity of suspensions. As a consequence, a control of the interparticle forces is necessary during all the stages of processing.

The net effect of attractive and repulsive forces between the surface of the particles determines the state of dispersion of colloidal suspensions. The magnitude of the attractive forces is mainly determined by the nature of the particles and the solvent and can be counteracted by repulsive forces. In general, suspensions can be dispersed by electrostatic, steric or electrosteric stabilization mechanisms [1]. Overlap of similar electric double layers implies electrostatic repulsion between particle surfaces, by generation of a common surface charge on the particles. The magnitude of both attractive and repulsive forces between particles can be modified by addition of organic or inorganic dispersants to the slurry, which are adsorbed at the solid/liquid interface. Steric stabilization is achieved by adsorption of polymeric additives, forming protective colloids.

Acidic, acrylic-based polymers, which are dissociated to form negatively ionized polyelectrolytes, are commonly used as dispersants, providing enhanced stability via electrosteric forces [2, 3]. The adsorption characteristics of these polyelectrolytes depend on the surface charge of the particles and on the polyelectrolyte and bulk solution chemistry. The adsorbed polyelectrolytes can change their conformation as a function of the suspension pH. In addition, by modifying the pH, the conformation of the polyelectrolyte can be altered in order to enhance the particle stability. The effectiveness of a polyelectrolyte in enhancing the particle stability is determined by the adsorbed amount, the total amount of the polyelectrolyte added, the dissociation degree and how far the adsorbed chain extends into the bulk aqueous phase to screen the van der Waals attractive interaction. Adsorption of a low molecular weight carboxylic acid can be explained as a simple exchange of the OH^- group for a $R–COO^-$ group without influence on the particle surface charge. A change of the surface charge can be achieved if either an additional dissociated group that is not coordinated to the surface is present in the molecule, two groups are coordinated to the same Lewis base center or one $-OH_2^+$ group is exchanged instead of one OH^- group [4, 5].

Polyacrylic acid dispersants have been used in the stabilization of slurries of mechanochemically synthesized HAP calcined at 700 °C [6]. The adsorption of sodium polyacrylate on HAP showed a Langmuirian shape, with the ionized polyacrylate ions of the salt repelling each other [7, 8]. The importance of heat treatment of HAP commercial powders was pointed out and stable suspensions were obtained with an anionic polyelectrolyte and powders calcined in the 500–900 °C range [9].

The objective of this work is to study the effect of

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some dispersants on the stability of HAP suspensions and to obtain high solids loading slurries under selected conditions of powder-specific surface area, pH range and type and concentration of deflocculants. In accordance with the observed effectivity of anionic organic dispersants on the stability of HAP slurries [6, 9] three different types of these dispersants were chosen for this study: citric acid, dispex N40 and dispex HDN.

2. Experimental

2.1. Materials

The hydroxyapatite powder (Merck 2196) used in the present experiments had an initial specific surface area, $A_s = 77\,\mathrm{m}^2/\mathrm{g}$. A temperature of 1000 °C was chosen to calcine the HAP powder, leading to a strong reduction of the specific surface area, $A_s = 6\,\mathrm{m}^2/\mathrm{g}$, and consequently to better rheological characteristics and higher green densities. As confirmed by XRD, HAP was the only crystalline phase present in powder. From ICP results, the ratio Ca/P was determined as 1.63, corresponding to a stoichiometric HAP.

Citric acid (Riedel de Haen) and two other commercially available dispersants – dispex N40 and dispex HDN (Allied Colloids, UK) – were chosen. Dispex N40 is a low molecular weight polyacrylic acid neutralized with sodium. Dispex HDN is an acrylic ester based copolymer. HNO_3 ($1\,\mathrm{mol\,dm^{-3}}$) and KOH ($1\,\mathrm{mol\,dm^{-3}}$) solutions were used to adjust the pH of suspensions.

2.2. Experimental methods

All suspensions were prepared by adding the powder gradually, and with continuous stirring, to the correct volume of water, which contained the dispersant. Subsequently the pH was adjusted to 10.5. The slurries used in rheological measurements were then ball-milled for 24 h, in plastic containers with alumina balls as milling media.

Rheological characteristics of aqueous suspensions were measured with a cone and plate viscometer (CLS Rheometer Carri-Med) in the shear rate range 0 to $1000\,\mathrm{s}^{-1}$. Pre-shearing was done for 1 min at the highest shear rate. All measurements were performed at $25 \pm 0.2\,^\circ\mathrm{C}$.

The adsorption isotherms of dispex N40 at HAP/electrolyte interface were determined by mixing the powder with the dispersant over two days and, after centrifuging and adjusting the pH of the supernatant to 10.5, the amount of dispersant in solution was determined by automatic titration with NaOH and HNO_3.

The measurements of the ESA signal as a function of the pH value were performed on 2 vol % HAP suspensions using a Matec ESA-8000 equipment (Matec Applied Sciences, Hopkinton, MA, USA). The suspensions were ultrasonicated before for 15 min (500 W Vibra-cell ultrasonic desintegrator VC 600, Sonics & Materials, USA). The ESA probe was calibrated using 10 vol % Ludox TM (Du Pont, Wilmington, DE, USA) in water. The ESA value for the Ludox solution was taken to be $-5.32 \times 10^3\,\mathrm{Pa.m.V^{-1}}$ at 25 °C [4]. All measurements were performed at $25 \pm 0.2\,^\circ\mathrm{C}$. The apparatus was calibrated before each titration, and was checked after the measurement. Potentiometric titration of the suspensions with either HCl (1 M) or KOH (1 M) was performed automatically, starting at basic conditions, where the suspension is stabilized, and reducing its pH. The magnitude of the ESA signal is related to the dynamic electrophoretic mobility, μ_d, of the particles by:

$$\mathrm{ESA}(\omega) = \mu_d(\omega)\, c\, \Delta_\rho\, \Phi\, G_f$$

where $\mu_d(\omega)$ is the electrophoretic mobility, c is the sound velocity in the suspension, Δ_ρ is the density difference between the particles and the solvent, Φ is the volume fraction of the particles, G_f is a geometrical factor for the electrode geometry and ω is the angular frequency of the applied field.

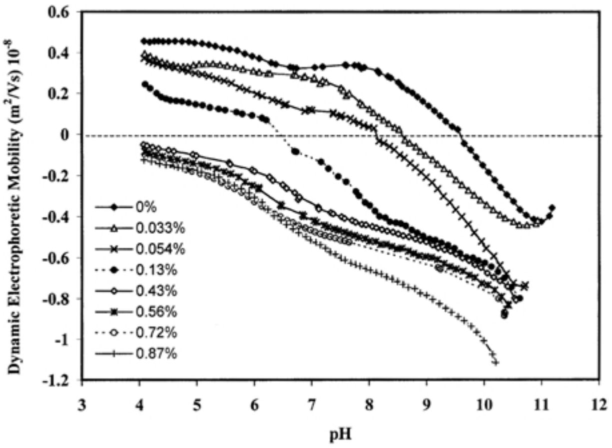

Figure 1 Dynamic electrophoretic mobility of HAP particles (2 vol. %) as a function of pH at various dispex N40 additions.

3. Results

3.1. Rheology of aqueous HAP suspensions

3.1.1. Electrophoretic mobility

In order to determine the stabilization conditions of the suspensions of HAP powder, electroacoustic measurements were performed. Results of the variation of the electrophoretic mobility (μ_d) of HAP particles as a function of pH and of the amount of dispex N40 added are shown in Fig. 1.

It can be seen that at pH around 10.50, the μ_d of the particles in the powder without any defflocculant addition is $\approx -0.4\,\mathrm{m^2\,V^{-1}\,s^{-1}}$. With decreasing pH, the μ_d of the particles in suspension becomes zero at pH 9.5–9.7 (the isoelectric point – i.e.p.), and then increases to $0.42\,\mathrm{m^2\,V^{-1}\,s^{-1}}$ at pH 5.5. Slurries are stabilized either at pH = 10.50 or at pH = 5.5, but at this lower pH value the powder starts to dissolve. It was then decided to use a value of pH = 10.50 in the subsequent comparative rheological studies with different deflocculants.

The addition of dispex to the suspensions leads to an increase of the negative charge on the particles, or, at lower pH values, to a reduction in the positive charges on the particle surface; the i.e.p. is shifted to lower pH values. Increasing the dispex concentration intensifies the effect of increasing the negative charge of the particles.

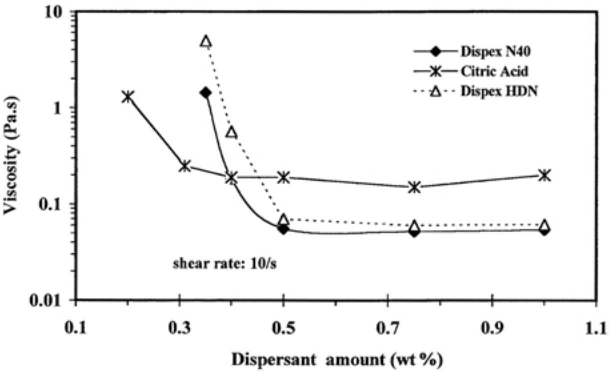

Figure 2 Viscosity of aqueous HAP suspensions (57 wt % solids loading; pH = 10.5) at various dispersants additions.

3.1.2. Viscosity as a function of different dispersants

The effect of dispex N40, citric acid and dispex HDN upon the plastic viscosity of slurries of HAP powder, with a solids loading of 57 wt %, at pH = 10.50, is shown in Fig. 2.

A large decrease in the viscosity of the suspensions with the addition of any of these dispersants can be observed. For an amount of dispex N40 and dispex HDN between 0.5–0.6 wt %, the stabilizing effect is saturated. Although this effect can be obtained for a slight lower amount of citric acid (0.4 wt %), the value of the minimum viscosity obtained is higher than for the other two dispersants. This effect can be attributed to the fact that its adsorption decreases with increasing pH and is maximum at acidic pH. As the viscosity measurements had been performed at pH = 10.50, the amount of acid adsorbed must be minimum (results of the adsorption of citric acid on alumina particles showed that for a concentration of 0.2 wt % and at pH lower than 7, ≈ 100% of dispersant is adsorbed, but for pH higher than 7 the adsorbed amount decreases to less than 20% [4]).

3.1.3. Viscosity as a function of solids loading

Fig. 3 shows the effect of solids loading upon the plastic viscosity of those suspensions, using a concentration of 1 wt % of each dispersant at pH = 10.50.

For solids loading lower than 74 wt % the effect of dispersants are similar to that observed in Fig. 2, i.e. for the same solids loading the slurries with dispex N40 and dispex HDN show close values of viscosity, which are lower than those obtained in slurries with addition of citric acid. For solids concentrations higher than 74% the increase of the viscosity of slurries with addition of dispex HDN is more pronounced than that observed for dispex N40. A higher solids loading (80 wt %) suspension with a viscosity still adequate for colloidal processing (≤ 1 Pa.s) can be obtained using dispex N40 as a deflocculant, where for the other two dispersants this upper limit value of viscosity was obtained at lower solids loading values (74–75 wt %). Such a high value of solids loading obtained with the use of dispex N40 at a basic pH = 10.50 is higher (maximum of solids loading 73 wt %) than those obtained in HAP similar studies [6, 9]. Based on these results dispex N40 was selected for further rheological characterization.

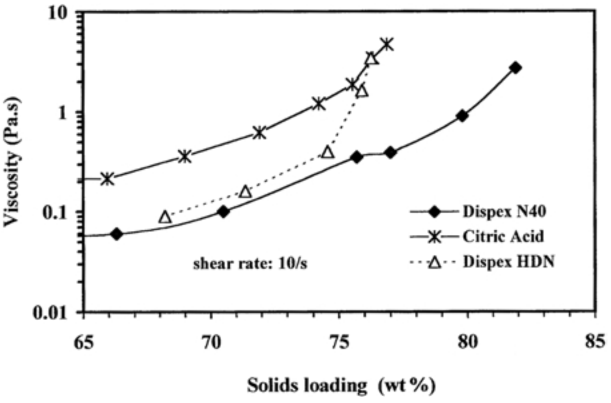

Figure 3 Viscosity of aqueous HAP suspensions (pH = 10.5) versus solids loading at various dispersants additions.

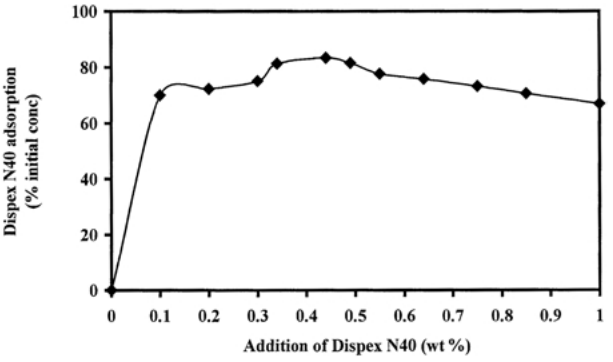

Figure 4 Adsorption curve of dispex N40 on HAP particles at pH = 10.5.

3.1.4. Adsorption of Dispex N40 on HAP surface

In Fig. 4 the adsorption of dispex N40 on HAP particles surface, in suspensions at pH 10.50, is plotted in ‘‘percent of the initial amount of dispersant’’ versus the addition of dispex, wt %, relatively to the weight of the powder.

The results display an increase of the adsorbed amount until around 0.5 wt % of added dispersant, in agreement with viscosity results (Fig. 2). Up to this value of added dispex, 84% of the deflocculant is adsorbed. For higher amounts, the percentage adsorbed is progressively lower and more deflocculant remains in solution, leading to an increase of the ionic strength (for an overall amount of 1% only ≈ 65% is adsorbed, remaining 35% in solution).

3.1.5. Effect of the pH on the viscosity

In Fig. 5 it is plotted the viscosity versus the pH of suspensions with dispex additions chosen as being close to its maximum effect as a dispersant. For pH values between 9.5 and 11 the suspensions show a minimum in viscosity for the three concentrations of dispex. When 0.75 wt % and 1 wt % of dispersant are added, the viscosity increases sharply at pH lower than 9.5.

These results conclude that the best conditions for the

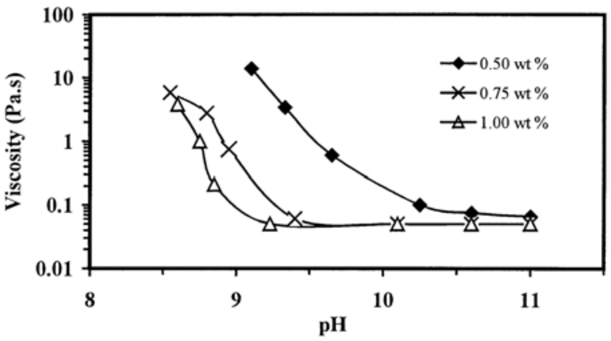

Figure 5 Viscosity of aqueous HAP suspensions (57 wt % solids loading) at different dispex additions.

stabilization of the suspensions are achieved for a pH around 10.50 (as already seen from electrophoretic mobility measurements) and for an addition of 0.75 wt % of dispex N40.

4. Discussion

The adsorption behavior of dispex is quite complex and dependent on the overall dispex concentration and on the pH of the suspension. Polyacrylic acid (PAA) with carboxyl groups along the backbone, possess different conformations at different pH, due to the pH dependent ionization ratio of COOH groups and interaction of these groups with other ions in the system [10]. Potentiometric titrations indicate that, with the increase of pH, ionization of PAA led to a configurational transformation from a compact random coil at low pH to a fully extended and rigid molecule at high pH. The carboxyl groups dissociate to produce a negatively ionized polymer with flexible molecular chains (at pH 10 it is fully ionized and exists in a stretched conformation) [11]. As a consequence, in alkaline media, these acrylic acid polymers interact strongly with basic powders, as HAP powders, because the native i.e.p. of the solid phase is in the pH region in which the polyelectrolytes are fully ionized and in a stretched configuration. Furthermore, the powder surface near the i.e.p. contains a relatively large population of both negative and positive sites, which are available for polymer attachment. At pH 10.50 the adsorption of the negatively charged polyelectrolyte creates a carboxylate – HAP complex which imparts a higher charge density on the particles surface. This interpretation is corroborated by electrophoretic mobility results (Fig. 1). The addition of dispex N40 shifts the i.e.p. to lower pH values and leads to an increase of the negative charge of the particles due to the charged carboxylate–HAP complex. Furthermore, the extended structure of the adsorbed polymer in alkaline media promotes electrosteric repulsion [12]. The coverage of the whole surface of the particles with a monolayer of dispex increases the minimum distance between the particles, leading to a steric barrier between them.

The effect of dispex concentration on the electrophoretic mobility at different pH values (Fig. 1) shows that for concentrations higher than 0.43 wt % the electrophoretic mobility is almost independent of the deflocculant amount, in a pH range from ≈ 4 to ≈ 10.50. At this pH value and up to ≈ 0.5 wt % of dispersant, almost all the dispex molecules are adsorbed on the HAP particles surface (Fig. 4) and do not contribute to the ionic strength of the slurry. For dispersant concentrations higher than this value the adsorption continues but the percentile adsorbed amount progressively decreases. However, for those higher concentrations (0.72 wt % and 0.87 wt %) the electrophoretic mobility is almost not affected in the acid media but increases progressively with pH in the basic region. The partial adsorption of the overall dispex with a tendency to an increase of the electrophoretic mobility in alkaline media suggests that an additional group that is not coordinate to the surface may occur in these conditions. The surface charge will not be affected and, on the other hand, the reduction of the Debye length by the increase of the ionic strength, will be counteracted by the opposite effect of the extended structure of the adsorbed polymer (which promotes electrosteric repulsion).

The viscosity data is in agreement with the electrophoretic mobility results. The dependence of the suspension viscosity on the dispersant concentration can be explained in terms of the DLVO theory [4]. The interaction potential between the particles depends on the adsorbed carboxylate ions on the surface (with a consequent increase of a negative particle charge) and on the presence of additional dissociate groups not coordinated to the surface (with an increase of the ionic strength). In the suspension without addition of dispex at pH 10.5, an attractive particle network is formed, due to the lack of a net repulsive potential, leading to a high viscosity and to the flocculation of the suspension. Electrophoretic results (Fig. 1) suggest that for additions of dispex higher than 0.43 wt % the particles do not attract each other anymore due to the formation of a primarium maximum and, as a consequence, the viscosity decreases (in agreement with results of Fig. 2). The range of the net repulsive potential is very large and in concentrated suspensions this combination of a long range repulsive double layer potential with a relatively high surface charge of the particles with their double layer fill the space completely [4]. For pH ≈ 10.5, at a minimum value of ≈ 0.5 wt %, a monolayer of dispex must be covering the particle surfaces, in agreement with electrophoretic mobility and adsorption results (Figs. 1 and 4) and a primary repulsive maximum is created. Accordingly, at that value of pH, the viscosity is kept almost constant for concentrations up to 0.5 wt % (Fig. 5), but the electrophoretic mobility may yet increase in the alkaline region, as observed in Fig. 1. This apparent discrepancy may be attributed to the presence of the, as refereed dissociated groups in dilute suspensions, as those used in the electrophoretic mobility measurements.

5. Conclusions

This work has shown that:

1. The addition of a low molecular weight polyacrylic acid neutralized with sodium (dispex N40) allows to obtain slurries with high solids loading (up to 80 wt %) and a reduced viscosity for HAP commercial powders

calcined at 1000 °C. Dispex HDN and citric acid are not so effective in the stabilization of high-solids suspensions.

2. The adsorption of the polyelectrolyte on the particles surface creates a charged carboxylate–HAP complex.

3. For the stabilization of the slurries an amount of polyelectrolyte of ≈ 0.75 wt % was determined by the minimum of the viscosity, which is in good agreement with the adsorption measurements and with the electrophoretic mobility of particles.

4. In the alkaline range (pH ≈ 10.50) the conformation of the adsorbed highly charged anionic polyelectrolyte extends far into solution. As a consequence its adsorption on HAP particles affects its surface charge and creates a steric barrier that inhibits their mutual approach. It can be concluded that the high effectivity of this deflocculant may be attributed to an electrosteric effect.

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Received 30 July
and accepted 22 October 2001