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Rheological properties of concentrated aqueous fluorapatite suspensions

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Abstract

The $Ca_3(PO_4)_2$ and CaF_2 powders were mixed in a 3:1.5 ratio, calcined at 1000 °C and then milled in an aqueous media with the pH initially adjusted at 9. The resulting powder had a Ca/P atomic ratio of 1.67, which corresponded to the theoretical composition of fluorapatite (FA), $Ca_{10}(PO_4)_6F_2$. Its reactivity in an aqueous solution having two initial pH values with a concentration of ammonium polyacrylate (NH_4PA) was investigated as a function of time. The adsorption behaviour of NH_4PA and the influence of NH_4PA addition on the rheological properties of 40 vol.% FA slips were studied. In addition, the influence of the volume fraction of solids on the rheological behaviour of stabilized FA slips was determined. Finally, the effect of poly(vinyl)alcohol (PVA) addition on the relative viscosity of 38 vol.% FA suspensions stabilized with NH_4PA was investigated. The dissolution of FA was enhanced by decreasing the pH to an acidic value; the increase in pH above 7 markedly reduced the Ca^{2+}/H^+ exchange reaction rate. As a result, well-stabilized aqueous suspensions could be obtained at pH close to 9 in a wide range of solids loading. The minimum viscosity of 40 vol.% slips at pH 8.9 occurred at 0.6 wt% of NH_4PA was added. An important increase in the yield stress was observed for suspensions with a volume fraction of solids higher than about 46 vol.%. The addition of 0.5–1 wt% PVA to a well-stabilized FA slip caused aggregation of particles by a depletion flocculation mechanism, thereby increasing the slip viscosity.
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Keywords: Fluorapatite; Surface reactivity; Rheological properties

1. Introduction

Because of its excellent biocompatibility, fluorapatite ($Ca_{10}(PO_4)_6F_2$) ceramic has been used in orthopedics and dental surgeries [1–3]. However, the low mechanical properties of bulk FA restricted its wider applications in the load-bearing compartments. Therefore, FA coating on a bioinert ceramic such as ZrO_2 has been introduced to achieve a high mechanical strength as well as a suitable biocompatibility of the system [4,5]. A relatively thick FA coating layer on ZrO_2 can be fabricated by a powder slurry method. One step in this process is the preparation of stable concentrated FA suspensions with the addition of a dispersant and a binder. Concentrated FA suspensions based on organic solvents have been prepared [5,6]. In recent years, environmental protection and safety reasons have induced the replacement of non-aqueous organic solvents for an aqueous media. However, the rheological behaviour of concentrated FA aqueous suspensions has not been studied.

Successful colloidal processing of fine ceramic powders requires accurate control of both rheological properties and the state of the dispersion. Anionic polyelectrolytes such as NH_4PA are commonly used as dispersant of ceramic powders in aqueous media [7,8]. The polyelectrolyte adsorbs at the solid–liquid interface and infers repulsive force between the particles which keeps the particles well dispersed; the repulsive interactions are caused by electrostatic and steric effects [9].

The preparation of stable suspensions in aqueous solution is strongly limited by the solubility of FA, which is rather high in acidic conditions. Little attention has been paid to the study of its surface reactivity in an aqueous solution with NH_4PA in weakly alkaline conditions, at which the anionic polyelectrolyte is dissociated. In order to produce well-stabilized slips, first its reactivity in an aqueous solution having two initial pH values with a concentration of NH_4PA was investigated as a function of time.

At high solids loading, relatively low slip viscosity can only be achieved in the presence of an optimum dispersion state of

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particles. Therefore, the adsorption behaviour of NH_4PA and the influence of NH_4PA addition on the rheological properties of 40 vol.% FA slips were studied. In addition, the influence of the volume fraction of solids on the rheological behaviour of stabilized FA slips was determined.

As we have mentioned the binder is an essential component for the effective processing of films on substrates. The binder provides strong adhesion between the ceramic particles and the substrate, preventing the powder from detaching off the substrate during thermal treatment. PVA is frequently used in an aqueous media due to its affinity with the processing liquid. Furthermore, it has an effective burnout profile without the formation of a deleterious residue. However, the addition of the organic binder affects the rheology of the suspension [10,11]. Therefore, the influence of PVA addition on the relative viscosity of 38 vol.% FA suspensions stabilized with NH_4PA was investigated.

2. Experimental procedure

2.1. Materials

The $Ca_3(PO_4)_2$ (Fluka, Germany) and CaF_2 (Aldrich) powders were mixed in a 3:1.5 ratio; thus, CaF_2 was in excess with respect to the stoichiometric ratio for the reaction:

$$3Ca_3(PO_4)_2 + CaF_2 \rightarrow Ca_{10}(PO_4)_6F_2 \quad (1)$$

The mixture of powders was calcined for 3 h at 1000 °C. Then, the powder was milled in an attrition mill using 1.6-mm zirconia balls with 0.047 wt% NH_4PA during 48 h. First distilled water with the pH adjusted at 9 was added to the attrition mill; then the dispersant, thereafter the powder and finally the zirconia balls were added. The powder was added in portions to the suspension and the pH was manually adjusted to be maintained at 9 during the additions. The milled powder was washed with distilled water and dried at 100 °C. This powder subsequently referred as FA was used for the experiments presented in this study.

A commercial ammonium polyacrylate solution (Duramax D 3500, Rohm & Haas, Philadelphia, PA, USA) and a 9 wt% PVA solution were used as deflocculant and binder, respectively. The degree of hydrolysis of PVA was 87–89% and the average molecular weight was in the range of 57,000–66,000 g/mol.

2.2. Powder characterization

The specific surface area of the calcined and FA powders was measured by single-point BET (Micromeritics Accusorb). The chemical composition of the powders was determined after alkaline fusion. The infrared spectra (FTIR-ATR) of the FA powder were obtained with an Espectrum One (Perkin Elmer) spectrometer using a 4 cm^{-1} resolution over the 4000–650 cm^{-1} region. The crystalline phases in the FA powder were determined by X-ray diffraction (XRD) using a diffractometer Philips PW3710.

2.3. FA surface reactivity measurements

In order to estimate the isoelectric point (IEP) of the FA, mean particle diameter measurements of 1.1 vol.% suspensions with 0 and 0.56 wt% NH_4PA at different pH values were developed using a Sedigraph (Micromeritics). The aqueous dissolution behaviour of FA with 0 and 0.6 wt% NH_4PA was study by measuring the pH of three suspensions as a function of time. The suspensions having a FA content of 10.4 vol.% were prepared as follows: (1) FA was added to distilled water, (2) FA was added to distilled water with 0.6 wt% NH_4PA at an initial pH 7.7, and (3) FA was added to an aqueous solution having an initial pH of 8.9 with 0.6 wt% NH_4PA. To aid in the interpretation of solubility measurements the infrared spectra (FTIR-ATR) of the three samples following their dissolution for 17 days and no reacted FA were determined. The Ca/P atomic ratio of the three samples after their dissolution was determined.

2.4. Slip preparation

40 vol.% aqueous FA slips with various amounts of deflocculant were prepared by suspending particles in deionized water via 20 min of ultrasound; the pH was manually adjusted to be maintained at 8.9. In addition, slips with 0.6 wt% NH_4PA and different solid contents were prepared at pH 8.9 to study the influence of the volume fraction of solids on the rheological properties. Finally, 38 vol.% suspensions with 0.6 wt% NH_4PA and two PVA concentrations were prepared.

2.5. Powder characterization and NH_4PA adsorption measurements

40 vol.% slips with NH_4PA were evaporated, afterwards the solid was dried at 100 °C and analyzed by FTIR-ATR. The spectra of this powder were compared with that of FA.

In order to determine the amount of NH_4PA adsorbed, slips were centrifuged for 30 min at 2500 rpm and washed twice with distilled water. Then, the solid was dried at 100 °C and analyzed by thermal gravimetric analysis (TGA) (Model STA 409, Netzsch, Inc., Germany) at a heating rate of 10 °C/min in air. The TGA data showed a water weight loss at temperatures near 100 °C and a weight loss due to the NH_4PA decomposition in a temperature range from 320 to 600 °C. This weight loss was used to determine the amount of NH_4PA adsorbed on each sample. Although the adsorption data obtained with this technique were semiquantitative, they provided a relative measure of the amount of NH_4PA adsorbed on the samples.

2.6. Rheological measurements

Steady state flow curves of FA slips were performed by measuring the steady shear stress value as a function of shear rate in the range of 0.5–542 s^{-1} using a concentric cylinder viscometer (Haake VT550, Germany) at 25 °C. A coaxial cylinder system with two gaps (sensor system NV Haake) was used. As soon as stationary conditions were reached at each shear rate, the shear rate increased in steps up to the maximum value and then decreased. The majority of the curves did not show hysteresis area. The relative viscosity $\eta_r = \eta_s/\eta_f$, where η_s and η_f are the viscosities of the suspension and the fluid medium (PVA + water + dispersant), respectively, was measured for 38 vol.% slips with 0.6 wt% NH_4PA and two PVA concentrations.

3. Results and discussion

3.1. Powder characterization

The milling of the calcined powder reduced the particle size, thereby increasing the specific surface area from 1.79 to 17.77 m^2/g. The particle size distribution curve of the FA powder showed an unimodal distribution with a mean particle diameter of 0.37 μm.

The Ca/P atomic ratio and the F content of the calcined and FA powders are shown in Table 1. The chemical composition of the calcined powder indicated an excess of Ca and F with respect to the theoretical composition of $Ca_{10}(PO_4)_6F_2$. This was attributed to the excess of CaF_2 used in the preparation of fluorapatite (Eq. (1)). Ca and F were removed during the milling and washing of the calcined powder, leading to an apatite with a Ca/P atomic ratio and a F content of 1.67 and 37,700 ppm, respectively, which were close to the theoretical one. Thus, the average composition of the FA powder was found to be $Ca_{10}(PO_4)_6F_2$. The XRD patterns of FA corresponded to JCPDS # 15-0876; no additional phases were revealed (Fig. 1).

3.2. FA surface reactivity

Fig. 2 shows the mean particle diameter (d_{50}) as a function of pH for FA with 0 and 0.56 wt% NH_4PA. The FA could be dispersed at pH values >6; the d_{50} slightly decreased with increasing pH from 6.5 to 9.9, reaching at this pH the lowest mean particle diameter of 0.75 μm. An important increase in the mean particle diameter was found with decreasing pH from 6 to 4; at pH ≤4 the d_{50} remained nearly constant.

Table 1
Ca/P atomic ratio and F content of different powders.

Powders	Ca/P atomic ratio	F content (ppm)
Calcined	1.81	>65,000
FA	1.67	37,700

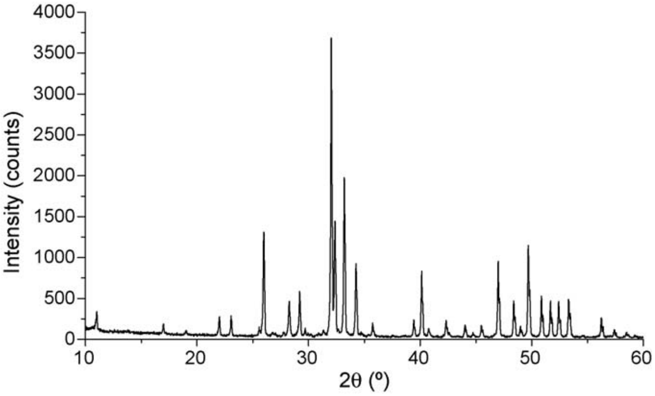

Fig. 1. XRD patterns of fluorapatite (FA).

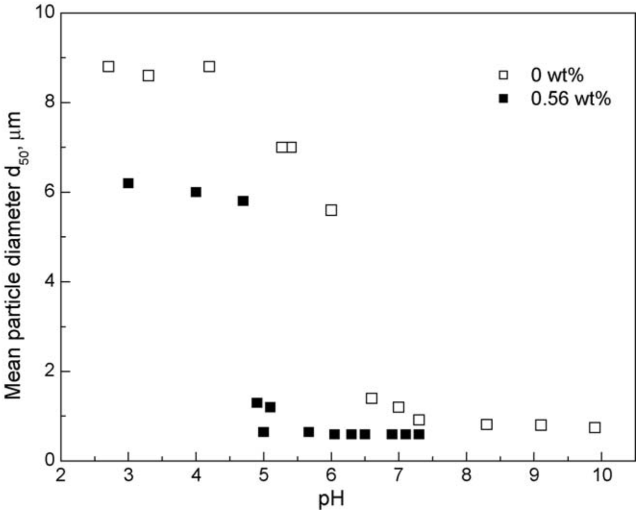

Fig. 2. Mean particle diameter (d_{50}) as a function of pH for FA with different NH_4PA contents: (a) 0 wt% and (b) 0.56 wt%.

The degree of aggregation of FA in aqueous dispersion was determined by the magnitude of the powder surface charge. At pH <6.5 a reduction in the electrostatic repulsion between particles was expected due to the strong flocculation; the Van der Waals attraction forces were dominant and caused aggregation of the particles. In the pH range from 6.5 to 10 the particles became well dispersed indicating an increase in the electrostatic repulsion between particles. At pH ≤4 an increase in the repulsion between particles could be expected due to the high positive charge of the FA powder; however, the aggregation between particles still remained. This behaviour could be attributed to proton exchange reactions at the FA surface under strongly acidic conditions, which will be explained later.

The IEP of FA seemed to be about pH 6. Therefore, a negatively charge FA surface at pH >6 could be expected and a positively one at pH values lower than the IEP. Fluorapatite surfaces are thought to consist of two distinct surface groups $\equiv CaOH_2^+$ and $\equiv PO^-$ [12]. According to Chaïrat et al. [13], in acid to neutral conditions, apatite surface protonation proceeds via the formation of $\equiv CaOH_2^+$ leaving phosphate surface sites deprotonated. The Ca sites loss a proton in strongly alkaline solutions according to the following reaction:

$$\equiv CaOH_2^+ \rightarrow \equiv CaOH^0 + H^+ \quad (2)$$

The $\equiv CaOH_2^+$ concentration decreases with increasing pH and at pH >9.5 the $\equiv CaOH^0$ sites predominate [13].

The addition of NH_4PA shifted the curve towards lower pH values (Fig. 2). A well dispersed FA suspension was found at pH ≥5, the mean particle diameter was nearly the same as the FA powder. At pH values lower than 4.5 flocculation occurred;

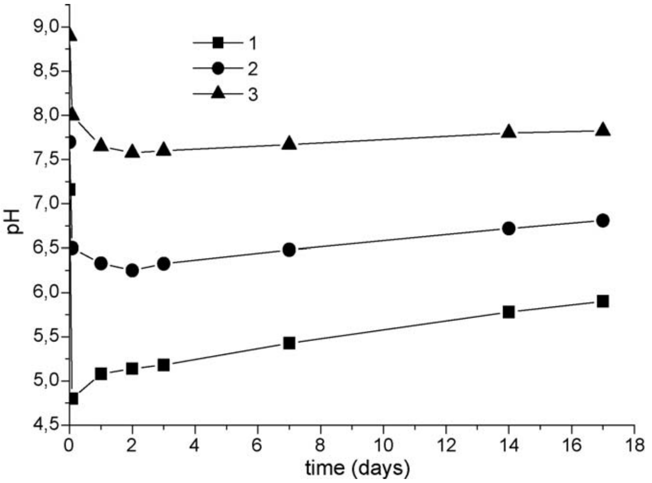

Fig. 3. pH as a function of time for three 10.4 vol.% FA suspensions: (1) FA added to distilled water, (2) FA added to distilled water with 0.6 wt% NH_4PA at an initial pH 7.7, and (3) FA added to an aqueous solution having an initial pH of 8.9 with 0.6 wt% NH_4PA.

however, aggregation of particles was lower than that observed in the absence of the dispersant. The ammonium polyacrylate dissociation according to the reaction:

$$RCOONH_4 \rightarrow RCOO^- + NH_4{}^+ \qquad (3)$$

begins at pH >3.5; at pH values ≥8.5 the polymer charge is negative with the degree of ionization approaching 1 [7]. The $RCOO^-$ groups of the deflocculant were adsorbed at the positive $\equiv CaOH_2{}^+$ sites of the FA powder surface. The anionic polyelectrolyte was only slightly dissociated at pH <8.5; consequently, the electrostatic repulsion between the polyelectrolyte chains was of less importance and the steric contribution started to dominate.

Fig. 3 shows the pH as a function of time for the 1, 2 and 3 suspensions. For the 1 slip, an important adsorption of OH^- was found upon the FA introduction in aqueous solution, since at pH 7, which was close to the IEP of the FA powder, a high amount of positive surface groups still remained. As a result, the pH decreased to an acidic value up to a minimum of 4.8. Afterwards, the pH increased with further time reaching a pH value of 5.9 for 17 days. According to Chaïrat et al. [14], at acidic conditions an exchange reaction between H^+ and Ca^{2+} was involved in the uptake of H^+ by FA surfaces. They observed an initial preferential release of Ca and F relative to P with respect to the stoichiometric dissolution in acidic solutions; they found that the F and Ca removal was coupled to phosphate hydrolysis and leaded to the formation of a protonated Ca-leached layer at FA surface. A possible dissolution mechanism could consist of the irreversible coupled removal of Ca and fluoride atoms located near the surface via proton for Ca exchange reactions, in accord with:

$$Ca_{10}(PO_4)_6F_2 + 2xH^+ \leftrightarrow [Ca_{10-x}(HPO_4)_{2x}(PO_4)_{6-2x}]^{2+} + xCa^{2+} + 2F^- \qquad (4)$$

The addition of FA to an aqueous solution with NH_4PA at pH 7.7 (2 slip), produced a lesser decrease in pH than that found for 1 slip. A minimum pH of 6.2 occurred after 2 days (Fig. 3). The lower adsorption of OH^- was due to: (1) the FA powder had few positive surface groups at pH 7.7 since this pH was far from the IEP of the FA with NH_4PA (Fig. 2) and (2) the anionic polyelectrolyte slightly dissociated was adsorbed at some of the positive sites on the FA powder surface, leaving less ones for the OH^- adsorption. An incomplete adsorption of the polyelectrolyte on the negatively charged FA surface could be expected, since the polymer and the surface had the same charge sign [15]; as a consequence, an excess of polymer remained in solution. After 2 days the pH increased with increasing time with a lower slope than that found for the 1 slip. This was attributed to the decreasing FA dissolution rate with increasing pH (Eq. (4)).

The introduction of FA in an aqueous solution with the pH adjusted at 8.9 with NH_4PA produced a scarcely lower decrease in pH than that observed for the 2 slip (Fig. 3). The $RCOO^-$ groups of the polyelectrolyte fully dissociated were adsorbed at some of the positive FA surface groups. However, as the amount of positive sites on the FA surface decreased with increasing pH, the powder had less positive groups at which the OH^- could be adsorbed. A minimum pH of 7.6 was found after 2 days; for longer time the pH increased with a lower slope than those observed for the 1 and 2 slips, as a consequence of the decrease in the Ca^{2+}/H^+ exchange reaction rate with increasing pH. Chaïrat et al. [13], demonstrated that the FA dissolution rate via Ca^{2+}/H^+ exchange markedly decreased in weakly alkaline conditions.

The FTIR-ATR spectra of unreacted FA, FA following its dissolution in an aqueous solution (1 powder), FA following its dissolution in an aqueous solution with 0.6 wt% NH_4PA at an initial pH 7.7 (2 powder), and FA following its dissolution in an aqueous solution with the pH initially adjusted at 8.9 with 0.6 wt% NH_4PA (3 powder) are presented in Fig. 4. In all the spectra the broad band at 3621 (Fig. 4a) was assigned to strongly adsorbed OH^- by coordination to $\equiv CaOH_2{}^+$ ions on the surface of the particles, whereas those at 960, 1017–1032 and 1090 cm^{-1} (Fig. 4b) to $PO_4{}^{-3}$ group. The intensity of the 3621 cm^{-1}band and consequently the amount of OH^- adsorbed by the powder increased in the following order: FA, 3, 2 and 1 powders. This behaviour was consistent with the decrease in pH observed (Fig. 3) upon the FA introduction in the respective solutions.

The anti-symmetric $PO_4{}^{-3}$ stretching band was observed at 1017 cm^{-1} on the FA powder and at 1020, 1023 and 1032 cm^{-1} on the 3, 2 and 1 powders, respectively. This peak shift was due to a change in the coordination environment of phosphate groups. The anti-symmetric $PO_4{}^{-3}$ stretching band of octa-calcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$) is located at 1038 cm^{-1}[16]. Thus, the shift of the peaks suggested the protonation of surface P–OH groups and the subsequent incorporation of protons into the FA structure. Chaïrat et al. [14] observed a shift in the phosphate stretching band position of FA dissolved in a pH 2 solution for 2 days. The greater shift of the 1 powder band indicated a greater incorporation of protons into the FA structure as a consequence of its dissolution in acidic conditions. The dissolution of FA in nearly neutral

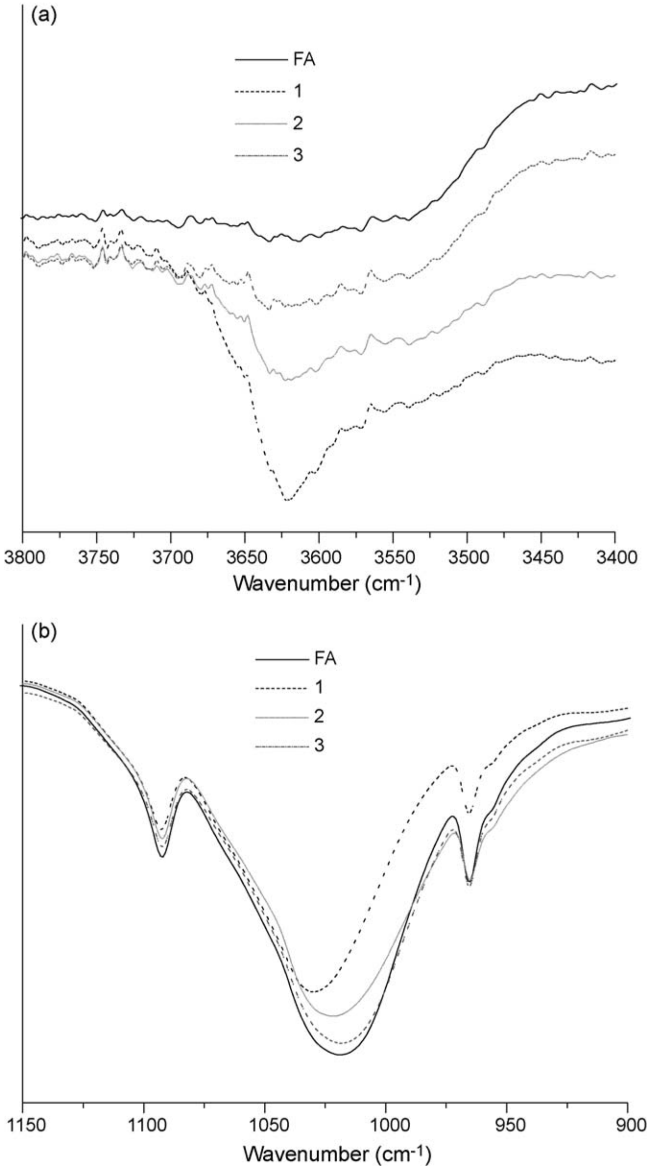

Fig. 4. FTIR-ATR spectra of unreacted FA, FA following its dissolution for 17 days in an aqueous solution (1 powder), FA following its dissolution for 17 days in an aqueous solution with 0.6 wt% NH_4PA at an initial pH 7.7 (2 powder), and FA following its dissolution for 17 days in an aqueous solution with the pH initially adjusted at 8.9 with 0.6 wt% NH_4PA (3 powder): (a) spectra over the 3800–3400 cm^{-1} range and (b) spectra over the 1150–900 cm^{-1} range.

solutions (2 and 3 powders) resulted in a lower proton penetration into the surface lattice of FA. These results confirmed the pH measurements, a proton–Ca exchange reaction occurred at FA surface during its dissolution leading to the formation of a protonated Ca-leached layer. As a result, the FA surface composition in contact with aqueous solution was expected to be different form its bulk composition.

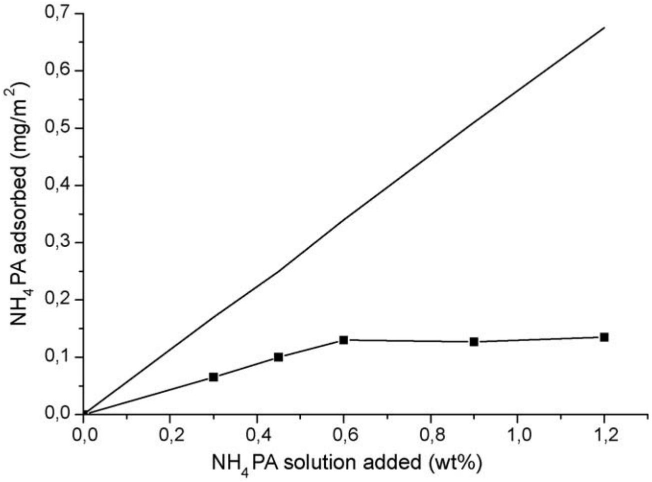

Fig. 5. Amount of NH_4PA adsorbed as a function of the amount of NH_4PA solution added at pH 8.9 for the FA powder. The diagonal line represents 100% of ammonium polyacrylate adsorption.

The Ca/P atomic ratio of the 2 and 1 powders was 1.50 and 1.33, respectively. These values were lower than that of the dissolving FA, suggesting that Ca was removed from the FA structure via exchange reactions. The Ca/P ratio decreased with decreasing the pH of the solutions as a consequence of the increase in the Ca^{2+}/H^+ exchange reaction rate. The Ca/P atomic ratio of the powder dissolved at the lower pH (1 powder), indicated that two calcium atoms were preferentially released from the FA surface during its dissolution for 17 days. This result and the FTIR spectra suggested that the leached surface layer might have a composition $[Ca_8(HPO_4)_4(PO_4)_2]^{+2}$ (Eq. (4)).

The results showed that the dissolution of FA was enhanced by decreasing the pH to an acidic value; the increase in pH above 7 markedly reduced the Ca^{2+}/H^+ exchange reaction rate.

3.3. Amount of NH_4PA adsorbed and powder characterization

Fig. 5 shows the amount of NH_4PA adsorbed as a function of the amount of NH_4PA solution added at pH 8.9 for the FA powder. The amount of NH_4PA adsorbed increased with increasing amounts of NH_4PA solution added up to reaching an adsorption plateau at 0.6 wt% of NH_4PA solution added. This plateau corresponded to the adsorption saturation limit of the polyelectrolyte on the FA powder at pH 8.9. The adsorption curve did not follow the 100% adsorption line, thus the adsorption plateau was reached with an appreciable amount of NH_4PA remaining in solution. At pH 8.9 the anionic polyelectrolyte was fully dissociated and the FA surface was negatively charged. The electrostatic repulsion at the surface imparts a barrier for adsorption which limited adsorption to low amounts [9]. However, the fact that adsorption occurred under these conditions indicated that there was a ‘‘specific’’ or ‘‘chemical’’ segment–surface interaction which overcompensated the repulsive electrostatic forces. Previous studies on alumina [7] and coated silicon nitride [17,18] also found a detectable adsorption of anionic polyelectrolytes when the polyelectrolyte and the surface have the same charge sign.

During the aqueous colloidal processing of the FA powder with 0.6 wt% NH_4PA the pH of the suspension was adjusted at 8.9. At this pH the Ca^{2+}/H^+ exchange reaction was markedly

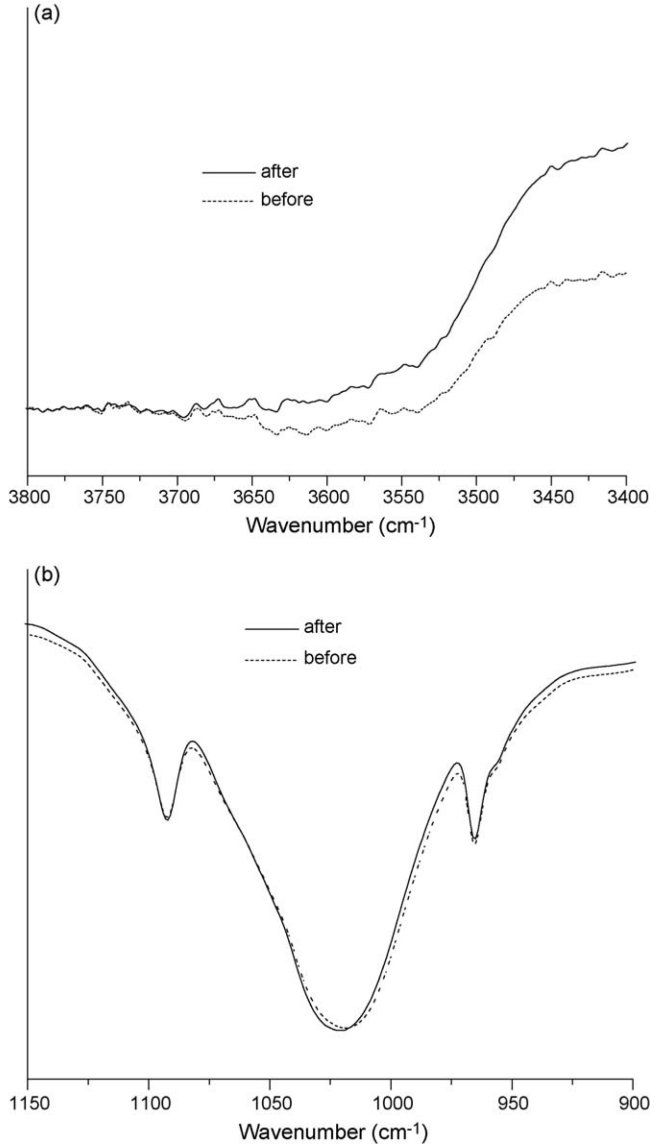

Fig. 6. FTIR-ATR spectra of the FA powder before and after its colloidal processing in an aqueous solution at pH 8.9 with NH_4PA: (a) spectra over the 3800–3400 cm^{-1} range and (b) spectra over the 1150–900 cm^{-1} range.

reduced, consequently a little change in the surface composition of the FA powder could be expected. Fig. 6 shows the FTIR-ATR spectra of the FA powder before and after its colloidal processing in an aqueous solution at pH 8.9 with NH_4PA. A similar intensity and position of the PO_4^{-3} bands (Fig. 6b) and a similar OH^- adsorption (Fig. 6a) were detected. This confirmed that the aqueous colloidal processing of FA with NH_4PA at pH 8.9 did not change the surface composition of the powder.

3.4. *Rheological properties*

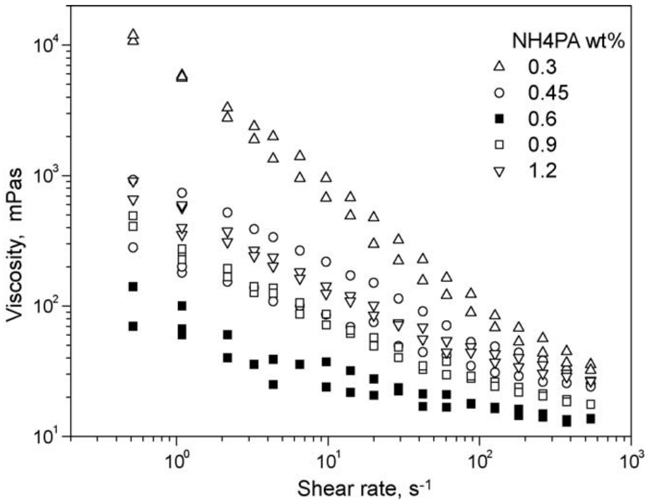

Fig. 7. Flow curves of viscosity versus shear rate as a function of the amount of NH_4PA solution added at pH 8.9 for 40 vol.% FA slips.

Fig. 7 shows the flow curves of viscosity versus shear rate as a function of the amount of NH_4PA solution added at pH 8.9 for 40 vol.% FA slips. All the curves showed a yield stress and the viscosity values were strongly dependent on the shear rate; thus, the suspensions exhibited a pseudoplastic behaviour. The measured flow curves were satisfactorily fitted with the Casson model ($R = 0.99$). The Casson model equation is:

$$\tau^{1/2} = \tau_0^{1/2} + (\eta_p \gamma)^{1/2} \quad (5)$$

where τ is the shear stress, γ is the shear rate, τ_0 is the yield stress and η_p represents the limiting viscosity at a high shear rate range. The τ_0 and η_p constants of the model could be used to represent the rheological properties of the slips.

The particles in a flocculated suspension form floc groups or a network, because of the mutual attraction between particles, and the yield value τ_0 of the Casson model could be used as a parameter that indicated the degree of aggregation and consequently the degree of flocculation. The η_p value becomes equal to the viscosity when $\tau_0 \rightarrow 0$.

Fig. 8 shows the effect of the amount of NH_4PA solution added on the τ_0 and η_p values. For the FA slip with 0.3 wt% NH_4PA the amount of NH_4PA adsorbed was lower than the adsorption saturation limit of the polyelectrolyte on the FA surface (Fig. 5), the suspension was flocculated and this condition resulted in high τ_0 and η_p values. The incomplete adsorption of the polyelectrolyte resulted in lower electrostatic

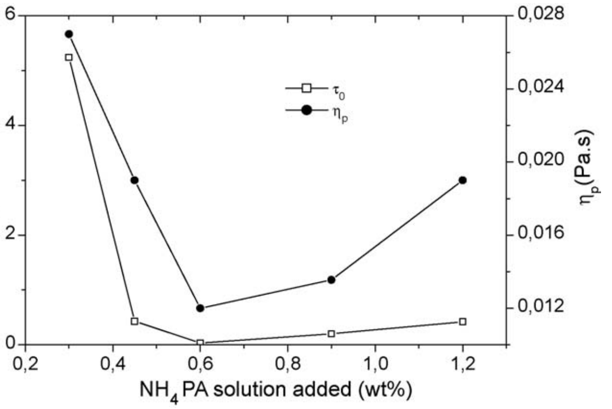

Fig. 8. Effect of the amount of NH_4PA solution added on the τ_0 and η_p values for 40 vol.% FA slips.

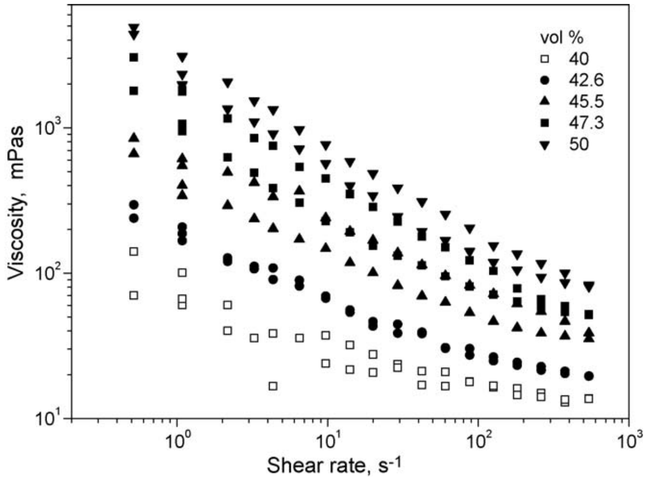

Fig. 9. Flow curves of viscosity versus shear rate of FA slips stabilized with 0.6 wt% NH_4PA for different volume fraction of solids.

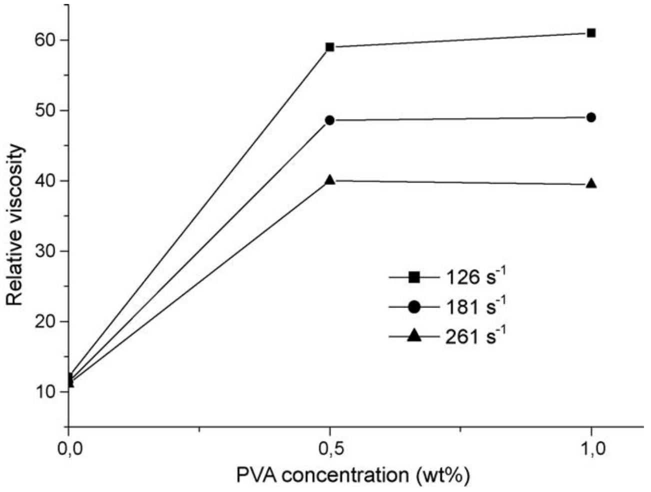

Fig. 11. Relative viscosity as a function of the PVA concentration for 38 vol.% suspensions stabilized with 0.6 wt% NH_4PA at three different shear rates.

repulsion between particles, thereby forcing particles together. Further additions of NH_4PA resulted in a decrease in the τ_0 and η_p values. The adsorption of the negatively charged polyelectrolyte enhanced the negative surface charge of the FA powder. In addition, at pH 8.9 the electrostatic repulsion between the charged carboxylate groups impedes the accumulation of groups at the surface, the polyelectrolyte adsorbs in a stretched-out configuration which results in long-range steric interactions of the NH_4PA at the solid–liquid interface [15]. Thus, the adsorbed molecules increased the electrosteric repulsion between particles, thereby decreasing the slip viscosity.

For 0.6 wt% NH_4PA the viscosity and consequently τ_0 and η_p attained the minimum values. As the adsorption coverage increased (Fig. 5) the negative surface charge density and the electrostatic repulsion between particles increased accordingly and, eventually, attained a level at 0.6 wt% NH_4PA that was strong enough to overcome the Van der Waals forces. At this NH_4PA concentration the suspension was dominated by repulsive forces, thus, it was stabilized. The viscosity at 400 s^{-1} was reduced to a low value of about 13 mPa s. As the NH_4PA addition increased over 0.6 wt% the slips changed from being well stabilized to weakly flocculated. The increase in the ionic strength due to the presence of a large amount of free polymer in solution decreased the negative surface charge of the FA powder due to the large compression of the double layer [19], which produced the increase in the slip viscosity. As a consequence an increase in the τ_0 and η_p values was found.

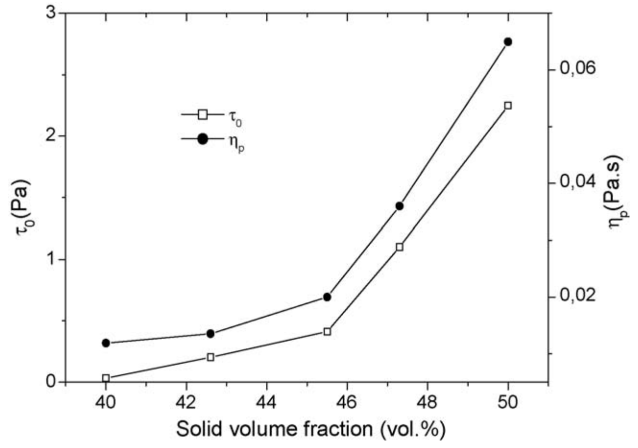

Fig. 10. Effect of the volume fraction of solids on the τ_0 and η_p values for slips stabilized with 0.6 wt% NH_4PA.

Fig. 9 shows the flow curves of viscosity versus shear rate of slips with 0.6 wt% NH_4PA for different volume fractions of solids. The suspensions exhibited a pseudoplastic behaviour, the viscosity increased with increasing the volume fraction of solids throughout the whole range of shear rates. As the volume fraction of solids increased from 40 to 50 vol.% the viscosity at 400 s^{-1} increased from 13 to 100 mPa s.

The effect of the volume fraction of solids on the τ_0 and η_p values is shown in Fig. 10. At high solids loading (>40 vol.%), the particles were constrained in their positions by electrostatic forces and the local stress might exceed a critical value (yield stress) in order to produce a continuous deformation (shear flow) of the particle network. An important increase in the yield stress was observed for suspensions with a volume fraction of solids higher than about 46 vol.%. At concentrations >50 vol.% the mean distances between particles decreased, consequently, the adsorbed polymeric layers were in close contact with one another and, the particle interlocking prevented the suspension from flowing; correspondingly, the yield stress went to a relatively high value. The increase in the solids loading increased the η_p parameter in a similar way. Zupancic et al. [20] observed a similar influence of the particle concentration on the rheological properties of aqueous α-alumina suspensions.

As we have mentioned, the addition of PVA can change the rheology of a dispersant stabilized suspension significantly [11]. Fig. 11 represents the relative viscosity at three different shear rates as a function of the PVA concentration for 38 vol.% suspensions stabilized with 0.6 wt% NH_4PA. At the three shear rates examined, the relative viscosity increased as the PVA concentration increased from 0 to 0.5 wt%; thereafter, the relative viscosity remained virtually unchanged. The increase in the relative viscosity was approximately four times as the PVA concentration increased from 0 to 0.5 wt%. The increase in the viscosity with the addition of PVA suggested that the PVA produced a flocculation of the FA particles. The degree of flocculation was more pronounced for the PVA concentration range between 0 and 0.5 wt%. Above 0.5 wt% PVA, there was little change in the degree of flocculation. Khan et al. [11] found a similar behaviour when PVA was added to stabilized alumina suspensions. They found that PVA did not adsorb to any measurable extent, on the alumina particles, therefore they explained that the aggregation of alumina particles was caused by a depletion flocculation process when PVA was added to the suspension.

The addition of PVA to stabilized FA suspensions might cause depletion flocculation, whereby the concentration of the non-adsorbing free PVA was effectively reduced between the particles, and the higher concentration outside the particle–particle approach zone, exerted an osmotic pressure causing the particles to flocculate. Thus, the addition of PVA promoted aggregation of particles by a depletion flocculation mechanism.

4. Conclusions

A fluorapatite with a Ca/P atomic ratio of 1.67 close to the theoretical one could be obtained by milling the calcined mixture ($Ca_3(PO_4)_2$:CaF_2; 3:1.5) in an aqueous media with the pH initially adjusted at 9.

The surface reactivity of fluorapatite in an aqueous solution with and without dispersant was investigated. The initial dissolution of fluorapatite in an aqueous solution produced a markedly decrease in pH to an acidic value, thereafter a proton consumption by Ca^{2+}/H^+ exchange reaction occurred with increasing pH accordingly. The addition of FA to an aqueous solution with NH_4PA in weakly alkaline conditions (pH $\sim$9) produced a lesser decrease in pH and consequently the up take of H^+ via proton–Ca exchange reaction was minimized.

The aqueous colloidal processing of FA with NH_4PA at pH 8.9 did not change the surface composition of the powder. The flow curves of the suspensions followed the Casson model. The τ_0 and η_p constants of the model were used to represent the rheological properties of the slips. The minimum viscosity of 40 vol.% slips at pH 8.9 occurred at 0.6 wt% of NH_4PA added. At this concentration, the saturation adsorption limit of fully dissociated NH_4PA was reached providing a high degree of particle stabilization. The yield stress increased with increasing the volume fraction of solids. An important increase in τ_0 was observed for suspensions with a volume fraction of solids higher than about 46 vol.%. At concentrations >50 vol.% the adsorbed polymeric layers were in close contact and, hence, the particle interlocking prevented the suspension from flowing.

38 vol.% FA slips stabilized with 0.6 wt% NH_4PA were selected to study the influence of the PVA binder on the rheological behaviour of the suspensions. The addition of 0.5 wt% PVA to a well-stabilized FA slip caused an aggregation of particles, thereby increasing the slip viscosity. The increase in viscosity was probably due to a depletion flocculation mechanism. The viscosity became nearly constant in the 0.5–1 wt% PVA concentration range.

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