

RHEOLOGICAL BEHAVIOR OF AQUEOUS SUSPENSIONS. OF FLUORAPATITE

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ABSTRACT

A fluorapatite with a Ca/P atomic ratio of 1.67 close to the theoretical one could be obtained by milling the calcined mixture ($\text{Ca}_3(\text{PO}_4)_2$: CaF_2 ; 3:1) in an aqueous media with the pH initially adjusted at 9. The influence of NH_4PA addition on the rheological properties of 40 vol.% FA slips was 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 minimum viscosity of 40 vol.% slips at pH 8.9 occurred at 0.6 wt% of NH_4PA 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.

Keywords: fluorapatite, NH_4PA adsorption, rheological properties.

1.INTRODUCTION

Because of its excellent biocompatibility, fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) 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 infer repulsive force between the particles which keeps the particles well dispersed; the repulsive interactions are caused by electrostatic and steric effects [9].

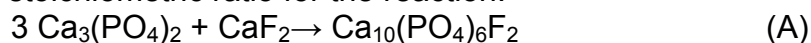
At high solids loading, relatively low slip viscosity can only be achieved in the presence of an optimum dispersion state of particles. Therefore, the adsorption behaviour of NH_4PA and the influence of NH_4PA addition on the rheological properties of 40 vol.% FA slips were studied. In addition, the 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 $\text{Ca}_3(\text{PO}_4)_2$ (Fluka, Germany) and CaF_2 (Aldrich) powders were mixed in a 3:1 ratio; thus the stoichiometric ratio for the reaction:



The mixture of powders was calcined 3 hs 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 hours. 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) 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 57000- 66000 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 Ca/P atomic ratio of the FA powder was determined by chemical analysis. The infrared spectra (FTIR-ATR) of the FA powder was obtained with an Espectrum One (Perkin Elmer) spectrometer using a 4 cm^{-1} resolution over the 4000-500 cm^{-1} region. The crystalline phases in the FA powder were determined by X-ray diffraction (XRD) using a diffractometer Philips PW3710.

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).

2.3 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.

2.4 NH_4PA adsorption measurements

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.

2.5 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 to 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 of the FA powder was 1.67, which was the theoretical one for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. The XRD patterns of FA corresponded to JCPDS # 15-0876; no additional phases were revealed. The FTIR-ATR spectra of the FA powder is presented in Figure 1.

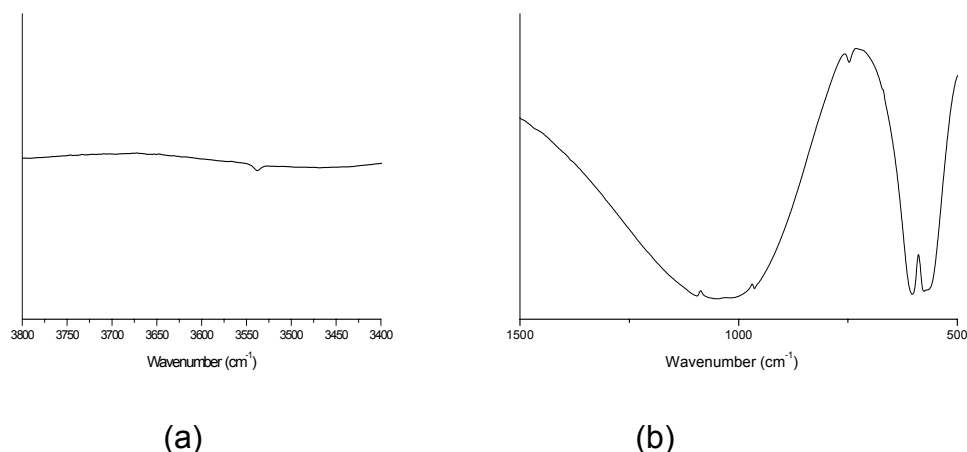


Figure 1: FTIR-ATR spectra of FA (a) spectra over the 3800-3400 cm^{-1} range, (b) spectra over the 1500-500 cm^{-1} range.

The FTIR-ATR spectra was typical for FA. The F-O stretching band was found at 3540 cm^{-1} (Fig. 1a). The strong bands at 570, 602, 960, 1035 and 1095 cm^{-1} were assigned to the fundamental vibrational modes of the tetrahedral phosphate ion (Fig. 1 b).

Figure 2 shows the mean particle diameter (d_{50}) as a function of pH for FA with 0 and 0.56 wt% NH_4PA .

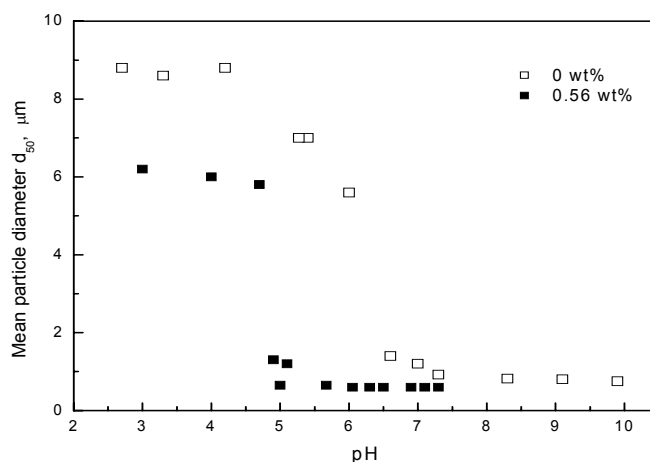


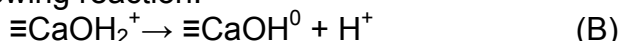
Fig. 2: Mean particle diameter (d_{50}) as a function of pH for FA with different NH_4PA contents: (a) 0 wt%, (b) 0.56 wt%.

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 $\text{pH} \leq 4$ the d_{50} remained nearly constant.

The degree of aggregation of FA in aqueous dispersion was determined by the magnitude of the powder surface charge. At $\text{pH} < 6.5$ 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

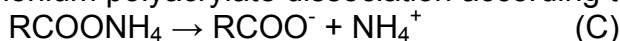
the pH range from 6.5 to 10 the particles became well dispersed indicating an increase in the electrostatic repulsion between particles. At $\text{pH} \leq 4$ an increase in the repulsion between particles could be expected due to the high positive charge of the FA powder; however, the aggregation between particles still remained. This behaviour could be attributed to $\text{Ca}^{+2}/\text{H}^{+}$ exchange reaction at the FA surface under strongly acidic conditions.

The IEP of FA seemed to be about pH 6. Therefore, a negatively charge FA surface at $\text{pH} > 6$ 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 $\equiv\text{CaOH}_2^{+}$ and $\equiv\text{PO}^{-}$ [12]. According to Chairat et al. [13], in acid to neutral conditions, apatite surface protonation proceeds via the formation of $\equiv\text{CaOH}_2^{+}$ leaving phosphate surface sites deprotonated. The Ca sites loss a proton in strongly alkaline solutions according to the following reaction:



The $\equiv\text{CaOH}_2^{+}$ concentration decreases with increasing pH and at $\text{pH} > 9.5$ the $\equiv\text{CaOH}^0$ 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 $\text{pH} \geq 5$, the mean particle diameter was nearly the same as the FA powder. At pH values lower than 4.5 flocculation occurred; however, aggregation of particles was lower than that observed in the absence of the dispersant. The ammonium polyacrylate dissociation according to the reaction:



begins at $\text{pH} > 3.5$; 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 $\equiv\text{CaOH}_2^{+}$ sites of the FA powder surface. The anionic polyelectrolyte was only slightly dissociated at $\text{pH} < 8.5$; consequently, the electrostatic repulsion between the polyelectrolyte chains were of less importance and the steric contribution started to dominate.

3.2 Amount of NH_4PA adsorbed

Figure 3 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.

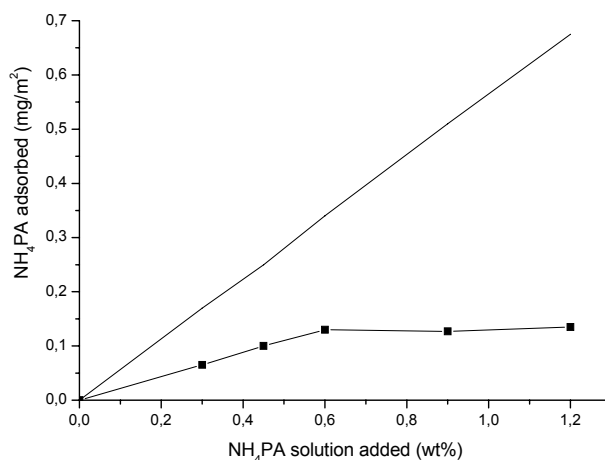


Figure 3: Amount of NH_4PA adsorbed as a function of the amount of NH_4PA solution added at pH 8.9 for the FA powder. The diagonal line represents 100% of ammonium polyacrylate adsorption.

The 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 [14, 15], also found a detectable adsorption of anionic polyelectrolytes when the polyelectrolyte and the surface have the same charge sign.

3.3 Rheological properties

Figure 4 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.

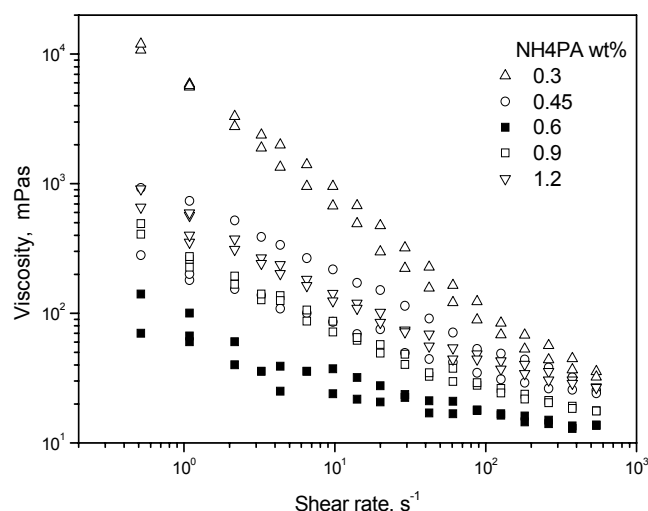


Figure 4: Flow curves of viscosity versus shear rate as a function of the amount of NH_4PA solution added at pH 8.9 for 40 vol% FA slips.

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:

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

where τ is the shear stress, $\dot{\gamma}$ 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 $\tau_0 \rightarrow 0$.

Figure 5 shows the effect of the amount of NH_4PA solution added on the τ_0 and η_p values.

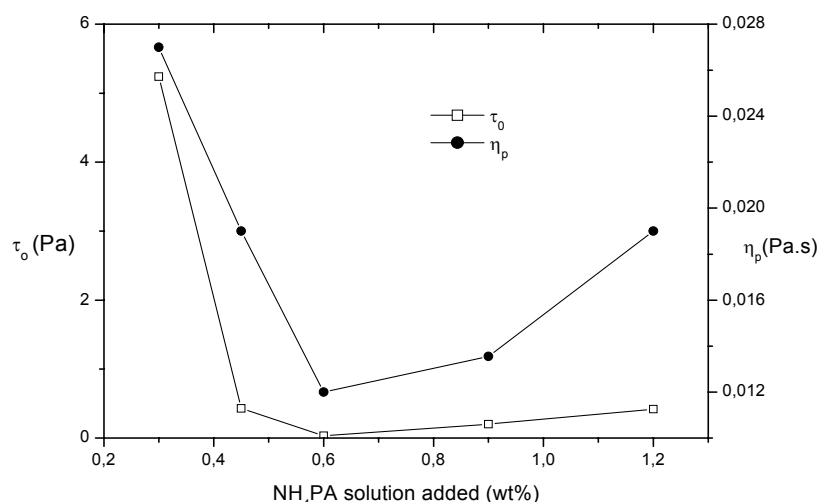


Figure 5: Effect of the amount of NH_4PA solution added on the τ_0 and η_p values for 40 vol% FA slips.

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. 3), 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 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 [16]. 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. 3) 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 [17], which produced the increase in the slip viscosity. As a consequence an increase in the τ_0 and η_p values were found. Figure 6 shows the flow curves of viscosity versus shear rate of slips with 0.6 wt% NH_4PA for different volume fraction of solids.

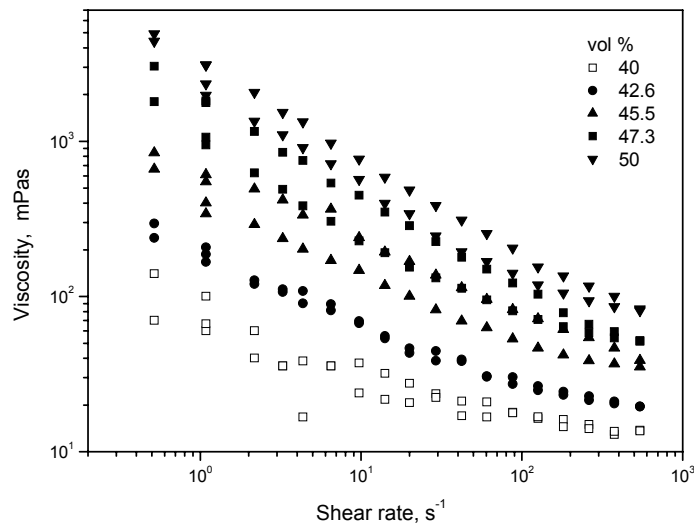


Figure 6: Flow curves of viscosity versus shear rate of FA slips stabilized with 0.6 wt% NH_4PA for different volume fraction of solids.

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 vol.% 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 Figure 7.

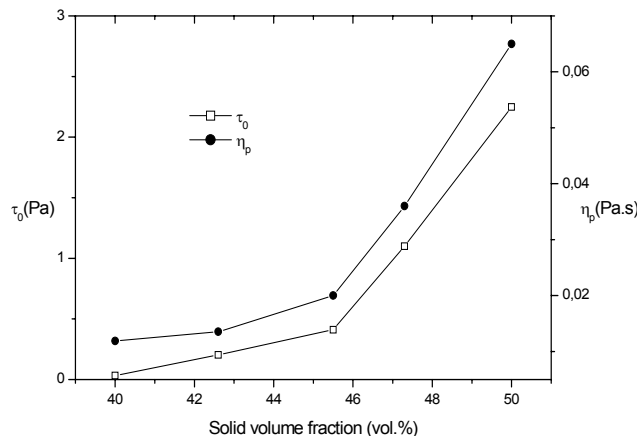


Figure 7: Effect of the volume fraction of solids on the τ_0 and η_p values for slips stabilized with 0.6 wt% NH_4PA .

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. [18] 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]. Figure 8 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 .

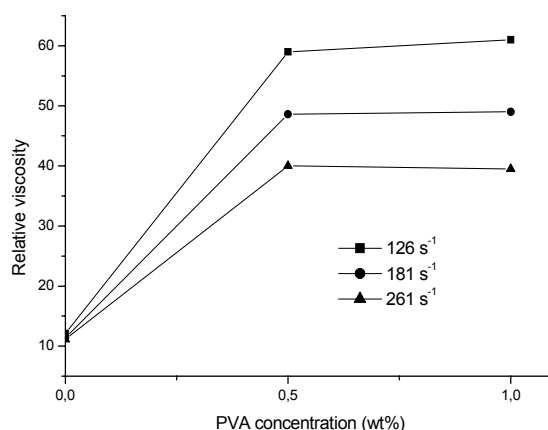


Figure 8: Relative viscosity as a function of the PVA concentration for 38 vol.% suspensions stabilized with 0.6 wt% NH_4PA at three different shear rates.

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.

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 ($\text{Ca}_3(\text{PO}_4)_2$: CaF_2 ; 3:1) in an aqueous media with the pH initially adjusted at 9.

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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