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Influence of powder pre-treatments and milling on dispersion ability of aqueous hydroxyapatite-based suspensions

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Abstract

The rheological properties and the dispersion stability of highly concentrated aqueous hydroxyapatite (HAP) powder suspensions in the presence of an anionic polyelectrolyte dispersant have been investigated. Dispersed suspensions with high content of HAP powder (up to 75 wt.%) and low viscosity were obtained. HAP suspensions with solids loading as high as 75 wt.% could be prepared following a slow process of increasing the solids weight fraction in steps of 3 wt.%, starting from 66 wt.%. After each increment of solids, ball milling was conducted for periods of 6 h, which then increased up to 24 h with solids loading increasing. Zeta potential measurements were conducted on HAP powders evaluate the influence of calcination on surface-charge properties of the particles.

It was concluded that both aqueous ball milling and calcining enhance the repulsive interaction forces between particles, like the presence of the dispersant.

Keywords: A. Calcination; Hydroxyapatite; Dispersion; Slurry; Zeta potential

1. Introduction

The colloidal consolidation technique involves the deflocculation and stabilization of micron/sub-micron sized ceramic powders dispersed in an aqueous or nonaqueous liquid medium before their consolidation. The spontaneously formed soft agglomerates due to van der Waals attractive forces between the powder particles are broken down into individual particles and dispersed by promoting interparticle repulsion by any or both of the following methods: (i) through the control of surface charges either by adjustment of pH of the medium or by adsorption of dispersants (electrolytes) on to the surface of powder particles (electrostatic stabilization) and (ii) through steric separation of individual particles by adsorption of neutral or charged large chain polymers on to the particle surface (steric or electrosteric stabilization) [1–4].

The colloidal approach to powder processing is based on the control of the interparticle forces through the modification of the reactivity at the solid–liquid interface [5–7]. The flowing properties of the slurry will be consequently tailored so as to match the rheological response required under the processing conditions. This can be achieved through the optimization of the type and quantity of the dispersing agent, solid loading, and the particle size distribution and shape of the powder particles. The addition of polyelectrolytes as dispersants prevents the agglomeration of the suspended ceramic powder, as a consequence of electrosteric stabilization. The adsorption of charged polyelectrolytes increases repulsive interparticle forces either by an increase in the surface charge of the particle (electrostatic repulsion) or by the action of the polymeric chains that hinder approaching particles (steric repulsion) [8,9].

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Hydroxyapatite (HAP)-based compositions are usually difficult to disperse in aqueous media, with the suspensions achieving only low or moderate solids concentrations. Nordstrom and Karlsson [10] found slip casting of the commercial HAP powder difficult, because of the lower zeta potential values for the slip.

In order to obtain dispersed slurries with high solid content it is necessary to study the different factors affecting their stability and rheology, such as the characteristics of the dispersing medium, type and amount of dispersant, powder characteristics (specific surface area, chemical composition and size distribution of the powder particles), preparation time of slurries and solid content. The surface properties play a critical role in the dispersing behavior in water. A successful processing requires the use of well-deagglomerated and relatively high concentrated suspensions. For obtaining such suspensions, the complex interfacial reactions between solvent media, dispersant, powders and additives must be taken into account. The present study is aimed at investigating the optimization of an aqueous dispersion of HAP powder synthesized by powder pre-treatments. In this work, the above-mentioned aspects were studied using powders of HAP calcined at temperatures ranging between 700 and 1000 °C. Slurries with high content of solid (up to 75 wt.%) and good fluidity were investigated.

2. Experimental procedure

2.1. Materials and methods

A commercial hydroxyapatite powder (Budenheim Company, Germany) with a stoichiometric ratio of Ca/P = 1.67 was used in this study. The mean particle diameter and the specific surface area were $4.9 \pm 1.1\ \mu m$ and 65.2 m^2/g, respectively. The particle size distribution and mean particle size (d_{50}) were determined by the laser diffraction method (Coulter LS230, USA). The specific surface area of HAP powder was determined by the BET method (Areameter; Model Strohlein, Germany).

Phase compositions of the samples were determined by X-ray diffraction (XRD; Model PW 1710, Philips, The Netherlands) using Cu Kα radiation. Additionally Fourier transform infrared spectroscopy (FTIR) (Bruker-vector 33, USA) was conducted since it allows analyzing materials characteristics that cannot be differentiated by means of X-ray diffraction. The powders and the crushed laser sintered samples were mixed with dried potassium bromide (KBr) powders at a concentration of 1 wt.% and subsequently compressed to produce a transparent tablet. The infrared spectrum with a resolution of 8 cm^{-1} and the scan number of 4 was adopted with a spectral region from 400 to 4000 cm^{-1}.

The zeta potential was determined with a zetasizer (Matec MBS-8000, USA) by measuring the electrophoretic mobility of the particles. The pH value of the slurries was adjusted through addition of 1 M KOH and 1 M HCl.

2.2. Slip preparation and characterization

The slips were prepared by dispersing HAP powder in deionized water, using mechanical stirring. Ammonium polyacrylate (NH_4PAA) solution (Dispex A40, Allied Colloids, Bradford, UK) as dispersant agent. The amount of NH_4PAA used here is expressed as a dry weight of the powder basis, equivalent to the w/w basis of the hydroxyapatite powder. For the rheological characterization of the suspensions, cases of the as-received powders and the pre-treated powders were used in different temperatures.

The slips were ball-milled for at least 6 h before incremental amounts of 3 wt.% solids have been added, up to final concentrations of 75 wt.% for the pre-treated powders. The dispersion behavior of the HAP particles was studied as a function of the pH of the slurry. All these rheological tests were carried out at 20 °C using a coaxial-cylinder measurement device, in the shear rate range of about 0.1–500 s^{-1}. The rheological characterization of the slurries was performed with a coaxial-cylinders shear-rate-controlled viscosimeter (Haake VT 550, Germany).

3. Results and discussion

3.1. Effects of powder pre-treatments on powder characteristics and surface charge of HAP suspensions

Fig. 1 shows the specific surface area as function of calcination temperature. A great decrease took place for powder calcined at temperature between 700 and 1000 °C. The surface area decreased from 65.2 m^2/g, for the as-received powder to 4.6 m^2/g for the powder calcined at 1000 °C.

The particle size distributions reported in Fig. 2 are evidence that as-received powder is characterized by larger agglomerates formed primary particles in comparison with

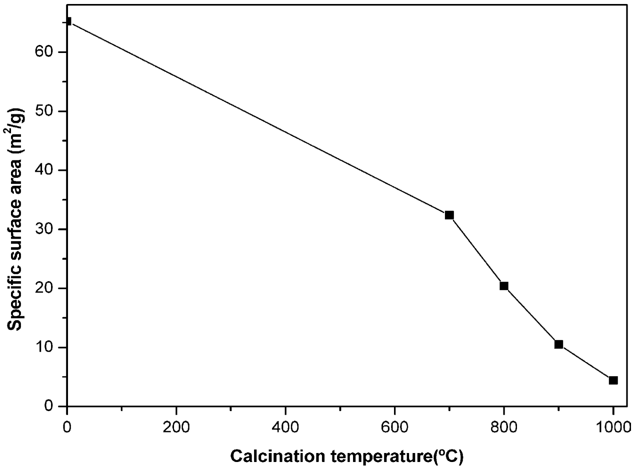

Fig. 1. Influence of the heat treatment on specific surface area (BET) of HAP powders.

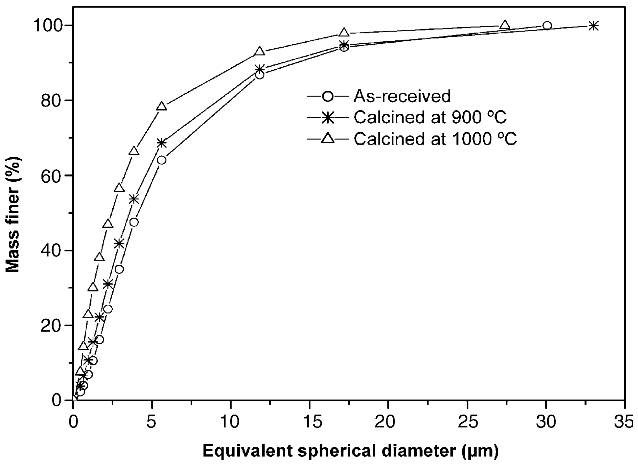

Fig. 2. Particle size distribution of HAP powders as-received and calcined at 900 and 1000 °C in the presence of 1 wt.% of dispersant NH_4PAA.

the pre-treatments powders at 900 and 1000 °C in the presence of 1 wt.% NH_4PAA as dispersing agent. It can be also observed that the as-received powder seems much more difficult to dispersing compared to the calcined powder. This confirms the increased difficulties in dispersing the as-received powders.

The calcination HAP powder at 1000 °C was pure single phase HAP, as shown by the X-ray diffraction presented in Fig. 3. The reflections of the XRD spectrum agree very well with as-received HAP powder.

FTIR spectra (Fig. 4a and b) provide evidence that the presence of a higher amount of HPO_4^{2-} and in powders as-received in comparison to powder calcined at 1000 °C. On the contrary, the O–H stretch band around 3450 cm^{-1} is more accentuated in powder calcined at 1000 °C, which shows small peaks for HPO_4^{2-}, and the associate broad peak, related to the hydration of the powder, is of minor importance for calcined powder at 1000 °C with respect to other. Also after calcinations, CO_3^{2-} group has been disappeared.

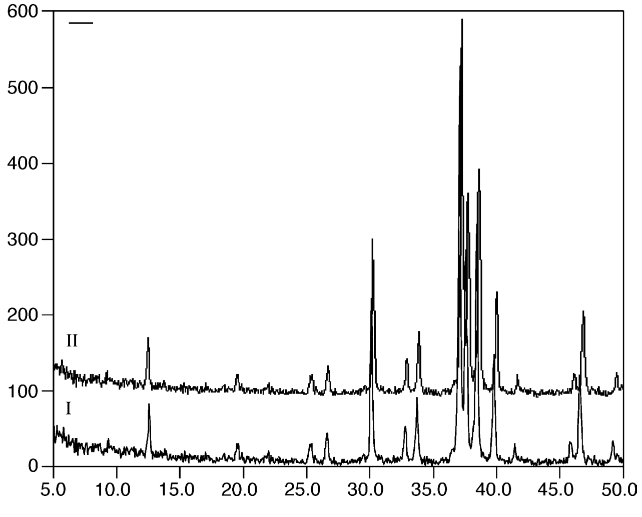

Fig. 3. XRD diffraction of HAP powders (I) as-received and (II) calcined at 1000 °C.

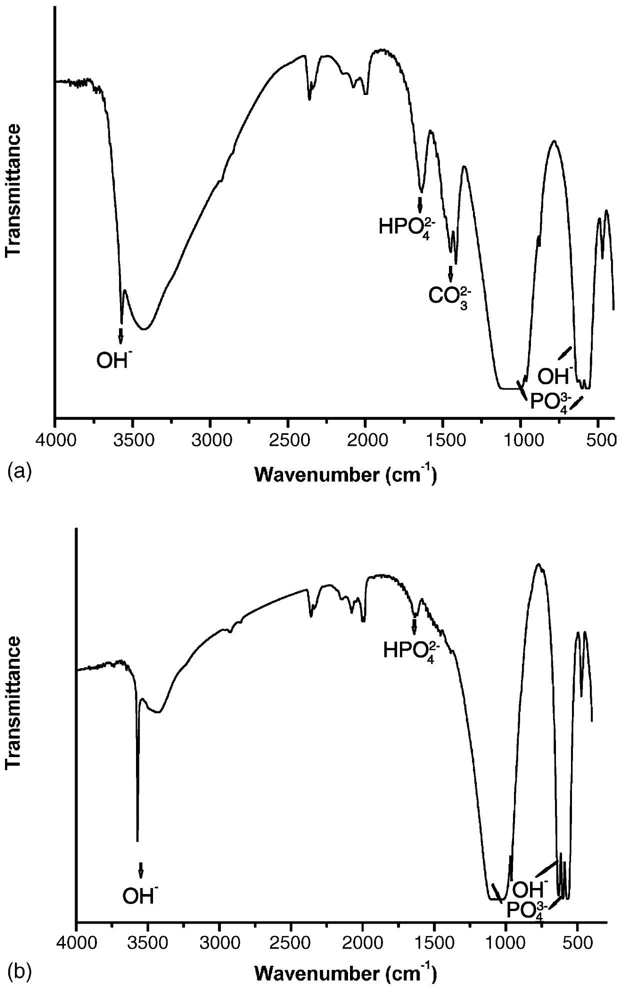

Fig. 4. FTIR spectra of powders (a) as-received and (b) calcined at 1000 °C. The main absorption bands are indicated.

On dispersion into aqueous media, the HAP particles could have on their surfaces various ions such as Ca^{2+}, $CaOH^+$, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and $CaH_2PO_4^+$, depending on the dissolution and the hydrolytic reactions in solution, bringing into play a set of complex flocculating/deflocculating mechanisms. However, because HAP slips could be dispersed and stabilized by the anionic polyelectrolytes, as well as by a polyphosphate, it can be concluded that the surface of HAP is positively charged and the positive charge attributed to the specific adsorption of Ca^{2+} ions or to preferential dissolution of phosphate ions from the apatite surface [11–13].

The study of the behavior of HAP powder in aqueous media gives information about its actual chemical reactivity in the biological environment because it is mainly based on aqueous salt solutions. For this purpose, the solubility of HAP in water has been extensively studied [14]. The stoichiometric dissolution of HAP is very low ($pK_{sp} = 115$) [15], but nonstoichiometric dissolution due to the formation of surface complexes was demonstrated to occur and to cause phenomena of metastable equilibrium solubility [16]. In particular, a solid surface complex $Ca_2(HPO_4)(OH)_2$, formed by HAP hydrolysis mechanism, controls the solubility equilibria, according to the following equations[14,17]:

$$Ca_{10}(PO_4)_6(OH)_2 + 6H_2O = 4Ca_2(HPO_4)(OH)_2 + 2Ca^{2+} + 2HPO_4{}^{2-} \quad (1)$$

$$4Ca_2(HPO_4)(OH)_2 = 8Ca^{2+} + 4HPO_4{}^{2-} + 8OH^- \quad (2)$$

The resulting nonstoichiometric Ca/P ratio in solution (1:1 for Eq. (1) or 2:1 for Eq. (2)) depends on which dissolution reaction prevails. If HAP is prepared in water, the surface is, presumably, just covered with surface complex $Ca_2(HPO_4)(OH)_2$ and subjected either to the equilibrium shown in Eq. (2) or to adsorption phenomena of ionic species present in solution [18].

Generally speaking, the surface charge of apatite solids is the result of pH and preferential dissolution or adsorption of calcium and phosphate ions, since H^+, OH^-, and lattice ions are the potential determining ions. The formation of surface complexes between potential-determining ions further complicates the estimation of ion activity product and surface potential [19].

Fig. 5 reports the influence of different pre-treatments on zeta potential of HAP powder. It can be seen that the isoelectric point of the as-received powder at pH 10.8 has shifted to about pH 9.5 in the calcined powder at 1000 °C. The zeta-potential curves for the as-received powder and calcined powders are almost consistent especially in the acidic side of pH range. For pH values higher than 9.5, the zeta potential of the calcined powder appears more negative compared to the as-received powder.

Therefore, calcinations would be responsible for an increase of the surface groups, enhancing a more negative potential and consequently, the repulsion between particles. The highest specific surface area of the as-received powder, reflecting in the formation of the highest quantity of the $Ca_2(HPO_4)(OH)_2$ complex, provides a shift of the natural pH toward the most basic value. The establishment of a cationic specific adsorption determines a shift of the pH_{iep} of as-received powder toward basic pH. This strong shift (about pH_{iep} 10.8) can be due either to the higher content of Ca^{2+} ions, leached from the surface complex. In the basic side of the titration curve, the absolute value of the zeta potential seems to be related to the Ca^{2+} concentration in the solution. In fact, above pH_{iep}, the absolute value of the zeta potential is smaller, with a higher content of Ca^{2+} in solution (the zeta potential at pH 12.2 is −29, −24, −20 and −14 mV for calcined powders in 1000, 900, 800 °C and as-received powder, respectively).

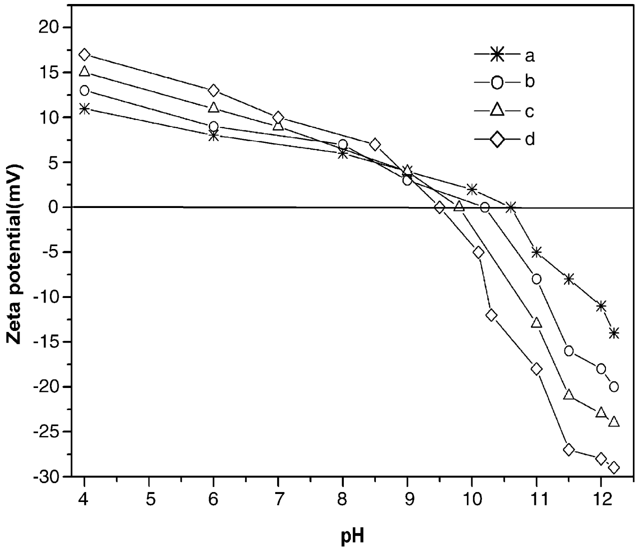

Fig. 5. Influence of pre-treatment on zeta potential of powders (a) as-received, (b) calcined at 800 °C, (c) calcined at 1000 °C in the presence of 1 wt.% of dispersant NH_4PAA.

The surface chemistry of powders dispersed in aqueous media can be modified in order to produce repulsive inter-particle forces that promote dispersion. Polyacrylates have proved to be effective dispersing agents for both clay- and nonclay-based ceramics, through an electrosteric mechanism of dispersing action. Their combination is important especially in the case of high solids concentration where the average inter-particle distance is short [20,21].

Calcination at 1000 °C resulted in a significant increase of the absolute value of zeta potential. Addition of the dispersant to the suspension of powder caused a shift of the pH_{iep} and of the whole electrophoretic curve similar to that promoted by calcining, attesting the anionic nature of the polyelectrolyte NH_4PAA. Above pH_{iep}, the particles become negatively charged and start to repel the dissociated groups of the polyelectrolyte chain.

Fig. 6 shows optimum values of dispersant for the 66 wt.% slurry at different calcination temperatures. At low amounts of dispersant, the electric double layer is not sufficient to achieve an effective inter-particle repulsion and prevails the attraction between them. When a higher amount

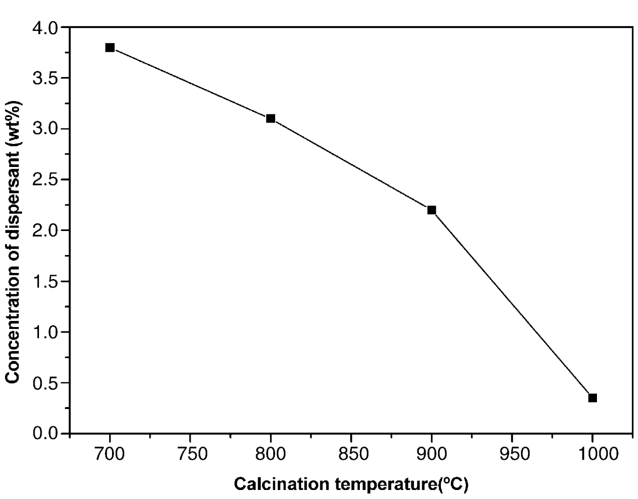

Fig. 6. Optimum values of dispersant for the 66 wt.% slurry vs. calcination temperatures.

of dispersant is added, the electric double layer is compressed by too high electrolyte concentration and the electrostatic repulsion is less effective and, therefore, the viscosity increases. Besides, an excess of nonadsorbed polyelectrolyte in solution could provoke a viscosity increase. It was observed that the lowest dispersant values were obtained when powder was calcined in 1000 °C. The minimum viscosity was reached with concentrations of 0.35 wt.% NH_4PAA with powder calcined at 1000 °C whereas for HAP calcined at 900 °C the best concentration was 2.2 wt.% NH_4PAA. A great decrease of viscosity was observed when HAP powder calcined from 1000 °C were used, being those slurries prepared with very fluid with viscosity of 0.24 Pa s at 100 s^{-1} for 66 wt.% solid.

In order to study the content of admissible solid, slurries containing 66 wt.% of the as-received HAP powder were prepared using a concentration of 3.5 wt.% NH_4PAA. The slurries had a paste-like consistency. In the case of the as-received powders, the starting solids loading could not exceed 41 wt.% due to more accentuated viscous character of these suspensions.

Therefore, besides chemical composition and surface area of the powder another factor influencing slurry fluidity should be present. Calcination affects on decrease of dispersant dramatically. This difference is significant and reveals that the as-received powders are more difficult to disperse than the heat-treated ones, as expected from the above discussion. The rheological behavior of the received powders suspensions would be mainly determined by the surface characteristics of the component.

3.2. Influence of deagglomeration time on dispersibility and rheology

Fig. 7 shows particle size distribution for HAP powder calcined at 1000 °C with 1 wt.% NH_4PAA dispersant in conditions of without milling and different times ball milling.

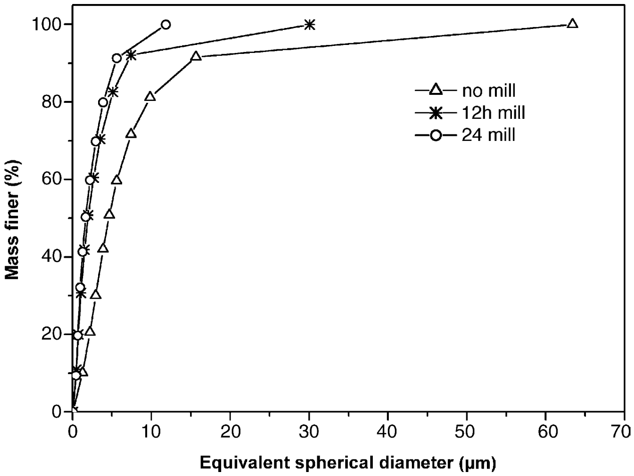

Fig. 7. Particle size distribution of HAP powders calcined at 1000 °C as a function of the milling time (with 1 wt.% NH_4PAA).

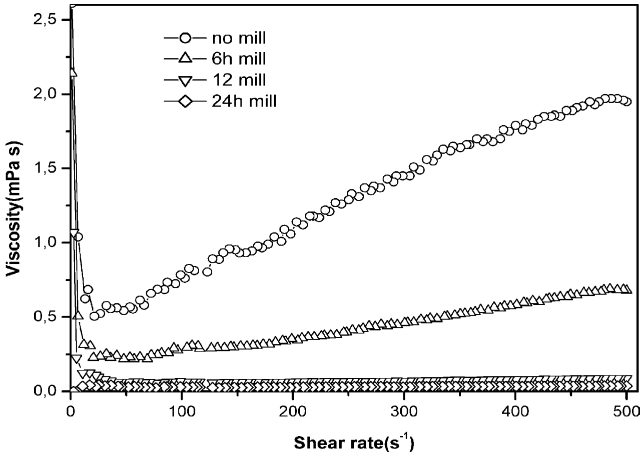

Fig. 8. Viscosity vs. shear rate for 66 wt.% HAP slurry as a function of the milling time.

Ball milling the suspension for 24 h caused a reduction in the number of agglomerates and the consequent increase in the number of the average sized particles.

The effect of deagglomeration time on the rheological characteristics of suspensions is reported in Fig. 8 for the 66 wt.% solid slurry. The shear-thinning character for a given solids volume fraction, decreases with increasing deagglomeration time.

The results presented in Fig. 8 show that viscosity decreases with increasing ball-milling time reaching an equilibrium situation of Newtonian suspension after 24 h ball milling. The shear-thinning character for a given solid decreases with increasing deagglomeration time.

The results presented above show that deagglomeration is promoted by ball milling and by the increasing duration of the contact between solid and liquid phases (at least up to 24 h). However, this is a long duration process and hydrolysis reaction of the HAP powder in water may increase the amount of OH^- in the powder surface. Fig. 9 proved this idea. This figure shows increasing pH with increasing ball milling time. These effects improve the dispersing ability of the

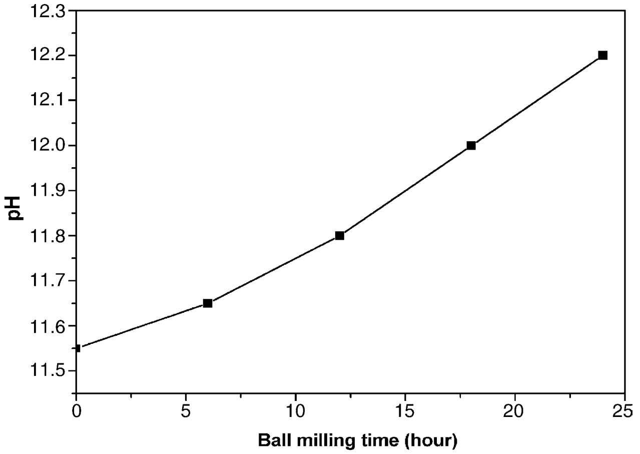

Fig. 9. pH of 66 wt.% slurry as a function of the milling time.

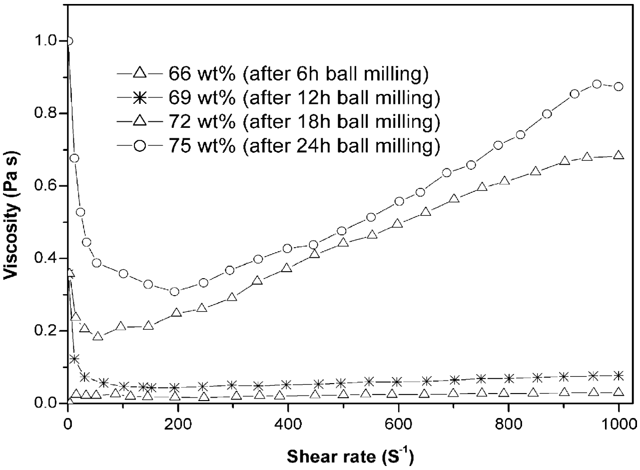

Fig. 10. Viscosity vs. shear rate for HAP slurries of the 1000 °C calcined powder in incremental process (3 wt.%) up to 75 wt.% and 24 h ball milling (with 0.75 wt.% NH_4PAA).

HAP-based compositions and enable the use of an incremental process to obtain highly concentrated (up to 75 wt.%) aqueous HAP-based suspensions. Fig. 10 shows viscosity versus shear rate for HAP slurries of the calcined powder at 1000 °C with 0.75 wt.% NH_4PAA in incremental process (3 wt.%) up to 75 wt.% and 24 h ball milling. The slips were ball-milled for at least 6 h before incremental amounts of 3 wt.% solids have been added, up to final concentrations of 75 wt.%. On the other hand, the suspensions of final slurry behave as pseudo-plastic fluids at shear rate lower of 200 s^{-1}. The shear-thinning character increase with increasing solids loading and deagglomeration process continues with the solids loading increasing, although at the lower rate as expected, since suspensions become more viscous. The viscosity of the slurries with 66 and 69 wt.% content of solid is very low and the suspensions exhibited a Newtonian behavior. The viscosity of slurries with 72 and 75 wt.% was higher but they were still fluid and easy to cast into the mould and they show a shear thinning behavior at low shear rate (100 and 200 s^{-1}, respectively).

4. Conclusions

The results presented in this work enable the following conclusions to be drawn:

1. The formation of a surface layer arises from the nonstoichiometric dissolution exhibited by HAP, and properties such as particle size, specific surface area, and solid loading strongly influence the change in composition of the saturated solution. The surface-charge characteristics of the HAP powders namely, the relative concentrations of OH^-, HPO_4^{2-} groups, and the adsorption of dispersant on the particles are the most relevant factors that control the dispersion ability of HAP-based suspensions.
2. It is believed that 1000 °C pre-treatment would enhance homogeneity and the electrostatic stabilization of hydroxyapatite powder in aqueous media, ball milling is also accepted to promote hydration of the particles surface. Calcination will lead to some surface dehydration and aggregation of the particles. In order to obtain colloidal slurries, it is necessary to use powders with low surface area, because powders with high surface area tend to form undesirable agglomerates.
3. Surface area and chemical composition of HAP powders played a fundamental role in the viscosity of slurries. Differences in surface charge characteristics may induce changes in the dispersant adsorption and therefore different amount of dispersant would be necessary to obtain fluid slurries. The highest concentration of solid was obtained with HAP calcined at 1000 °C. The concentration of dispersant, which provides the minimum viscosity, was the lowest for slurry using HAP calcined at 1000 °C.
4. Deagglomeration and calcinations at 1000 °C improved the positive ionic character of the surfaces powders favoring the adsorption of the anionic dispersant. The same pre-treatment given to HAP resulted in an interface shifting the isoelectric point to the acidic side, favoring the electrostatic stabilization at pH 9.5. The zeta potential measurements as a function of pH, conducted to investigate the complex surface chemical reactivity in water, provided evidence that the formation of a surface complex promotes the interplay of dissolution and adsorption, the former governed by the specific surface area and the later determining the resulting surface potential. The presence of different amounts of HPO_4^{2-} and OH^- groups on as-received and the 1000 °C calcined powder is confirmed by FTIR analyze.
5. Well-dispersed aqueous HAP-based suspensions with concentrations up to 75 wt.% could be prepared from the 1000 °C pre-treated powders by using a continuous deagglomeration process. This suspension presented a shear-thinning behavior characteristic of fine particles suspensions at low shear rate but viscosity values low enough for casting operations.
6. This clearly suggests that aqueous processing of HAP-based ceramics is suitable to prepare complex shapes by pressureless sintering at moderate temperatures. These processing methods also enable to control and manipulation of the forces between particles within a liquid and improve the homogeneity of the green compacts, which is essential for the sintering behavior and the ultimate material properties.

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