Journal of the European Ceramic Society 19 (1999) 469–477

PII: S0955-2219(98)00224-6
0955-2219/99/$—see front matter

Rheological Characteristics of Alumina Platelet–Hydroxyapatite Composite Suspensions

S. Gautier, E. Champion,* D. Bernache-Assollant and T. Chartier

Laboratoire de Matériaux Céramiques et Traitements de Surface, UPRESA CNRS 6015, 123, avenue Albert Thomas, 87060 Limoges Cedex, France

(Received 12 April 1998; accepted 3 September 1998)

Abstract

The rheological behaviour of aqueous suspensions of alumina platelet–hydroxyapatite mixtures for slip casting was investigated. The stabilisation of the suspensions requires the use of a dispersing agent and the breakdown of powder agglomerates. The addition of alumina platelets to the HAP powder does not modify significantly the behaviour of the suspensions which remains always quasi-Newtonian. Nevertheless, this behaviour becomes shear-thinning at low shear rates for high alumina contents when platelets of small size are used. The viscosity increases at low shear rates with the increase of small platelets content. These modifications are assumed to result from orientation phenomena of alumina disks under shear stress in the direction of flowing. The disk-shaped morphology of alumina is detrimental to the preparation of high density green composites. Suspensions containing between 50 and 70 wt% of powder are castable but the best rearrangement of solid particles during the casting process is reached for suspensions containing 65 wt% of powder. *© 1999 Elsevier Science Limited. All rights reserved*

Keywords: suspensions, composites, platelets, Al_2O_3, apatite.

1 Introduction

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$–HAP, due to its excellent biocompatibility with the surrounding bone tissues, constitutes a ceramic material of interest for orthopaedic applications.[1–4] But, dense polycrystalline HAP exhibits a great brittleness with a low fracture toughness (about 1 MPa $m^{1/2}$).[5–7] The incorporation of a ceramic second phase in a ceramic matrix is a way to improve the mechanical properties.[8] We have demonstrated in a previous paper that the introduction of alumina platelets in HAP matrices enhances the mechanical reliability by increasing the fracture toughness, though platelet agglomerates remained in these composites.[9] The mechanical characteristics of brittle ceramic materials are critically limited by the largest flaws.[10] Therefore, it is all the more important to avoid the initial agglomerates and to prevent or reduce the formation of microstructural defects during the elaboration process.

The use of slip casting of colloidal suspensions is known to be a way of forming green ceramic bodies with optimal properties. Slip casting is also considered as a potential method to improve the dispersion of a second phase within ceramic matrices.[11,12] The homogenisation, dispersion and stability of solid particles in the liquid are of primary importance in the processing of high-performance ceramics produced by this conventional consolidation method and the microstructure of the green piece will greatly depends on the rheological properties of the suspension.[13] Whereas the influence of the particle size distribution of the powder on the rheological behaviour is well known, the effects of powder mixtures with different particle shapes are not clearly understood, yet. Only few studies concerning the effect of whisker morphology on the rheological behaviour of composite suspensions have been published.[14] On these bases, our work consisted in the elaboration of composite materials by slip casting of stable slurries with the aim of achieving a homogeneous distribution of alumina platelets within the HAP matrix. In a first paper devoted to the elaboration of composites, we have demonstrated that a high fracture toughness can be reached with K_{Ic} values of 2·9 MPa $m^{1/2}$ for a 20 vol% Al_2O_3-HAP material compared with 0·75 MPa $m^{1/2}$ for the monolithic HAP matrix.[15] This result was obtained only using an appropriated slurry composition which was found to be

*To whom correspondence should be addressed

composed of 65 wt% of powder and 3·1 wt% of dispersant on a dry weight powder basis.

Starting from these results, the present study is concerned with the influence of the size and volume fraction of alumina platelets on the rheological behaviour of HAP based suspensions and with some correlations between characteristics of the slurries such as composition and viscosity and the density of the green body.

2 Experimental Procedure

2.1 Composite preparation

A commercially available hydroxyapatite powder (Bioland, France) was used for the preparation of composite materials. This HAP was calcined at 750°C and has a stoichiometric atomic ratio Ca/P = 1·667. Its specific surface area, measured by the BET method (Surface analyser, Micromeritics ASAP-2010) on powder outgased at 350°C, is $21{\cdot}2 \pm 0{\cdot}2\ m^2\ g^{-1}$. SEM micrograph (Fig. 1) shows that the as received HAP powder was formed of agglomerates which were constituted of elementary grains of about 50–100 nm. The agglomerate size distribution of the as received powder was determined using a Laser granulometer (Cilas 715) and is given in Fig. 2 This distribution can be divided in two domains of particle size, the first one is below 20 μm and the second between 20 and 100 μm, each one of them represents about 50 wt% of the powder.

Alumina platelets (Elf Atochem, France) were monocrystals of corundum phase (α-Al_2O_3) showing a hexagonal or disk-shaped morphology. Two different grades of platelets were used, their main characteristics are listed in Table 1. T'0 alumina was in the form of platelet agglomerates with a size which could reach 300 μm. Platelets of a larger size (grade T2) were less agglomerated.

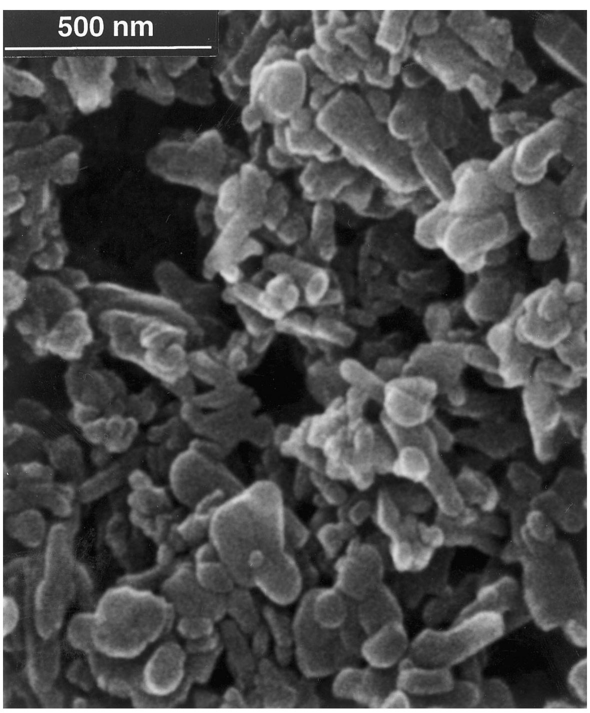

Fig. 1. SEM micrograph of the as received HAP powder.

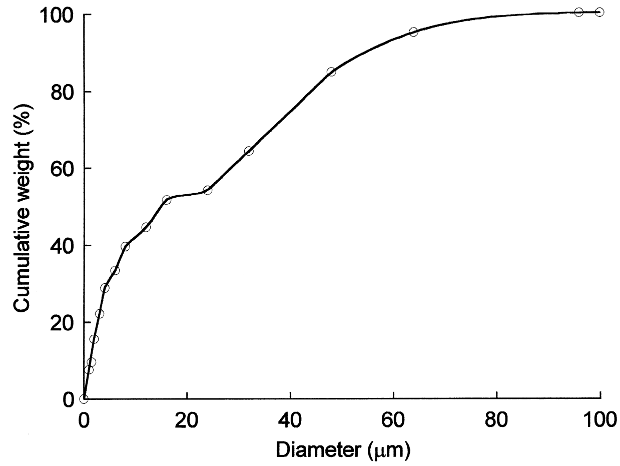

Fig. 2. Particle size distribution of the as received HAP powder.

As the initial powders were strongly agglomerated, the elaboration of a homogeneous mixture required the use of grinding. To this end, composite mixtures containing up to 50 vol% of alumina platelets were homogenised in demineralized water containing ammonium polymethacrylate as deflocculant, and planetary ball milled with alumina balls in an alumina container. The choice of ammonium polymethacrylate as dispersing agent was derived from literature data on the aqueous dispersion and stabilisation of HAP and alumina powders.[16,17] Green compacts of composite materials (ϕ = 30 mm, h = 12 mm) were produced by slip casting of the slurries in plaster moulds and were dried at 40°C for 24 h.

2.2 Characterisation

The rheological behaviour of Al_2O_3–HAP suspensions was investigated at a constant temperature of 25°C using a coaxial cylinder viscometer (Haake Rotovisco RV 20). The viscosity of the slurries was determined at constant shear rates of either 10 or 350 s^{-1} applied for 2 min. The lowest value of 10 s^{-1} was chosen to have an estimation of the viscosity of the suspensions during their casting. The highest value of 350 s^{-1} was used to overcome upsetting phenomena linked to the morphology of alumina platelet particles which lead to different behaviours depending on their volume ratio in the suspension and on their size. These modifications of the flow were more particularly encountered at low shear rate, as it will be seen hereafter. The values of the viscosity were measured with a relative accuracy of at least 5%. The rheological

Table 1. Main characteristics of alumina platelets (* supplier data)

Grade (ref.)	*Diameter* Φ (μm)*	*Average thickness* h (μm)*	*Aspect ratio* Φ/h*	*Specific surface area Ss (m^2g^{-1})*
T'0	3–7	0·6	5–12	$0{\cdot}83 \pm 0{\cdot}04$
T2	10–15	1·0	10–15	$0{\cdot}48 \pm 0{\cdot}02$

behaviour was obtained from the measurement of shear stress and viscosity versus applied shear rate. The shear rate was linearly increased up to $450\,s^{-1}$ in 2 min and then decreased down to $0\,s^{-1}$ for the same duration.

The compaction ratio of cast green composites was calculated from geometrical measurements. Theoretical densities of Al_2O_3–HAP composites were calculated from a mixture rule of the starting powders (HAP and Al_2O_3 theoretical densities were assumed to be 3·156 and 3·98, respectively).

Scanning electron microscopy (SEM–Philips XL30) was used for microstructural observations. More details concerning the elaboration of composite materials and characterisation methods are described elsewhere.[15]

The different compositions will be defined as follows:

1. For composite compositions, the alumina and/or HAP volume contents are expressed on the total volume of dry powders (HAP + Al_2O_3) basis,
2. For suspension compositions, the powder (HAP + Al_2O_3) loading (wt%) is expressed on the total weight of dry powders plus water. It must be cared that the volume content of alumina, which will be often mentioned to differentiate the suspensions, will remain always referred to the composite composition.

3 Results and Discussion

3.1 Viscosity of composite suspensions

3.1.1 Effect of ball milling time

Figures 3 and 4 give the viscosity, determined at a constant shear rate of $10\,s^{-1}$, versus ball milling time of suspensions containing 65 wt% of powder (HAP + Al_2O_3) and 3·1 wt% of dispersant, for composite compositions containing T'0 and T2 platelets, respectively. Whatever the suspension, the plots showed two different stages. An important drop in the measured values of the viscosity was observed during the first 3 h of milling. Then, for a longer duration, the viscosity remained almost constant.

In the first step of homogenisation, the decrease of viscosity is directly associated to the progressive reduction of powder agglomerates which is achieved by ball milling. As indicated in another work,[18] a part of the water is initially included inside agglomerate pores. The progressive breakdown of agglomerates releases this immobilised liquid which enhances flow. The plots show that the partial substitution of HAP powder by alumina platelets does not modify significantly this phenomenon, since these powders were also agglomerated. However, the viscosity reaches lower values when alumina platelets of large size were used (T2 grade). This last result can be explained by the less agglomerated state of T2 platelets which facilitates the dispersion.

During this phase of mixing, an important reduction of HAP grain size is achieved, as shown

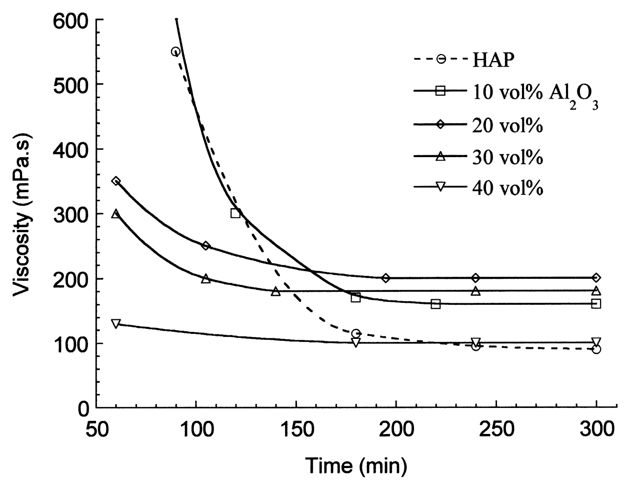

Fig. 3. Viscosity of composite suspensions (65 wt% of powder) containing T'0 platelets versus ball milling time ($\dot{\gamma} = 10\ s^{-1}$).

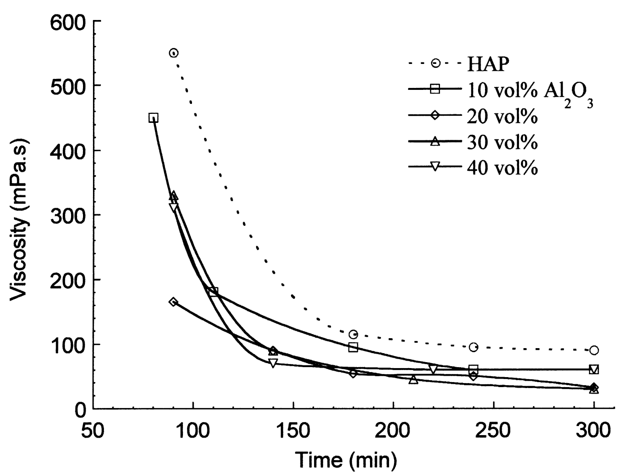

Fig. 4. Viscosity of composite suspensions (65 wt% of powder) containing T2 platelets versus ball milling time ($\dot{\gamma} = 10\ s^{-1}$).

in Fig. 5 which represents the grain size distribution of HAP after 5 h of milling. In comparison with the initial grain size distribution, the largest agglomerates have disappeared. The remaining agglomerates do not exceed a size of 30 μm and 70 wt% of the powder has a particle size below 5 μm. This simultaneous breakdown of HAP elementary particles and agglomerates leads to an increase of the specific surface area of the HAP powder from 21 m^2 g^{-1} up to $26{\cdot}2^{\pm 0{\cdot}3}$ m^2 g^{-1}. No quantitative measurement of changes in specific surface area or size of alumina platelets was performed but microstructural observations of cast composites (Fig. 6) showed no evidence for the presence of more broken platelets in cast compacts than in the initial alumina powders. These observations indicated that the breakdown of alumina agglomerates was achieved during milling without fracturing the individualised platelets. Finally, the ball milling process mainly leads to a deagglomeration of hard HAP agglomerates and to a grinding of HAP particles with a dispersion of alumina platelets in the HAP slurry.

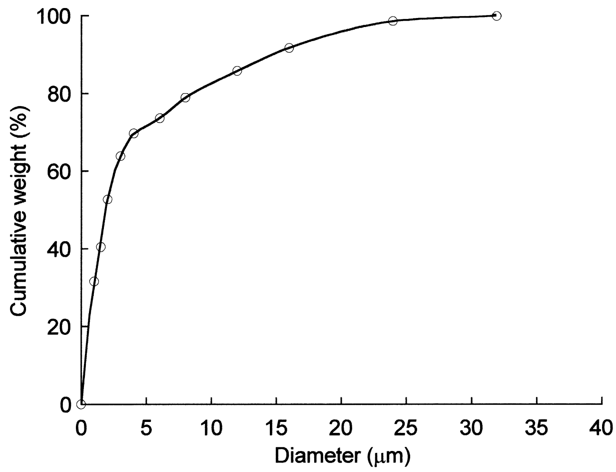

Fig. 5. Grain size distribution of the HAP powder after 5 h of ball milling.

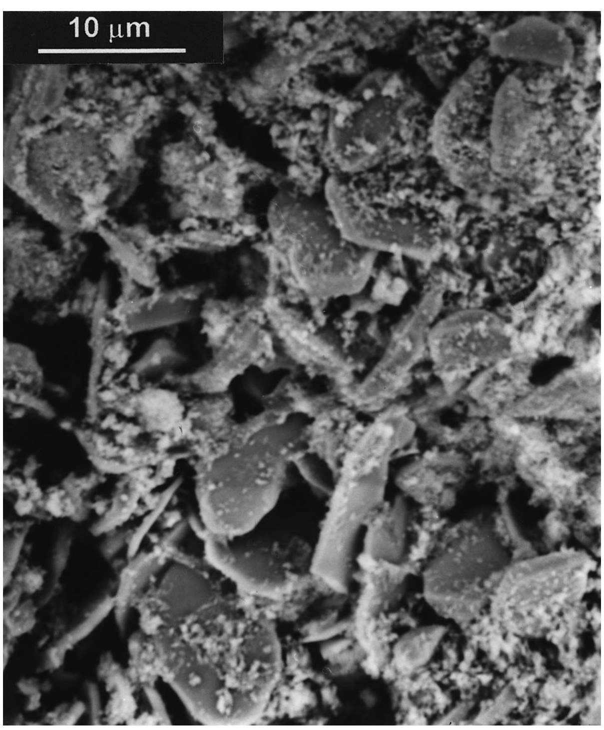

Fig. 6. SEM micrograph of a cast sample (composite containing 40 vol% of Al_2O_3 T'0).

After about 3 h of milling the viscosity of the slurries remains constant. The composite suspensions are stable with values of viscosity ranging from 50 to 200 MPa s which are compatible with the slip casting process.

3.1.2 Influence of dispersant content

The amount of dispersant required to obtain the best state of dispersion and a good stability of a slurry is usually assumed to correspond to the minimum of the viscosity of the suspension, though it does not necessary corresponds to the quantity really adsorbed at the solid particle surface. Figure 7 gives the viscosity, determined at a shear rate of 350 s^{-1}, versus dispersant concentration for single suspensions of alumina platelets and HAP powder ball milled during 5 h. The amount of added dispersant has been normalised with regard to the specific surface area of each powder.

For the HAP powder, the minimum value of the viscosity is reached for an added amount of dispersant close to 2 mg m^{-2}, which is in agreement with other studies.[16,19] Due to the low variations of the measured viscosities around the minimum value, a standard deviation of 0·3 mg m^{-2} was considered acceptable. In a similar way, an effective dispersion of alumina platelets may be obtained with $1{\cdot}3^{\pm 0{\cdot}4}$ mg m^{-2} of dispersant. Considering the specific surface area of HAP and alumina powders (i.e. 26 m^2 g^{-1} and between 0·5 m^2 g^{-1} and 1 m^2 g^{-1}, respectively) the average

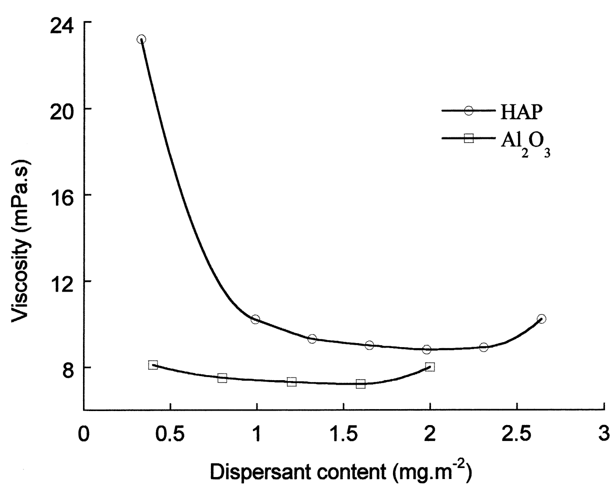

Fig. 7. Viscosity of alumina and HAP suspensions versus normalised dispersant content ($\dot{\gamma} = 350\ s^{-1}$).

amounts of dispersant leading to the best dispersion of alumina and HAP suspensions are of about 0·1 wt% and 4·5 wt%, respectively. On the assessment that the dispersion of composite slurries might be deduced from a single mixture rule of the data determined on the HAP and alumina suspensions, the amount of dispersant required to be incorporated in the composite slurries would be given by the following equation:

$$\text{wt\% Dispersant} = \left(2^{\pm 0\cdot 3}\frac{d_{HAP}}{d_{composite}}\cdot Ss_{HAP}\cdot \text{vol\%}_{HAP} + 1\cdot 3^{\pm 0\cdot 4}\cdot\frac{d_{Al_2O_3}}{d_{Composite}}\cdot Ss_{Al_2O_3}\cdot \text{vol\%}_{Al_2O_3}\right)\times 10^{-3} \quad (1)$$

where d_{HAP}, $d_{Al_2O_3}$ and $d_{composite}$ are the theoretical densities of the subscript compounds.

This equation is also based on the hypothesis that there is no preferred adsorption of the dispersant on the alumina or HAP powder. According to this expression, a wide range of dispersant content may achieve an efficient dispersion of composite suspensions. For instance, a 20 vol% Al_2O_3–HAP composite composition would require between about 2·8 and 4 wt% of dispersant. To validate this last hypothesis, suspensions containing 65 wt% of powder (composite composition: 20 vol% Al_2O_3–80 vol% HAP) with varying dispersant contents were prepared. The minimum value of viscosity (35 MPa s) is obtained for an addition of 3 wt% of dispersant (Fig. 8). A good agreement was found between the experimental measurements and the domain of viscosity defined by the calculated values of dispersant addition [eqn (1)]. Nevertheless, this result does not necessarily mean that there is no preferred adsorption of the dispersant on one of the two powders, because, due to their respective specific surface area and weight ratio, the contribution of alumina to the calculated amount of dispersant is much smaller than the contribution resulting from the HAP.

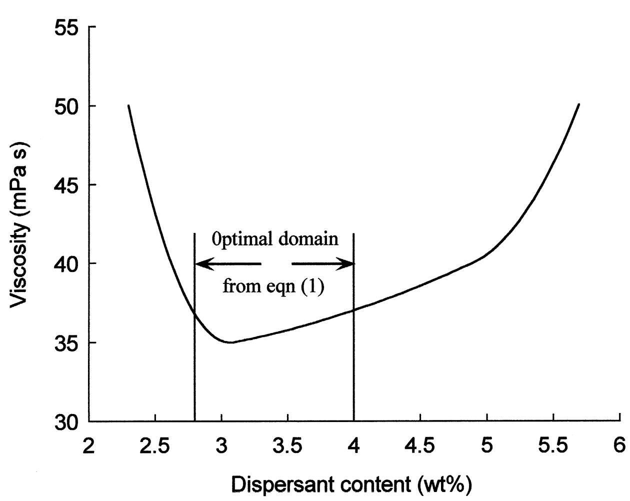

Fig. 8. Viscosity versus dispersant content for a composite (HAP-20 vol% Al_2O_3 T'0) slurry containing 65 wt% of powder ($\dot{\gamma} = 350\ s^{-1}$).

The mixture rule given in eqn (1) is also based on the hypothesis that a change of the powder ($HAP + Al_2O_3$) loading in the slurry would not modify the value of the concentration of dispersant required to minimise the viscosity of the suspension. This means that the optimal concentration of dispersant must remain constant for any powder content. But, from a theoretical point of view, the stability of a suspension depends on the total interparticle energy which results from the combination of different types of interactions (Van Der Walls, electrostatic, steric).[13,20] As the interparticle energy depends on the interparticle distance, the solid content in the suspension will influence the dispersion, independently on the concentration of dispersant. This means that eqn (1) can be satisfactory used for similar powder concentrations in the composite suspensions than in the single phased suspensions.

3.1.3 Influence of powder content

In respect to the latest comment, it appears important to investigate the simultaneous influence of powder and dispersant concentrations on the viscosity of composite slurries. The individual and combined effects of dispersant and powder contents have been evaluated using a two-variable experimental design.[15] HAP based composite suspensions (containing 20 vol% of alumina platelets T'0), mixed during 5 h, were used in this experiment. The total powder content ranged from 50 to 70 wt% and the dispersant content varied from 3 to 5 wt%. The minimum value of the viscosity, measured at the shear rate of $350\ s^{-1}$, was 25 MPa s at 50 wt% of powder and the maximum value was 70 MPa s at 70 wt% of powder. The experimental design allowed computation of the following empirical expression of the viscosity of suspensions in function of the powder (P) and dispersant (D) concentrations given in a system of reduced [-1, + 1] coordinates:

$$\eta_{(\text{MPa s})} = \exp\big(3\cdot 43 + 0\cdot 52P + 0\cdot 24P^2 + 0D - 0\cdot 1D^2 + 0P.D + (P, D)\big) \quad (2)$$

with:

$$P = \left(\frac{\text{wt\% of powder} - 60}{10}\right);$$

$$D = (\text{wt\% of dispersant} - 4)$$

In this expression $\varepsilon(P,D)$ is the standard deviation (equal to 0·09). More details concerning the construction and the statistical treatment of this experimental design can be found elsewhere.[15]

It must be noted that eqn (2) is only a statistically accurate mathematical expression which represents the experimental values of viscosity inside the investigated domain. Though this mathematical model should not be considered as a phenomenological equation, it is in good agreement with the known theoretical approaches concerning the effect of powder concentration on the viscosity of a suspension. Indeed, it is generally accepted that the viscosity depends on the volume fraction of particles in accordance with exponential relationships or power laws.[21] The computed equation shows the predominant effect of powder content on the viscosity of the suspensions. The empirical coefficients associated to the dispersant content is equal to zero at the first order and is very low at the second order ($0{\cdot}1\,D^2$ with $D \in [-1, +1]$). This relation allows to validate the hypothesis of an insignificant combined effect of powder and dispersant contents on the viscosity since no coefficient associated to $P.D$ appears in eqn (2). In this respect, the mixture rule established to evaluate the relative quantity of dispersant required to obtain stable composite suspensions (eqn (1)) can be satisfactory used for the elaboration HAP–Al_2O_3 suspensions containing between 50 and 70 wt% of powder (i.e. for slurries containing approximately a total of 25–40 vol% of solid).

All the composite slurries containing up to 70 wt% of solid presented viscosities compatible with slip casting. Above this powder loading, the viscosity becomes too high and the suspensions are not suitable for slip casting. Figure 9 gives the effect of the powder concentration in the slurry on the relative density of cast samples in the case of a 20 vol% Al_2O_3–HAP composite. The arrangement of particles in cast samples increased with increasing powder content to reach a maximum value close to 51% for a slurry containing about 65 wt% of powder. Then, the compaction decreased drastically for higher powder contents. This behaviour is likely exacerbated by the low compaction ability associated to the disk-shaped morphology of alumina platelets. A too high viscosity of the slurry is detrimental for the rearrangement of solid particles during the formation of the green composite compact.

3.2 Rheological behaviour of composite suspensions

This part of the study has been performed on suspensions containing 65 wt% of powders (Al_2O_3 + HAP). Typical plots of shear stress (τ) versus shear rate ($\dot{\gamma}$) after different times of ball milling for a composite composition containing 30 vol% of Al_2O_3 T2 are given in Fig. 10, similar plots were registered for the others composite compositions. For a milling time shorter than 210 min the slurries exhibit a thixotropic hysteresis. This phenomenon is associated to a shear-thinning behaviour of the suspensions and indicates a flocculated state of particles within the liquid. Thixotropy as well as shear-thinning decrease with increasing milling time. Thixotropy disappears after 3–4 h of mixing, depending on the slurry composition, and can be attributed to the presence of powder agglomerates. Then, after 4 h of milling the behaviour of the slurries becomes time-independent, corresponding to a complete desagglomeration.

The plots of shear stress versus applied shear rate of stable suspensions milled during 5 h are given in Figs 11 and 12 for composite compositions containing T'0 and T2 alumina platelets, respectively. Whatever the composition studied, no yield stress was detected ($\tau_0 = 0$). The behaviour can be

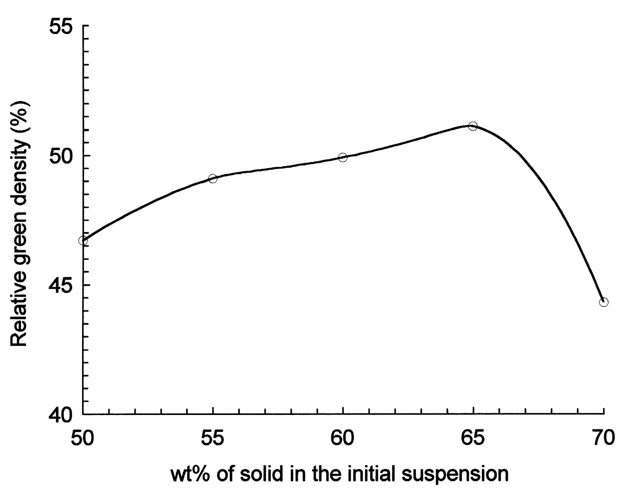

Fig. 9. Relative densities of cast composites (HAP-20 vol% Al_2O_3 T'0) versus initial powder content in the slurry.

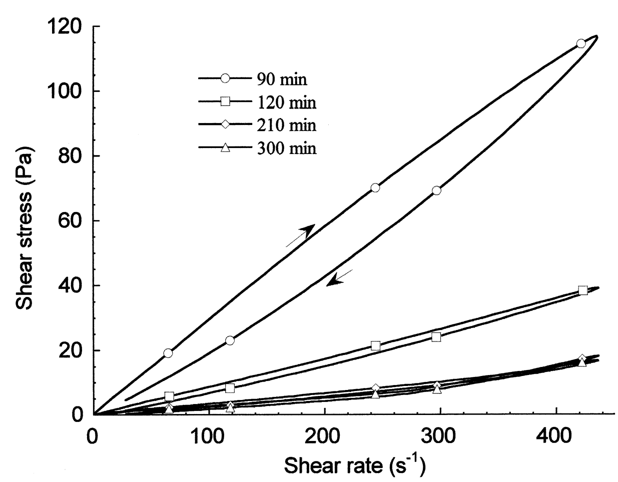

Fig. 10. Rheological behaviour of a composite (HAP-30 vol% Al_2O_3 T2) suspension (65 wt% of powder) versus ball milling time.

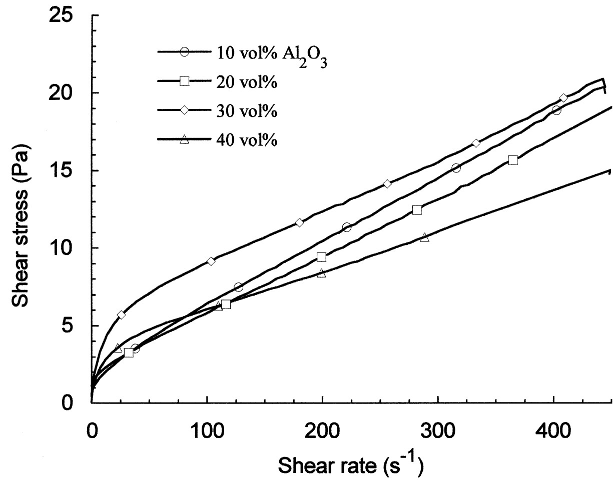

Fig. 11. Rheological behaviour of composite suspensions (65 wt% of powder) containing T'0 platelets.

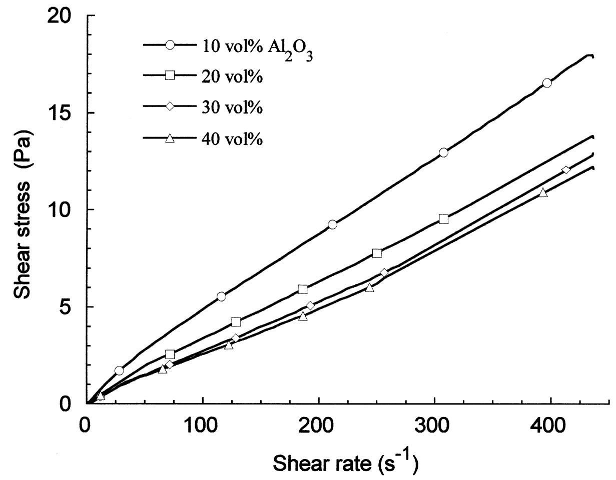

Fig. 12. Rheological behaviour of composite suspensions (65 wt% of powder) containing T2 platelets.

divided in two distinct domains depending on the shear rate.

1. At low shear rates ($\dot{\gamma} \leq 100\,s^{-1}$), the behaviour of the slurries is more or less shear-thinning. It can be described through the Ostwald's power law:[22]

$$\tau = k \cdot \dot{\gamma}^n$$

Table 2 summarises the fitted values of the shear rate exponent n for the different suspensions. For the majority of the investigated suspensions the value of the shear rate exponent n was close to 1 for $\dot{\gamma} \leq 450\,s^{-1}$ (Newtonian behaviour) except for the suspensions of composite compositions containing 30 and 40 vol% of small platelets (T'0) for which a value of $n = 0{\cdot}45$ (shear-thinning behaviour) was calculated when $\dot{\gamma} \leq 100\,s^{-1}$.

2. At high shear rates ($\dot{\gamma} > 100\,s^{-1}$) the behaviour becomes linear (i.e. Newtonian).

Table 2. Shear stress exponent of the Ostwald's law calculated for $0 \leq \dot{\gamma} \leq 450\,s^{-1}$ on suspensions containing 65 wt% of powder and milled during 5 h

Al_2O_3 Grade	*T'0*				*T2*			
Al_2O_3 vol% (in composite)	*10*	*20*	*30*	*40*	*10*	*20*	*30*	*40*
exponent n	0·9	0·9	0·45[a]	0·45[a]	0·9	0·95	1	1

[a] Values calculated for $0 \leq \dot{\gamma} \leq 100\,s^{-1}$.

These results show that, at low shear rates, the presence of alumina platelets can modify the behaviour of slurries or not, depending on their size and/or on their volume content. The disk-shaped alumina particles may be oriented by a sufficient value of applied shear rate in the direction of flowing. And, it appears more difficult to achieve an orientation of small platelets (T'0) than of large ones (T2). This could be explained by the lower aspect ratio of T'0 platelets as well as its initial high agglomerate state, compared with T2 platelets.

Figure 13 gives typical viscosity/shear rate plots for different composite suspensions (containing 65 wt% of powder). As previously described, the incorporation of small or large platelets leads to two different types of rheological behaviour. For all the slurries containing T2 platelets, the viscosity remains always quasi-constant with increasing shear rate. On the opposite, the viscosity of suspensions containing T'0 platelets decreases with increasing shear rate to become quasi-constant at high shear rates. These variations of viscosity remain low for platelet contents below 30 vol% but become important for larger alumina contents.

Considering the possible orientation of alumina platelets in the direction of flowing under the effect of shear stress, it could have been thought that the incorporation of platelets would have induced more significant modifications of the rheological behaviour. Nevertheless, the incorporation of platelets of large size enhances the flow whereas smaller ones makes it more difficult. Several explanations may be taken into account for these apparent controversial results:

1. When large platelets are used (grade T2) increasing their volume content from 10 up to 50% of the powder contained in the suspension induces a slight lowering of the measured viscosity from about 35 MPa s at 10 vol% of alumina down to 20 MPa s at 50 vol% (Fig. 13). For a given weight ratio of powder in the suspension (fixed at 65 wt% in this part of the experiment) an increase of the alumina content from 10 to 50 vol% in the composite compositions, corresponds to a total decrease of volume of solid contained in the suspension

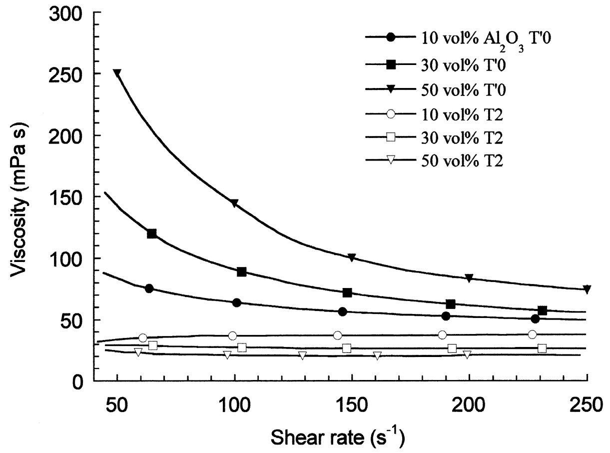

Fig. 13. Viscosity versus shear rate of HAP based composite suspensions (65 wt% of powder).

from 36·5 vol% to 34·3 vol%. This slight decrease of powder volume concentration may explain the decrease of viscosity. This can also justify the slight decrease of the measured shear stress as the alumina content in the suspension was increased (Fig. 12).

2. When small platelets are used (T'0), an opposite situation is observed. Increasing the volume content of alumina leads to an increase of the viscosity though the total volume content of solid in the suspension also decreases in this case. It could be considered that the size of these platelets is too small to allow an easy orientation in the flow direction. This would explain that an important shear rate is required to induce a preferred orientation, and, then to decrease the viscosity of the suspension.

Whereas the evolution of both the shear stress and the viscosity with alumina content could be explained in the case of the suspensions containing large platelets, no satisfactory explanation was found for the evolution of the shear stress in suspensions containing small alumina platelets.

4 Conclusion

This study demonstrates that the homogenisation of alumina platelets in a hydroxyapatite matrix may be performed using slip casting of stabilised composite slurries. The stabilisation of the suspension requires the reduction of powder agglomerates and the action of a dispersant. For the casting process, it is possible to predict the concentration of dispersant required to the best dispersion of composite suspensions in a wide range of powder concentration (50–70 wt%) from a single mixture rule of data registered on a suspension of alumina and on a suspension of HAP.

The disk morphology of alumina platelets has minor effects on the rheological behaviour providing the incorporated volume ratio is not to high. A quasi-Newtonian behaviour can be maintained in a wide range of composite compositions. Only a great quantity of small platelets (from 30 vol%) can modify the flow which becomes shear-thinning.

Finally, in most of cases, the incorporation of alumina platelets does not affect the viscosity of suspensions to a significant extent. Similar results were found in another study on composite containing 30 vol% of whiskers which concluded to a probably too low fraction of added whiskers to modify the viscosity of suspensions.[14]

Similarly to whisker-like particles, which are known to present a poor packing ability,[23] a platelet morphology is also detrimental to obtain high packing volume fractions of powders. From this point of view, slip casting of stable suspensions is an appropriate method since it allows the dispersion and a possible orientation of disk-shaped particles which enhances the packing. The solid concentration in the initial suspension was adjusted to obtain an optimal rearrangement of particles and high relative density of the green composite materials after casting (d/d_{th} = 51%).

References

1. De Groot, K., *Bioceramics of Calcium Phosphate*, ed. K. de Groot. CRC press, Boca Raton, FL, USA, 1983, pp. 99–114.
2. Jarcho, M., Calcium phosphate ceramics as hard tissue prosthetics. *Clin. Orthop. Rel. Res.*, 1981, **157**, 259–278.
3. Heise, U., Osborn, J. F. and Duwe, F., Hydroxyapatite ceramic as a bone substitute. *Int. Orthopaedics*, 1990, **14**, 329–338.
4. Oonishi, H., Orthopaedic applications of hydroxyapatite. *Biomaterials*, 1991, **12**, 171–178.
5. De With, G., Van Dijk, H. J. A., Hattu, N. and Prijs, K., Preparation, microstructure and mechanical properties of dense polycrystalline hydroxyapatite. *J. Mater. Sci.*, 1981, **16**, 1592–1598.
6. Akao, M., Miura, N. and Aoki, H., Fracture toughness of sintered hydroxyapatite and β-tricalcium phosphate. *Yogyo Kyokai Shi*, 1984, **92**(11), 672–674.
7. Halouani, R., Bernache-Assollant, D., Champion, E. and Ababou, A., Microstructure and related mechanical properties of hot pressed hydroxyapatite ceramics. *J. Mat. Sci. Mater. Med.*, 1994, **5**, 563–568.
8. Rice, R. W., Mechanisms of toughening in ceramic matrix composites. *Ceram. Engng Sci. Proc.*, 1981, **2**, 661–701.
9. Champion, E., Gautier, S. and Bernache-Assollant, D., Characterization of hot pressed Al_2O_3-platelet reinforced hydroxyapatite composites. *J. Mat. Sci. Mater. Med.*, 1996, **7**, 125–130.
10. Freiman, S. W., Brittle fracture behavior of ceramics. *Ceram. Bull.*, 1988, **67**(2), 392–402.
11. Belmonte, M., Moreno, R., Moya, J. S. and Miranzo, P., Obtention of highly dispersed platelet-reinforced Al_2O_3 composites. *J. Mat. Sci.*, 1994, **29**, 179–183.
12. Nischik, C., Seibold, M. M., Travitzky, N. A. and Claussen, N., Effect of processing on mechanical properties of

platelet-reinforced mullite composites. *J. Am. Ceram. Soc.*, 1991, **74**(10), 2464–2468.
13. Pugh, R. J., Dispersion and stability of ceramic powders in liquids. *Surf. Sci. Ser., Surf. Coll. Chem.*, 1994, **51**, 127–192.
14. Bergström, L., Rheological properties of Al_2O_3-SiC whisker composite suspensions. *J. Mat. Sci.*, 1996, **31**, 5257–5270.
15. Gautier, S., Champion, E. and Bernache-Assollant, D., Processing, microstructure and toughness of Al_2O_3-platelet reinforced hydroxyapatite. *J. Eur. Ceram. Soc.*, 1997, **17**, 1361–1369.
16. Lelièvre, F., Bernache-Assollant, D. and Chartier, T., Influence of powder characteristics on the rheological behaviour of hydroxyapatite slurries. *J. Mat. Sci. Mater. Med.*, 1996, **7**, 489–494.
17. Cesarano III, J., Aksay, A. and Bleier, A., Stability of aqueous a-Al_2O_3 suspensions with poly(methacrylic acid) polyelectrolyte. *J. Am. Ceram. Soc.*, 1988, **71**(4), 250–255.
18. Merle, S., Caractéristiques de poudres d'alumine: influence sur le broyage, la dispersion et le frittage. Thesis, University of Limoges, France, 1996.
19. Toriyama, M., Ravaglioli, A., Krajewski, A., Galassi, C., Roncani, E. and Piancastelli, A., Slip casting of mechanochemically synthesized hydroxyapatite. *J. Mat. Sci.*, 1995, **30**, 3216–3221.
20. Bergström, L., Rheology of concentrated suspensions. *Surf. Sci. Ser., Surf. Coll. Chem.*, 1994, **51**, 193–244.
21. Chow, T. S., Viscosities of concentrated dispensions. *Phys. Rev. E*, 1993, **48**(3), 1977–1983.
22. Couarraze, G. and Grossiord, J. L., Initiation à la rhéologie. Lavoisier Tech. & Doc., Paris, 1991.
23. Milewski, J. V., Efficient use of whiskers in the reinforcement of ceramics. *Adv. Ceram. Mat.*, 1988, **3**(3), 257–262.