

# Effect of an excess of polyelectrolyte on viscoelastic properties of suspensions of alumina and zircon mixtures

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## Abstract

Aqueous suspensions of alumina and zircon mixtures which are of practical interest in ceramics forming process were stabilized with an ammonium salt of a polycarboxylic acid as a dispersant (an anionic polyelectrolyte). Rheological properties of highly concentrated suspensions were determined by measuring shear viscosity and dynamic tests in the linear viscoelastic region. The effects of the degree of dispersion and solid volume fraction of the suspension  $\phi$  between 0.45 and 0.57 on dynamic viscoelastic properties were studied. Flow behavior of the suspensions changed from predominantly viscous to more elastic at a critical solid content  $\phi_c$ , which depends on the polyelectrolyte addition. If a high amount of non-adsorbed polyelectrolyte was in solution, the suspension flocculated and exhibited a relatively low  $\phi_c$  at which viscous to elastic transition occurred. The storage modulus reached a plateau in the high frequency region and gradually reduced at very low frequencies indicating a certain breakdown in the formed structure. The  $G'$  at the plateau increased significantly with increasing  $\phi$ . Contrarily, heterocoagulated suspensions due to insufficient dispersant addition showed a predominant elastic behavior with viscoelastic parameters almost independent in the frequency region studied. Moreover, both moduli sharply increased with increasing  $\phi$  and achieved a magnitude of several orders higher than that of the flocculated suspension. Changes in the storage  $G'$  and the loss  $G''$  moduli due to the different additions of polyelectrolyte provided information about modifications on the suspension structure.

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## 1. Introduction

Reaction sintering of a mixture of alumina and zircon powders at high temperatures is a relatively easy and a low cost way to produce mullite–zirconia composites [1–3]. The powder mixture must be dispersed in water to achieve optimum particle packing through colloidal processing. This requires the preparation and dispersion of highly concentrated suspensions which are fundamental steps in the colloidal processing of ceramics.

Derived polymers of acrylic and methylacrylic acids are substances commonly used as dispersants for effective stabilization of many ceramic suspensions. These polyelectrolytes provide stabilization of suspension by a combination of electrostatic and

steric (electrosteric) mechanisms. Dispersion occurs by an electrostatic repulsion with a steric contribution originating from the adsorbed polyelectrolyte layer [4–6].

The degree of dispersion of suspended particles is related to the polyelectrolyte adsorption on the solid surface. Adsorption depends on nature and surface charge of solid, ionic strength and pH of suspension. The adsorption mechanism is essentially controlled by factors affecting several characteristic of polyelectrolyte, such as dissociation, ionization degree and conformation of the molecule in solution that control charge and adsorbed layer thickness [5,6]. The presence of non-adsorbed polyelectrolyte in solution may affect the suspension stability and consequently flocculation can occur in concentrated systems [7].

Ceramics slips of practical interest for industrial applications consists in dispersions of mixtures of various ceramic phases with multiple processing aids. These complex compositions determine the flow and consolidation behavior of the

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suspensions. Changes in the interparticle interaction forces, relative particle number or weight ratios, sizes ratio, solid loading of suspensions, applied shear, etc. may be responsible for different suspension structures which can, in turn, affect these properties [8,9].

It is well known the importance of the unstable suspensions (in which interparticle forces are attractive) and the resultant structures that they formed during the consolidation process of the green compact in ceramics. Depending on the strength of the aggregation, particle rearrangement can occur during the consolidation. Therefore, it is essential to understand the effect of different aggregation conditions on the size and structure of the flocs formed. Besides of the aggregation condition, the interparticle distance is not a fixed quantity but a variable during consolidation process. When interparticle distance becomes smaller as the water content of the suspension reduces, the balance of interparticle interactions may change, and consequently can vary the particle network that develop.

In addition to providing information on compositional effects, viscoelastic measurements constitute an easy and adequate technique to indirectly examine interactions between particles and also give useful information about the formed network structure [10–12]. As compared with viscometry, oscillatory tests are advantageous because the suspension is subjected to very small strains or stresses and the sample structure is not disturbed from its condition at rest. Since the influence of hydrodynamic interactions due to the applied movement on the rheological response is minimal, viscoelastic measurements are very convenient to study the relation between rheology and interparticle colloidal forces.

In this work, rheological properties of highly concentrated suspensions of alumina and zircon mixture in the presence of non-absorbed polyelectrolyte were examined. Such mixture represents a system of colloids with size ratio (large to small) equal to 4 having opposite electrical charges. The variation of viscoelastic parameters of well stabilized, partially heterocoagulated (by insufficient dispersant addition) and flocculated (by an excess of polyelectrolyte in solution) suspensions with the volume fraction  $\phi$  was shown. Microstructure modification by the initial destabilization methods used was evidenced by a comparison between elastic and viscous components.

## 2. Experimental

### 2.1. Materials and methods

Alpha-alumina (A-16 SG, Alcoa Inc., USA) powder with a mean particle diameter of 0.45  $\mu\text{m}$  and a BET surface area of 9.5  $\text{m}^2/\text{g}$  was used. Zircon (Mahlwerke Kreutz, Mikron, Germany) powder was characterized by a large mean particle diameter (2  $\mu\text{m}$ ) and 4  $\text{m}^2/\text{g}$  BET surface area. The contents of alumina and zircon in the mixture were 45.5 and 54.5 wt%, respectively. The mixture exhibited a mean particle size of 0.9  $\mu\text{m}$  (Sedigraph 5000D, Micromeritics) with broad and bimodal particle size distribution.

### 2.2. Suspension preparation

Previously, we used [13] an ammonium salt of a polycarboxylic acid as dispersant (Dolapix CE64 (Zschimmers and Schwartz, Germany) to electrosterically stabilize the mixed alumina–zircon suspensions. The detailed method of suspension preparation is given elsewhere [13]. Briefly, the concentrated aqueous suspensions of the mixture were prepared by dispersion of the powder in distilled water containing different amounts of dispersant at pH 9 by ultrasonic treatment.

Well-stabilized suspensions were achieved by control of the zeta potential of the powders. According to the zeta potential versus pH curves previously determined through the electroacoustic ESA technique [13], iep of alumina and zircon powders were at pH 8.5–9 and 5, respectively. In this pH range, individual particles were oppositely charged and therefore developed mutual flocculation (heterocoagulation). In absence of dispersant at pH near 9 (i.e. close to  $\text{pH}_{\text{iep}}$ ), alumina particles exhibited a slightly neutral charged surface. Adsorption of dispersant (an anionic polyelectrolyte) increased mainly the negative zeta potential of alumina as compared with that of the original. Thus, the adsorbed polyelectrolyte layer provided a sufficiently high electrostatic repulsion and imparted some steric repulsion promoting stabilization of mixed suspension. Low amounts of polyelectrolyte of 0.20–0.4 wt% (dry solid basis) was found to be effective to stabilize the suspension of the powder mixture at pH 9. Therefore, partially heterocoagulated suspensions with below optimum dispersant concentration, i.e. 0.04, 0.06 and 0.12 wt% were achieved at pH 9. Contrarily, to examine the effect of the concentration of non-adsorbed polyelectrolyte in solution, suspensions containing 0.6, 0.9 and 1.2 wt% were prepared. These suspensions were flocculated by excessive amount of dispersant in solution.

To study the effect of increasing solid volume fraction of the suspension  $\phi$  on rheological properties, series of suspensions at each condition (stable, partially heterocoagulated and flocculated) were prepared at solid concentrations of 78, 80, 81.5, 83 and 85 wt%. These solid contents correspond to a range of  $\phi$  variable between 0.45 and 0.57.

### 2.3. Rheological characterization

#### 2.3.1. Viscometric measurements

Steady state flow curves of concentrated mixed suspensions were performed using a concentric cylinder viscometer (Haake VT550, Germany) at 25 °C. Shear stress was measured by increasing the shear rate in steps from 0.1 to a maximum of 550  $\text{s}^{-1}$  and then decreased.

#### 2.3.2. Viscoelastic measurements

Dynamic measurements were carried out with a parallel plate geometry on a stress controlled rheometer (Haake, RS 600 Germany). The diameter of the plate was 60 mm and the gap between the two plates was 1 mm. The viscoelastic parameters were measured as a function of frequency at small stress magnitude in the linear viscoelastic region. The temperature was 25 °C for all runs. A frequency sweep experiments was used to determine the

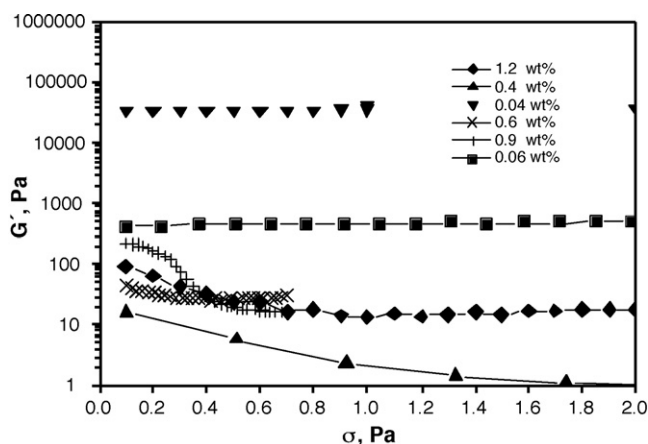


Fig. 1. Stress  $\sigma$  sweeps tests (at 1 Hz) of 48 vol% suspensions of alumina and zircon mixture containing different amounts of polyelectrolyte as a dispersant.

elastic and viscous parameters. In the experiment, a stress  $\sigma$  is applied as a sinusoidal time function at a fixed small amplitude. Stress frequency is stepwise increased and at any frequency step resulting measurements are transformed in the elastic and viscous components. The range of frequency used was from near 0.04 to 100  $\text{s}^{-1}$ . For small frequencies, tests are very prolonged being evaporation of the sample difficult to avoid. Therefore, the measuring system was covered with a special device to prevent even small drying of wet samples.

To determine the limit of linear viscoelastic region, dynamics tests were performed at fixed frequency (1 Hz–6.28  $\text{s}^{-1}$ ) and amplitude of the stress  $\sigma$  was stepwise increased. From a  $G'$  versus  $\sigma$  curves, the amplitude range where  $G'$  remained constant (is independent of the applied amplitude) was obtained. Above a critical stress at which  $G'$  became to decrease, the viscoelastic functions exhibited a non-linear dependence with  $\sigma$  and equations are not appropriate.

Fig. 1 shows sweeps of  $\sigma$  at fixed frequency of 1 Hz for various suspensions in different conditions. In some cases, the critical stress  $\sigma$  shifted to low values while a rapid decrease in  $G'$  can be observed. Then to perform frequency sweeps in the linear region a  $\sigma$  of 0.1 Pa or less was chosen.

The variation of storage  $G'$  and loss  $G''$  moduli, tangent of phase angle  $\tan \delta$  (where  $\delta$  is a phase angle shift) as a function of frequency  $\omega$  at a fixed stress amplitude for each type of suspension with different  $\phi$  were determined.

Generally, the dependence of the viscoelastic parameters on frequency  $\omega$  is explained in terms of the concept of relaxation time  $\tau$  of the material [11,12,14]. This is a useful parameter to compare with an experimental characteristic time (which is calculated as the reciprocal of the applied frequency) and to describe the tendency of the flow properties of the material. According to previous works [14,15], a rough estimation of the  $\tau$  is obtained as  $\tau = 1/\omega_c$  where  $\omega_c$  is the critical frequency expressed in rad/s, i.e. the frequency at which the crossover of the  $G'$  and  $G''$  versus frequency curves occurred. This approximation considers the use of a single Maxwell model to represent the linear viscoelastic response of the material.

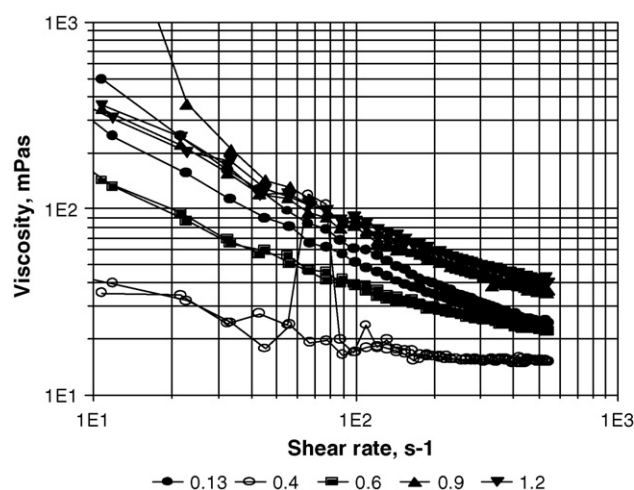


Fig. 2. Effect of addition of polyelectrolyte on the apparent viscosity of 48 vol% suspensions of alumina and zircon mixture at pH 9.

### 3. Results and discussion

#### 3.1. Effect of dispersant addition on shear flow of 48 vol% suspensions ( $\phi = 48$ )

Fig. 2 shows the apparent viscosity versus shear rates curves for  $\phi = 48$  (80 wt%) suspensions of the mixture of alumina and zircon containing different amounts of polyelectrolyte. Apparent viscosity (measured as the shear stress to shear rate ratio) and thixotropy (hysteresis of the flow curve) decreased with increasing dispersant addition and showed a minimum at 0.20–0.4 wt%. At the concentration required to attain the minimum, the suspension exhibited a nearly Newtonian flow behavior. Further increase in dispersant concentration from 0.40 to 1.2 wt%, gradually changed the rheological behavior of these suspensions from Newtonian to shear thinning. Nevertheless, in the high shear rate region a nearly Newtonian plateau in viscosity was reached. Viscosity at the plateau increased with increasing polyelectrolyte addition up to 1.2 wt% demonstrating flocculation of the particles. The high viscosity was attributed to an increase in the effective volume fraction of solids due to the volume of immobilized liquid between the flocs [13].

Variation in the flow behavior of the suspensions as a function of added amount of polyelectrolyte was explained by the following mechanisms: highest viscosity was observed for the suspension containing less than 0.1 wt% of dispersant at pH 9 due to the insufficient amount of adsorbed polyelectrolyte. At 0.20–0.4 wt%, a minimum viscosity was reached as heterocoagulation between components was prevented. Adsorption isotherm of dispersant on the powder mixture at pH 9 was showed previously [13]. The maximum adsorbed amount was slightly lower than that required to saturate the alumina surface. Because of the low-affinity adsorption type behavior [4,13] most of the added amount of polyelectrolyte remained free in solution. Many authors have demonstrated that free polyelectrolyte promoted flocculation of ceramic suspensions [4–7,11]. In particular, the excess of polymer has a detrimental effect on stability of alumina suspensions which increases

as the molecular weight [7]. Free unadsorbed polyelectrolyte resulted in a high ionic strength that therefore decreased the range of the double layer repulsion. Therefore, low electrostatic repulsion caused flocculation. Also, the number of dissociated carboxylic groups reduces at high ionic strength which would have a critical influence on the conformation and adsorption of the molecule. Other destabilization mechanism called depletion flocculation [6,7] may be a possibility. Briefly, depletion flocculation is the result of an osmotic pressure increase due to polymer in solution thereby forcing the particles together [7]. This mechanism was used to explain the destabilization of anionic latex by free polycations after saturated adsorption on the surface [16]. However, some discrepancy even exists about the importance of this mechanism.

Viscosity versus shear rates curves of suspensions for a range of  $\phi$  between 0.51 and 0.57 (not shown) exhibited a similar behavior than that shown in Fig. 2. Moreover, as expected, viscosity increased and even the well stabilized suspension exhibited a slight shear thinning character with increasing  $\phi$ .

### 3.2. Effect of polyelectrolyte addition on viscoelastic properties of $\phi = 0.48$ suspensions

The influence of the dispersant addition on viscoelastic properties was examined for 48 vol% (80 wt%) suspensions. Fig. 3 shows the variation of  $G'$  and  $G''$  as a function of frequency  $\omega$  for polyacrylate additions of 0.4–1.2 wt%.

At 0.4–0.6 wt% of added polyelectrolyte, very low  $G'$  and  $G''$  which linearly increased with applied frequency were observed in the frequency sweeps. In the low frequency region,  $G''$  was higher than  $G'$  indicating a predominant viscous behavior. An intersection point of the curves occurred at a critical frequency  $\omega_c = 8 \text{ s}^{-1}$ . Thus, a certain  $\tau$  lower than 0.1 s (which is estimated as the inverse of  $\omega_c$ ) was an indication of low elasticity.

It is well known that  $G'' > G'$  indicates a viscous liquid-like flow behavior and thus the dissipation of the introduced energy is lost as heat. When  $G' > G''$  the material shows an elastic behavior which is associated with the stored energy that can be recovered [14]. Although, for suspensions containing 0.6 wt% (Fig. 3) the

magnitude of both dynamic moduli at  $\omega_c$  remained near 1 Pa, the curves approached each other from a lower limit of frequency than that for 0.4 wt% suspension. Such behavior indicated a similar viscous to elastic contribution.

With increasing polyelectrolyte addition to 0.9 wt%, the  $G'$  modulus increased significantly and became less dependent on frequency reaching a plateau in the high frequency region. Moreover,  $\omega_c$  shifted to less than  $0.1 \text{ s}^{-1}$  indicating a predominant elastic behavior in the frequency range studied. The estimated  $\tau$  of 10 s is an indication of the relative increase in the elastic component. The  $G'$  at the plateau was one order of magnitude larger than that of the viscous. This is a typical response of a weak gel structure [14].

A similar frequency sweep was obtained by addition of 1.2 wt%. However, the suspension exhibited more solid like characteristics with both moduli almost constant in the frequency range studied. Also,  $G'$  at the plateau increased to 100 Pa while  $G''$  slightly reduced with increasing frequency. This type of behavior is typically observed with an elastic solid. High elasticity  $\omega_c < 0.1 \text{ s}^{-1}$  (i.e.  $\tau$  increased approximately to 10 s) indicated the formation of structure from increased attraction between particles.

For polymer melts the existence of both a plateau region in the  $G'$  or a minimum in the  $G''$  versus frequency curves, indicate the formation of a gel structure due to the crosslinking by intermolecular interactions [14]. However, in colloidal gels network structure is formed by particle to particle linkages. These systems are more complicated as network structure that develop strongly depends on the experimental conditions [8,9].

The tendency of the suspension to show more fluid or solid like behavior may also be confirmed by determining the variation of  $\tan \delta$  with increasing frequency [14]. Fig. 4 shows that  $\tan \delta$  of 0.4–0.6 wt% suspension reduced to a well defined minimum, similar to a Newtonian liquid-like behavior. The response gradually changed for the other concentrations. Thus,  $\tan \delta$  rapidly reduced up to  $\omega_c$  and then reached a very low value in the high frequency region where the elastic behavior dominated. Low  $\tan \delta$  (near to 0.5) at high frequencies confirmed the more elastic characteristic for suspensions having high dispersant addition.

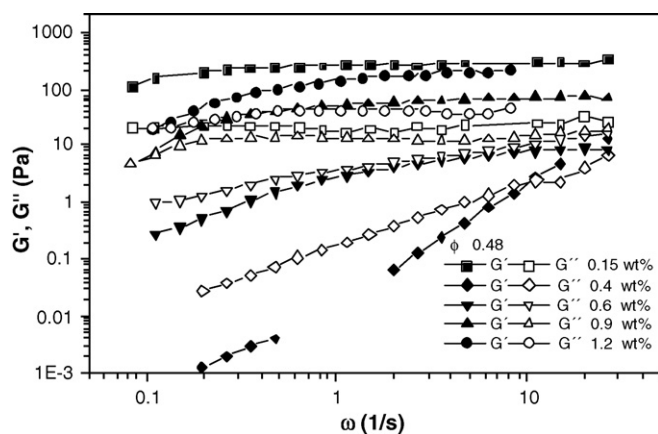


Fig. 3. Effect of added amount of polyelectrolyte on the storage  $G'$  and loss  $G''$  moduli vs. frequency curves for 48 vol% suspensions of alumina and zircon mixture.

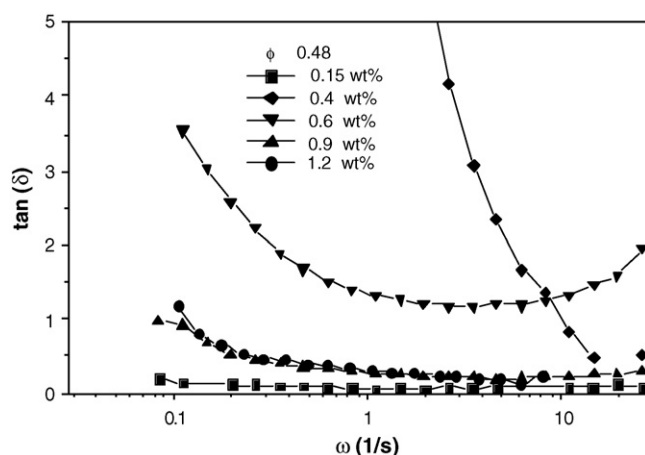


Fig. 4. Effect of addition of polyelectrolyte on the  $\tan \delta$  vs. frequency curves for 48 vol% suspensions of alumina and zircon mixture.



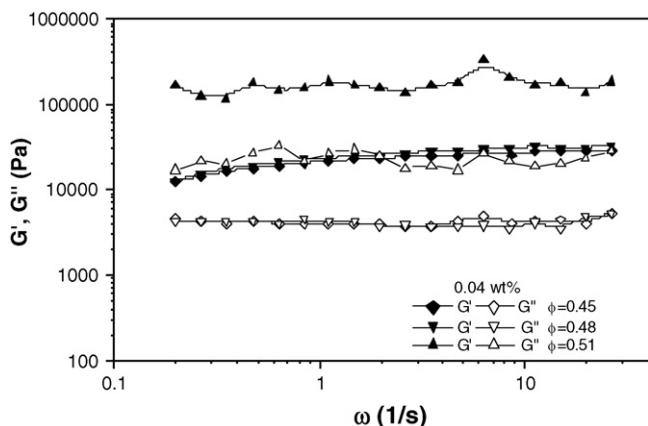


Fig. 5. Frequency sweep tests of the storage  $G'$  and loss  $G''$  moduli of suspensions of alumina and zircon mixture containing 0.04 wt% of dispersant for different volume fractions.

Figs. 5 and 6 show the frequency sweeps for suspensions containing 0.04 and 0.06 wt% (i.e. destabilized by insufficient addition of dispersant).  $G'$  and  $G''$  were nearly independent on frequency being  $G'$  significantly larger than  $G''$ . Therefore, the solid like behavior dominated even at very low frequencies ( $\omega_c \ll 0.10 \text{ s}^{-1}$ ). This result may be an indication of the appreciable strength of the structure. However, Fig. 6 shows that the magnitude of  $G'$  at the plateau strongly decreased with the slight increase in dispersant addition at a given  $\phi$ . The decrease in  $G'$  and  $G''$  was sensitive to the dispersant addition because of the high electrostatic contribution to formation of the structure.

Figs. 3 and 5 evidenced a different viscoelastic behavior between unstable suspensions. Particularly the magnitude of  $G'$  in the high frequency region and the dependence of  $G'$  at very low frequencies indicated the formation of different network structures. Fig. 3 shows the elastic behavior of suspensions flocculated by an excess of polyelectrolyte in solution. Assuming the presence of a polyelectrolyte layer on the surface, short-range repulsive forces between particles probably developed and prevented a relatively strong attractive interaction. Many previous studies reported that weak flocculation occurs

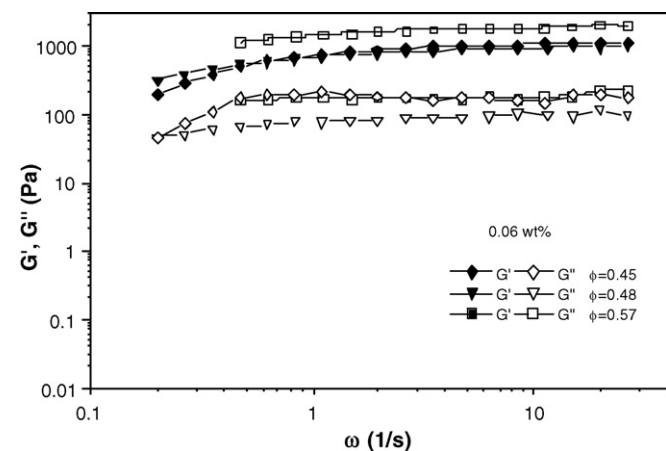


Fig. 6. Frequency sweep tests of the storage  $G'$  and loss  $G''$  moduli of suspensions of alumina and zircon mixture containing 0.06 wt% of dispersant for different volume fractions.

under similar experimental conditions [17–19]. Fig. 5 shows elastic properties of heterocoagulated suspension due to electrostatic attraction between oppositely charged particles where low adsorbed amount of polyelectrolyte (i.e. low surface charge) resulted in stronger attraction. This is consistent with typical viscoelastic behavior of strongly flocculated suspensions, such as that formed at the  $\text{pH}_{\text{iep}}$ , and sterically stabilized suspensions in poor solvents [17,20,21]. In these cases, flocs are strongly interconnected in the network compared with those in weakly coagulated suspensions [8,9]. Previous results [19] showed that this result was due to stronger interparticle interactions.

In an earlier work [13], the different packing behavior of unstable suspensions was shown. When flocculated suspensions were consolidated by pressure filtration, packing density of the green compact improved as compared with that achieved from coagulated ones having similar viscosity. This result was in good agreement with previously reported improvements in the consolidation and forming using weakly flocculated suspensions (alumina, zirconia, silicon nitride, etc.) [21–23].

### 3.3. Effect of volume fraction $\phi$ on viscoelastic properties

The evolution of  $G'$  and  $G''$  with frequency of stable and unstable suspensions was determined for a range of  $\phi$  between 0.45 and 0.57.

Fig. 7 shows the frequency sweeps of well-dispersed suspension. For  $\phi \leq 0.5$ , there was a mainly viscous behavior with very low values of the viscoelastic parameters. The transition from the viscous to viscoelastic behavior ( $G' \approx G''$ ) occurred at  $\phi_c \approx 0.53$  (83 wt%). At  $\phi = 0.57$ , the elastic behavior predominated in the frequency range studied. The increase in the elastic contribution with increasing  $\phi$  may be explained by the overlap of electric double layer or by compressibility of the adsorbed polyelectrolyte layer as the interparticle distance reduced [11,17]. At low  $\phi$  (high separation distance), interparticle interactions are less important. Atomic force microscopy (AFM) measurements confirmed the existence of a thin layer of the polyelectrolyte on the alumina surface [24], in which the thickness varied between

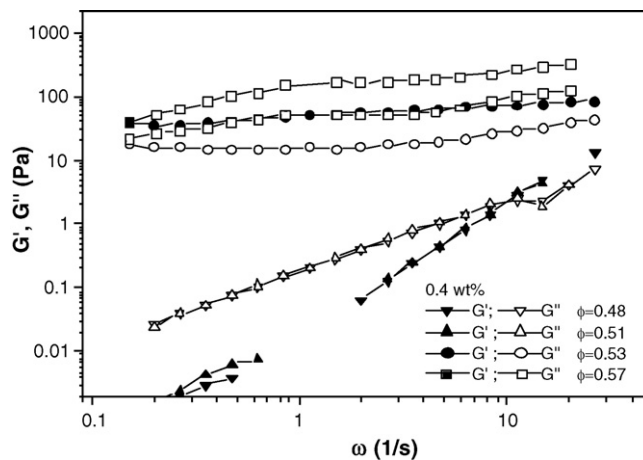


Fig. 7. Effect of volume fraction on the storage  $G'$  and loss  $G''$  moduli vs. frequency curves of well-stabilized suspensions of alumina and zircon mixture (0.4 wt% of dispersant addition).

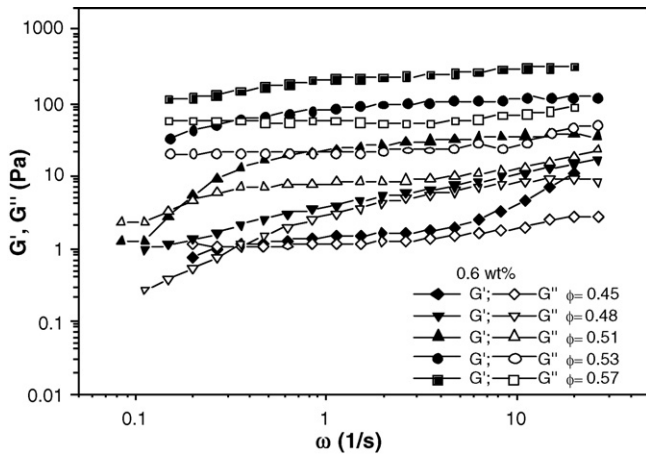


Fig. 8. Frequency sweep tests of the storage  $G'$  and loss  $G''$  moduli of suspensions of alumina and zircon mixture containing 0.6 wt% of dispersant for different volume fractions.

of 2.5 and 6 nm depending on the ionic strength of the solution. This thickness may be non-significant relative to interparticle separation distance. Consequently, the elastic contribution may be attributed to the compressibility of the electrical double layers indicating the relative high importance of the electrostatic repulsion.

Fig. 8 shows the frequency sweeps of suspensions containing 0.6 wt% of dispersant for different  $\phi$ . In this case, elastic behavior became to be dominant at  $\phi_c = 0.53$  (83 wt%). Since  $\phi_c$  is slightly lower than that for 0.4 wt% the beginning of flocculation reflected the higher attraction promoted by the increase in the amount of non-adsorbed polyelectrolyte. At  $\phi = 0.57$  storage modulus at the plateau exceeded 100 Pa.

Fig. 9 shows that  $\phi_c$  shifted to 0.45 for a polyelectrolyte addition of 0.9 wt%. For  $\phi \geq 0.53$  (83 wt%), the storage modulus at the plateau reached a moderate value (500 Pa) showing the relatively high attraction between particles. When addition of polyelectrolyte increased to 1.2 wt%, Fig. 10, suspensions exhibited a viscoelastic response with more elastic than viscous behavior even for  $\phi \leq 0.48$ . Moreover, high  $G'$  and  $G''$  values

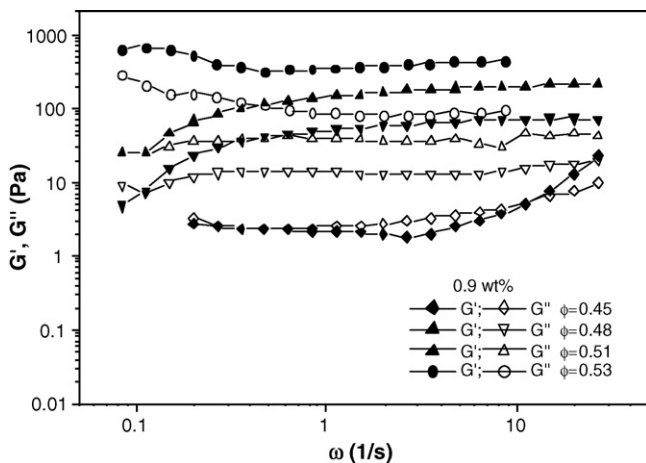


Fig. 9. Frequency sweep tests of the storage  $G'$  and loss  $G''$  moduli of suspensions of alumina and zircon mixture containing 0.9 wt% of dispersant for different volume fractions.

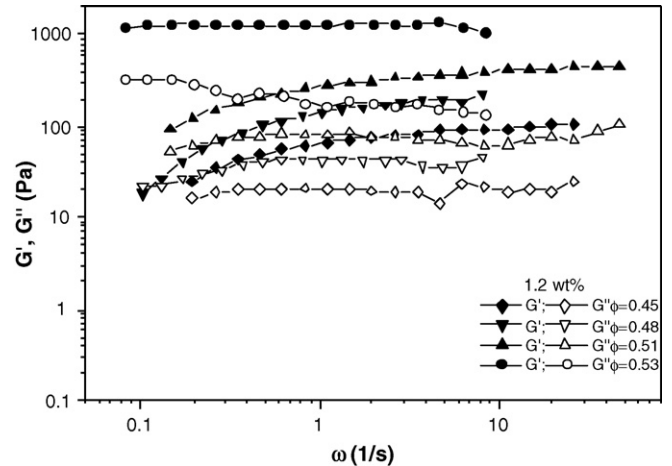


Fig. 10. Frequency sweep tests of the storage  $G'$  and loss  $G''$  moduli of suspensions of alumina and zircon mixture containing 1.2 wt% of dispersant for different volume fractions.

were less dependent on frequency.  $G'$  at the plateau gradually increased near to 500 Pa. With increasing  $\phi$  up to 0.50,  $G' \gg G''$  for the frequency range studied being  $G'$  at the plateau as high as  $10^3$  Pa indicating enhanced particle attraction.

The variation of  $G'$  and  $G''$  (at 1 Hz) as a function of  $\phi$  for suspensions at different degree of dispersion are shown in Fig. 11. Viscoelastic parameters strongly depended on  $\phi$ . The viscous to elastic transition occurred at  $\phi_c > 0.53$  for the stabilized suspension. The  $\phi_c$  shifted from 0.53 for 0.6 wt% to  $\phi_c < 0.48$  for 1.2 wt%.

The dependency of  $G'$  with the volume fraction  $\phi$  for the elastic part of the curves shown in Fig. 11 may be satisfactorily described following:

$$G' \approx K \phi^m$$

where a similar exponent  $m$  of approximately 16 was obtained for dispersant additions between 0.6 and 1.2 wt%. Although a

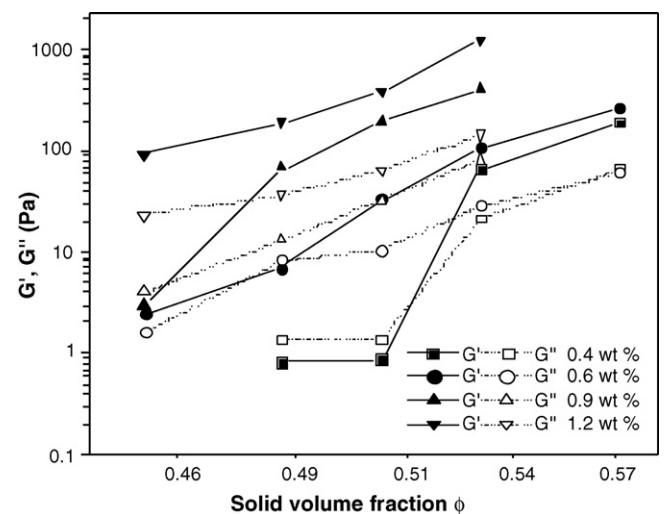


Fig. 11. Effect of volume fraction on the storage  $G'$  and loss  $G''$  moduli (at 1 Hz) of suspensions of alumina and zircon mixture containing different amounts of polyelectrolyte.

relatively wide range of  $\phi$  is necessary to clearly show the dependence of  $G'$  with  $\phi$ , a powder law behavior was in agreement with that predicted by a network consisting in closed packed fractal flocs. In very diluted systems, the exponent was near 2 suggesting the fractal dimensions of flocs [11,12,20]. For concentrated systems in which occurred the interpenetration or interconnection of flocs, the resulting structure is not uniform because the density of the individual particle in the floc varies with the distance from this center. Then according to the theory of interconnected fractal clusters, the exponent gradually increases up to 4–5 [25]. As  $\phi$  approached to the maximum random packing (as used in this work) this value would not be appropriate and a very high exponent was obtained. Examples include suspensions of latex particles electrostatically stabilized at low electrolyte concentration and sterically stabilized suspensions, where elasticity was explained by the compressibility of the extended electric double layers and the adsorbed polyelectrolyte layer, respectively [11,12,20].

Therefore, the high value of exponent  $m$  obtained in this study may be attributed to the heterogeneity of the particle distribution in the floc [25]. Also, the system studied differs from that of an ideal model (monomodal dispersion of spherical particles) because is constituted of two components having different nature and dimensions.

However, fractal models suggest that there is no a lower threshold of volume fraction for the onset of elasticity [26]. Therefore, a percolation theory that suggests a scaling of  $G'$  of the form of a power law dependence on the distance of  $\phi$  from the percolation threshold ( $\phi - \phi_g$ ) over a wide range of  $\phi$  may be more appropriate. Following the percolation model, the exponent characterizes the structure and the pre-exponential factor characterizes the elasticity of the bonds [26]. We found that data of  $G'$  in Fig. 11 may be satisfactorily described with this type of dependence by assuming  $\phi_g \approx \phi_c$ . The resulting exponent and prefactor increased from 1.35 and 3.9 for 0.6 wt% to 1.93 and 5.14 with increasing polyelectrolyte addition up to 1.2 wt%.

#### 4. Conclusions

The viscoelastic behavior of a highly concentrated suspensions of an alumina and zircon mixture containing an anionic polyelectrolyte acting as dispersant was studied. Variation of viscoelastic parameters was used to examine the changes of network structure produced by dispersant additions and solid loadings. The well-dispersed suspension exhibited a predominantly viscous response showing a transition to a slight elastic behavior at a high critical solid content  $\phi_c$ . The elastic contribution increased with increasing the concentration of free polyelectrolyte in solution as particle attraction enhanced. Thus,  $\phi_c$  reduced from 0.57 for the stable suspension to 0.48 for suspension with 1.2 wt% of polyelectrolyte addition. The storage modulus  $G'$  for these flocculated systems attained a relatively low value and exhibited strong  $G'$  dependence in the low frequency region indicating an easy disruption of the formed

network structure. Contrarily, heterocoagulated suspensions by an insufficient dispersant addition showed a predominantly elastic behavior. Both moduli remained relatively higher and almost constant in the frequency range studied. The attainment of high values was indicative of an inhomogeneous and strongly interconnected network. The differences between the corresponding values of the storage modulus at low and high frequency limits evidenced the presence of a layer of adsorbed polyelectrolyte for flocculated particles. Therefore, dense aggregates formed a weakly attractive particle network. The mechanical behavior was dominated by the weakness of inter-aggregate bonds. Therefore, the good consolidation behavior observed in an earlier study may be explained by the different strength of the structure.

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