Rheological properties of concentrated alumina slurries: influence of pH and dispersant agent

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Abstract

The relationship between the pH, the electrolyte concentrations and the rheological properties of high concentrated alumina slurries in aqueous medium is of great importance because it is considered to be the key to control the stability of the slurries from flocculation. Zeta potential of alumina slurries with and without Duramax C (dispersant agent) as a function of pH was studied. Two pH's around the zero point of charge of alumina slurries were selected for the investigation of rheological properties. The rheological properties of aqueous alumina slurries with respect to different parameters, e.g.: viscosity, elastic modulus (storage modulus G') and viscous modulus (loss modulus G"), were investigated. Viscosity measurements of the slurries as a function of Duramax C content at both pH's 8.4 and 9.4) were used to determine the state of slurries. Three states of slurries, termed flocculated, partially deflocculated and fully deflocculated, were selected for further investigation. The viscosity of the three slurries at both pH's as a function of shear rate was determined. Fully deflocculated slurry shows Newtonian behavior at all shear rates at both tested pH's compared by the partial deflocculated and flocculated system. Results of investigation of G' and G'' at pH of 9.4 as a function of applied stress explored the critical stress

(τ_c) at which well-deflocculated alumina slurries can be prepared to cast green body with high bulk density and uniform microstructure.

Key words: Alumina suspensions, Zeta potential, Rheology, Viscosity, Loss modulus, Storage modulus, Critical stress

1. Introduction

Forming via colloidal processing including slip casting, gelcasting and direct coagulation casting has been suggested as methods to produce high quality ceramic green body[1-13]. These types of processing are still the main large-scale production method. However, understanding the mechanism of particle interactions is necessary for process optimization and best design of the initial formulations[14]. In these methods, a well-dispersed suspension of high solids loading with responsible low viscosity to facilitate the mold filling process is required. Therefore, the rheological properties of the concentrated suspensions play a key role in controlling the shape forming behavior and subsequently, the green body properties. Adapting of the surface properties of the ceramic powders and choosing the suitable dispersant as well as optimizing its content offer a route to reduce viscosity and hence aid processing.

According to DLVO(Derjaguin-Landau-Verway-Overbeek) theory [15-16], the stability of colloidal sized particles depends essentially on the balance of attractive and repulsive forces surrounding the suspended particles. Surface potential (zeta potential), electrolyte concentration, particle size and Hamaker constant are four major parameter that control the stability of the suspension, in particular electrostatically stabilized suspension[17]. Accordingly, controlling the pH of an aqueous suspension can develop charges on the particle surface. In most cases, these charges may not provide enough energy barrier between particles to overcome the Van der Waal attractive force between the particles. So these particles tend to flocculate. From this point of view, a dispersant agent is necessary to build up an electrical double layer and, in turn, to generate enough repulsive force and consequently, to increase the particles dispersability.

Extensive studies on dispersing alumina in aqueous medium using different dispersant agent e.g. Tri-ammonium citrate, Doplax CE 64, Duramax D3005 & Duramax C and polyethyl acrylic acid have been reported[18-20].

In the present work, the influence of the pH and Duramax C on rheology of high concentrated aqueous alumina slurries were studied. We used alumina in our work, because it has both industrial applications and academic interests. While aqueous dispersing media are preferred due to environmental consideration.

2. Experimental procedure

2.1. Materials

Alumina (A14) used in this study was obtained from Alcoa Co., USA. Their mean particle size is 5 microns as measured by coulter L.S. 100. (Coulter Scientific Inst. Hialeah, FL), see Table(1). Duramax C which was used as dispersant agent was supplied by Rohm & Haas Company Inc., USA.

Table. 1. Particle size distribution of Alumina.

Volume %.	<10	<25	<50	<75	<90
Particle Size, mm	1.573	2.168	3.332	5.242	7.91

2.2. Zeta Potential measurements (ζ)

Electrokinetic studies were performed on two sets of alumina suspensions prepared by deionized pure water and in a solution containing 1mg/(g solids) of Duramax C. The pH of the first and second set of samples was adjusted to different values from 2 up to 10 using fisher brand HCl and NH_4OH, respectively. Zeta potential measurements were carried out using Coulter Scientific Instrument (Hialeah, FL). The sample was loaded into the cell of the instrument and multiple measurements of the zeta potential of the particles were made at room temperature (20 °C). Zeta potentials of another sets of alumina with different concentrations of Duramax C were carried out at the same conditions but at pH of 9.4.

2.3. Rheological characterization

The rheological properties of high concentrated alumina (65 wt.%) dispersed in deionized water at different pH's around the point of zero charge i.e. at 8.4 and 9.4 , and at different concentrations of Duramax C were determined. Viscosity measurements were measured using Brookfield viscometer, Model RVTD,™. Single point viscosity measurements were made at a constant shear rate of 5 rpm. The viscosity values were plotted as a function of deflocculant added until the minimum viscosity of the slurry was achieved.

Dependence of shear viscosity and dynamic stress sweep test was performed on three slurries with contents of Duramax C of $1x10^{-5}$, $4x10^{-5}$ and $9x10^{-5}$ ml /g solid of alumina. Such tests were performed using TA instrument (Rheolyst AR 1000 Rheometer New Castle, DE, USA). Dependence of shear viscosity flow curves of three slurries at both pH's (8.4 and 9.4) was constructed by increasing shear rate from 1-100 sec^{-1}, and measuring the viscosity. In case of dynamic stress sweep test, slurries at pH value of 9.4 was presheared at 100 S^{-1} for 60 seconds, then the structure was allowed to rebuild. The response of the material to increase stress amplitude was monitored at constant frequency (1rad/sec) and constant temperature 20°C. The viscoelastic parameters G′ (elastic or storage modulus) and G″ (viscous or loss modulus) were computed automatically as a function of applied stress. The elastic modulus is an indication of the energy stored elastically in the system after a shear perturbation while the loss modulus is a measure of the energy lost as heat against friction. The strength of the structure in term of critical stress (τ_c) was also determined. τ_c is magnitude of the stress that defines the end of the linear viscoelastic region of the materials at which G′ is independent of the applied stress or the stress value at which G′ approaches zero or deviates from its original measurements [21].

3 Results and discussions

3.1. Electrokinetic studies

It is well-known that well dispersed aqueous system can be achieved by dispersing the powder in aqueous medium having a pH adjusted far way from the point of zero charge[3,22]. This should confirm enough electrostatic stabilization from the development of charge onto the surface of solid particles. The electrokinetic behavior results here are for aqueous dispersions of alumina particle using Duramax C. The isoelectric point of this system in absence of dispersant is found in the pH range of 7.7 to 9.2. As the pH of the suspension increased from 2 to 10, the surface charge of alumina will change from positive to a negative value. In this pH range, Duramax C will change the surface of the particles from an effectively uncharged state in particular at point of zero charge to a moderately charged. However, it changes the surface charge of the particle to a highly negative charge above zero point. This change could be result from the polyectrolyte and the surface, which have either an electrostatic attraction at low levels of pH or an electrostatic repulsion at higher pH levels.

The variation of zeta potential of alumina as a function of pH is shown in Fig. 1. It is clear that zeta potential of alumina in absence of Duramax C doesn't exceed –10 mV in the pH range of 8-10 and reaches zero point of charge (zpc) at pH of 8.6. This means that using of pH alone to generate high surface charge and, in turn, to prepare stable colloidal system from alumina particle in aqueous media is difficult in this case. However, zeta potential in the presence of Duramax retained negative values over a pH range of 2-10 and exceeds -20 mV reaching to `-40mV in a pH range of 8-10. It was also observed that there is no indication of zero point charge in presence of Duramax. This means that the addition of Duramax C generates a highly charged surfaces of the particles that will result in a strong double layer repulsion. Limited ranges of pH near zpc showed higher values for zeta potentials. This range could be able to overcome the adsorption barrier for Duramax C and, in turn, generate higher repulsive forces and decreases the electrostatic attractive forces[23]. This means that at this range, it is possible to achieve stable aqueous colloidal dispersion. Since most of changes of alumina particle surface charge has been nearly beside the isoelectric point at very limited range of pH, therefore the study of rheology of concentrated alumina suspension around this pH (e.g. 8.4 and 9.4) will help in understanding the state of the slurry.

Zeta potentials as a function of dispersant agent content at pH of 9.4 were investigated as shown in Fig. 2. Increasing the contents of dispersant agent was accompanied by significant increase in zeta potentials from –6 to –15 with additions of Duramax C up to $5x10^{-5}$ ml/g solid. Whereas, there is no significant change in zeta potential with further additions of Duramax C beyond 5x 10^{-5} ml/g solid as the changes in zeta potential is very small and the curve shows nearly plateau in this range of addition. This means that the content of dispersant agent has significant effect on the particle surface charge in specific limit but with increasing its content is insignificant.

3.2. Rheological behavior results

3.2.1. Variation of viscosity with Duramax C dosage

Two deflocculation curves were generated to examine the dispersant demand for the alumina system at two pH's (8.4&9.4) as shown in Fig. 3. These curves show the viscosity of the suspensions decreases from 4000 Pa.s at pH of 8.4 and 3500 Pa.s at pH of 9.4 to less than 30 Pa.s with the addition of Duramax C up to $1.11x10^{-4}$ ml/g solid. As it is found from zeta potential measurements that at the same content of dispersing agent zeta potential was about –16 mV at pH of 8.4 and ~30 mV at pH of 9.4 so the surface of the particles is not highly charged. By investigation the effect of the content of Duramiax C on the surface charge as previously discussed, there is no significant enhancement in the surface with increasing the content of Duramax C. This means that achieving of stable colloidal system according to zeta potential figures is difficult. However, from viscosity measurements, the amount of dispersant agent significantly contributed to decreasing the viscosity and determining the effective concentration of the dispersant that allows the viscosity to reach a minimum steady. Accordingly, The optimum concentration of deflocculant to obtain a minimum steady viscosity is started at $8x10^{-5}$ ml/g solid at both pH's.

As it is well known that there is a close relationship between zeta potential and the rheological properties of oxide slip(24). Consequently, the characteristic amount that occurs in the apparent viscosity-pH curves for oxide slip could be explained in term of zeta potential of the dispersed powder. Higher zeta potential is a measure of improved dispersion resulting from increased interparticular electrostatic repulsion between the similar surface charges acquired by the particles in the medium. However, from the investigated results of the present work, there is an agreement in specific range but not in all ranges of addition. This is concluded from the decreasing of viscosity with increasing the zeta potential and the dosage of dispersant. While reaching to minimum steady viscosity with insignificant increasing the zeta potential and increasing the dosage content of dispersant could be explained in another issue like steric stabilization not zeta potential dependent. As it is reported in some cases(25) at high pH value, an inferring adsorption occurs for polyelectrolyte that exists in a highly dissociated state molecules in stretched confirmations. These types of molecules provide a high repulsive barrier that favor low viscosity. This occurs regardless of the predominantly negative surface of alumina particles at high pH.

Therefore, although the dispersiblity of particles around zero point of charge is difficult from zeta potential point of view. I think that the rheology in term of viscosity as a function of the amount of dispersant agent could be used as criteria to judge if the dispersiblity of the particles can be achieved or not. In this case as discussed , and around zero point of charge, a minimum steady viscosity was reached at both pH's whatever the concentration of the dispersant agent increased or not beyond $8x10^{-5}$ ml/g solid.

Since the role of pH is not very clear in explanation of the viscosity of suspension as a function of dispersant agent so a further rheological studies will be carried out. Accordingly, a three states of concentrated alumina slurry at both pH's named in Fig. 3; undeflocculated state (a), partially deflocculated state (b) and fully deflocculated state (c) on the curve, were chosen for the investigation of their rheology in terms of viscosity as function of shear rate, viscoelastic behavior.

3.2.2. Viscosity-shear rate relationship

Viscosity flow curves for undeflocculated, partially deflocculated and fully deflocculated suspensions as a function of shear rate at pH of 8.4 and 9.4 are shown in Figs.4 and 5 respectively. It is observed from these figures that the suspensions in terms of undeflocculated and partially deflocculated at both pH's exhibited a high viscosity in the range of shear rate tested compared by suspension in term of fully deflocculated. But both suspensions have a significant shear thinning behavior at intermediate shear rates followed by a tendency to Newtonian plateau at higher shear rates. This is due to breakdown of flocculated structure and release of entrapped liquid at high shear rate[26]. However, the viscosity of both suspensions at pH value of 9.4 is less than viscosity at lower pH. The higher viscosity of suspension can be explained in view of insufficient electrostatic repulsion forces to overcome the Van der Waal attraction force at these levels of dispersant agent and pH. These results are consistent with zeta potential measurements and verify the correlation between the rheological properties and charged particle surface. In contrast, the viscosity of suspensions in term of fully deflocculated at both pH's exhibited less shear thinning at the most shear rates values. This means that the particle surface coverage of adsorbant increases and in turn the repulsion forces increases to attains a level that is strong enough to overcome the Van der Waal forces[27]. At low pH, viscosity is higher compared to the viscosity at high pH with considering the Newtonian behavior in both cases. This eventually ensures that the role of pH and its effect on rheological properties of suspension. It can also be concluded that the Newtonian behavior of the viscosity at low zeta potentials at both pH's, means that rheology can be used as criteria for stability of the colloidal system.

3.2.2. Viscoelastic – dynamic stress sweep relationship

In further examining the rheological behaviors of the above dispersions, I present in this section the viscoelastic-dynamic stress sweep measurements that correspond to the suspensions of Fig. 6 at pH of 9.4. pH of 9.4 was selected for this study because at which it gave significant effect from viscosity and zeta potential. It means that the state of the suspensions in all terms is clear. From this point of view, the results of viscoelastic measurements could be enough to figure out the behavior of suspensions in all terms and to propose how can deal with each suspension. Over the range of stresses where G′ shown in Fig. 6 is greater in magnitude than G″ shown in Fig. 7. This means that all suspensions behave more elastic than viscous. At lower stress the elastic modulus(G′) is independent of the applied stress and the materials are behaving as an elastic solids and obeys Hook's law[28]. It can be seen from G′ and G″ of stress dependence of the suspensions represented in figures (6 and 7) that flocculated suspensions show the highest critical stress(τ_c =7.72 Pa) necessary to break down the structure. The suspension in term of partially deflocculated shows the lowest critical stress(τ_c =5.14Pa), , and therefore, the weakest structure. However, fully deflocculated suspensions shows a sharp drop off in G' and a more distinct critical stress level(τ_c ~2.98Pa). It can also be concluded that flocculated and partially deflocculated systems i.e. gelled slips, G′ doesn't drop to zero once yield occurs due to the effective of particle-particle association. In contrast, fully deflocculated system, G′ drops to zero once yield occurs due to the ineffective particle-particle separations. It can be understood from this measurements that there is specific or certain value of applied energy at which the flocs or agglomerates breakdown and obtain a more non-associated type of particle arrangement. This means that the processing of suspensions can be achieving under conditions of applied external stress above critical stress (τ_c)[29]. This in turn, causes particles to dissociate. Consequently, the stability of suspensions improve leading to achieve particle packing and high green bulk density of cast body with more uniform microstructures.

4. Summary and Conclusions

It can be concluded from the study of the influence of pH and Duramax C as dispersant agent on the rheological properties of high concentrated alumina slurries that:

1. Zeta potential of dispersed alumina in aqueous media was improved with addition of Duramax C and variation of pH. The content of the dispersing agent made little bit enhancement in the zeta potential at pH value of 9.4 but to a certain limit. Over the ranges of pH's in presence of dispersing agent, surface charge of the particles based on zeta potential as a function of pH can not be used as representative tool to express for state of suspension stability.
2. Rheological studies of slurries in term of viscosity at pH's around zero point of charge explored that there is three states of slurries termed; flocculated, partially deflocculated and fully deflocculated. Viscosity of fully deflocculated slurries at both pH's as a function of shear rate behave like Newtonian compared by the other two states. The viscosity

decreased at pH value of 9.4 rather than at pH value of 8.4. Viscosity measurements of the slurries as a function of shear rate gave indication to state of dispersed alumina particles in aqueous media and contributed in effective amount of dispersant agent required.

3. Further rheological study but in term of dynamic stress sweep for three states of slurries at pH value of 9.4 illustrated that elastic modulus(storage modulus), G′, was higher than viscous modulus(loss modulus), G″, of most slurries whatever their states. However, G′ or G″ values decreased with change states of slurry from flocculated to fully deflocculated. Critical stress calculated for flocculated, partially deflocculated and fully deflocculated states from viscoelastic terms as a function of applied stress were 7.72 Pa, 5.14Pa and ~2.98 Pa, respectively. Preparation of stable slurry could be achieved at applied external stress above these critical stress value.
4. Rheological measurements could be proposed as a route for designing the casting technique that causes particles to dissociate. Consequently, the stability of suspensions improve leading to achieve particle packing and high green bulk density of cast body with more uniform microstructures.

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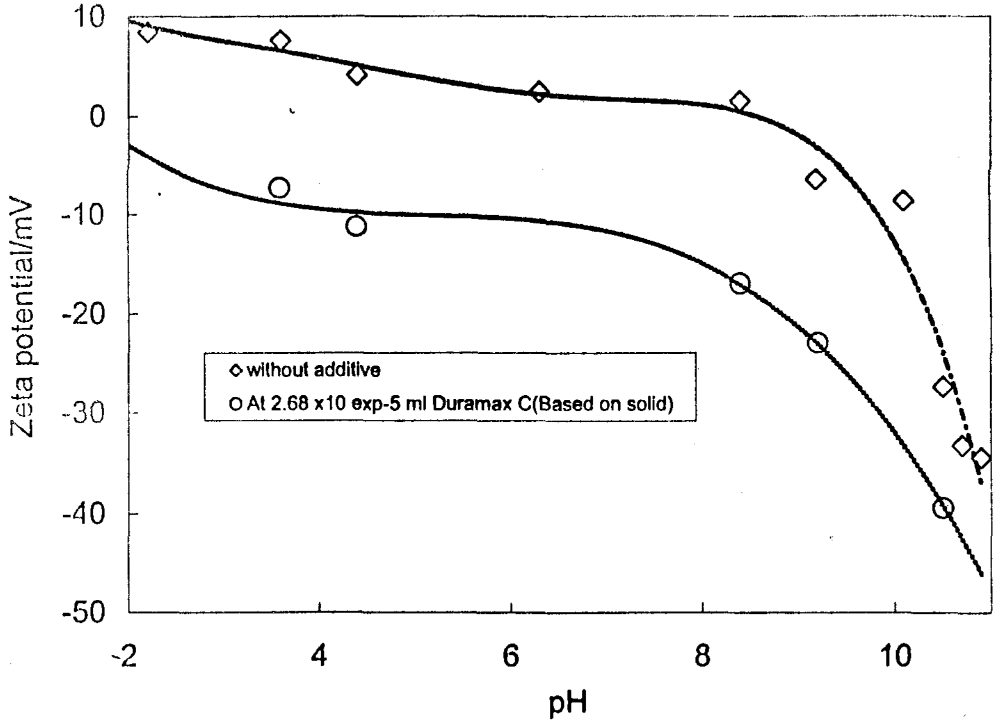

Fig. (1) Varation of zeta potential of alumina suspension as a function of pH

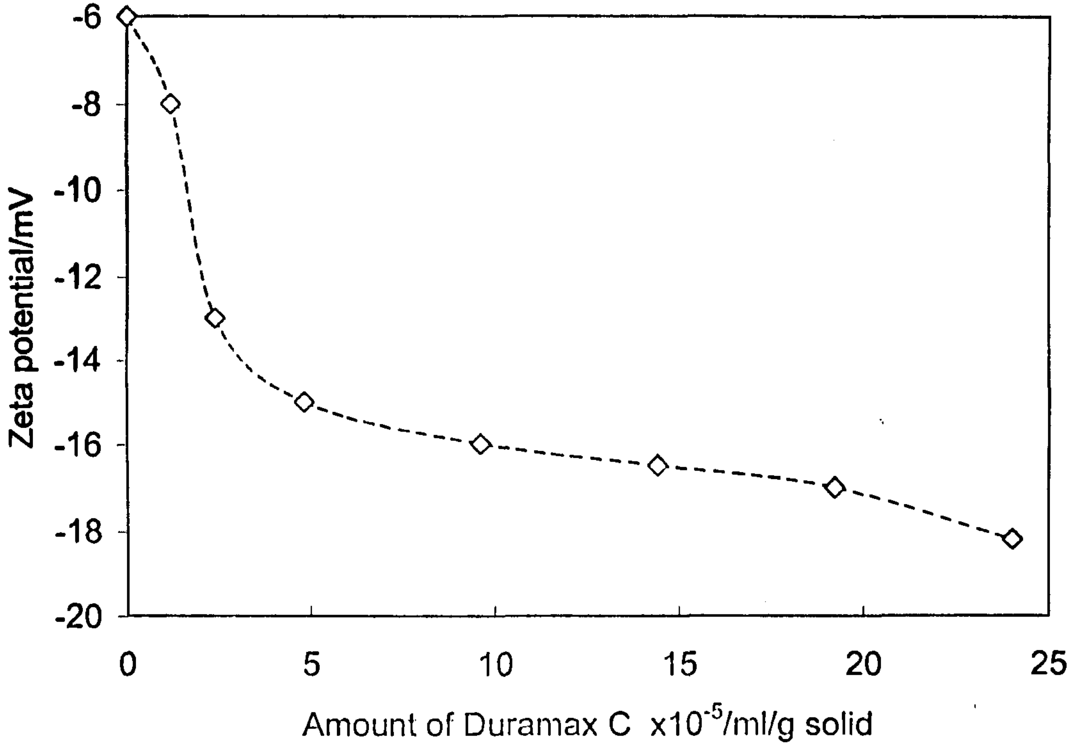

Fig.(2) Varation of zeta potential of alumina suspension as a function of Duramax C concentration at pH value of 9.4

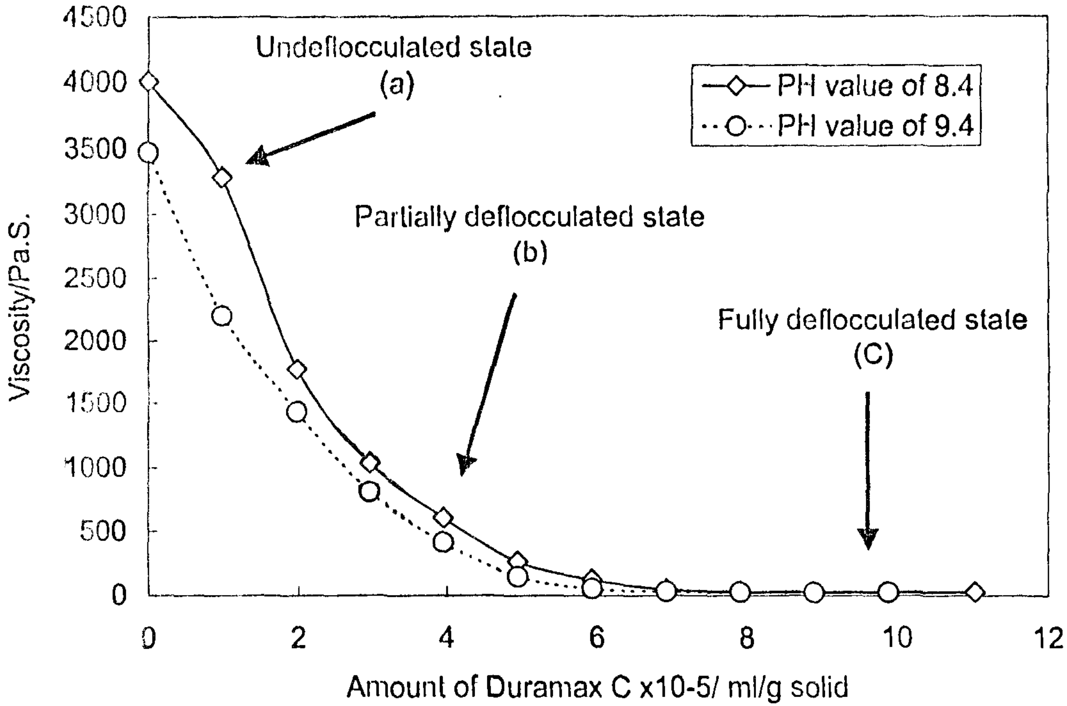

Fig. (3) Viscosity of alumina suspension as a function of Duramax concentration at pH value of 8.4 and 9.4

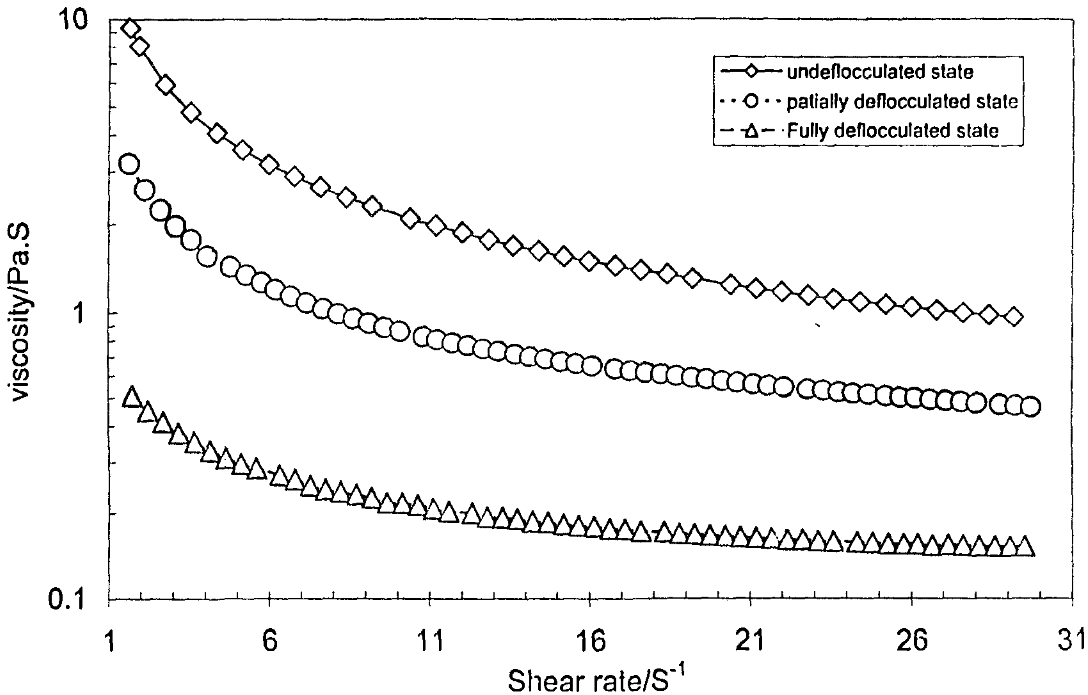

Fig. (4) Viscosity of alumina suspension with different states as a function of shear rate at PH value of 8.4

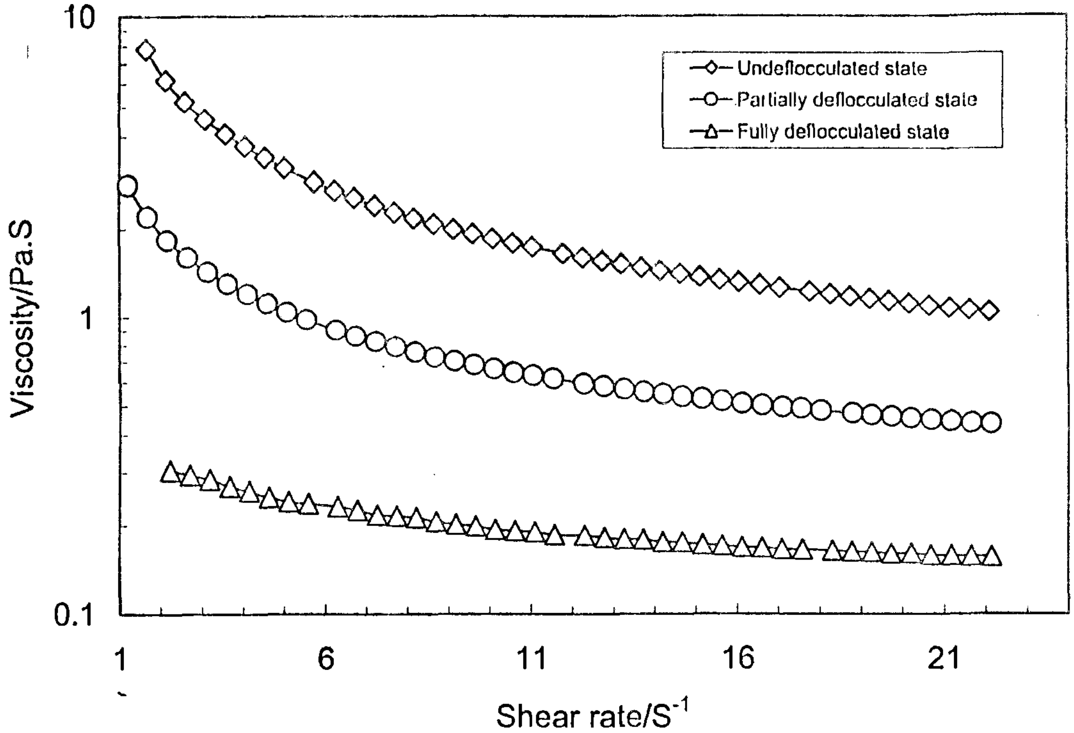

Fig. (5) Viscosity of alumina suspension with different states as a function of shear rate at PH value of 9.4

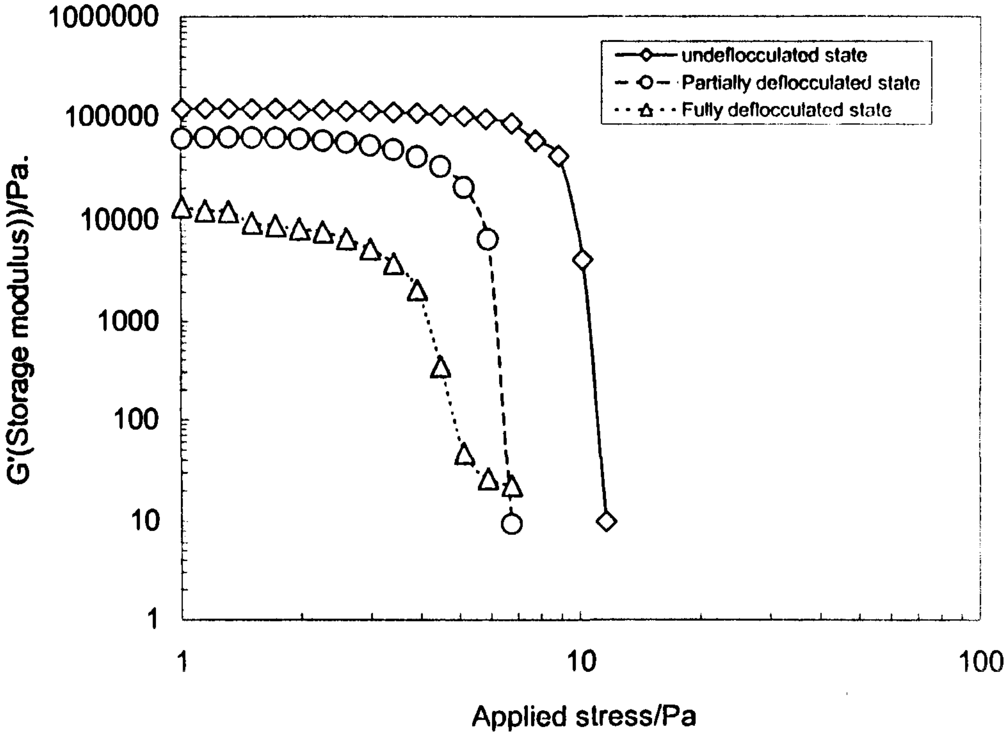

Fig.(6) Dynamic stress sweep in term of elastic modulus for alumina suspension with different states as a function of applied stress at pH value of 9.4

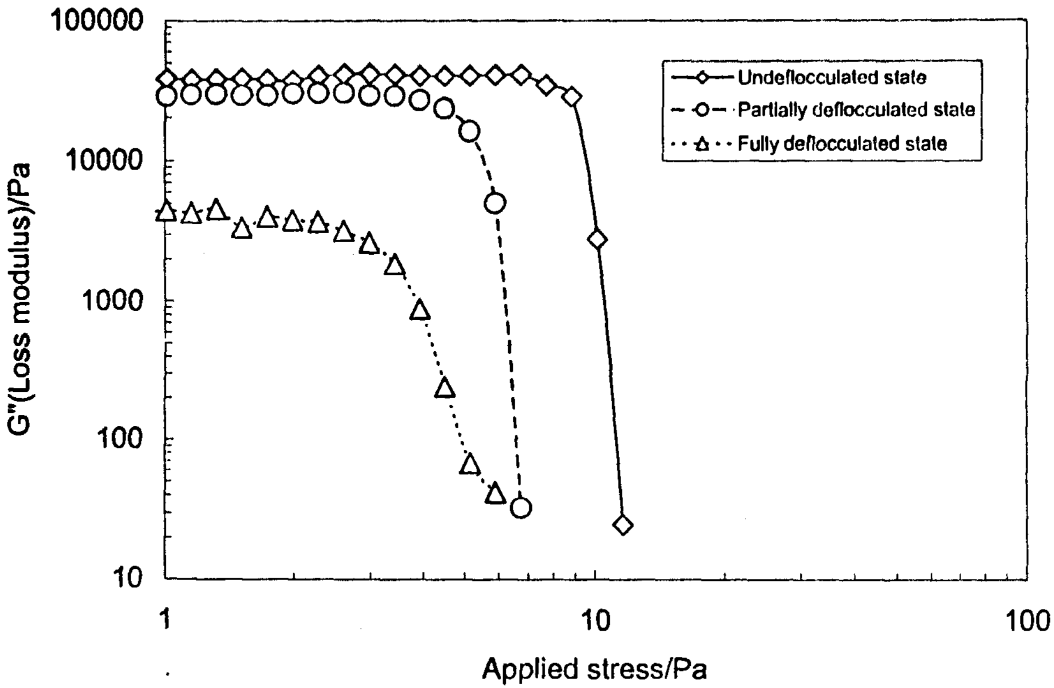

Fig.(7) Dynamic stress sweep in term of viscous modulus for alumina suspension with different states as a function of applied stress at pH value of 9.4