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RHEOLOGY OF ALUMINA SLIPS

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The aim of the present work is to study the rheological behaviour of concentrated aqueous alumina suspensions. Aqueous alumina suspensions were prepared at various solid contents (65 to 77.5 wt%). Rheological tests were carried out at 25±0.1°C by using the rate controlled coaxial cylinder viscometer Rotovisko-Haake 20, system M5-osc., measuring device SV2P with serrated surfaces. The tests were performed under both continuous and oscillatory flow conditions. All the suspensions studied show a rheological behaviour of the shear-thinning type; in addition, the presence of a yield stress is noticed. Some rheological equations of both $\tau=f(\dot{\gamma})$ and $\eta_r=f(\Phi,\dot{\gamma})$ type have been taken into consideration for describing the flow behaviour of the alumina slips investigated. A master-curve procedure was applied in order to give a compact representation of the flow curves drawn for the alumina suspensions examined. Finally, the effect of the addition of a dispersing agent (sodium polyphosphate) on the rheology of alumina slips was investigated and its optimum dosage was determined as well.

Introduction

For the preparation of ceramic suspensions by means of techniques such as slip casting and tape casting, submicron sized ceramic powders are needed. However, since very fine ceramic particles spontaneously agglomerate owing to attractive van der Waals forces, they must be dispersed in liquid phase using suitable dispersing agents. Moreover, different polymeric binders as well as processing aids are usually added to the suspension in order to obtain final products with the optimum properties. The mixing of dispersants, binders and processing aids greatly complicates the rheology of the system.

Alumina is a material widely used in a lot of industrial applications which presuppose the presence of concentrated suspensions. In the light of what said above, the knowledge and control of the rheological properties of alumina suspensions is of paramount importance for improving both the production processes and the quality of final products. However, the rheology of concentrated alumina suspensions is very complex, it being dependent on several factors, which include solid content as well as particle morphology, size and size distribution, surface charge, presence of impurities, aggregation conditions; these latter are strongly influenced by the addition of dispersing agents and/or pH. Hence, concentrated alumina suspensions clearly show non-Newtonian flow characteristics as well as viscoelastic properties.

This article is part of a research program which has been undertaken in order to thorougly characterise the rheological behaviour of alumina suspensions under both continuous and oscillatory flow conditions. Particular attention will be focused on the employment of deflocculants of different chemical nature and concentration. Here, the aim is to contribute deeper understanding of the applicability in continuous flow conditions of some rheological equations to alumina suspensions prepared at different solid content as well as to investigate their oscillatory shear behaviour and the effect of addition of a commercial dispersing agent on the flow characteristics of these materials.

In the last years, several papers regarding the rheology of alumina suspensions have been published; here, mention is made of most papers [1-7].

Experimental Section

Materials employed

Suspensions were prepared with a vane stirrer (Ultra-Turrax T50, Janke & Kunkel, IKA-Labortechnik) from deionized water and an alumina powder, whose

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Table 1 Description of the alumina powder employed

Trade name:	H.P. Alumina AKP-15, Sumitomo Chemical Co. Ltd. (Japan)
Purity:	99.99 %
d_{50}	0.68 µm
Particle size distribution:	83 % < 1 µm
Density:	3.97 g/cm^3
Specific surface:	3.8 m^2/g
Chemical composition:	Si=22 ppm; Na=5 ppm; Mg= 6 ppm; Cu< 1 ppm; Fe= 19 ppm

characteristics are reported in *Table 1*. Solid volume fractions varied in the range 0.319 to 0.464 (65 wt% to 77.5 wt% of solid content). Solid contents higher than 77.5 wt% were not taken into consideration owing to the very high viscosity of samples. A sodium polyphosphate (molecular weight=1733.39) by Aldrich-Sigma was selected as dispersing agent; different dispersant concentrations were considered, ranging from 0.01 to 1.0 wt% as calculated on the alumina powder, solid dry weight basis.

Apparatus and experimental procedure

Rheological measurements were carried out using the rate controlled coaxial cylinder viscometer Rotovisko-Haake 20, system M5-Osc., measuring device SV2P with serrated surfaces. Temperature was kept strictly constant at 25 ±0.1°C. The tests were accomplished under both continuous and oscillatory flow conditions. Flow curves were achieved under continuous flow conditions by ascending shear rates ramps from 0 to 389 s^{-1} at the constant shear acceleration of 6.49 s^{-2}, after preshearing at a high constant shear rate carried out in order to suppress the previous rheological history of the sample tested; down curves from 389 to 0 s^{-1} at the constant deceleration of 6.49 s^{-2} were also determined. A 0.1 to 1 Hz frequency sweep with a 0.7 rad of constant strain was applied as oscillatory testing procedure, in the region of linear viscoelasticy, which was previously determined by applying a 0.2 to 1.3 rad strain sweep with a 0.1 Hz constant frequency.

Results, Data Reduction and Discussion

Continuous flow tests

Time-dependent effects under continuous shearing conditions were negligible with all the alumina suspensions examined. A rather good superposition of up and down curves is observed in the whole range of particle concentration. Hence, in the present work attention has been essentially focused on the shear-dependent behaviour of alumina suspensions.

The shear stress vs. shear rate flow curves obtained for the alumina slips investigated are drawn in *Fig.1*: it can be seen that all the alumina suspensions studied

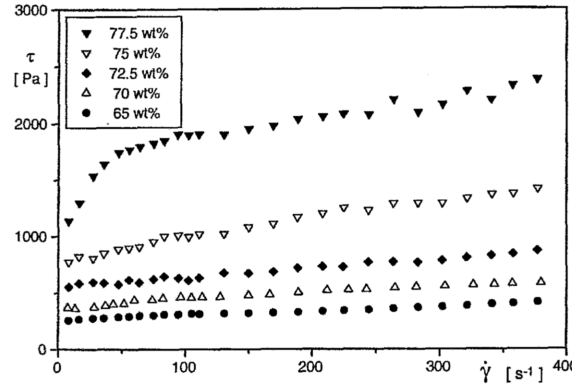

Fig.1 Shear stress (τ) vs. shear rate ($\dot{\gamma}$) flow curves for the alumina suspensions studied.

show a rheological behaviour of the shear-thinning type; in addition, the presence of a yield stress is made evident. A great increase in viscosity is noticed by passing from 75 to 77.5 wt%. In order to obtain the most suitable equation for describing as well as predicting the rheological behaviour of alumina aqueous suspensions some models of the literature of both $\tau=f(\dot{\gamma})$ and $\eta_r=f(\Phi,\dot{\gamma})$ type were taken into consideration.

Models of the $\tau=f(\dot{\gamma})$ type

Among the rheological models which correlate shear stress with shear rate, only the following literature equations which take into consideration the presence of yield stress were tested:

The Bingham model

$$\tau=\tau_o+\eta_p\dot{\gamma} \tag{1}$$

The Casson model

$$\tau=\tau_o+\eta_\infty\dot{\gamma}+2[\tau_o\eta_\infty]^{1/2}\dot{\gamma}^{1/2} \tag{2}$$

The generalized Casson model

$$\tau^n=\tau_o{}^n+[\eta_\infty\dot{\gamma}]^n \tag{3}$$

The Herschel-Bulkley model

$$\tau=\tau_o+K\dot{\gamma}^n \tag{4}$$

The Sisko modified model

$$\tau=\tau_o+\eta_\infty\dot{\gamma}+K\dot{\gamma}^n \tag{5}$$

From a deep examination of *Figs.2-5* the following general considerations can be put on:

1) No satisfactory correlation with solid volume fraction can be noticed for the generalized Casson infinite viscosity; on the other hand, a distinct fitting was obtained by correlating with Φ the η_∞ values determined with Eqn. (5) and using the sigmoidal Boltzman equation :

Table 2 Standard deviations (STD) and coefficient of determination values (COD) for the alumina suspensions studied

		Alumina concentration (wt%)				
		65.0	70.0	72.5	75.0	77.5
Eqn.(1)	STD	5.78	14.9	17.8	31.1	131
	COD	0.982	0.955	0.965	0.976	0.807
Eqn.(2)	STD	8.26	8.07	21.5	20.7	98.4
	COD	0.963	0.987	0.950	0.989	0.892
Eqn.(3)	STD	5.90	8.15	18.0	20.2	85.4
	COD	0.982	0.987	0.966	0.990	0.922
Eqn.(4)	STD	5.91	8.04	18.0	20.0	84.3
	COD	0.982	0.988	0.966	0.991	0.924
Eqn.(5)	STD	5.81	7.99	18.3	19.9	85.0
	COD	0.983	0.988	0.966	0.991	0.924

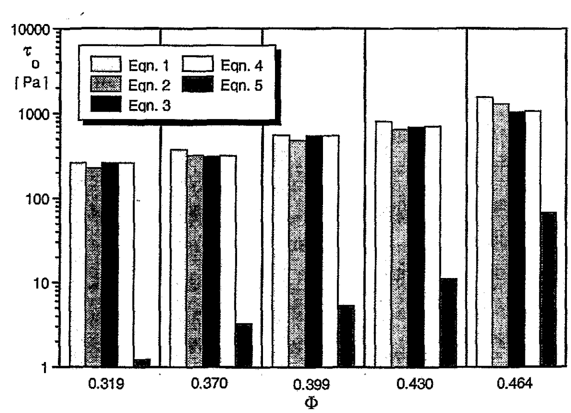

Fig.2 Yield stress (τ_o) variation with solid volume fraction (Φ) for the alumina suspensions studied.

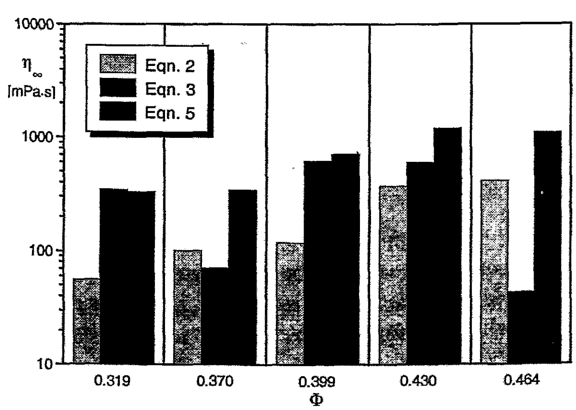

Fig.3 Infinite viscosity (η_∞) variation with solid volume fraction (Φ) for the alumina suspensions studied.

$$\eta_\infty = A + (B-A)/(1+\exp\{(\Phi-\Phi')/d\Phi\}) \qquad (6)$$

The following values for the Boltzman parameters were determined: A=0.809; B=0.336; Φ'=0.399; $d\Phi=3.05\cdot10^{-4}$; STD=0.0768; COD=0.991.

2) An irregular variation of the Herschel-Bulkley consistency with Φ can be observed.
3) An irregular variation with Φ can also be noticed for the n parameter of Eqn. (5).
4) Very close τ_o values were obtained with Eqns. (1-4).

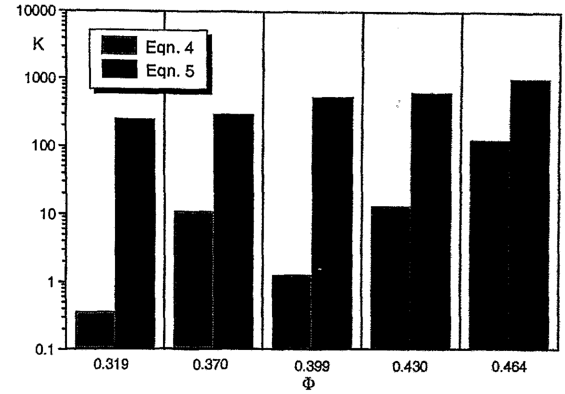

Fig.4 Consistency values (K) variation with solid volume fraction (Φ) for the alumina suspensions studied.

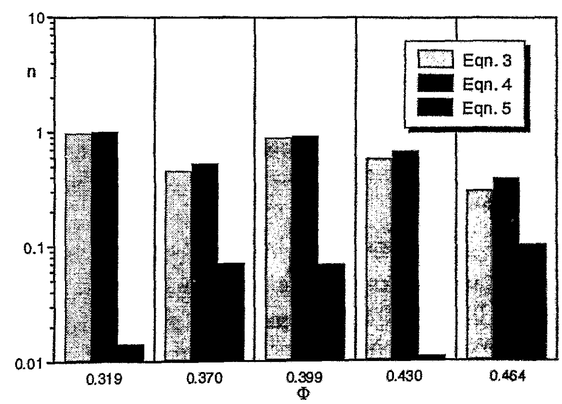

Fig.5 n parameter values variation with solid volume fraction (Φ) for the alumina suspensions studied.

5) Higher values of the Casson generalized n parameter were obtained with respect to those determined by Zupancic *et al.* in (2).

As can be seen from an examination of both standard deviations estimates (STD) and determination coefficient values (COD), which are reported in *Table 2*, all the models considered gave a distinct fitting for all the slips investigated except for the most concentrated suspension. Obviously, a slightly superior fitting was achieved by applying Eqn. (5), it being a model with four adjustable parameters. In addition, as regards the choice of the most suitable model for application to alumina suspensions, no indication can be obtained by comparing experimental and calculated shear stress data. Hence, a final contribution to screening among the models proposed may be gained by considering another criterion of choice, i.e. that consisting of checking whether the parameters of the selected models can be assigned a physical meaning. Accordingly, the physical consistency of the yield values determined by fitting was checked by using the following equation:

$$\tau_o = K'[(\Phi-\Phi_o)/(\Phi_m-\Phi)]^m \qquad (7)$$

where Φ_o (percolation threshold) is the volume fraction corresponding to transition from the Newtonian or shear-thinning behaviour to the plastic one, i.e. the

Table 3 Parameters of Eqn. (7)

Model	K'	Φ_0	Φ_m	m	STD	COD
Eqn.(1)	284	0.170	0.496	0.769	32.1	0.999
Eqn.(2)	256	0.183	0.487	0.648	37.7	0.998
Eqn.(3)	291	0.116	0.563	1.01	82.2	0.980
Eqn.(4)	330	0.144	0.565	1.03	82.3	0.984
Eqn.(5)	10.4	0.264	0.602	4.73	4.16	0.989

Table 4 Variation of Quemada intrinsic viscosities k_o and k_∞ and critical shear rate $\dot{\gamma}_c$ with solid volume fraction

Φ	k_o	k_∞	$\dot{\gamma}_c$ (s^{-1})
0.319	6.27	5.76	1790
0.370	5.41	5.03	1220
0.399	5.01	4.20	14700
0.430	4.65	4.41	1710
0.464	4.31	3.74	36400

lower limit of the solid volume fraction at which the disperse phase behaves as a three-dimensional network structure, and Φ_m is the maximum volume fraction, i.e. that corresponding to the maximum particle packing in quiet conditions. Eqn. (7) has been already applied to alumina slips by Kristoffersson *et al.* in [1] and by Zupancic *et al.* in [2]. As can be seen in *Table 3*, data regression according Eqn. (7) gave the best fitting by using the τ_0 values given by Eqns. (1) and (2); moreover, both the Bingham and the Casson τ_0 parameters can be assigned a physical meaning, in that a good agreement has been evaluated between the Φ_m values calculated by means of Eqn. (7) and that experimentally determined by centrifugation ($\Phi_{m,exp}$=0.51).

Very low values of Φ_0 with respect to the volume fraction of random particle packing Φ_{rp}, calculated equal to 0.64 in [8] for suspensions of monomodal non-interactive hard spheres, denote the presence of strong attractive forces among particles, i.e. the formation of flocs and/or clusters. The size distribution of the alumina particles used being not monomodal, the Φ_{rp} should be slightly higher than 0.64. For the alumina suspensions investigated pecolation limit values lower than those found by Zupancic *et al.* in [2] were determined; this means that the formation of a three-dimensional network can be expected at solid volume fractions considerably lower than Φ_{rp}=0.64.

Models of the $\eta_r=f(\Phi,\dot{\gamma})$ type

As far as the $\eta_r=f(\Phi,\dot{\gamma})$ rheological models are concerned only the Quemada equation [9-11] in its first formulation was considered. This model, which is based on the dissipation energy by viscous friction, can be written as follows:

$$\eta_r=(1-k\Phi/2)^{-2} \tag{8}$$

$$k=[k_0+k_\infty(\dot{\gamma}/\dot{\gamma}_c)^p]/[1+(\dot{\gamma}/\dot{\gamma}_c)^p] \tag{9}$$

where k is an intrinsic viscosity with the limiting values k_0 and k_∞ for very low and very high shear rates, respectively, $\dot{\gamma}_c$ is a critical shear rate, beyond which the disaggregation process of the disperse phase prevails over the aggregation one, and p is an empirical exponent, lying in the range 0 to 1. The p quantity was tentatively associated by Quemada with particle shape (p=0.5: asymmetric particles; p=1: symmetric particles); better, the p parameter should be connected to the shape of the minimum-dimension aggregates, present even at very high shear rates. By a previous linear regression on the four Quemada parameters, p values slightly superior to 0.5 were found, in accordance to the asymmetric shape of alumina particles. Accordingly, a new fitting was performed keeping p equal to 0.5. The application of the Quemada equation with three adjustable parameters provided very satisfactory results. As for the k_0-Φ dependence, the hyperbolic law $k_0=2/\Phi$ was found; as for the k_∞-Φ dependence, a satisfactory correlation was also found by using the law of hyperbolic type: $k_\infty=1.8/\Phi$. Accordingly, the Quemada equation becomes a model with only one adjustable parameters ($\dot{\gamma}_c$), which can be rewritten in this very simple form:

$$\sqrt{\eta_r}=10\cdot(1+1/\sqrt{\dot{\gamma}_r}) \tag{10}$$

where:

$$\dot{\gamma}_r=\dot{\gamma}/\dot{\gamma}_c \tag{11}$$

Accordingly, the Quemada model leads to the Casson one. The Quemada k_0, k_∞ and $\dot{\gamma}_c$ values are listed in *Table 4*: no regular variation of $\dot{\gamma}_c$ with Φ has been noticed, even if their evident increase with solid volume fraction is in fully agreement with its physical meaning.

In the light of the above reported considerations, the Casson equation seems to be the most suitable model for correlating shear stress and shear rate data for the alumina slips investigated.

Finally, in order to give a compact representation of the flow behaviour of the individual members for the alumina suspensions family a master-curve was traced. The master-curve of reduced viscosity, η_R, vs. reduced shear stress, τ_R, is shown in *Fig.6*. For the alumina suspensions family considered the flow curve at Φ =0.319 was assumed as reference curve; reduced variables are defined as follows:

$$\eta_R=a_\eta\eta \qquad \tau_R=a_\tau\tau \tag{12}$$

Shift factors a_η and a_τ were evaluated starting from the τ_0 and η_∞ values determined by fitting the experimental data with the Casson equation. So, they are defined as:

$$a_\eta=\eta_{\infty,ref}/\eta_{\infty,\Phi} \qquad a_\tau=\tau_{0,ref}/\tau_{0,\Phi} \tag{13}$$

Where:

Table 5 Shift factors

	Alumina concentration (wt%)				
	65.0	70.0	72.5	75.0	77.5
a_τ	1.00	0.712	0.473	0.350	0.176
a_η	1.00	0.549	0.471	0.150	0.136

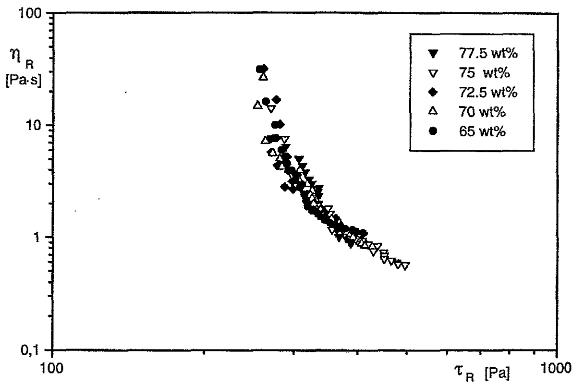

Fig.6 Reduced viscosity (η_R) vs. reduced shear stress master-curve for the alumina slips investigated.

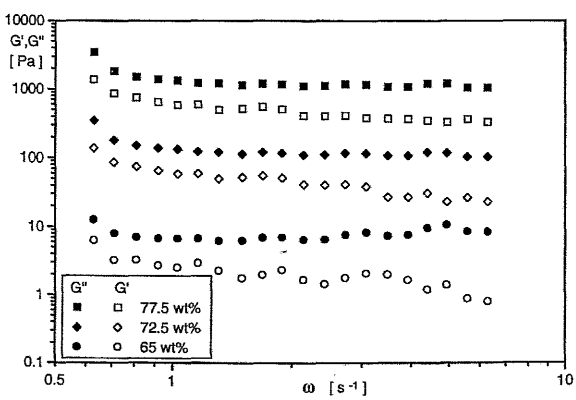

Fig.7 Storage (G') and loss (G") moduli variation with angular velocity (ω) for some of the alumina suspensions studied (0.7 rad of constant strain).

$\eta_{\infty,ref}$ and $\tau_{0,ref}$ are the Casson parameters of the reference curve (Φ =0.319), whereas $\eta_{\infty,\Phi}$ and $\tau_{0,\Phi}$ are the corresponding parameters of the suspension at Φ solid volume fraction.

Shift factors a_η and a_τ are reported in *Table 5*.

Oscillatory tests

It can be observed that dynamic viscosity always decreases monotonically with frequency for all the alumina slips investigated. An inspection of the mechanical spectra determined for the alumina slips formulated without deflocculant, i.e. the plots of storage (G') and loss (G") moduli vs. angular velocity, shows that G" is always greater than G'; hence, one can state

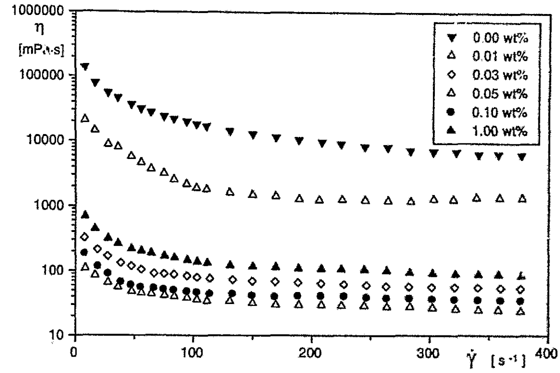

Fig.8 Apparent viscosity (η) vs. shear rate ($\dot{\gamma}$) flow curves for the 77.5 wt% alumina + sodium polyphosphate suspensions studied.

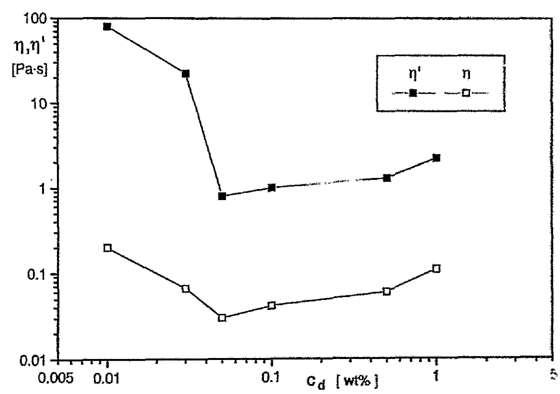

Fig.9 Apparent (η) and dynamic (η') viscosity vs deflocculant concentration ($\dot{\gamma}$ =200s^{-1};ω =2s^{-1}).

that no gel-like to sol-like transition occurred over the all frequency sweep explored. In addition, it results that both G' and G" are nearly independent of ω within the whole frequency range investigated. An example of both G' and G" variation with angular velocity is reported in *Fig.7*.

Effect of deflocculant addition

Figure 8 reports the apparent viscosity vs. shear rate flow curves obtained for the 77.5 wt% alumina slip to which a sodium polyphosphate was added as dispersing agent. From an examination of *Fig.8* a shear-thinning behaviour is registered within all the deflocculant concentration range examined: hence, sodium polyphosphate behaves in a different manner than in kaolin suspensions, where its presence involves a dilatant behaviour beyond a critical concentration [12]. In addition, a viscosity collapse is made evident by adding a 0.01 wt% of deflocculant and passing from 0.01 to 0.03 wt% as well. Finally, by examining the results shown in *Figs.9* and *10* the optimum dosage for sodium polyphosphate was determined for c_d=0.05 wt%.

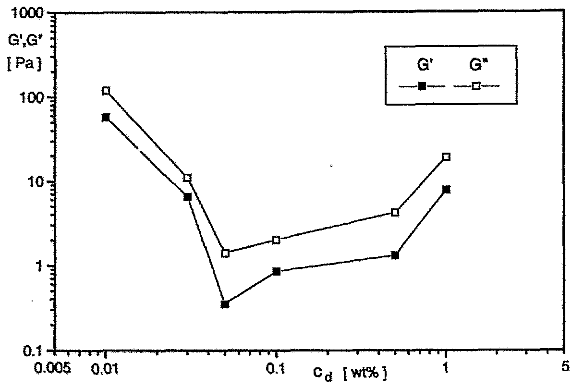

Fig.10 Storage (G') and loss (G") moduli vs. deflocculant concentration ($\omega = 2s^{-1}$).

Conclusions

As far as the rheological models of the $\tau = f(\dot{\gamma})$ type are concerned, the Casson model proved to be the most suitable to describe the flow behaviour of alumina concentrated suspensions in the shear rate range explored and for any alumina concentration examined as well. As for the rheological models of the $\eta_r = f(\Phi, \dot{\gamma})$ type, the Quemada model gave satisfactory results, it reducing to the Casson equation for the alumina slips investigated; in addition, the Quemada p parameter can be associated tô the asymmetric shape of aggregates. The application of oscillatory techniques did not prove the existence of a gel-like to sol-like transition. Finally, the optimum dosage for a sodium polyphosphate employed as dispersing agent was determined by means of rheological techniques.

SYMBOLS

a_η, a_τ	Shift factors
A, B, $d\phi$	Parameters of Eqn. (6)
c_d	Deflocculant concentration, wt%
COD	Determination coefficient values
G'	Storage modulus, Pa
G"	Loss modulus, Pa
k	Parameter of the Quemada equation
k_o	Quemada intrinsic viscosity for a very low shear rate
k_∞	Quemada intrinsic viscosity for a very high shear rate
K	Consistency in Eqns. (4-5)
K'	Constant in Eqn. (7)
m	Exponent in Eqn. (7)
n	Exponent in Eqns. (3-5)
p	Exponent in the Quemada equation
STD	Standard deviations estimates

Greek letters

$\dot{\gamma}$	Shear rate, s^{-1}
$\dot{\gamma}_c$	Critical shear rate in the Quemada equation, s^{-1}
$\dot{\gamma}_r$	Reduced shear rate in Eqn. (11)
ϕ	Solid (nominal) volume fraction
ϕ'	Parameter of Eqn. (6)
ϕ_{eff}	Effective volume fraction
Φ_o	Percolation threshold [see Eqn. (7)]
Φ_m	Maximum solid volume fraction
Φ_{rp}	Volume fraction of random particle packing
η	Apparent viscosity, mPa·s
η'	Dynamic viscosity, Pa·s
η_p	Plastic viscosity [see Eqn. (1)], Pa·s
η_r	Relative viscosity
η_R	Reduced viscosity , Pa s
η_∞	Viscosity at infinite shear rate, mPa·s
τ	Shear stress, Pa
τ_o	Yield value, Pa
τ_R	Reduced shear stress, Pa
ω	Angular velocity, s^{-1}

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