RHEOLOGICAL BEHAVIOR OF CONCENTRATED ALUMINA SUSPENSION: EFFECT OF ELECTROSTERIC STABILIZATION

HAMID SARRAF, JIŘÍ HAVRDA

Department of Glass and Ceramics, Institute of Chemical Technology Prague
Technická 5, 166 28, Prague, Czech Republic

E-mail: sarraf_20002000@yahoo.com

Submitted March 13, 2007; accepted June 6, 2007

Keywords: α-Al_2O_3, Electrosteric polyelectrolyte (Dolapix CE64), Shear-thinning behavior, Yield stress, Flow models

The aim of the present work was to investigate the rheological behavior of highly (43 vol%) concentrated sub-micron α-Al_2O_3 aqueous suspensions containing different amounts of electrosteric polyelectrolyte (Dolapix CE64) as dispersant. It was found that in an aqueous alumina/dispersant system, as the amount of dispersant increased up to its optimum, the viscosity and yield stress of the suspension decreased. The flow curves of alumina suspensions illustrated typical shear-thinning behavior and were fitted satisfactorily to the power law, Herschel-Bulkley and Bingham models. The application of various flow models on the alumina systems confirmed that the optimum dispersant concentration which will impart the minimum viscosity to prepare stable suspensions is 0.4 wt.% of Dolapix CE64. Finally, the results obtained from rheological measurements indicated that dispersant Dolapix CE64 has great efficiency in electrosterically dispersing of concentrated alumina suspension and enables the preparation of lower viscous suspensions, suitable for colloidal processing such as slip-casting.

INTRODUCTION

Colloidal processing of advanced ceramics has received an increasing amount of attention in recent years. Colloidal processing techniques such as slip casting, tape casting, centrifugal casting, injection moulding and dip coating are employed to produce advanced ceramics of improved reliability. In all types of suspension shape forming techniques of ceramic materials, the rheological properties of the concentrated suspension play a key role in controlling the shape forming behaviour and optimising the properties of the green body [1,2]. Fundamentally, the rheological properties of concentrated colloidal suspensions are determined by an interplay of thermodynamic and fluid mechanical interactions. This means that there exists an intimate relation between the particle interactions, including Brownian motion, the suspension structure (i.e. the spatial particle distribution in the liquid), and the rheological response. Furthermore, the prevailing trend in ceramic processing is the development of very fine colloidal particles (at least one dimension < 1 μm), in order to enhance sintering rates as well as to reduce the size scale for mixing uniformity in powder blends. However, the combination of high solids loading and small particles leads to a viscosity increase because of increased particle-particle interactions and, consequently, to difficulties in slurry handling [3]. Dispersant addition can dramatically reduce the viscosity of slurries with very high solids content, thus ceramic industry has a constant demand for effective dispersants or deflocculants [4,5]. The kind of a dispersant to be used with a particular ceramic powder as well as its optimum quantity, have to be determined in order to prepare stable slurries of high solids content that can produce defect-free, high quality products. The systems that contain a polyelectrolyte dispersant, which is functioning via electrosteric stabilization mechanism, have an especially important role in colloidal processing [6-8]. Polyelectrolytes exhibit several advantages over inorganic dispersants, including greater stability, greater control of the thixotropy or flocculation state, the possibility to prepare highly concentrated suspensions, with higher consolidated density for slip casting, and greater flexibility for processing multiphase systems [9-11]. The application of polyelectrolytes as dispersants has been developed to a substantial degree [10], and the understanding of the mechanisms in such systems has also been largely deepened through many investigations. However, previously several researchers examined various water-soluble anionic polyelectrolyte dispersants such as PAA, PMAA, Darvan, etc. for the stabilization of oxide powder slurries (alumina, titania, zirconia, etc.) [11-13]. Those results indicated that the stability of systems that have a polyelectrolyte is very sensitive to the concentration of the polyelectrolyte. However, some notable phenomena and issues remain yet unclear. One of them, to our knowledge is the effect of a new commercial type of electrosteric polyelectrolyte (Dolapix CE64, Zschimmer & Schwartz GmbH Co., Germany) concentration on the stability of aqueous sub-micron α-Al_2O_3 ceramic suspensions at high solids loading. Therefore, in this work Dolapix CE64 was the focus of investigation. Further, to be able to fully control the stability and the rheological properties, proper evaluation of suspension stability is very important [14,15]. Sedimentation and apparent-viscosity measurement at fixed shear rates are widely used in assessing stability. For concentrated systems, however, their limitations are obvious [16]. Instead, a rheological flow curve can be used, which can provide information that relates to the interactions among the particles, the polymer, and the media. Furthermore, the strength of the interactions can be estimated with the information at various shear-rate conditions [17]. In particular, if the data can be represented by an appropriate model, the evaluation may become more convenient and effective [18]. Several models have been developed for non-Newtonian systems, including the Oswald-de Waele power law, Bingham plastic model, the Herschel-Bulkley model, and the Casson model [17]. These models have been widely and successfully used to explain, characterize, and predict flow and shear-thinning behaviors for various systems; nevertheless, not much has been reported in regard to the study of shear-thinning behavior of high concentrated sub-micron α-Al_2O_3 suspension/Dolapix CE64 systems by means of these models.

Thus, the primary purpose of the present study has been to investigate the efficiency of dispersant (Dolapix CE64) concentration in dispersing sub-micron α-Al_2O_3 suspensions at a constant high solids loading of 77 wt.% (~ 43 vol.%) through rheology study. We also intend to demonstrate the electrosteric effect of adsorbed Dolapix CE64 on stabilization. Consequently, viscosity measurements were carried out to discuss shear thinning behavior and to correlate the rheological (viscosity, yield stress and shear rate) properties and dispersion effects of the anionic polyelectrolyte dispersant with three different rheological flow models of the α-Al_2O_3 aqueous suspensions at a constant high solids loading of 77 wt.% (~ 43 vol.%).

EXPERIMENTAL

Materials

Table 1 shows the main characteristics of the commercially available sub-micron α-Al_2O_3 (high purity, AA04, Sumitomo Co., Japan) powder used in this study. A commercially available alkali-free anionic polyelectrolyte (Dolapix CE64, Zschimmer & Schwarz GmbH Co., Germany) dispersant was used in the study. This particular dispersant is based on a polycarboxylic acid that imparts stability by electrosteric interactions, with a *pH* of 9 [19]. In this study, dispersant concentration is expressed in weight % on dry powder basis.

Table 1. Characteristics of powder used in the experiments.

Powder characteristics	α-Al_2O_3
Manufacturer	Sumitomo Co., Japan
Type	AA04, α-Alumina
Mean particle size	0.514 (μm)
BET S.S. Area* (m^2/g)	13.57
Bulk density (g/cm^3)	~ 4.0
Purity	99.99 %
Impurity Y_2O_3 (%)	-
Al_2O_3 (%)	-
SiO_2 (%)	-
Fe_2O_3 (%)	2
Na_2O (%) (ppm)	4
W. loss at 110°C (%)	~ < 0.2
Green density (g/cm^3)	2.28
Shrinkage (1550°C) (%)	17.1
Flexural Strength* (MPa)	570

** The specific surface area measured by BET (Brunauer-Emmett-Teller) single point nitrogen adsorption experiment (Norcross, USA) [11].*

Suspension preparation

In this investigation, composition of three different aqueous suspensions (samples of: A, B, C) of selected high solid (77 wt.%) concentrated α-alumina powder by dispersing into the mixture of doubly distilled water containing different amounts of dispersant (Dolapix CE64) in the range of 0.3-0.5 wt.% was formulated, as shown in Table 2. The table lists the composition of three different α-Al_2O_3 suspension batches prepared in this study. After the addition of different amounts of dispersant into the suspensions of a given (77 wt.%) solid loading, the resulting suspensions were dispersed by using a planetary ball-mill (Pulverisette 6, Fritsch, Germany) for a period of 30 min at a rate of 500 rad/min. Subsequently, deagglomeration was performed in vacuum (laboratory desicator) to remove gas bubbles for 5 min. Then suspensions were additionally deagglomerated with a high-energy ultrasonic horn for 5 min and again degassed for an additional 5 min for removal

Table 2. Composition of examined suspensions (wt.%) of the applied α-Al_2O_3 powder.

Sample	Water (total, wt.%)	Powder (wt.%)	Dispersant * (wt.%)
A	23	77	0.3
B	23	77	0.4
C	23	77	0.5

** wt.% , ~ means weight percent based on the applied α-Al_2O_3 dry powder.*

of air bubbles and better homogeneity, which is essential prior to the rheological measurements as well as for slip casting. pH of all suspensions during suspension preparation was determined in the range of 9-10 depending on dispersant concentration. At least ten suspensions were prepared for each different suspension compositions, in order to determine the optimal amount of dispersant to give the lowest viscosity and control reproducibility of suspensions. Then suspensions were evaluated with respect to their rheology, by means of viscosity measurements.

Viscosimetry and rheological characterization

Immediately, after all suspensions with constant high (77 wt.%) solids loading and different dispersant concentrations were prepared, the rheological measurements of all studied suspensions were carried out by pouring of suspensions into a concentric cylindrical Rheometer (Thermo Haake Ltd., Sensor Z41-DIN measurement system, RV1, Germany). The flow curves were automatically recorded via a built-in program at a particular temperature 23 ± 1°C. Experimentally for measuring of all suspensions a volume of about 14 ml was obtained and used in cylinder. Before performing rheological characterization, to avoid undesired influence from different mechanical histories, the fresh samples were pre-sheared by shearing at an identical rate of 100 s^{-1} for 1 min, followed by an equilibrium period of 2 min prior to measurement. Then, immediately rheology (viscosity) of suspensions was determined. The measurements were performed with the following input conditions: The shear rate (γ) increased (forwards) continuously, and then also reversed (backwards) to 0 s^{-1} with 21 equal steps in the range of shear rates from 0.03 s^{-1} to 1000 s^{-1} over a time period of 20 min. This range was scanned forwards and then backwards in order to check if a given sample was shear-stable or thixotropic. Thrice measurements were made for each suspension, and each result was identical on the whole. The influence of dispersant concentration on the viscosity and yield stress (τ_0) of concentrated α-Al_2O_3 suspensions are investigated by using of different rheological flow models and the flow curves (shear stress- vs- shear rate, viscosity- vs- shear rate) at a particular shear rates between the range of γ < 0.03 s^{-1} - 1000 s^{-1} > are calculated automatically by Rheowin software (Rheometer, Haake Instrument, Germany), compared and corrected by excel software programme. The yield stress (τ_0) was calculated directly by Rheowin software program for both the rheological flow models of: Herschel-Bulkley and Bingham models and compared by shear stress obtained at 0.03 s^{-1}.

RESULTS AND DISCUSSION

Optimization of the rheological properties

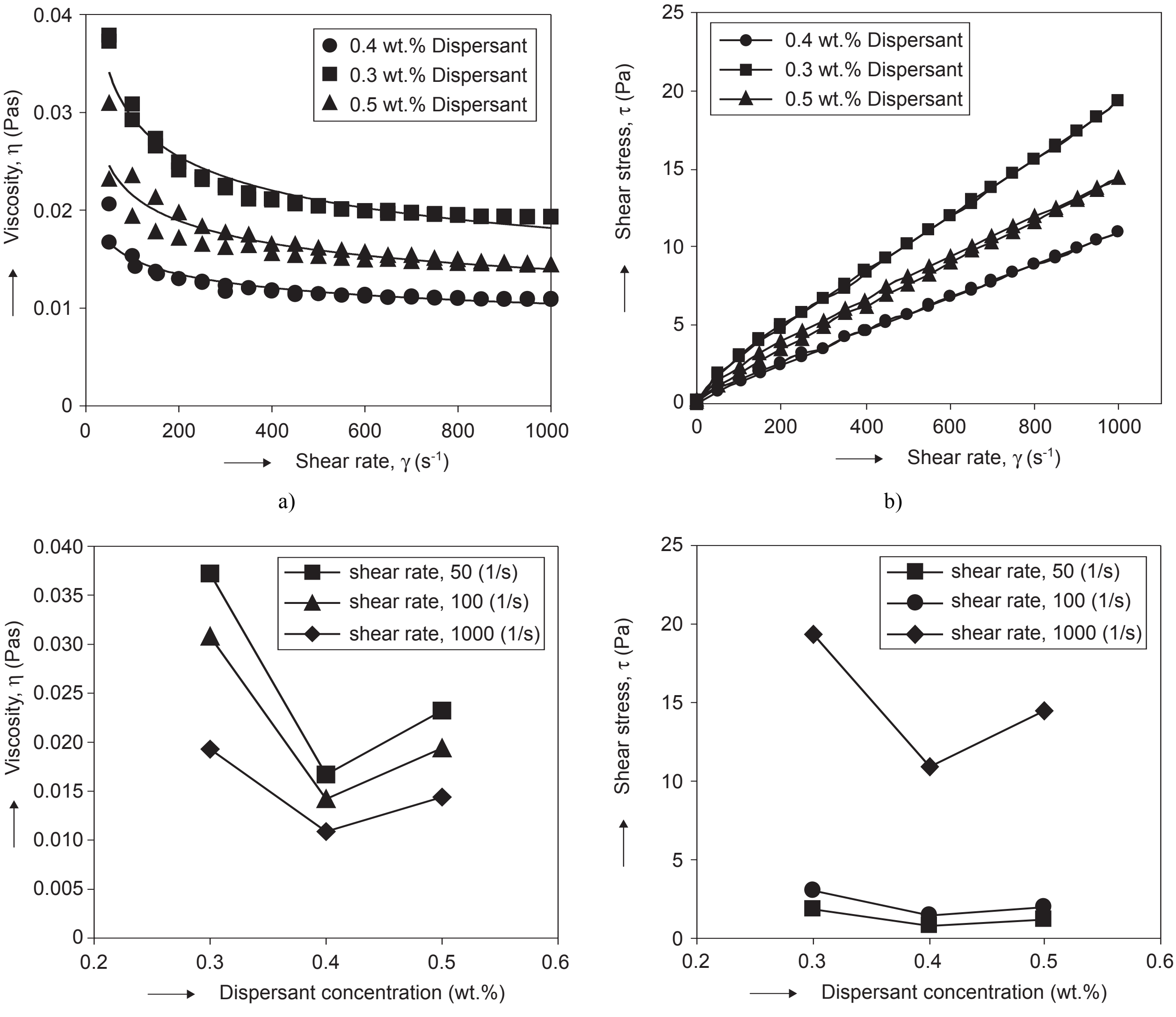
The optimum amount of Dolapix CE64 was investigated by rheological measurements for the α-Al_2O_3 suspension batches as formulated in Table 2, and its concentration was varied from 0.3 to 0.5 wt.% by measuring the suspension viscosity (η) and shear stress (τ), where the solid loading of the suspensions was held at constant 77 wt.%. Figure 1 shows the variation in the rheological behavior (viscosity and shear stress) of concentrated α-Al_2O_3 suspensions as a function of both shear rate γ (< 0.03-1000 s^{-1} >) and Dolapix CE64 concentration in the range of 0.3-0.5 wt.%. The results observed from Figure 1 indicate that alumina suspension with 77 wt.% solids content and dispersant concentration of 0.4 wt.% exhibits the minimum viscosity (~ 0.017 Pa.s at shear rate 50 s^{-1}) as an optimum dispersant concentration compare with the other suspensions at room temperature. This minimum viscosity corresponds to the best dispersion of the suspension, i.e. a suspension system free from significant flocculation of raw powder. So that it can be handled easily and used successfully for slip-casting. In contrast, Figure 1 exhibits that both the suspension viscosity and shear stress increase in the whole range of shear rates for suspensions with inappropriate amounts 0.3 and 0.5 wt.% of Dolapix CE64. This is because, outside the range of dispersant concentration where minimum viscosity is achieved (> 0.017 Pa.s <, in this case) due to the high suspension solids content, a flocculated network structure is formed which causes increasing viscosity of suspensions.

Relationship between viscosity measurement and shear-thinning behavior: Using various rheological flow models

As evident from Figure 1 (a,b), the measured flow curves (the behavior of the shear stress as a function of shear rate) and viscosity-shear rate data in the range of the whole shear rates γ (s^{-1}) between 0.03 s^{-1} - 1000 s^{-1}, the suspensions present typical shear thinning (or pseudoplastic) behavior, (i.e., the viscosity decreases as the shear rate increases) and can be fitted well by the following three different flow models of: Power law model (the Oswald model) [20] (Herschel-Bulkley relation [20,21] with zero shear stress) given by: $\tau = k\,\gamma^n$, Herschel-Bulkley model given by: $\tau = \tau_0 + k\,\gamma^n$, and Bingham model given by: $\tau = \tau_0 + \rho\,\gamma$, where τ is shear stress (Pa), k is consistency coefficient (flow index), γ is shear rate (s^{-1}), ρ is plastic viscosity (Pa.s), n is shear rate exponent and τ_0 is yield stress (Pa), as mentioned in

Table 3. Therefore, the τ, τ_0 and γ values that were obtained were used to assess the suspensions, as shown in Table 3. Table 3 shows the influence of dispersant concentration on the rheological properties (viscosity, yield stress and relative variations) of highly concentrated (77wt.% solid loading) alumina suspensions with different amounts of Dolapix CE64 at two different shear rates γ of 50 s^{-1} and 100 s^{-1}, which estimated by different flow models as follows: Power law, Herschel-Bulkley and Bingham models.

The table shows that the flow behavior of different suspensions follows by the Power law (Oswald de



a) b)

c) d)

Figure 1. Influence of dispersant concentration (wt.%) on the rheological behavior of the highly concentrated (77 wt.%, *pH* = 9–10) aqueous α-Al_2O_3 suspensions at different shear rates γ (s^{-1}) in the range of 0.03–1000 s^{-1}. a) viscosity (Pa.s) vs. shear rate (s^{-1}); b) shear stress τ (Pa) vs. shear rate g (s^{-1}) at different dispersant concentration (wt.%); c) viscosity (Pa.s) vs. dispersant concentration (wt.%); d) shear stress t (Pa) vs. dispersant concentration (wt.%) at different shear rates γ (s^{-1}). All points are measured with increasing shear rate.

Table 3. Comparison of flow variations of different alumina suspensions obtained from different flow models.

Sample L*	Viscosity η (Pa s)		Power law $\tau = k\gamma^n$			Herschel-Bulkley $\tau = \tau_0 + k\gamma^n$				Bingham $\tau = \tau_0 + \rho\gamma$		
wt.%	γ =50 s^{-1}	100 s^{-1}	k	n	r	τ_0	k	n	r	τ_0	ρ	r
0.3	0.037	0.031	0.0	0.86	0.999	0.619	0.030	0.92	0.999	1.05	0.018	0.999
0.4	**0.017**	**0.014**	**0.02**	**0.91**	**0.999**	**0.126**	**0.017**	**0.92**	**0.999**	**0.38**	**0.010**	**0.999**
0.5	0.023	0.019	0.03	0.89	0.999	0.182	0.024	0.918	0.999	0.56	0.014	0.999

** L ~ denotes the dispersant (Dolapix CE64) loading in weight percent (wt.%); r ~ Correlation coefficient.*

Waele), Herschel-Bulkley and Bingham models very well in the observed range of coverage by 0.4 wt.% as an optimum addition of dispersant. As shown in Table 3, the shear rate exponent *n* (by Power law model) of weakly flocculated structure of suspension with 0.3 wt.% Dolapix CE64, is low (i.e., high shear thinning tendency) of ~ 0.86 and insufficient amount of (0.3 wt.%) dispersant is slightly off from the optimum dispersant concentration by means of 0.4 wt.% where has shear rate exponent of *n* ~ 0.91 shear thinning flow by nearly to newtonian flow behaviors (where *n* = 1). Hence, much above the optimum dispersant concentration by means of 0.5 wt.% the flocs should be more rigid (due to bridging or depletion flocculation) leading to relative low shear thinning and shear rate exponent (*n*) of ~ 0.89. Also, the consistency coefficient k attains values of 0.05, 0.02 and 0.03 for the suspensions with 0.3 wt.%, 0.4 wt.% and 0.5 wt.% of alumina suspensions. A more interesting feature of this table is the significant reduction in the maximum yield stress (τ_0 obtained by both Herschel-Bulkley and Bingham models) as a result of the anionic polyelectrolyte addition. The extent of reduction increases with increasing dispersant. A limiting τ_0 of about 0.126 (Pa) by Herschel-Bulkley and 0.38 (Pa) by Bingham models are reached at a concentration of 0.4 wt.% Dolapix CE64. However, according to the Bingham model, the particles in a flocculated suspension form floc groups or a network, because of the mutual attraction between particles, and the Binham yield value (τ_0) can be used as a parameter that indicates the degree of flocculation. Hence, the reduction in τ_0 is attributed to the adsorbed anionic polyelectrolyte providing a steric barrier of interaction between the Al_2O_3 particles. Commonly it can be conclude that shear thinning conditions obtained by optimum amount (0.4 wt.%) of Dolapix CE64 are convenient for processing as at low shear rates (i.e., in the range of 0.03 to 50 s^{-1}), the viscosity is high enough to delay sedimentation, whilst at high shear rates more ordered structure in the flow direction is formed and the viscosity is low enough to produce a castable state.

CONCLUSIONS

The following conclusions have been drawn on the basis of the rheological measurements of highly concentrated α-Al_2O_3 aqueous suspensions:

1) Studies of the rheological behavior has allowed to determine alumina suspension with high 77 wt.% solids loading, well-dispersed, stable and easily processable with low viscosity of 0.017 Pa.s at shear rate 50 s^{-1} (where the shear rate of 50 s^{-1} is similar to that used for slip-casting work) with an optimum amount 0.4 wt.% of Dolapix CE64 at 23 ± 1°C, suitable for colloidal processing such as slip-casting.
2) The flow curves of alumina suspensions show typical shear thinning behavior and were fitted well by three different rheological flow models of: (i) Power law (Oswald-deWaele), (ii) Herschel-Bulkley and (iii) Bingham model. The application of different flow models on the α-Al_2O_3 systems illustrated that the optimum dispersant concentration which will impart the minimum viscosity to prepare stable suspensions is 0.4 wt.% of Dolapix CE64. It was evident that using different rheological flow models can give better attribution and prediction of shear thinning behavior.
3) Further, comparison between Herschel-Bulkley and Bingham models of different alumina suspensions showed obviously that the minimum yield stress value (τ_0) is reached for at a concentration of 0.4 wt.% Dolapix CE64, which is attributed to the adsorbed anionic polyelectrolyte providing an electrosteric interactions between the Al_2O_3 particles.
4) Finally, the results obtained from rheological measurements indicated that dispersant Dolapix CE64 has great efficiency in electrosterically dispersing of highly concentrated alumina suspension and enables the preparation of lower viscous slips. A fact that gives an advantage to use this particular dispersant.

Acknowledgement

The authors would like to acknowledge the funding from the Institute of Chemical Technology (I.C.T-Prague), Czech Republic. First author Hamid Sarraf is also gratefully acknowledge the Ph.D. scholarship awarded to him through this study by the Czech government and the Institute of Chemical Technology (I.C.T, Prague), Czech Republic.

References

1. Chang, J. C., Velamakanni B.V., Lange F. F., Pearson D. S.: J.Am.Ceram.Soc. *74*, 2201 (1991).
2. Bergstrom L., Schilling C.H., Aksay I.A: J.Am.Ceram. Soc. *75*, 33115 (1992).
3. McCauley, R.A. in: *Ceramic Monographs - Handbook of Ceramics*, pp. 1-7, Verlag Schmid GmbH, Freiburg 1983.
4. Sheppard L.M.: Cer.Bull. *69*, 802 (1990).
5. Moreno R.: Am.Ceram.Soc.Bull. *71*, 1521 (1992).
6. McHale, A.E. in: *Engineered Materials Handbook*, Vol. 4, Ceramics and Glasses, pp. 115-121, American Technical Publishers, Herts 1991.
7. Brinker C., Scherer G.: *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing*, Academic Press, New York 1990.
8. Pugh R.J., Bergstrom L.: *Surface and Colloid Chemistry in Advanced Ceramic Processing*. Surfactant Science Series, Marcell Dekker, New York 1994.

9. Fuerstenau D.W., Urbina R.H., Hanson J.S.: Ceramic Transactions *1*, 333 (1988).
10. Alston E.: Trans.Br.Ceram.Soc. *74*, 279 (1975).
11. Cesarano III J., Aksay I. A., Bleier A.: J.Am.Ceram. Soc. *71*, 250 (1988).
12. Foissy A., Attar A. E., Lamarche J.M.: J.Colloid Interface Sci. *96*, 275 (1983).
13. Guo L., Zhang Y., Uchida N., Uematsu K.: J.Eur. Ceram.Soc. *17*, 345 (1997).
14. Pugh R. J. in: *Surface and Colloid Chemistry in Advanced Ceramics Processing*, pp. 127-30, Edited by R. J. Pugh and L. Bergström, Marcel Dekker, New York 1994.
15. Lange F.F.: J Am.Ceram.Soc. *72*, 3 (1989).
16. Bell S.H., Crowl V.T. in: *Dispersion of Powders in Liquids*, pp. 291-305, Edited by G. D. Parfitt. Applied Science, London 1973.
17. Darby R. in: *Encyclopedia of Fluid Mechanics*, Vol. 5, Slurry Flow Technology, pp. 49-65, Edited by N. P. Cheremisinoff. Gulf Publishing, Houston 1986.
18. Hiemenz P.C.: *Principles of Colloid and Surface Chemistry*, pp. 207-17, Marcel Dekker, New York 1986. (b) ibid, pp. 753-57. (c) ibid, pp. 659-65.
19. Graule Th., Hidber P. C., Hofmann, H., Gauckler L.J.: Proc. of the 2nd Euro Ceramic, Vol. 1, pp.299-305, Ausburg 1991.
20. Herschel W.H., Bulkley R.: Proc.Am.Soc.Testing Mater. *26*, 621 (1926).
21. Rangaranjan S., Qi, G., Venkataraman, N., Safari A., Danforth S.C.: J.Am.Ceram.Soc. *83*, 1663 (2000).

REOLOGICKÉ VLASTNOSTI KONCENTROVANÉ SUSPENZE OXIDU HLINITÉHO: VLIV ELEKTROSTERICKÉ STABILIZACE

HAMID SARRAF, JIŘÍ HAVRDA

Ústav skla akeramiky,
Vysoká škola chemicko-technologická v Praze,
Technická 5, 166 28 Praha 6

Práce se zaměřuje na prozkoumání reologických vlastností vysoce koncentrované (43 vol%) submikronové vodné suspenze α-Al_2O_3 s obsahem elektrosterického polyelektrolytu (Dolapix CE64) jako dispergačního činidla. Bylo zjištěno, že ve vodném systému oxid hlinitý/dispergační činidlo se se zvyšováním obsahu dispergačního činidla až na optimální hranici snižovala viskozita a mez průtažnosti suspenze. Tokové křivky suspenze oxidu hlinitého ukázaly typické snižování smykové síly a uspokojivě se řídily zákonem sil, Herschel-Bulkleyovým i Binghamovým modelem. Použití různých modelů toku v systému oxidu hlinitého potvrdil, že optimální hodnota koncentrace dispergačního činidla Dolapix CE64, která ovlivněním minimální viskozity přispěje k získání stabilní suspenze, je 0,4 hm.%. Závěrem lze konstatovat, že výsledky získané z reologického měření prokázaly, že dispergační činidlo Dolapix CE64 je velice účinné pro elektrosterickou dispergaci koncentrovaných suspenzí oxidu hlinitého a umožňuje připravit suspenze s nižší viskozitou vhodné pro koloidní zpracování, jako je například lití licí břečkou.