Iranian Polymer Journal
15 (11), 2006, 879-889

Available online at: http://journal.ippi.ac.ir

Effect of Polymeric Binder and Dispersant on the Stability of Colloidal Alumina Suspensions

Hossain Karimian and Ali Akbar Babaluo*

Research Center for Polymeric Materials, Sahand University of Technology, P.O. Box: 51335/1996, Tabriz, Iran

Received 26 April 2006; accepted 10 December 2006

ABSTRACT

Polymeric additives include dispersants and binders which play a key role in processing of colloidal ceramic suspensions. In this work, the dispersion behaviour of colloidal Al_2O_3 suspensions in the presence of polymeric binder (polyethylene glycol) and dispersant (ammonium salt of polyacrylic acid) was investigated by sedimentation technique, viscosity measurement and FTIR method. The effects of polymeric binder molecular weight and concentration and its interaction with polymeric dispersant were investigated. The results showed that PEG 6000 can be used as a suitable polymeric binder in colloidal processing of alumina suspensions. The optimum concentration of polymeric binder which results in optimum stability conditions was obtained 5 wt% PEG 6000 based on the dry powder weight. Further increasing of binder concentration causes instability of the alumina suspensions via depletion mechanism. In the optimum range of the dispersant concentration (0.2-0.3 mL/100 g powder), suspensions with optimum binder concentration have lower stability compared to those with only dispersant as a polymeric additive. This behaviour is confirmed by FTIR spectra analysis of the polymeric species remained in supernatant liquid. The stability behaviour of the colloidal alumina suspensions with different contents of polymeric binder and dispersant was also evidenced by scanning electron microscopy imaging of the sediment layers after 3 weeks.

Key Words:

alumina;
binder;
dispersant;
stability;
interaction.

INTRODUCTION

Polymeric additives include dispersants and binders which are used extensively to facilitate the processing of ceramic bodies [1]. Polymeric dispersants result in well dispersed and stable suspensions based on electrosteric stabilization mechanism. The stabilization of different aqueous ceramic powder suspensions with ammonium salt of poly(acrylic acid) were investigated systematically in order to understand the basic mechanism of dispersion [2-8]. In these works, the effect of different parameters such as pH [2,3,5,7,8], dispersant

(*) To whom correspondence to be addressed.
E-mail: a.babaluo@sut.ac.ir

cocentration [3,7], molecular weight [6], and structure [4] were investigated on ceramic powder suspensions stability. Also, the stability of ceramic powder suspensions was investigated in the presence of polyacrylic acid [9,10], anionic polyelectrolyte (PMAA-NH_3) [11], acrylic acid/acrylate copolymer [12] and etc.

Binders provide sufficient strength to the body such that the green bodies can be moulded and retained in desired shape without breaking or damage before and during sintering. The ideal binder should be compatible with the dispersant, perhaps also function as stabilizer, to induce no interference with the solvent quality and should not produce foaming upon air entrainment. Also, the objective of some new research works is to define and synthesize molecules with a double function of dispersant and binder [13,14].

The effect of different binders on the stability behaviour of colloidal suspensions has been studied by several researchers [13-21]. But, very little investigations have been done on the more complex binder-dispersant interactions in special colloidal suspensions [13,18-21]. Dasgupta [18] investigated the adsorption isotherms of nitrocellulose, polyurethane and phenoxy binder resins as well as organic phosphate and lecithin dispersants on colloidal magnetic particles in non-aqueous solutions by spectroscopic studies. Khan et al. [13] investigated the rheological response of selected aqueous alumina suspensions, stabilized with a polyelectrolyte dispersant and including poly(vinyl alcohol) (PVA) as a binder. Kristofferson et al. [19] studied the influence of varied polyelectrolyte concentrations in alumina suspensions with and without the addition of a latex binder using rheological measurements. Paik et al. [20] investigated the interaction of binder and dispersant on the stability of aqueous ceramic powder suspensions. Singh et al. [21] have studied the synergistic effects of different surface-active agents (dibasic ammonium citrate as dispersant, albumin as binder and octanol-2 as an antifoaming agent) on the stability of aqueous alumina suspensions by factorial design of experiments. But, the same results have not been obtained. As in some systems, the binder-dispersant interaction was not significant, but in some other different systems, binders have more significant effects on the stability of the colloidal ceramic powder suspensions. Therefore, study on the binder-dispersant interactions in different colloidal suspensions is necessary.

The aim of this work is to investigate the effect of polyethylene glycol (PEG) as a polymeric binder and ammonium salt of polyacrylic acid (Darvan 821A) as a polymeric dispersant and their interactions on stability of colloidal alumina suspensions. The effects of different parameters such as binder molecular weight, binder concentration and dispersant concentration were examined by several methods include sedimentation experiments, viscosity measurements and FTIR spectroscopy method. Also the microstructure of the sediment layers was studied by the scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The characteristics of materials used in this work are given in Table 1 and also Figure 1.

Suspension Preparation

Colloidal suspensions were prepared based on the designed experiments (Table 2) by adding required amount of binder, dispersant and alumina powder in the deionized water. Each suspension was stirred about 24 h under 300 rpm with magnetic stirrer. The pH value of the suspensions was adjusted by 0.1 N NaOH solution at pH 10.

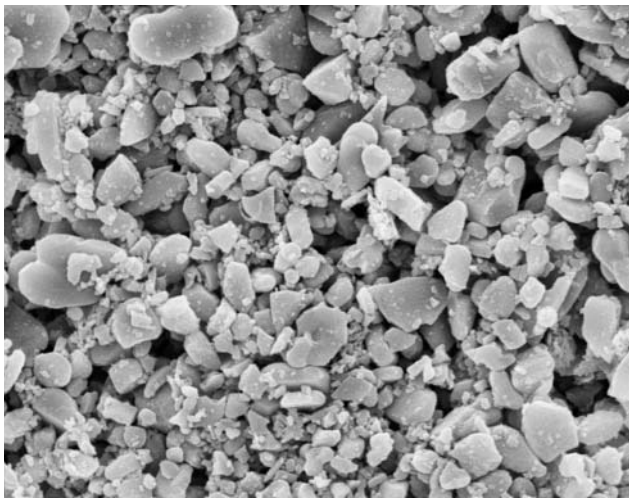


Figure 1. SEM Micrograph of alumina powder.

Table 1. Characteristics of materials.

Materials	Function	Molecular formula	Characteristics	Supplier
α-Alumina	Matrix phase	α-Al_2O_3	Ave. particle size: 1μm, Ave. surface area : 6.55 m^2/g	Fibrona[1]
Polyethylene glycol	Binder	$HO(C_2H_4O)_n H$	Ave. molecular weight: 2000, 6000,10000,35000	Merck[2]
Ammonium salt of polyacrylic acid	Dispersant	$(C_4H_5O_2 - NH_4^+)_n$	40 wt% Aqueous suspension, Darvan 821A	R.T Vanderbilt[3]
Water	Dispersing media	H_2O	Deionized	Ghazi[4]

(1) Fibrona, 215 M. Tehran, Iran; (2) E. Merck, D 6100 Darmstadt, Germany; (3) R.T. Vanderbilt Co, Norwalk, CT, USA; (4) Shahid Ghazi Pharmaceutical Co., Tabriz, Iran.

Methods

The 5 wt% alumina suspensions with different binder and dispersant contents were prepared at pH=10. Several methods were used to study the stability of suspensions include sedimentation technique, viscosity measurements, and FTIR spectroscopy method. In sedimentation experiments, 5 mL of prepared alumina suspensions were put in volumetric cylinders to meas-

Table 2. Characteristics of samples.

Sample No	Binder molecular weight	Binder concentration (based on dry powder weight) wt%	Dispersant concentration (based on 100 g dry powder) (mL)
1	---	0	0.0
2	2000	5	0.0
3	6000	5	0.0
4	10000	5	0.0
5	35000	5	0.0
6	6000	5	0.0
7	6000	10	0.0
8	6000	15	0.0
9	6000	20	0.0
10	6000	5	0.1
11	6000	5	0.2
12	6000	5	0.25
13	6000	5	0.3
14	6000	5	0.4
15	6000	5	0.5
16	---	0	0.1
17	---	0	0.2
18	---	0	0.25
19	---	0	0.3
20	---	0	0.4
21	---	0	0.5

ure the sedimentation volume as a function of time. The cylinders were capped to minimize solvent loss during the sedimentation experiments. For a good dispersion state, the height of interface between clear and cloudy liquid after 24 h should be high; i.e. the powder should not have settled out of suspension in a short time, and the sedimentation height after 3 weeks should be low; i.e. the powder should pack very well when it does finally settle out of suspension. The viscosity of alumina suspensions were measured with Cannon-Fenske type viscometer at 25°C. Suspensions with lower viscosity would have better dispersion state than suspensions which have low fluidity. The effect of free polymer species on the stability of alumina suspensions was studied qualitatively using FTIR spectra of remained polymeric species (binder and dispersant) in the supernatant liquid of suspensions with Fourier transform infrared instrument, Matson 1000, UK.

Characterization

Several methods were used for the characterization of the ceramic powders and sediment layers. The BET (CHEMBET 3000, Quantachrome, US) measurements were performed to determine the surface area of alumina powder. The Zeta potential of alumina dispersed in deionized water was measured with Zetasizer instrument (Zetasizer 3000HS, Malvern, UK). The morphology of the alumina powder and microstructure of the sediment layers was investigated with scanning electron microscopy (SEM, LEO 440I, 3×10^5, LEO, UK and CamScan MV2300, US).

RESULTS AND DISCUSSION

Zeta Potential

The study of the electrokinetic behaviour through measurement of zeta potential becomes important for understanding of dispersion state of colloidal particles in a liquid medium. The zeta potential values of alumina suspensions at different pH values are presented in Figure 2. According to IEP of the alumina powder, pH 10 has been selected as an operating pH. In this pH, alumina particles have negative surface charge equal to -18.2 mV which is suitable in processing of colloidal alumina suspensions stabilized by electrosteric mechanism [4,22].

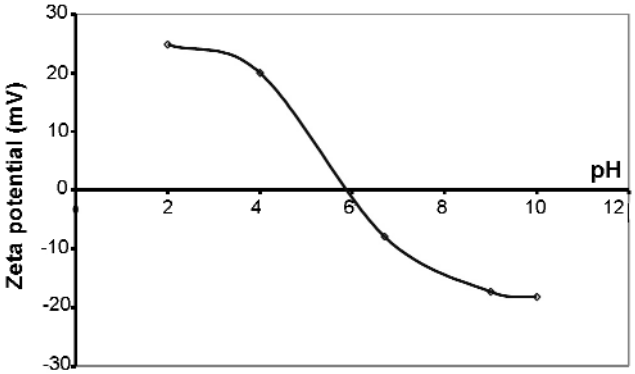
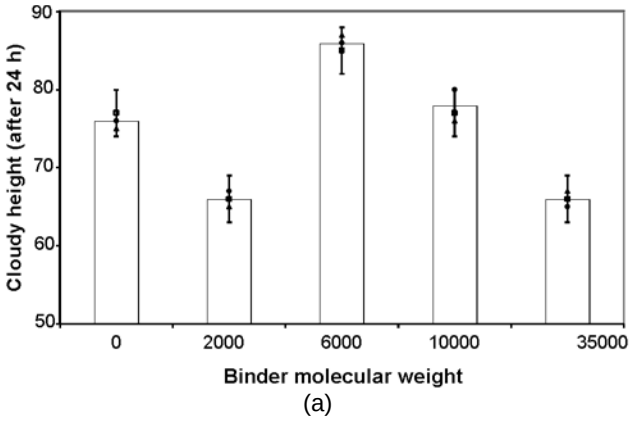


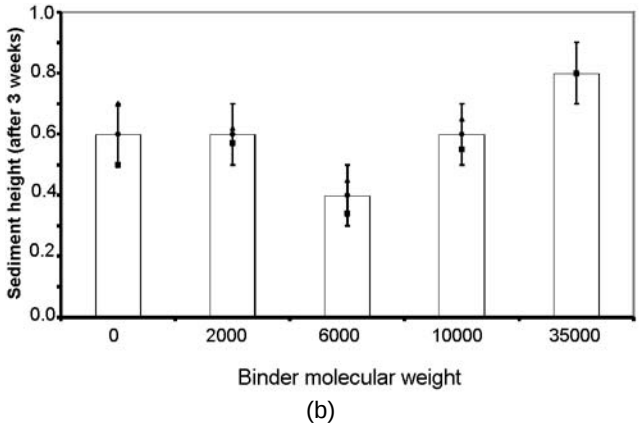
Figure 2. Zeta potential of alumina particles as a function of pH.

Binder Molecular Weight Effect

Figure 3 shows the cloudy height and sediment height of 5 wt% alumina suspensions with different binder



(a)



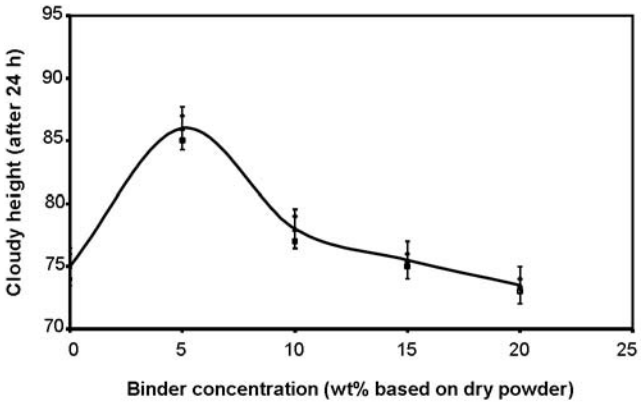
(b)

Figure 3. (a) Cloudy height (% of initial suspension height) after 24 h, (b) sedimentation height (mm/1wt% powder) after 3 weeks as a function of binder molecular weight.

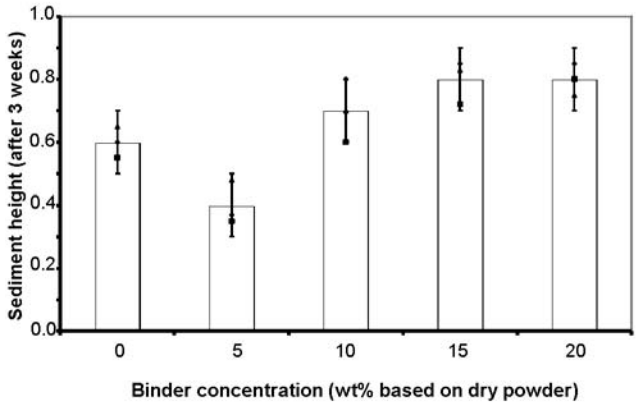
molecular weights at pH 10 including three times repetitions. Addition of 5 wt% (based on dry powder) PEG 2000 results in decreasing of cloudy height compared to suspension without binder. Even if very short chains of this polymeric binder (PEG 2000) adsorb on the surface of alumina particles, they are not able to provide significant steric restriction between colloidal particles. Therefore, the adsorbed short chains of PEG 2000 increase the weight of alumina particles and cause instability of alumina suspensions. When the binder molecular weight reaches 6000, the cloudy height reaches its maximum value about 86% of initial suspension height. PEG 6000 chains are adsorbed on the surface of alumina particles and stabilize them with the steric mechanism. Further increase in binder molecular weight results in decreasing cloudy height due to bridging flocculation that was expected according to the literature [23]. As shown in Figure 3b, the suspension with PEG 6000 has the lowest sedimentation height which is in good agreement with the cloudy height results. Therefore, PEG 6000 can be used as a suitable polymeric binder in colloidal processing of alumina suspensions and manufacturing of ceramic articles.

Binder Concentration Effect

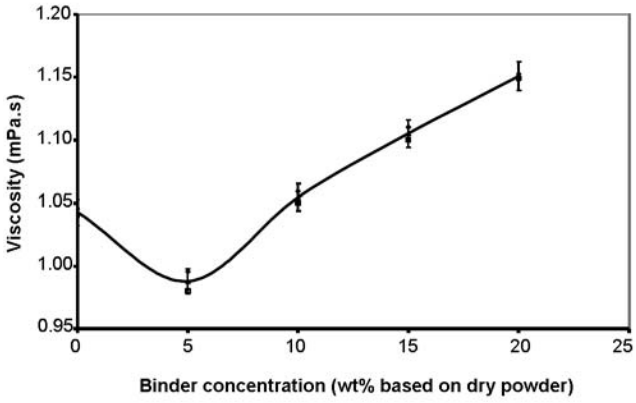
Effect of binder concentration (PEG 6000) on cloudy height, sedimentation height and viscosity of 5 wt% alumina suspensions was shown in Figure 4 with three times repetitions. The suspension with 5 wt% (based on dry powder) PEG 6000 has the highest cloudy height. With further increasing of binder concentration, the cloudy height begins to decrease. At binder concentration higher than 5 wt% there were excess free polymeric binder chains in solution which increase the viscosity and cause instability of alumina suspensions (Figure 4c). Also, the sediment layer obtained from 5 wt% PEG 6000, has the lowest height, i.e. the powder packed very well after settlement of the initial alumina suspension. Diminution of the suspension stability with increasing binder concentration is due to the increasing of interparticle interactions in the system and these enhanced interactions cause an aggregation of particles by a depletion mechanism. The term "depletion" describes the exclusion of adsorbed polymeric chains from the gap region between colloidal particles that arises when



(a)



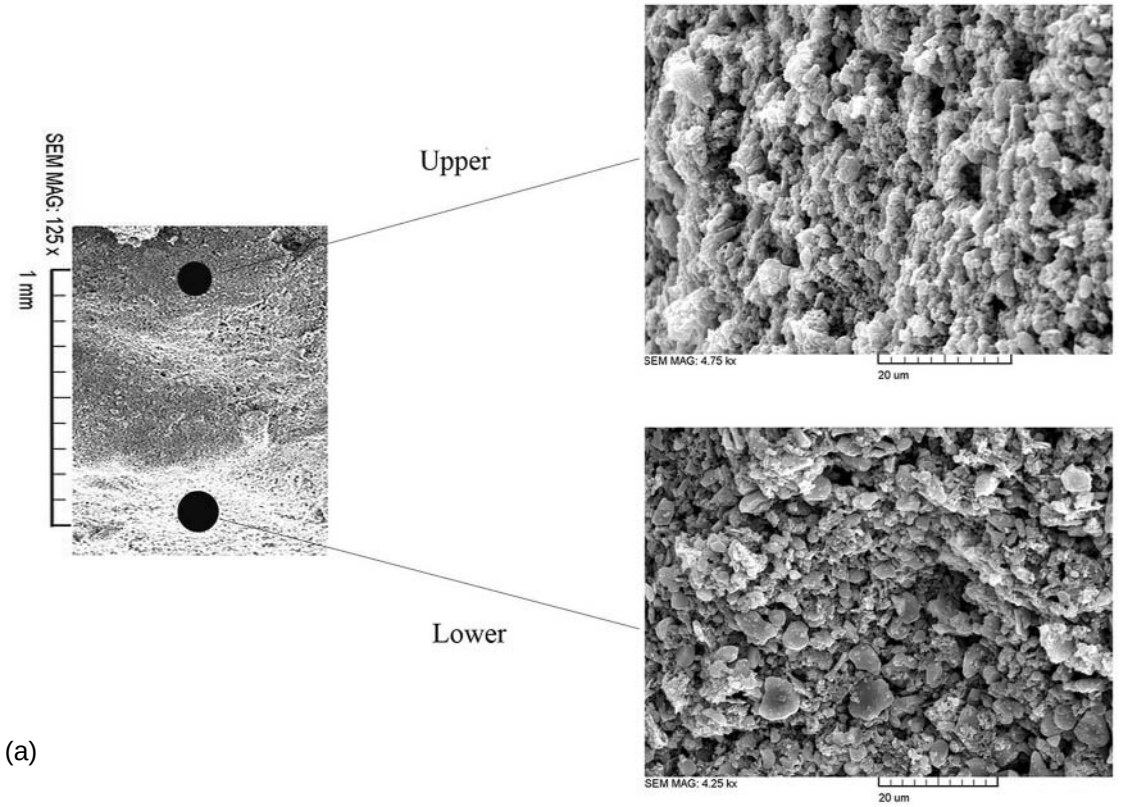
(b)



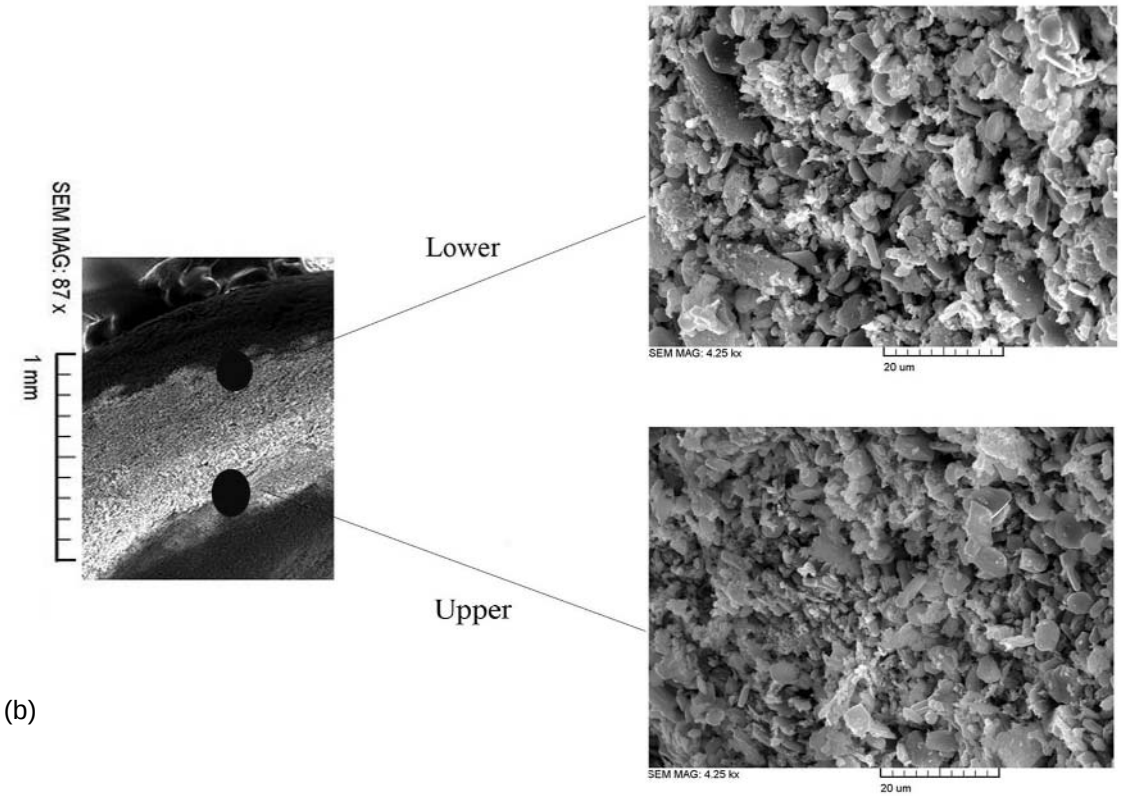
(c)

Figure 4. (a) Cloudy height (% of initial suspension height) after 24 h, (b) sedimentation height after 3 weeks (mm/1wt% powder), and (c) viscosity of alumina suspensions as a function of binder (PEG 6000) concentration.

their separation distance becomes less than the characteristic depletant size. The resultant concentration gradient between the gap region and bulk solution gives rise to a net attraction due to difference in osmotic pressure [13,19,24]. SEM Micrographs (Figure 5) of the sediment layers cross-section



(a)



(b)

Figure 5. SEM Micrograghs of the sediment layer obtained from suspension: (a) without binder, and (b) with 5 wt% PEG 6000.

obtained from suspensions with optimum binder concentration and without binder show that in former case fine and large alumina particles settle out simultaneously from initial suspension compared to the latter case. This reveals the positive role of PEG as an unconventional polymeric dispersant on stability of alumina suspensions in short time (after 24 h) which results in relative homogeneous microstructure in sediment layers at long time.

Binder and Polymeric Dispersant Interaction

To investigate the dispersant-binder interactions, the alumina suspensions with optimum binder concentration (5 wt% PEG 6000) and without polymeric binder were prepared with different amounts of polymeric dispersant. The results of dispersant concentration effect on stability criteria of colloidal alumina suspensions were presented in Figure 6. Also, the cloudy height of suspensions in the absence of polymeric binder was shown in Figure 6a. The experimental results of the cloudy and sediment heights were repeated twice and the viscosity results were repeated three times which were shown in Figure 6 as error bars. Although at dispersant concentration of 0.2-0.3 mL/100 g powder the maximum cloudy height is obtained, but in the absence of PEG the suspensions give higher cloudy height values. These results show that presence of the polymeric binder decreases the electrosteric effect of dispersant on stability of the alumina suspensions [13,19]. In low concentration of polymeric dispersant, the surface of the colloidal alumina particles are not covered completely with polyelectrolyte chains, hence the cloudy height does not change compared to suspension without dispersant (only with 5 wt% PEG 6000). When the dispersant concentration increases, the surface of the alumina particles are covered with the charged polyelectrolyte chains, completely. Adsorption of the polymeric dispersant restricts adsorption of the polymeric binder. In this condition, stability of alumina suspensions is due to the electosteric effect of adsorbed dispersant chains on the surface of the colloidal particles. Although the uncharged binder chains remain in the bulk of solution, however, the electrosteric repulsion induced by polyelectrolyte adsorption is sufficiently strong which prevents instability of suspension by attractive depletion forces induced by the presence of free binder chains in the bulk of solution. In this range of dispersant concentration (0.2-0.3 mL/100 g powder), the lowest sediment height and viscosity was observed which is in good agreement with cloudy height results. At dispersant concentration higher than 0.3, the excess amount of dispersant remains in the continuous medium and functions as an electrolyte and compresses the range of the double layer (reduction of the

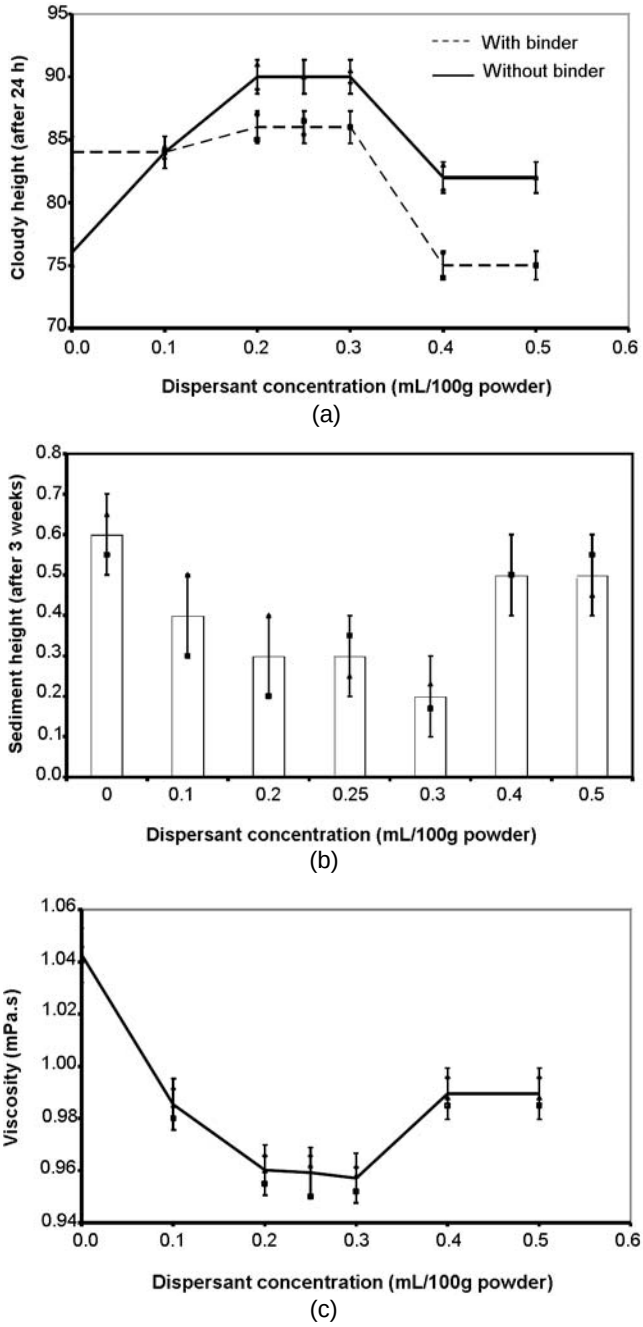


Figure 6. (a) Cloudy height (% of initial suspension height) after 24 h, (b) sedimentation height (mm/1wt% powder) after 3 weeks, and (c) viscosity of alumina suspensions as a function of dispersant concentration.

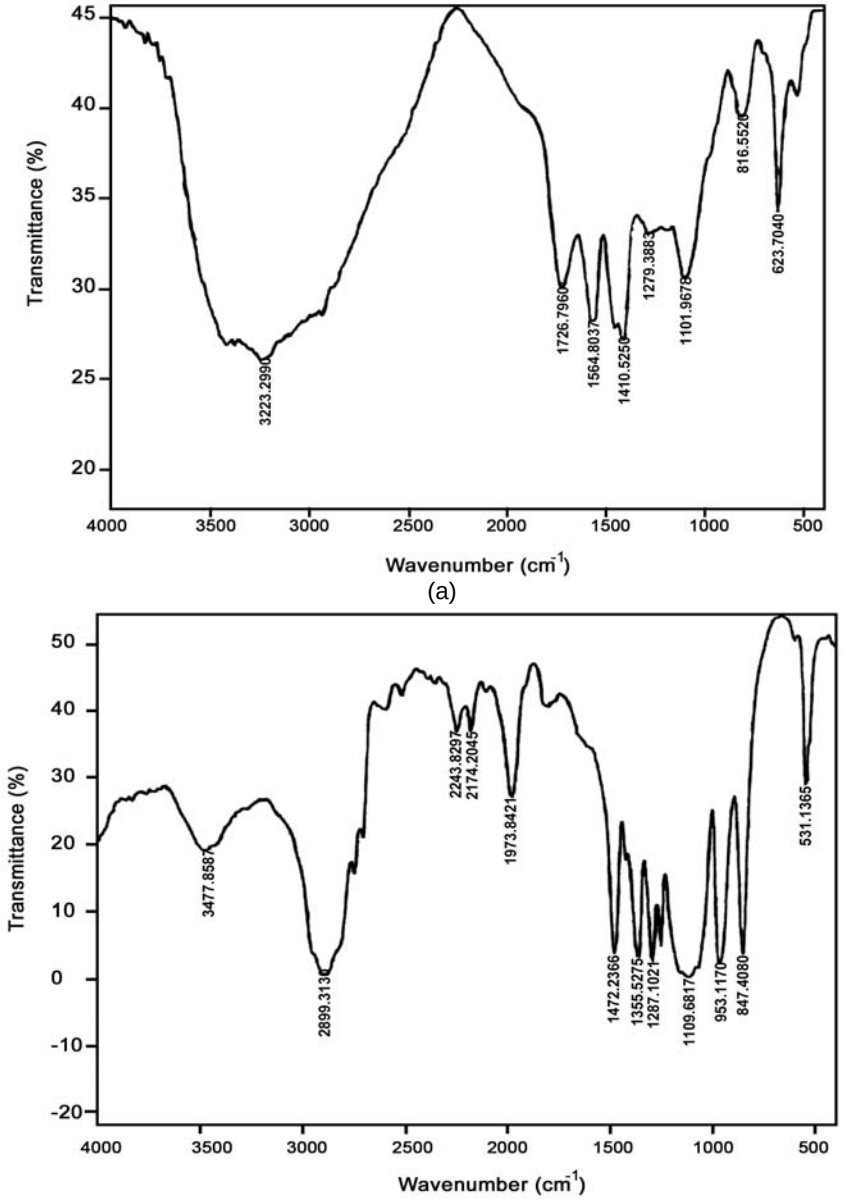


Figure 7. FTIR Spectra of: (a) ammonium salt of polyacrylic acid (Darvan 821A), and (b) polyethylene glycol 6000.

repulsive electrostatic effect) and hence decreases the stability of suspensions [3,10-11].

Figure 7 shows FTIR spectra of polymeric dispersant (Darvan 821A) and polymeric binder (PEG 6000). As shown in this figure, at 1500-1800 cm^{-1} wavenumbers, the peaks of two polymeric additives interfer with each other. Therefore, these peaks cannot be used for qualitative analysis of free polymeric species in the supernatant liquid. Polyethylene glycol has a characteristic peak in 1973 cm^{-1}, but Darvan 821A has no detectable peak in this region. Therefore, this peak may be suitable for determination of the remained free polymeric species in the supernatant

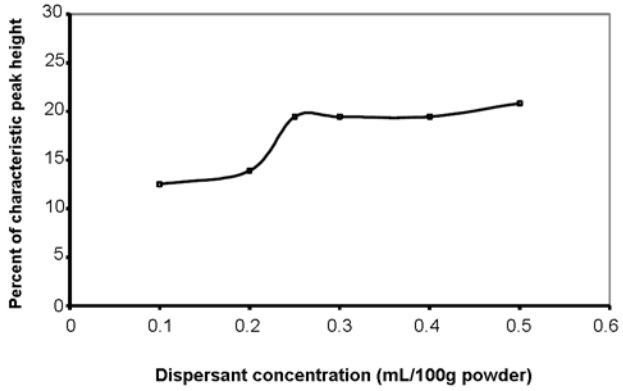
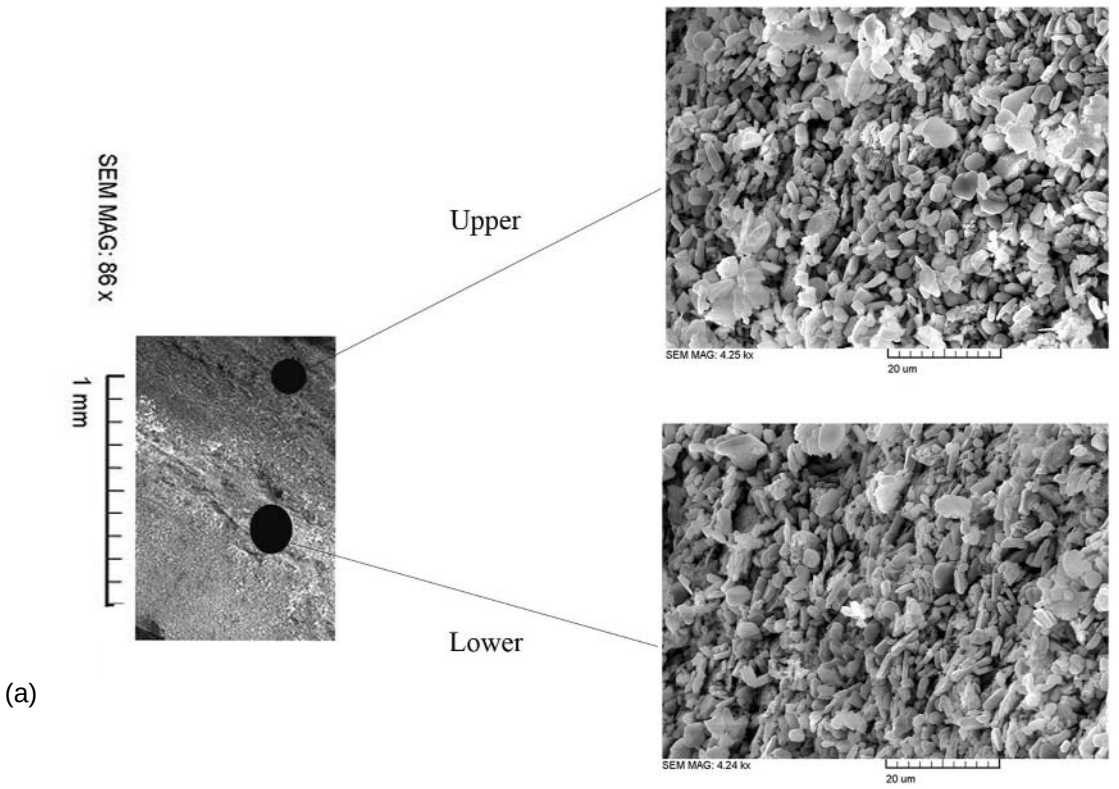
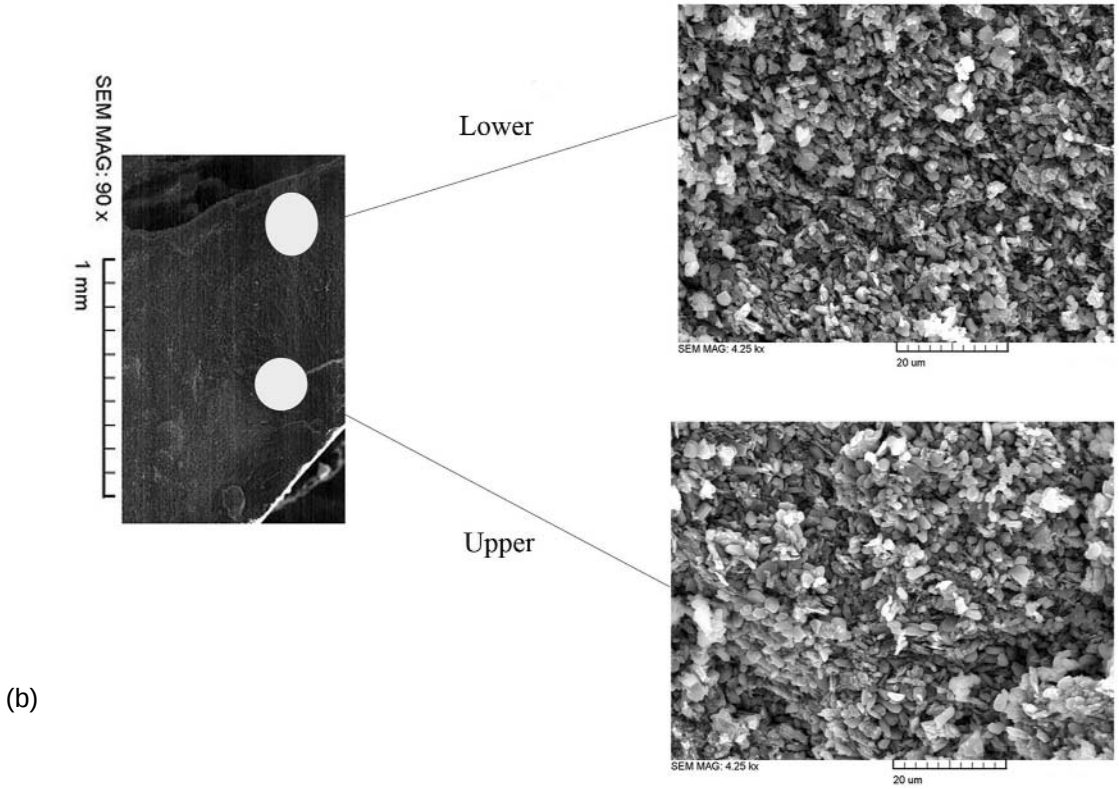


Figure 8. Effect of dispersant concentration on remained polymeric binder in the supernatant liquid.



(a)



(b)

Figure 9. SEM Micrographs of the sediment layers obtained from suspension with: (a) optimum dispersant concentration, and (b) optimum dispersant and binder concentration.

liquid. Analysis of FTIR spectra of the remained polymeric species has been shown in Figure 8 as percentage of characteristic peak height versus dispersant concentration. As shown in Figure 8, increasing thedispersant concentration results in increase of thecharacteristic peak height which confirms the increasing the free polymeric binder in the bulk of solution. characteristic peak height which confirms the increasing the free polymeric binder in the bulk of solution. These results are in good agreement with the sedimentation experiments data.

For illustration the effect of the presence of dispersant-binder on the stability of alumina suspensions in long times, SEM micrograph of cross-section of sediment layers obtained from suspension containing optimum dispersant and optimum binder-dispersant concentrations are presented in Figure 9. The presence of binder causes non-homogeneity of sediment layer microstructure compared to suspension which has only dispersant as polymeric additive. These results confirm the results obtained from the sedimentation experiments, viscosity measurements and FTIR analysis.

CONCLUSION

Based on the work done in this research, the following conclusions can be presented:

- Binder molecular weight

The stability behaviour of 5 wt% alumina suspensions in the presence of different PEG molecular weights ranging from 2000 to 35000 was investigated by a sedimentation technique. The PEG molecular weight which corresponded to the optimum dispersion state was determined to be 6000. Higher increase of PEG molecular weight causes instability of the alumina suspensions via bridging flocculation.

- Binder concentration

The effect of binder concentration on stability of the alumina suspensions was critical. At 5 wt% (based on powder weight) of PEG 6000 a good dispersion of alumina particles was obtained which is attributed to steric stabilization mechanism due to adsorption of binder chains on the surface of colloidal particles. Further increase in binder concentration results in flocculation of the alumina particles by depletion mechanism.

- Binder and polymeric dispersant interaction

The results of sedimentation experiments and FTIR spectra analysis of the remained polymeric species in the supernatant liquid showed that the presence of polymeric binder decreases the electrosteric effect of polymeric dispersant on stability of the alumina suspensions. Increasing the dispersant concentration results in increasing the free polymeric binder in the bulk of solution which causes instability of alumina suspensions via depletion mechanism. In spite of the negative effect of the polymeric binder in the presence of the polymeric dispersant on the colloidal alumina suspensions stability, the optimum value of dispersant concentration was determined to be 0.2-0.3 mL/100 g powder which is in good agreement with literature [25].

On the basis of these conclusions, process guidelines can be established for fabricating ceramic articles from the colloidal alumina suspensions with different polymeric additives.

ACKNOWLEDGEMENT

The authors wish to thank Sahand University of Technology (SUT) for the financial support of this work. Also, we thank co-workers and technical staff in the Research Centre for Polymeric Materials at SUT for their help during various stages of this work.

REFERENCES

1. Sundlof R.B., Perry R.C., Klingenberg H.E., Schultz A.L., Additives interactions in ceramic processing, *Am. Ceram. Soc. Bull.*, **79**, 67-72, 2000.
2. Shi C.Y., Wu S.Y., Li G.J., Li Z.G., Surface and rheology characterization of NH_4PAA-stabilized nanosized TiO_2 suspensions, *J. Dispersion Sci. Technol.*, **24**, 739-743, 2003.
3. Shen G.Z., Chen F.J., Zou K.H., Yun J., Dispersion of nanosized aqueous suspensions of barium titanate with ammonium polyacrylate, *J. Colloid Interface Sci.*, **275**, 158-164, 2004.
4. Kamiya H., Fukuda Y., Suzuki Y., Tsukada M.,

Effect of polymer dispersant structure on the electrosteric interaction and dense alumina suspensions behavior, *J. Am. Ceram. Soc.*, **82**, 3407-3412, 1999.
5. Shih J.C., Hon M.H., Stabilization of aqueous Si_3N_4 suspensions with ammonium salt of poly(acrylic acid) at various pH, *Mater. Chem. Phys.*, **57**, 125-133, 1998.
6. Davis J., Binner J.G.P., The role of ammonium polyacrylate in dispersing concentrated alumina suspensions, *J. Eur. Ceram. Soc.*, **20**, 1539-1553, 2000.
7. Sun J., Gao L., Guo J., Influence of the initial pH on the adsorption behavior of dispersant on nano zirconia powder, *J. Eur. Ceram. Soc.*, **19**, 1725-1730, 1999.
8. López M.C.B., Rand B., Riley F.L., Polymeric stabilisation of aqueous suspensions of barium titanate, Part I: Effect of pH, *J. Eur. Ceram. Soc.*, **20**, 1579-1586, 2000.
9. Santhiya D., Nandini G., Subramanian S., Natarajan K.A., Malghan S.G., Effect of polymer molecular weight on the adsorption of polyacrylic acid at the alumina-water interface, *Colloids Surf. A: Physicochem. Eng. Aspec.*, **133**, 157-163, 1998.
10. Greenwood R., Bergström L., Electroacoustic and rheological properties of aqueous Ce-ZrO_2 (Ce-TZP) suspensions, *J. Eur. Ceram. Soc.*, **17**, 537-548, 1997.
11. Shojai F., Pettersson A.B.A., Mäntylä T., Rosenholm J.B., Electrostatic and electrosteric stabilization of aqueous slips of 3Y-ZrO_2 powder, *J. Eur. Ceram. Soc.*, **20**, 277-283, 2000.
12. Liu Y., Gao L., Sun J., Effect of acrylic copolymer adsorption on the colloidal stability of a 3Y-TZP suspension, *J. Eur. Ceram. Soc.*, **22**, 863-871, 2002.
13. Khan A., Brisco B., Luckham P., Interaction of binders with dispersant stabilized alumina suspensions, *Colloids Surf. A: Physicochem. Eng. Aspec.*, **161**, 243-257, 2000.
14. Romdhane M.R.B., Baklouti S., Bouaziz J., Chartier T., Baumard J.F., Dispersion of Al_2O_3 concentrated suspensions with new molecules able to act as binder, *J. Eur. Ceram. Soc.*, **24**, 2723-2731, 2004.
15. Walker W., Reed J., Adsorption behavior of poly(ethylene glycol) at the solid/liquid interface, *J. Am. Ceram. Soc.*, **82**, 585-590, 1999.
16. Yoon D., Lee B., Processing of barium titanate tapes with different binders for MLCC applications, Part I: Optimization using design of experiments, *J. Eur. Ceram. Soc.*, **24**, 739-752, 2004.
17. Yoon D., Lee B., Processing of barium titanate tapes with different binders for MLCC applications, Part II: Comparison of the properties, *J. Eur. Ceram. Soc.*, **24**, 753-761, 2004.
18. Dasgupta S., Adsorption behavior of macromolecules on colloidal magnetic oxide particles: Interfacial interaction and dispersion characteristics, *Prog. Org. Coat.*, **19** , 123-139, 1991.
19. Kristoffersson A., Lapasin R., Gallasi C., Study of interactions between polyelectrolyte dispersant, alumina and latex binders by rheological characterisation, *J. Eur. Ceram. Soc.*, **18**, 2133-2140, 1998.
20. Paik U., Hackley V.A., Lee H.W., Dispersant-binder interactions in aqueous silicon nitride suspensions, *J. Am. Ceram. Soc.*, **82**, 833-840, 1999.
21. Singh B.P., Besra L., Bhattacharjee S., Factorial design of experiments on the effect of surface charges on stability of aqueous colloidal ceramic suspension, *Colloids Surf. A: Physicochem. Eng. Aspec.*, **204** , 175-181, 2002.
22. Wei W.C.J., Lu S.J., Yu B.K., Characterisation of submicron alumina dispersion with poly-(methacrylic acid) polyelectrolyte, *J. Eur. Ceram. Soc.*, **15**, 155-164, 1995.
23. Liufu S., Xiao H., Li Y., Adsorption of poly(acrylic acid) onto the surface of titanium dioxide and colloidal stability of aqueous suspension, *J. Colloid Interface Sci.*, **281**,155-163, 2005.
24. Mao Y., Cates M.E., Lekerkerker H.N.W., Depletion force in colloidal systems, *Physica A*, **222**, 10-24, 1995.
25. Barati A., Kokabi M., Babaluo A.A., Effect of poly(methacrylic acid) polyelectrolytes on stability of alumina suspension systems, *Iran. Polym. Sci. Tech. (Persian Ed.)*, **15**, 131-141, 2002.