

# Stabilization of alumina with polyelectrolyte and comb copolymer in solvent mixtures of water and alcohols

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## Abstract

Solvent mixtures of water and ethanol and water and isopropanol have been evaluated for processing of concentrated alumina suspensions. The addition of alcohols may increase the long-term stability of suspensions with soluble ceramic species such as magnesia, which is added as a sintering aid. A poly(acrylic acid) and a hydrophilic comb copolymer were used as dispersants for the different solvent mixtures. The aim was to compare the stabilization efficiency at normal processing conditions, pH 9–10, through rheological measurements and to develop a robust system including magnesia with long-term stability. The electrostatic stabilization of the dispersants in the different solvent mixtures was studied by zeta potential measurements. Highly negative zeta potentials were observed for the poly(acrylic acid) at pH 9–10 in the solvent mixtures. A charge contribution was also seen from the adsorbed comb copolymer, however smaller than for the poly(acrylic acid). Low viscosity was obtained for suspensions stabilized with poly(acrylic acid) in solvent mixtures with either 25 vol% ethanol or isopropanol. Higher alcohol to water ratio led to flocculation of the suspension when poly(acrylic acid) was used as dispersant. Alumina suspensions with added magnesia in isopropanol:water 25:75 and poly(acrylic acid) as dispersant showed long-term stability. The viscosity remained almost constant during 4 days of aging. Suspensions stabilized with the comb copolymer dispersant gave stable systems with ethanol and isopropanol concentrations between 25 and 75 vol%. The superior dispersing efficiency of the comb copolymer at alcohol contents above 25 vol% was believed to originate from steric stabilization in combination with low effective particle size, giving low viscosity through lower apparent solid contents of the suspension.

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**Keywords:** Suspensions; Dispersants; Shaping; Al<sub>2</sub>O<sub>3</sub>; MgO

## 1. Introduction

Many ceramic forming-processes involve the preparation of highly concentrated powder suspensions prior to the shaping step. High solid loading is desirable since it normally promotes high shaped density and, therefore, reduces stresses induced by large shrinkage during drying and sintering.<sup>1</sup> The stability and rheological behavior of the suspension are important for the final quality of the ceramic component. A well-dispersed system with low viscosity will enable proper mould-filling and result in dense/homogeneous compacts in casting operations. Voids from air entrapment can be avoided by low viscosity and good wetting performance. Furthermore, milling of the powder suspension

minimizes defects due to poor deagglomeration. After milling, the particles should be stabilized by electrostatic and/or steric dispersants to remain separated.

Owing to environmental and health aspects there is a need for using non-organic solvents in the ceramics industry today. Thus, for many established and novel shaping techniques for ceramics such as slip casting, tape casting and gel casting, water-based systems with acceptable performance have been developed.<sup>2–7</sup> However, there are a few drawbacks of using water to replace common organic solvents. The high surface tension of water results in poor cavity filling in moulds, problems with air entrapment as well as deformations of ceramic tapes due to poor wetting of the carrier during tape casting. Moreover, many ceramic materials show substantial solubility and/or reactivity in water. The dissolved species may cause inhomogeneous chemical composition of the final material, as they will precipitate at the surface of the components during drying. They may also

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destabilize the suspensions through increased ionic strength, and even react with other additives in the suspension. One example is aqueous processing of barium titanate, which is used for multilayer capacitors for high frequencies. The  $\text{Ba}^{2+}$  ions will dissolve selectively, and the divalent ions increase the ionic strength of the suspension. The selective dissolution also changes the surface properties of the remaining powder by changing the zeta potential. Furthermore, the dissolved barium ions tend to react with some water soluble polymers that are often used as binders, and create cross linking.<sup>8</sup> Another example is when magnesia is used as a sintering aid to obtain high sintered densities in alumina components. It is known that aqueous suspensions of alumina and magnesia often show low stability,<sup>9,10</sup> which is attributed to high dissolution rates of divalent  $\text{Mg}^{2+}$  ions. Some of these problems may be overcome by using solvents that are environmentally acceptable yet have lower surface tension than water and suppress dissolution of ceramic powders. Alcohols with low molecular weights are interesting, as they have low toxicity, low surface tension and medium polarity. They are not new in ceramic processing, although very few studies of water-based solvent mixtures are reported. Successful processing of barium titanate in water and 22 vol% isopropanol<sup>11</sup> as well as the use of water and 1,2-propanediol for dispersions of nano-sized zirconia<sup>12</sup> has been described. The use of pure alcohols in milling operations prior to granulation and drying gives a highly fluid powder, resulting in high compaction density in the subsequent pressing operation compared to water.

Furthermore, the properties of the dispersant must be taken into account in ceramic processing. The stabilization efficiency of poly(acrylic acid)s as dispersants for aqueous ceramic systems is well established.<sup>13–16</sup> The ionic strength of the suspension affects the efficiency of commonly used polyelectrolyte dispersants, which act mainly by electrostatic stabilization. They are very effective at moderately high ionic strengths, but they may lose some of their electrostatic repulsion ability at high salt concentrations due to counter ion screening of the charges.<sup>17,18</sup>

Moreover, when alcohols are used as solvent, their low permittivity leads to compression of the diffused double layers of the particles. Thus, electrostatic stabilization may not be effective, although high zeta potentials have been reported for alumina dispersed in ethanol at low concentrations.<sup>19</sup> However, in suspensions with high solid-loadings, the ceramic particles are mechanically forced close to each other. This may lead to instability in suspensions that are stabilized by electrostatic repulsion only,<sup>16</sup> since the electrostatic double layers of the particles begin to overlap when the particles are forced together. Due to this, the efficiency of commonly used polyelectrolyte dispersants such as poly(acrylic acid)s may be reduced. Instead, a dispersant with the possibility of providing steric repulsion may be more efficient. Steric stabilizers are often block copolymers, with the backbone adsorbing strongly to the surface to be stabilized, and with grafted chains as brushes that move freely in the solvent.<sup>20</sup> Non-ionic comb copolymers are relatively insensitive to high ionic strengths, and may be efficient stabilizers in highly concentrated ceramic suspensions. Adsorbed on alumina in water,

they have shown to provide steric stabilization.<sup>21</sup> Dispersion stability was also observed with a comb copolymer for barium titanate in water/isopropanol mixture.<sup>11</sup>

The aim of this study has been to evaluate the rheological and wetting behavior of solvent mixtures of ethanol/water and isopropanol/water. Alumina suspensions were prepared with a poly(acrylic acid) as well as a comb copolymer with grafted poly(oxyethylene) chains as dispersants. Charge properties of alumina particles with adsorbed dispersants were studied by zeta potential. Stability of suspensions was evaluated by viscosity measurements at different alcohol/water ratios. A stable system based on alcohol/water as solvent was developed for alumina suspensions with addition of magnesia.

## 2. Experimental procedure

### 2.1. Materials

Alumina powder (AKP30, Sumitomo Chemicals Ltd., Japan) was used as received for all rheological experiments. The powder has a mean particle diameter of 270 nm and a specific surface area of 6.8 m<sup>2</sup>/g. Deionized water, 99.5% ethanol (Kemetyl AB, Sweden) and analytical grade isopropanol, 99.8% (Analytical grade, Merck KGaA, Germany) were used as solvents. The dispersants were commercial products provided by the manufacturers. They were used as received. The poly(acrylic acid) (Dolapix PC21, Zschimmer & Schwartz GmbH & Co, Germany) is linear with  $\text{NH}_4^+$  as counter ion and has a molecular weight of about 4500. A hydrophilic comb copolymer with a polymethylmethacrylate anchor chain and grafted poly(oxyethylene) chains (Hypermer KD7, Uniqema Chemie BV, Netherlands) and a molecular weight of 3000 was also used.

### 2.2. Viscosity measurements

Samples with 50 vol% alumina for rheological evaluations were prepared by ball-milling for 24 h in plastic containers with  $\text{Si}_3\text{N}_4$  balls. The suspensions were equilibrated on a magnetic stirrer prior to characterization. The processing experiments were done at the natural pH  $9.5 \pm 0.5$  of the suspensions. For long-term stability experiments, 0.05 wt% magnesia based on solid matter was added to the suspensions before milling. Rheological characterization of suspensions was done at steady shear conditions. Viscosity was measured in a rotational stress controlled rheometer (StressTech, Reologica Instruments AB, Sweden) with cup and couette at different shear rates. The samples were pre-sheared at 400 s<sup>-1</sup>, at rest for 60 s, and then equilibrated at each shear rate for 60 s followed by a measurement period of 60 s. For pure solvent mixtures the viscosity was determined with a viscosimeter (Rheomat 30, Contraves, Switzerland) equipped with a measure device (MS-0) with a double gap.

### 2.3. Zeta potential and surface tension measurements

Samples with 1 vol% alumina in different solvent mixtures and 0.01 M KCl as background electrolyte were prepared

by ball-milling for 24 h in plastic containers with  $\text{Si}_3\text{N}_4$  balls. pH adjustments were done with analytical grades of NaOH and HCl. Zeta potential measurements were done with an Acoustosizer (Matec Applied Sciences) by means of electrokinetic sonic amplitude, ESA. Details about the technique can be found elsewhere.<sup>22</sup> The dynamic mobility was measured by means of automatic titration between pH 12 and 2.

Surface tension was measured with a Wilhelmy plate set-up.

### 3. Results and discussion

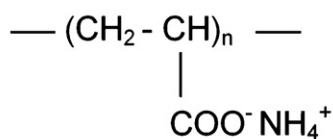
#### 3.1. Structures of the dispersants used

The structures of the dispersants are schematically illustrated in Fig. 1. The poly(acrylic acid) has a molecular weight of 4500 and  $\text{NH}_4^+$  as counter ion. NMR analysis indicates that the comb copolymer is a copolymer between methacrylic acid and ethoxylated hydroxyethylmethacrylate. The mass of the poly(oxyethylene) (PEO) chains constitutes about 60% of the total molecular mass of 3000.

#### 3.2. Surface tension

The surface tension was measured for a solvent mixture with 25 vol% isopropanol and found to be 28 mN/m, i.e. close to the value 21 mN/m for pure isopropanol, and considerably lower than 73 mN/m for water. Low surface tension of 33 mN/m was also observed in a suspension prepared with 50 vol% alumina in 25% isopropanol. Hence, the wetting properties can be expected to improve considerably for solvent mixtures already at moderate alcohol addition.

#### (a) Polyacrylic acid



#### (b) Comb copolymer (PMMA/PEO)

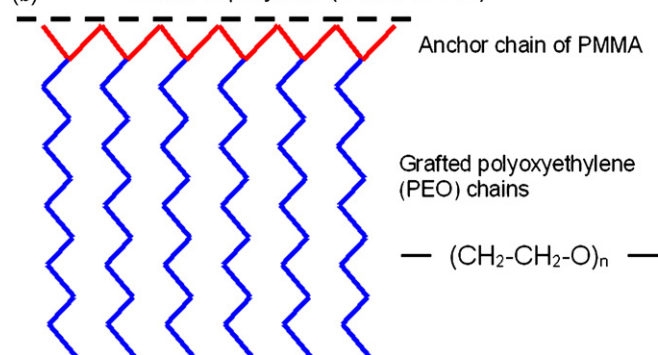


Fig. 1. Schematic drawing of the structure of (a) ammonium salt of poly(acrylic acid) and (b) poly(methyl methacrylic acid)-graft-poly(oxyethylene) comb copolymer.

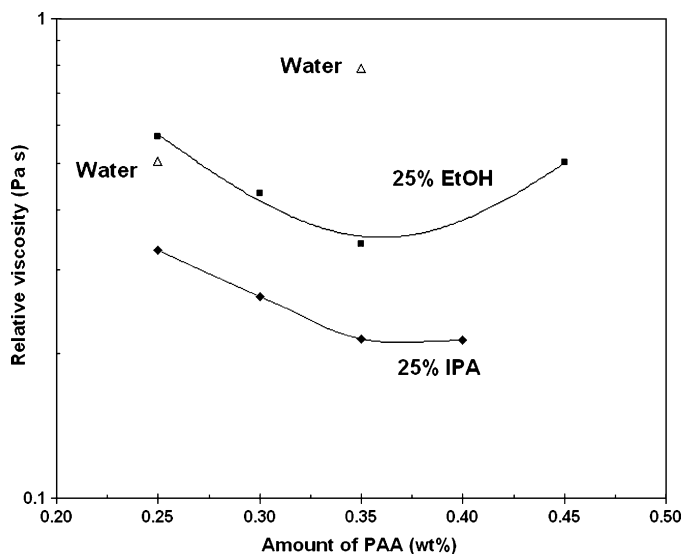


Fig. 2. Relative viscosity at  $1 \text{ s}^{-1}$  vs. amount of added poly(acrylic acid) (PAA) for suspensions with 50 vol% alumina in solvent mixtures of water and either isopropanol (IPA) or ethanol (EtOH).

#### 3.3. Optimization of amount of dispersant by viscosity measurements

In order to compare the relative efficiency of the dispersants for different solvent mixtures, the rheological response is shown as relative viscosities in the optimization experiments presented in Figs. 2–4. The relative viscosity was calculated from experimental data of the steady shear viscosity divided by the viscosity of the pure solvent mixture. The equilibrium viscosities for the pure solvent mixtures are shown in Table 1, and are in close agreement with literature values.<sup>23</sup> A viscosity maximum is observed for the alcohol/water ratio of approximately 1 for both ethanol and isopropanol. Hence, a corresponding influence on the viscosity of a powder suspension can be expected.

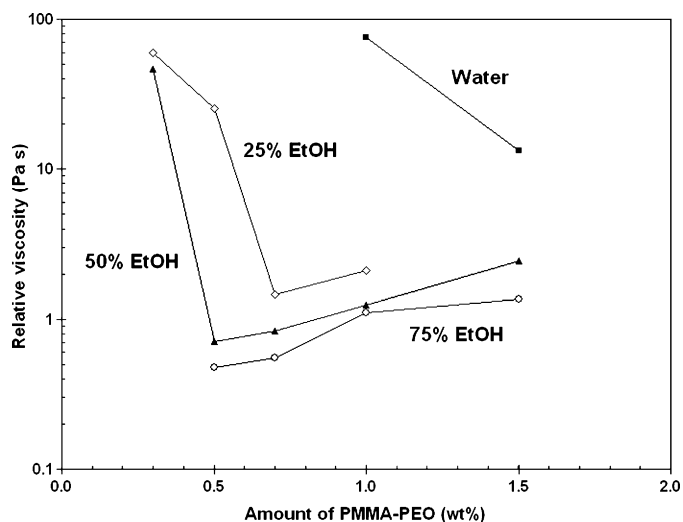


Fig. 3. Relative viscosity at  $1 \text{ s}^{-1}$  vs. amount of added comb copolymer (PMMA-PEO) for suspensions with 50 vol% alumina in solvent mixtures of water and ethanol (EtOH).

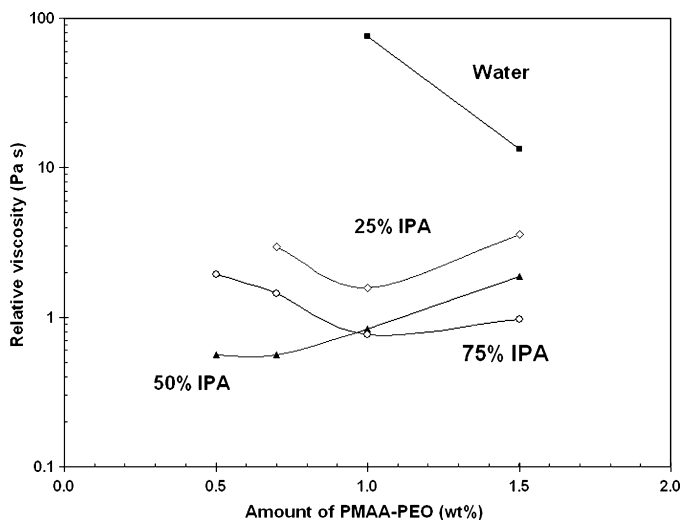


Fig. 4. Relative viscosity at  $1\text{ s}^{-1}$  vs. amount of added comb copolymer (PMMA-PEO) for suspensions with 50 vol% alumina in solvent mixtures of water and isopropanol (IPA).

The optimum dispersant concentration is the one that gives the lowest suspension viscosity. At that concentration, coverage of the surfactant in a monolayer is considered,<sup>24</sup> the particles are effectively kept apart and high fluidity is obtained. At lower dispersants concentration the surface is not fully covered by surfactant. Then flocculation may occur due to attraction between positively charged bare surface patches and negatively charged surfaces with adsorbed polyelectrolyte. On the other hand, excess of dispersant can cause flocculation due to bridging or depletion effects, leading to increased viscosity.

### 3.3.1. Poly(acrylic acid) (PAA)

Fig. 2 shows relative viscosities vs. amount of added poly(acrylic acid) for suspensions with 50 vol% alumina in solvent mixtures with either 25 vol% ethanol or 25 vol% isopropanol. At higher additions of alcohol the suspensions became unstable with poly(acrylic acid) as dispersant, and could not be processed due to flocculation. As seen, the lowest viscosity levels are obtained with 0.35 wt% poly(acrylic acid) for the ethanol and in the range of 0.35–0.40 wt% for the isopropanol mixture. The relative viscosity level of the suspension with ethanol is already close to that of water with 0.25 wt% of poly(acrylic acid) (also shown in Fig. 2), which has previously been shown as an optimal amount in water.<sup>21</sup> At the optimal dispersant level for the alcohol mixtures, the relative viscosity is clearly lower than with pure water at similar dispersant concentration. With 25% isopropanol, the viscosity level is even lower than with the pure water system at its optimal dispersant

Table 1  
Equilibrium viscosities for solvent mixtures without ceramic powder

Alcohol concentration (vol%) in alcohol/water mixture	Equilibrium viscosity (mPa s)	
	Ethanol	Isopropanol
0	1.0	1.0
25	2.2	2.5
50	2.5	3.8
75	2.2	3.3

concentration, indicating a highly dispersed suspension. Here, it could be expected that the charges would be less effective due to less extended double layers as well as lower dissociation, since the solvent mixture has lower dielectric constant than water.<sup>25</sup> However, considerable electrostatic repulsion has been observed previously for alumina in ethanol, which is less polar than water.<sup>19</sup> Moreover, the poly(acrylic acid) will have higher affinity for the particle surface in alcohols compared to water due to lower solubility, which would lead to a higher number of ionizable groups at the surface. Thus, more efficient adsorption of the poly(acrylic acid) in the mixed system could contribute to electrostatic stabilization. Moreover, steric repulsion is possible if the adsorbed dispersant is extended in a loop conformation at the surface rather than in a flat adsorption.<sup>17</sup> Flat adsorption is expected in water, but lower dissociation degree in alcohol mixtures would favor the formation of loops. The extension of loops from the surface in combination with denser packing could give steric repulsion in addition to the electrostatic stabilization.

### 3.3.2. Comb copolymer (PMMA-PEO)

The results from relative viscosity measurements vs. added amount of comb copolymer dispersants are shown in Fig. 3 for solvent mixtures of water and ethanol and in Fig. 4 for water and isopropanol mixtures. Clearly, stabilization is obtained in alcohol mixtures with this dispersant, as it was possible to process well dispersed suspensions with low viscosities both at 50 and 75 vol% alcohol for both systems, in contrast to the poly(acrylic acid) suspensions. The figures also show that the viscosity for pure water suspensions stabilized with this comb copolymer is very high, and thus, the dispersant is not efficient in water. Both the relative viscosity and the amount of dispersant needed to obtain low viscosity decrease with increased ethanol concentration, as seen in Fig. 3.

The amounts giving the lowest viscosities are in the range of 0.7 wt% for mixtures with 25 vol% ethanol and 0.5 wt% for both 50 and 75 vol% ethanol. As seen in Fig. 4, the optimum amounts of comb copolymer are around 1.0 wt% for both 25 and 75 vol% isopropanol, whereas for 50% isopropanol/water mixture about 0.5 wt% is needed.

The superior performance of the comb copolymer at high alcohol concentrations compared to the poly(acrylic acid) may be explained by the steric stabilization possibility from the extending poly(oxyethylene) chains. In water, the extension of these chains may not be long enough to overcome the van der Waals attraction between the particles, and thus, stabilization is insufficient. However, as the alcohol concentration increases, the van der Waals attraction decreases, since it depends on the Hamaker constant which is lower in less polar media due to the lower dielectric constants.<sup>12</sup> Therefore, it may be possible for the extending chains to give sufficient steric repulsion.

### 3.4. Suspension viscosity with optimized amount of dispersant

For industrial processes, the actual viscosity of a ceramic suspension is more important than the relative viscosity values

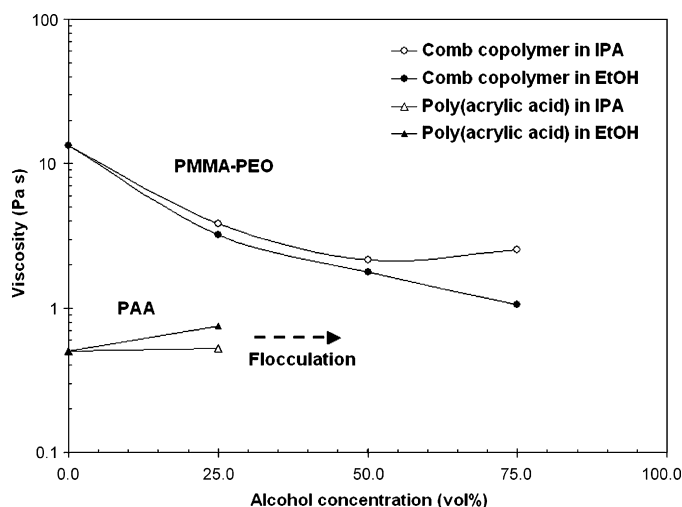


Fig. 5. Viscosity at a shear rate of  $1 \text{ s}^{-1}$  vs. alcohol concentration for 50 vol% alumina suspensions with optimized amounts of poly(acrylic acid) (PAA) and comb copolymer (PMMA-PEO) in various solvent mixtures.

used for the optimization above. In contrast to relative viscosity values, the suspensions viscosity will be higher for a mixed system with higher alcohol concentration compared to a pure water system. This is shown in Fig. 5 for alumina suspensions with the different solvent mixtures stabilized with optimized amounts of either poly(acrylic acid) or comb copolymer. From the figure it is clear that the lowest viscosity is obtained with a poly(acrylic acid) as dispersant for pure water and for 25 vol% isopropanol/water. However, this dispersant did not give stable systems at higher alcohol concentrations due to flocculation. If more alcohol is needed in the system due to, for example, high dissolution rate of the ceramic powder, it is still possible to obtain a highly dispersed system by using the comb copolymer as dispersant. However, the viscosity for such a system will be higher than the corresponding system with pure water or 25% alcohol and poly(acrylic acid). All of the suspensions have viscosity levels low enough to be successfully processed in for example a tape casting operation.

### 3.5. Long-term stability of alumina suspensions with magnesia

Magnesia is often added to alumina suspensions as a sintering aid to suppress grain growth. However,  $\text{Mg}^{2+}$  dissolves selectively in water-based systems, which increases the ionic strength and gives low long-term suspension stability<sup>9,10</sup> as well as inhomogeneous chemical composition. For industrial purposes it is not only important to have low viscosity, but also that the process parameters are constant over time, i.e. the viscosity should not change. Here, the possibility of increasing the stability by adding alcohol was studied. The system with the highest stability from the optimization experiments, i.e. 25-vol% isopropanol and 0.35-wt% poly(acrylic acid) was compared to an optimized water suspension with 0.25 wt% poly(acrylic acid). Fig. 6 shows the results from aging experiments of 50 vol% alumina suspensions with additions of 0.05 wt% magnesia (MgO). As shown, the initial viscosity level, directly after preparation, is low for the

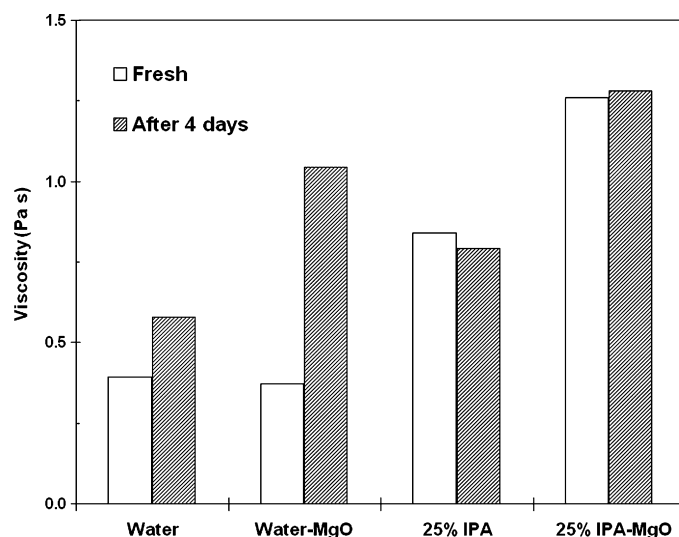


Fig. 6. Steady shear viscosity at  $1 \text{ s}^{-1}$  of 50 vol% alumina suspensions with and without addition of 0.05 wt% magnesia in water and 25 vol% isopropanol/water.

water-based systems, and no negative effect of magnesia addition is observed. The viscosity for the suspension containing isopropanol is higher than the water systems, and the addition of magnesia has a negative influence. After 4 days of aging, the viscosities for suspensions with isopropanol are very similar to the initial values. However, the viscosity has increased considerably for the water-based system, containing magnesia, and a slight increase is also seen in water without the addition of magnesia. Hence, by adding a relatively small amount of the low molecular weight alcohol, the long-term stability of the suspensions can be increased.

### 3.6. Zeta potentials of alumina in solvent mixtures

#### 3.6.1. Without adsorbed dispersants

Zeta potentials were calculated from measured dynamic mobility values according to the Smoluchowski equation<sup>26</sup>

$$\mu = \frac{\xi \varepsilon}{\eta} \quad (1)$$

where  $\mu$  is the dynamic mobility,  $\xi$  is the zeta potential,  $\varepsilon$  is the permittivity of the solvent and  $\eta$  is the solvent viscosity. For the calculations, input values of viscosity of the mixtures with different alcohol/water ratios were measured (Table 1), and the dielectric constants were estimated by linear extrapolation from literature values of the pure solvents.<sup>23</sup> In systems with different solvent mixtures, the zeta potential will increase with increasing solvent viscosity as well as decreasing permittivity of the solvent. Moreover, the dissociation degree of the background electrolyte may vary slightly for the different solvent mixtures, which leads to small variations in ionic strength. Thus, in this study, general trends of the different systems were compared, rather than absolute values of the zeta potentials.

In Fig. 7 the zeta potentials of pure alumina suspended in solvent mixtures of water and isopropanol are shown. The isoelectric point (iep) for pure alumina in water was found to be approximately 8.1, which is in agreement with previous

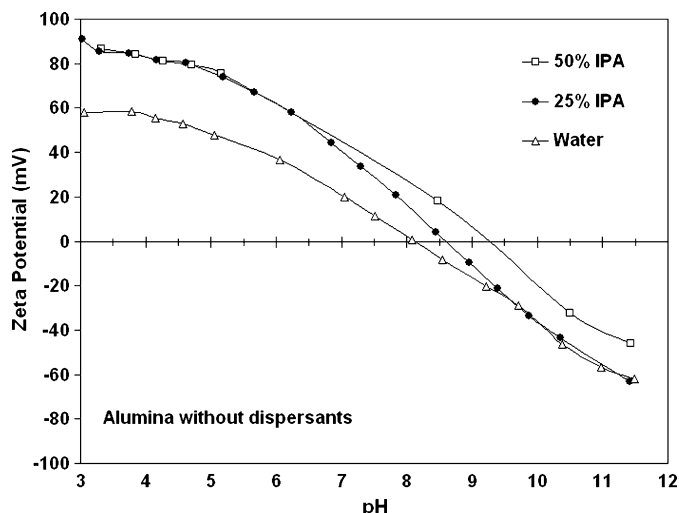


Fig. 7. Zeta potentials of pure alumina in solvent mixtures of water and isopropanol. Titration conducted from high to low pH.

reports.<sup>27</sup> High zeta potentials are observed at high and low pH, not only for the water system but also for the solvent mixtures with isopropanol. Earlier studies of alumina in pure ethanol have shown similar, high zeta potentials far from the iep.<sup>19</sup> A small shift in the isoelectric point towards higher pH is observed with increasing alcohol concentration, also in agreement with earlier observations.<sup>19</sup>

Previous studies have shown that high stability in terms of low viscosity can be obtained with alumina in pure ethanol at pH far from the iep without the addition of dispersants.<sup>19</sup> However, in the system presented here, the normal processing pH is around 9.5, i.e. fairly close to the shifted iep in the alcohol mixtures. A zeta potential of at least  $\pm 30$  mV is said to be a requirement for electrostatic stabilization without the need for dispersants.<sup>28</sup> As the iep shifts towards higher pH in the mixtures containing alcohol, the zeta potential without dispersants becomes too low for efficient stabilization at pH 9–10. A reliable industrial system must be insensitive to small changes in pH, and thus a dispersant is added to improve the stabilization by electrostatic and/or steric repulsion.

### 3.6.2. With adsorbed dispersants

Fig. 8 shows zeta potentials for alumina in solvent mixtures of isopropanol and water with adsorbed poly(acrylic acid) and comb copolymer. It can be seen that both the poly(acrylic acid) and the comb copolymer shift the isoelectric point of alumina to lower pH, which is a clear indication of adsorption of dispersant onto the alumina surface. The strongest shift in iep is observed for the poly(acrylic acid), to pH 4.6 for water and 5.0 for water/isopropanol. The slightly higher iep for the alcohol containing system is consistent with the observations for pure alumina in Fig. 7. High zeta potential is observed far from the iep. The poly(acrylic acid) will be less dissociated in alcohols compared to water, and one may then expect lower zeta potential values. However, the poly(acrylic acid) has lower solubility in alcohol compared to water,<sup>29</sup> and will thus adsorb more strongly to the oxide surface in a suspension containing alcohol. This was

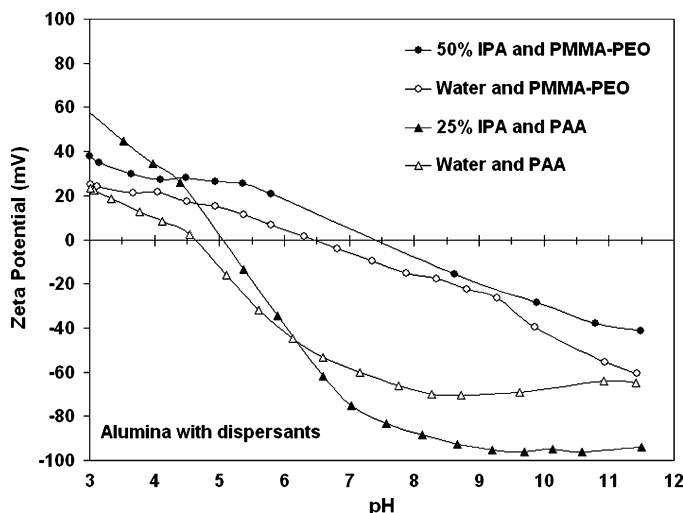


Fig. 8. Zeta potentials of alumina with adsorbed poly(acrylic acid) and comb copolymer in solvent mixtures of water and isopropanol. Titration conducted from high to low pH.

also found in the optimization step, where 0.35 wt% PAA gave the lowest viscosity for both ethanol and isopropanol compared to 0.25 wt% PAA in water (Fig. 2). More adsorbed PAA could counteract the lower charge due to lower dissociation degree, and thus result in retained high zeta potential. The shift in iep is less-pronounced for alumina with adsorbed comb copolymer, with new isoelectric points of 6.5 for the water-based system and 7.4 with 50% IPA. Interestingly, fairly high zeta potential is observed near processing pH of 9–10 also for the comb copolymer, which brings a possibility for electrostatic interaction in addition to steric repulsion.

### 3.7. Effective particle size with comb copolymer in different solvent mixtures

The solubility of PEO chains is progressively poorer in ethanol and isopropanol compared to water due to less hydrogen bonding and polar interactions.<sup>30</sup> Thus, the PEO chains can be fully stretched in water, whereas in ethanol and even more so in isopropanol, the chains will adopt a more coiled conformation at the oxide surface. The less extended conformation is expected to decrease the possibility for steric stabilization. However, less extended chains will give a thinner dispersant layer, which could be beneficial in a highly concentrated particle suspension. The reduced thickness will give a smaller effective particle size,<sup>31</sup> resulting in lower apparent solids content of the ceramic suspension. This could account for the observed decrease in viscosity at higher alcohol concentrations for the suspensions stabilized with the comb copolymer. Moreover, the volume of solvent associated with the comb copolymer layer will be lower for ethanol, and in particular for isopropanol, compared to pure water systems.<sup>30</sup> This will also contribute to a smaller hydrodynamic particle diameter and thus, smaller effective particle volume. The proposed effect of decreasing solvency of the PEO chains is illustrated in Fig. 9. However, above 75% alcohol, the dispersant layers collapse and the stabilization

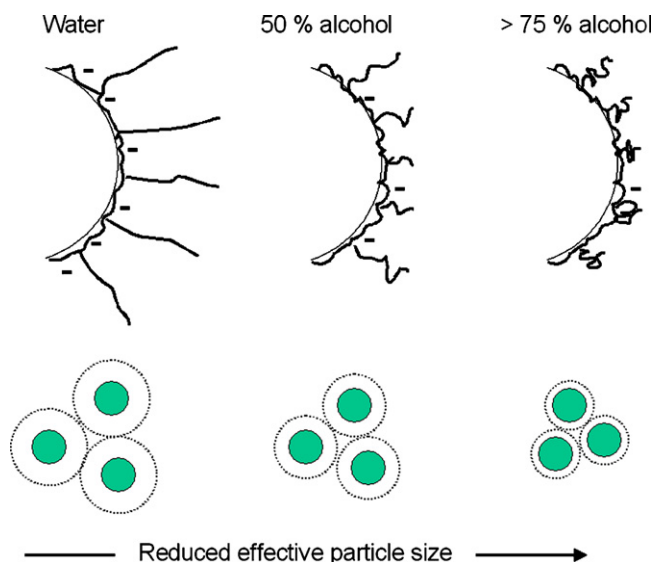


Fig. 9. Illustration of proposed reduction in effective particle size with increasing alcohol content for the comb copolymer dispersant.

properties are lost due to insufficient solubility. This results in flocculation.

#### 4. Conclusions

In this study, solvent mixtures of water and ethanol and water and isopropanol have been evaluated for processing of concentrated alumina suspensions. Adsorption of both poly(acrylic acid) and a comb copolymer on alumina was evident from shifts in the isoelectric point to lower pH for both dispersants. It was also shown, that stable, concentrated alumina suspensions with low viscosity can be achieved with the poly(acrylic acid) dispersant in solvent mixtures of water and up to 25 vol% ethanol or isopropanol. Alumina suspensions with added magnesia in solvent mixtures of water and 25% isopropanol and poly(acrylic acid) as dispersant showed long-term stability. The viscosity remained almost constant during 4 days of aging.

Furthermore, the comb copolymer showed superior stabilization properties to the poly(acrylic acid) for solvent mixtures with alcohol concentrations above 25 vol% for both ethanol and isopropanol.

The proposed reason for this is that the lower solubility of the PEO chains at higher alcohol contents allows for a more coiled conformation at the surface, with retained stabilization properties. The less-extended conformation of the polymer chains leads to reduced effective particle size and hence, low viscosity through lower apparent solid content in the suspension. As a result of this study, it was concluded that the addition of moderate amounts of low-molecular weight alcohols could increase the long-term stability of suspensions with soluble ceramic species such as magnesia. This is important in ceramic applications where high solid-loadings are used, and at the same time low viscosity is required for successful processing. Moreover, emerging techniques for the production of ceramic powders in the nano-size range will increase the demand for smaller dispersants that minimize the effective particle diameters with simultaneous high

dispersing efficiency. For such systems, the short comb copolymer may provide steric stabilization in solvent mixtures of water and alcohols.

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#### References

- Sevostianov, I. B., Levin, V. M. and Pompe, W., Evolution of the mechanical properties of ceramics during drying. *Phys. Stat. Sol. A*, 1998, **166**, 817–828.
- Kristoffersson, A. and Carlström, E., Tape casting of alumina in water with an acrylic latex binder. *J. Eur. Ceram. Soc.*, 1997, **17**, 289–297.
- Smay, J. E. and Lewis, J. A., Structural and property evolution of aqueous-based lead zirconate titanate tape-cast layers. *J. Am. Ceram. Soc.*, 2001, **84**, 2495–2500.
- Bell, N. S., Wang, L., Sigmund, W. M. and Aldinger, F., Temperature induced forming: application of bridging flocculation to near-net shape production of ceramic parts. *Z. Metallkd.*, 1999, **90**, 388–396.
- Bengisu, M. and Yilmaz, E., Gel casting of alumina and zirconia using chitosan gels. *Ceram. Int.*, 2002, **28**, 431–438.
- Lyckfeldt, O. and Ferreira, J. M. F., Processing of porous ceramics by “starch consolidation”. *J. Eur. Ceram. Soc.*, 1998, **18**, 131–140.
- Sigmund, W. M., Bell, N. S. and Bergström, L., Novel powder-processing methods for advanced ceramics. *J. Am. Ceram. Soc.*, 2000, **83**, 1557–1574.
- Paik, U. and Hackley, V. A., Influence of solids concentration on the isoelectric point of aqueous barium titanate. *J. Am. Ceram. Soc.*, 2000, **83**, 2381–2384.
- Tari, G., Ferreira, J. M. F. and Lyckfeldt, O., Influence of magnesia on colloid processing of alumina. *J. Eur. Ceram. Soc.*, 1997, **17**, 1341–1350.
- Dakskobler, A., Kocevar, K. and Kosmac, T., Short-range repulsive potential by the addition of Mg(II) ions to aqueous alumina slurries. *J. Eur. Ceram. Soc.*, 2001, **21**, 2361–2368.
- Vamvakaki, M., Billingham, N. C., Armes, S. P., Watts, J. F. and Greaves, S. J., Controlled structure copolymer for the dispersion of high-performance ceramics in aqueous media. *J. Mater. Chem.*, 2001, **11**, 2437–2444.
- Renger, C., Kuschel, P., Kristoffersson, A., Clauss, B., Oppermann, W. and Sigmund, W., Colloidal probe investigation of the stabilization mechanism in aqueous 1,2-propanediol nano-zirconia dispersions. *Phys. Chem. Chem. Phys.*, 2004, **6**, 1467–1474.
- Baklouti, S., Pagnoux, C., Chartier, T. and Baumard, J. F., Processing of aqueous  $a\text{-Al}_2\text{O}_3$ ,  $a\text{-SiO}_2$  and  $a\text{-SiC}$  suspensions with polyelectrolytes. *J. Eur. Ceram. Soc.*, 1997, **17**, 1387–1392.
- Briscoe, B. J., Khan, A. U. and Luckham, P. F., Optimising the dispersion on an alumina suspension using commercial polyvalent electrolyte dispersants. *J. Eur. Ceram. Soc.*, 1998, **18**, 2141–2147.
- Cesarano, J. and Aksay, I. A., Processing of highly concentrated aqueous  $a\text{-alumina}$  suspensions stabilized with polyelectrolytes. *J. Am. Ceram. Soc.*, 1988, **71**, 1062–1067.
- Tari, G., Ferreira, J. M. F. and Lyckfeldt, O., Influence of the stabilising mechanism and solid loading on slip casting of alumina. *J. Eur. Ceram. Soc.*, 1998, **18**, 479–486.
- Fleer, G. J., Stuart, M. A. C., Scheutjens, J. M. H. M., Cosgrove, T. and Vincent, B., *Polymers at Interfaces*. Chapman & Hall, London, 1993 [chapter 1].
- Rojas, O. J., Claesson, P. M., Muller, D. and Neuman, R. D., The effect of salt concentration on adsorption of low-charge-density polyelectrolytes and

- interactions between polyelectrolyte-coated surfaces. *J. Colloid Interf. Sci.*, 1998, **205**, 77–88.
19. Wang, G. and Nicholson, P. S., Influence of acidity on the stability and rheological properties of ionically stabilized alumina suspensions in ethanol. *J. Am. Ceram. Soc.*, 2001, **84**, 1977–1980.
  20. Tadros, T. F., *Handbook of Applied Surface and Colloid Chemistry, vol 1*, ed. K. Holmberg. Wiley, New York, 2001 [chapter 16].
  21. Palmqvist, L., Lyckfeldt, O., Carlström, E., Davoust, P., Kauppi, A. and Holmberg, K., Dispersion mechanisms in aqueous alumina suspensions at high solids loadings. *Colloid Surf. A*, 2006, **274**, 100–109.
  22. O'Brien, R. W., Cannon, D. W. and Rowlands, W. N., Electroacoustic Determination of Particle Size and Zeta Potential. *J. Colloid Interf. Sci.*, 1995, **173**, 406–418.
  23. Lide, D. R., *Handbook of Chemistry and Physics*. CRC Press, Boca Raton, 1999 [chapter 8].
  24. Greenwood, R. and Bergström, L., Electroacoustic and rheological properties of aqueous Ce–ZrO<sub>2</sub> (Ce–TZP) suspensions. *J. Eur. Ceram. Soc.*, 1997, **17**, 537–548.
  25. Shaw, D. J., *Introduction to Colloid and Surface Chemistry*. Butterworth–Heinemann, Oxford, 1991.
  26. Hiemenz, P. C. and Rajagopalan, R., *Principles of Colloid and Surface Chemistry*. Marcel Dekker, New York, 1997 [chapter 12].
  27. Pettersson, A., Marino, G., Pursiheimo, A. and Rosenholm, J. B., Electrosteric stabilization of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and 3Y-ZrO<sub>2</sub> suspension: effect of dissociation and type of polyelectrolyte. *J. Colloid Interf. Sci.*, 2000, **228**, 73–81.
  28. Pugh, R. J., Surface and colloid chemistry in advanced ceramics processing. In *Surfactant Science Series, vol 51*, ed. R. J. Pugh and L. Bergström. Marcel Dekker, New York, 1994 [chapter 4].
  29. Hou, Z. C., Chen, S. and Sheng, K. L., Distribution of acrylic acid grafted chains introduced into polyethylene film by simultaneous radiation grafting with water and ethanol as solvents. *J. Appl. Polym. Sci.*, 2007, **103**, 1570–1577.
  30. Müller, M. T., Yan, X., Lee, S., Perry, S. S. and Spencer, N. D., Lubrication properties of a brush-like copolymer as a function of the amount of solvent absorbed within the brush. *Macromolecules*, 2005, **38**, 5706–5713.
  31. Cohen-Stuart, M. A., Biopolymers at interfaces. In *Surfactant Science Series, vol 110*, ed. M. Malmsten. Marcel Dekker, New York, 2003 [chapter 1].