

Colloidal processing of aluminum oxide powder for membrane applications

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Abstract

The properties of dip-coating slips were varied by adjusting pH, by using nonionic or ionic additive polymers and by using different electrolytes and concentrations. Electrostatic stabilization of the slip with poly(vinyl alcohol) (PVA) addition led to the smallest particle size resulting in the highest density and the lowest permeability of the dip coated layer. Only small amounts of nonionic PVA adsorbed on the particles, which decreased the zeta potential slightly by charge shielding. The measured particle size decreased when the PVA concentration increased. The PVA addition did not affect the isoelectric point (i.e.p.) of the alumina particles. Strongly adsorbed sodium poly(metacrylic acid) (Na-PMAA) changed the pH_{iep} from ~ 9 to ~ 4 . The smallest particle size was measured at pH values 7–9. The zeta potential of particles with Na-PMAA addition decreased when the ionic strength was increased. Low zeta potential values resulted in flocculation of the slip and larger flock size. The flocculated slips led to fast growth, high porosity and high permeability of the layer.

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1. Introduction

The aim of the colloidal processing of the ceramics is to consolidate the particles in a controlled manner. A uniform and dense green microstructure is vital for processing of homogenous ceramic membranes where the desired properties are narrow pore size distribution and controlled thickness. The ceramic membranes usually have a multi-layer structure [1]. Each layer should have a well-controlled pore size to provide the desired stepwise decrease in pore size and controlled thickness to minimize the flow resistance. To produce such the layered structures with slip based methods the dispersion properties must be optimized. The key for the desired properties is the controlled state of the suspension. Careful control of the stability with suitable

additive system ensures required properties for the final, sintered structure.

Aluminum oxide particles can be stabilized by an electrostatic mechanism through careful pH-control. At low pH (pH 3.5–4.5) the positively charged particles repel each other and prevent flocculation. The alumina dispersions can be also stabilized by an electrosteric mechanism, which combines both electrostatic and steric mechanisms. Sodium poly(metacrylic acid) (Na-PMAA) is a widely used polyelectrolyte for stabilization of alumina suspensions [2–5]. Na-PMAA has carboxylic acid (COOH) sites, which dissociate in water and form negatively charged sites (COO⁻). The dissociation reactions occur at pH range 4–5. At higher pH all functional groups are dissociated and the molecule has high negative charge. The dissociated molecules adsorb on positively charged alumina surface resulting both steric and static repulsion between the particles [6–8].

In casting processes different kind of additives are used to control casting kinetics and to strengthen the unfired structure. Poly(vinyl alcohol) (PVA) is a non-ionic, commonly used binder, which has also effect on

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the solution viscosity and on the rheological properties of the slip [9–12].

The ceramic membrane processing requires a controlled shape forming technique. One of such techniques is dip-coating. A suspension is put in contact with a porous substrate and the suspension medium (solvent) is continuously sucked by capillary force [13]. The particles of the suspension accumulate on the substrate surface and form a porous layer. The mechanism of capillary suction, the effect of additives on absorption rate and evaluation of layer permeability during dip-coating were studied in our previous works [14,15].

In this work the adsorption of PVA and Na-PMAA on the alumina as well as the flock size and zeta potential of the particles were measured at different pH and with different electrolytes. The slips were used for dip-coating onto the two-layered substrate. The real-time layer growth during dip-coating was monitored and the layer permeability evaluated. The layer properties, such as porosity and permeability were finally compared with the dispersion properties.

2. Experimental

The powder used was high purity, sub-micron size α -Al₂O₃ (Baikalox CR6, Baikowski International Corp.). The powder purity was 99.99%, the specific surface area 6.2 m²/g and the mean particle size 0.25 μ m (agglomerate size 0.55 μ m).

The studied polymers were Na-PMAA (molecular weight 13 000 g/mol, Rohm and Haas Company) and PVA (molecular weight 22 000 g/mol, Fluka). Analytical grade KCl and CaCl₂ were used to adjust the ionic strength. The pH values were adjusted by 1 M HNO₃ (Titrisol, Merck) and NH₄OH (Aldrich). The minimum resistivity of deionized water used was 18 M Ω /cm.

The studied slips are given in Table 1. The slips were prepared by mixing the powders with solution to have

solid load of 10 wt.%. The mixing was confirmed by ultrasonification and 24 h stirring.

For adsorption isotherm measurement, Al₂O₃ (2.8 g), polymer solution (25 ml), electrolyte, and appropriate amount of HNO₃ or NH₄OH were mixed and centrifugated. The adsorbed amount of polymer was calculated from the difference between the amount of polymer added and that remaining in the supernatant. The zeta potential and the flock size were measured by the AcoustoSizer (Matec Applied Sciences), which allows the simultaneous measurement of the particle size and charge.

Dip-coating was done onto two-layered porous alumina substrate disc. The substrate disc consisted of thick, silica glass bonded, alumina layer and thin alumina top-layer. The coarse layer was 16 mm thick with porosity of 40%, the mean pore diameter of 35 μ m and had measured permeability of 4.1×10^{-12} m². The alumina top-layer had thickness of 250 μ m, porosity of 40%, pore size of 600 nm and permeability of 4.56×10^{-15} m² [14,15]. The substrate sides were sealed with plastic film so that only the top-layer came in contact with the slip.

Dip-coating was done with the arrangement described in Fig. 1. The slip was brought into contact with the substrate when the capillary absorption started to suck the solvent into the pores of substrate. The flocks started to accumulate on the top-layer. Weight change was recorded as a function of dipping time by computer connected to scale. Dipping time varied from 40 to 120 s depending on weight increase. After dip-coating the substrate was pulled out from the slip, weighted and dried. The dried discs were calcined at 600 C (3C/min) to burn out organic additives. After calcination the sample was weighted again. The porosity of sample was calculated from the mass and the volume of the layer.

The permeability of the layer during dip-coating was calculated from the mass increase versus time curve. The mass increase was converted to the layer thickness by using the measured porosity. The permeability was

Table 1

Composition of the slips. Powder concentration in all dispersions is 10 wt.%; polymer concentrations are expressed in dry weight basis

Sample	PVA (wt.%)	Na-PMAA (wt.%)	C _{KCl} (mM)	C _{CaCl₂} (mM)	pH24 h
I	0.5				4.4
II	2.15				4.5
III	0.5				9.8
IV	2.15				9.8
V		0.5			9.3
VI		0.5	1		9.3
VII		0.5	10		9.4
VIII		0.5	100		9.2
IX		0.5		1	9.2
X		0.5		10	7.6

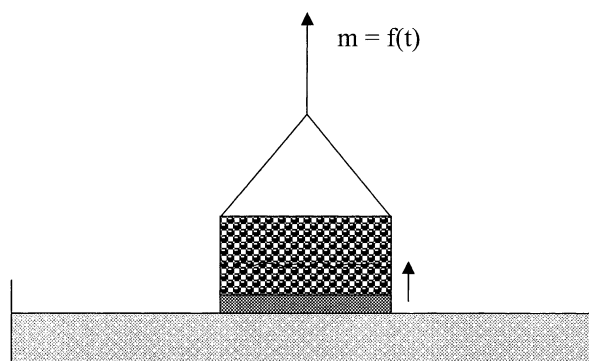


Fig. 1. Schematic presentation of the arrangement used for measuring layer growth during dip-coating.

calculated with the method described in our earlier work [14]. The first 15–30 s were used in the calculation in order to avoid the effect of sedimentation on the layer build-up. Possible sedimentation was evaluated from the solid content of adsorbed slip. The solid content of adsorbed slip was calculated from the mass of the dried layer and the mass of the adsorbed slip. When the solid content of adsorbed slip was smaller than the solid content of the original slip (10 wt.%), sedimentation had occurred. For the permeability calculations the pure polymer solutions were characterized separately from dispersions. Surface tension (KSV Instruments Ltd, Sigma 70), density (Anton Paar Densitometer, DMA 60) and kinematic viscosity (Scott geräte capillary viscometer, AVS measuring unit) of polymer solutions were measured.

3. Results and discussion

PVA had low adsorption ability on Al_2O_3 surface as shown in Fig. 2. Adsorption isotherms were rounded shape indicating low-affinity adsorption. At pH 4.3 the amount of adsorbed PVA was leveling off at $0.32 \times 10^{-8} \text{ mol/m}^2$, which is clearly higher than $0.17 \times 10^{-8} \text{ mol/m}^2$ at pH 9.85. The PVA adsorption is reported to increase on the positively charged oxide surface when pH approaches the isoelectric point and to decrease on the negatively charged surface at higher pH values [8,9]. From the 0.5 wt.% PVA solution only 5% of PVA was

adsorbed on alumina at pH 4.3 and the rest 95% remained in the solution. From 2.15 wt.% PVA solution the adsorbed fraction was even lower, 2.1%.

Fig. 3 shows that the due to non-ionic nature of PVA, the PVA addition had no effect on the isoelectric point (i.e.p.) of the alumina. The zeta potential value anyhow decreased from 60 to 40 mV, probably due to a charge shielding effect of the adsorbed polymer. A dispersion is classified as stable when zeta potential value is 40 mV or over. In Fig. 4 is shown that the smallest particle sizes appeared around pH 4 where the zeta potential had its maximum absolute. The particle size had a maximum at pH value near the i.e.p. of alumina, suggesting flocculation. The particle size decreased when PVA was added. The adsorbed PVA seems to have some steric stabilizing effect. Small amount of adsorbed PVA suggests flat configuration of the molecules on the alumina surface and therefore the adsorbed layer is probably thin. The particle size measurement method is based on mobility and it measures the particle size with the adsorbed layer. Since the slip without PVA neither contained electrolyte, the electrostatic double layer was probably very thick and measured particle size therefore large.

The adsorption of Na-PMAA on alumina surface with different electrolyte concentrations is shown in Fig. 5. Without an electrolyte the adsorption is low-affinity type but adsorbed amount, $0.50 \times 10^{-8} \text{ mol/m}^2$, is much higher compared with PVA. The negatively charged molecules adsorb on the positive surface sites

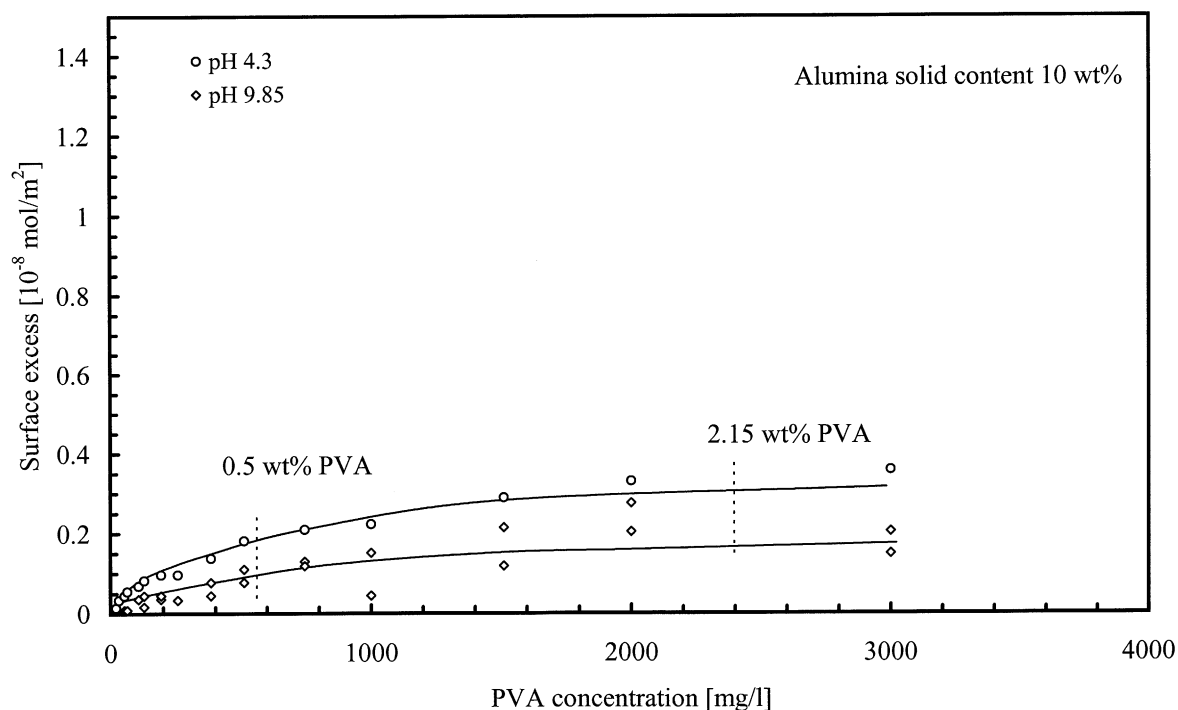


Fig. 2. Adsorption of PVA on α -alumina as a function of polymer concentration at different pH. Dashed lines represent PVA concentrations of the studied slips.

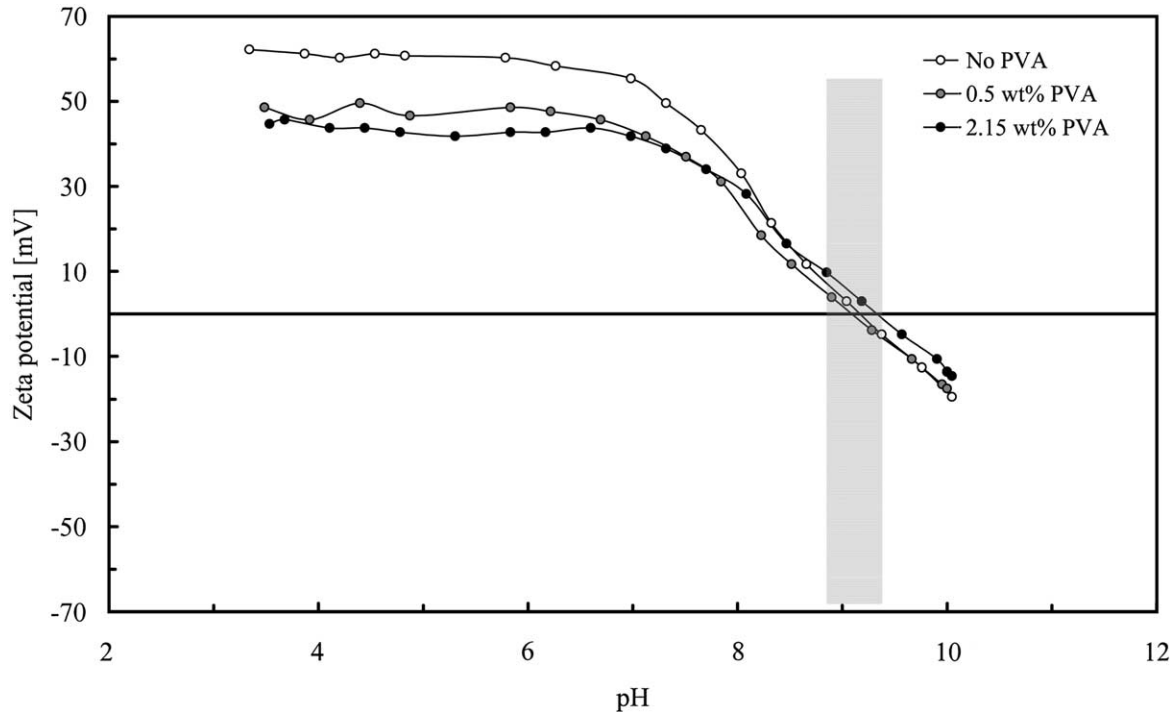


Fig. 3. The zeta potential of the α -alumina particles as a function of pH with the different PVA concentrations. Shaded area represents the i.e.p. of alumina.

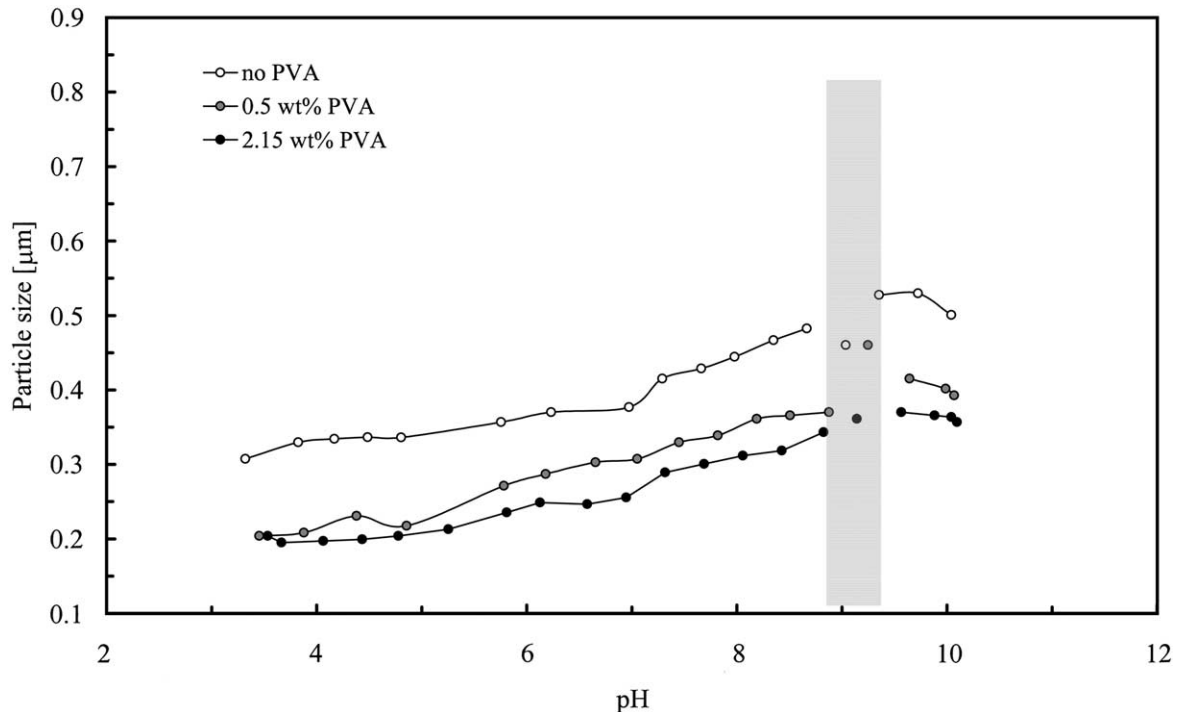


Fig. 4. The effect of pH on the particle size with different concentrations of PVA. Shaded area represents the i.e.p. of alumina.

still present at alumina near pH_{iep} . The adsorption of Na-PMAA increased to $0.95 \times 10^{-8} \text{ mol/m}^2$ and further to $1.13 \times 10^{-8} \text{ mol/m}^2$ when monovalent and divalent electrolytes were introduced. The shape of adsorption isotherm also changed to high-affinity type. This suggests

that the multivalent ions will compact the double layer leading to adsorption by van der Waals forces. The effect of electrolyte on adsorption of Na-PMAA has also been reported earlier [2]. With polymer concentration of 0.5 wt.% of Na-PMAA the adsorbed polymer

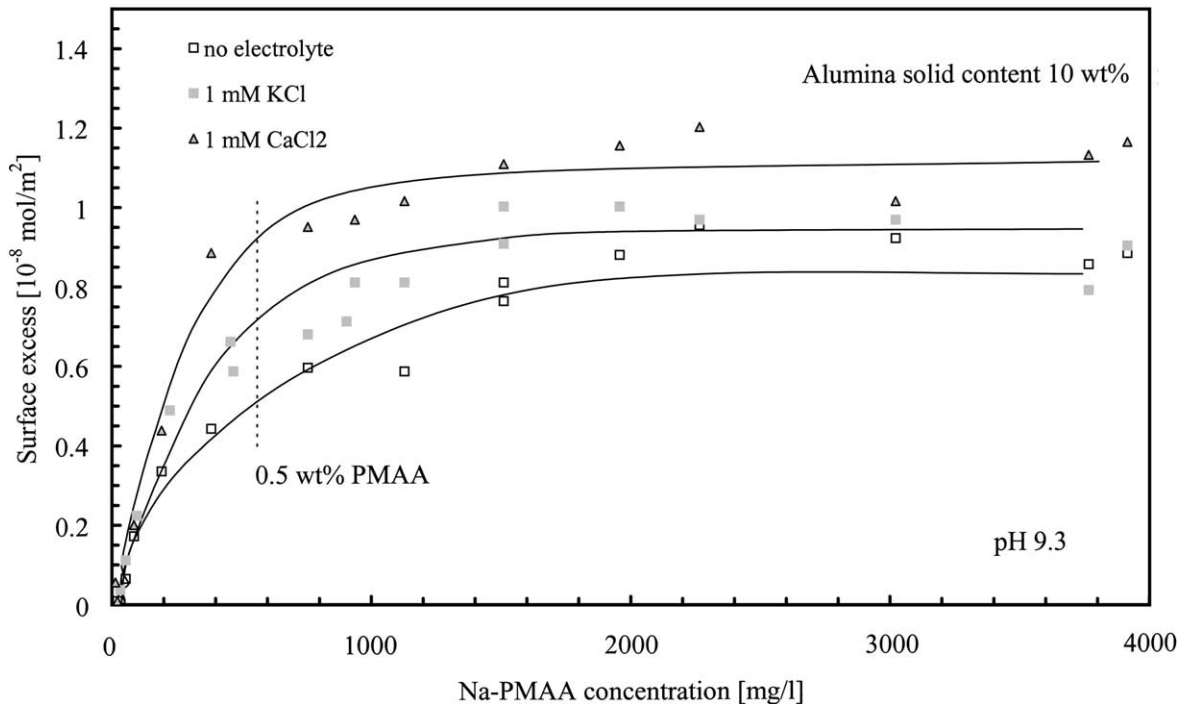


Fig. 5. Adsorption of Na-PMAA on α -alumina as a function of concentration with different electrolyte concentrations at pH 9.3. Dashed line represents Na-PMAA concentration of the studied slips.

fractions were 9, 11 and 14% for slips with no electrolyte, 1 mM KCl and 1 mM CaCl_2 . The adsorbed fractions are much higher compared with PVA.

The Na-PMAA addition shifted the i.e.p. to pH 4–4.5, where the dissociation reaction of carboxylic groups occurs. Use of monovalent electrolyte, KCl, decreases the absolute value of zeta potential only slightly by the compression of electrosteric layer of adsorbed polyelectrolyte as shown in Fig. 6. Only at high concentration, 100 mM, the absolute value of zeta potential decreases near the 40 mV. All the KCl containing slips can be therefore classified as stable. Divalent electrolyte, CaCl_2 , had stronger effect on the absolute value of the zeta potential. Concentration of 10 mM decreased the zeta potential down to 20 mV and at 100 mM concentration the charging effect disappeared almost totally.

The particle sizes had the maximum near i.e.p. at pH 4–4.5 as expected as shown in Fig. 7. Interestingly, the particle size of the slip without any electrolyte had rather big particles in spite of the large net charge. Low ionic strength causes the protrusion of adsorbed polymer into the solution which is observed as larger particle size. The 1 and 10 mM KCl addition decreased the particle size significantly by compressing the adsorbed electrosteric polymer layer. High, 100 mM, KCl concentration gave big particle size again, which may be due to flocculation of the slip. CaCl_2 had similar effect on the particle size as KCl, but the effect was anyhow stronger. Flocculation occurred at 10 mM CaCl_2 concentration. With 100 mM CaCl_2 concentration the slip flocculate

clearly having the flock size of 5.14 μm . The strong effect of electrolyte concentration on the zeta potential and the particle size indicates that the Na-PMAA works by the electrosteric stabilization mechanism. If the electrostatic effect is hindered by the high ionic strength of the solution the steric stabilization mechanism is not strong enough to deflocculate the slip.

In Fig. 8 the weight versus dipping time curves are presented for the deflocculated (2.15 wt.% PVA and pH 4.4) and the flocculated (0.5 wt.% PVA and pH 9.8) and slip. The mass increase during the dip-coating with the deflocculated slip was slow and dipping was stopped after 110 s. The dipping curve was strongly curved, indicating that the growing layer restricted the flow of liquid. The peak in dipping curves is a surface tension effect when the sample was removed from contact with slip. The weight increase during dip-coating with the flocculated slip was fast, 65 s, and the mass increase curve was almost straight at longer dipping times. The straight curve is indication that only liquid is absorbed into sample at long dipping times, since thin top layer and particle layer with constant thickness causes a constant pressure drop for absorbing liquid. The solid content of absorbed slips for the slips with 0.5 and 2.14 wt.% PVA at pH 9.8 was 3.7 wt.% and for the slip with Na-PMAA with 10 mM CaCl_2 was 4.2 wt.%. The solid content of original slips was 10 wt.%. The low solid contents of absorbed slips indicate that the substrate had adsorbed only liquid phase of the slip while flocks were lying at the bottom of the slip reservoir. For

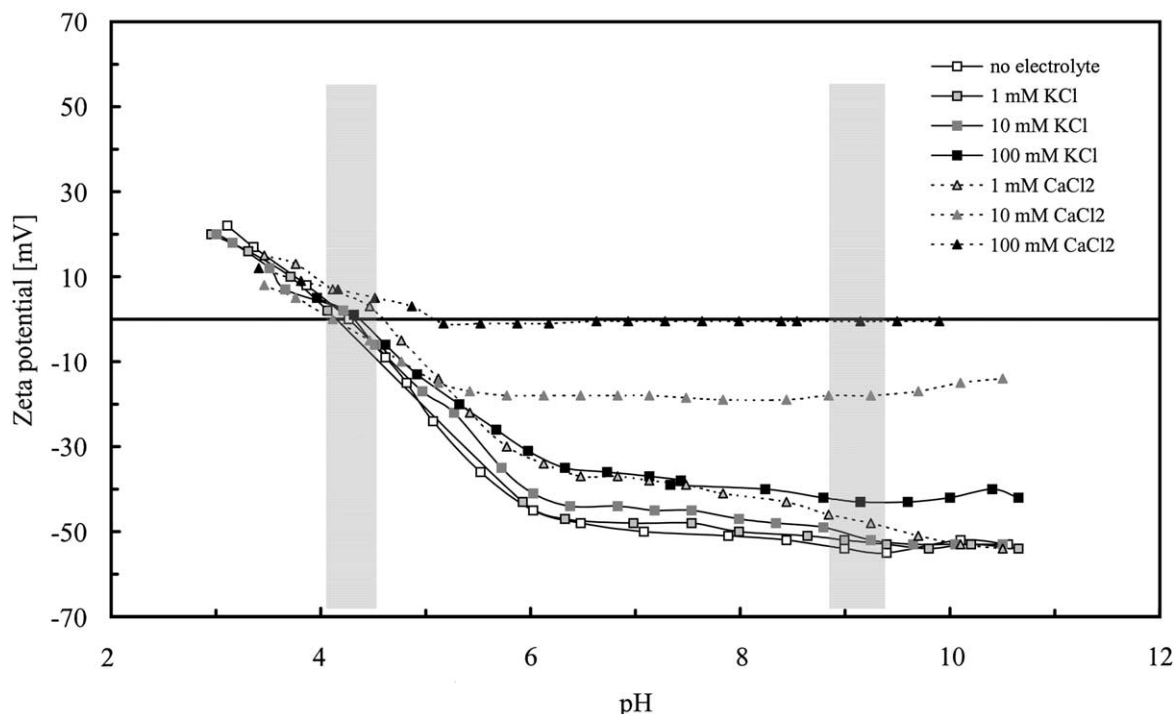


Fig. 6. The effect of electrolyte and concentration on the zeta potential of α -alumina particles as a function of pH. Concentration of Na-PMAA is 0.5 wt.%. Shaded area at pH 4–4.5 represents dissociation range of COOH. Shaded area at pH \sim 9 represents the i.e.p. of alumina.

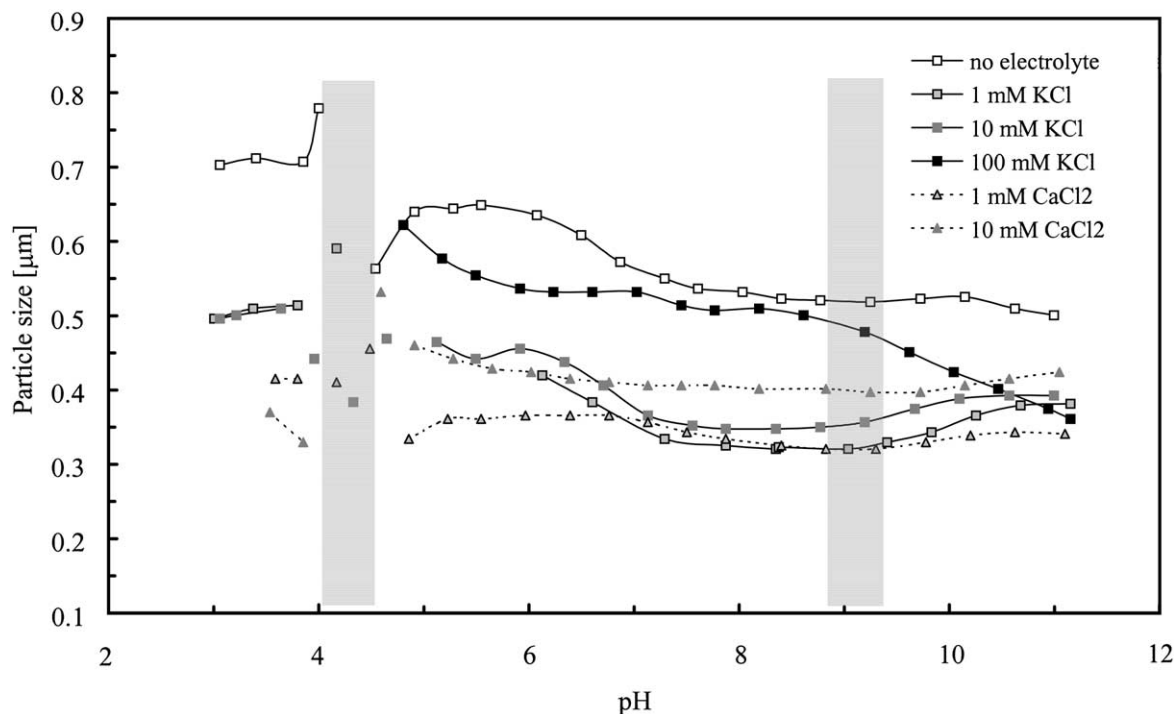


Fig. 7. The particle size of the slips with 0.5 wt.% Na-PMAA as a function of pH with different electrolytes and concentrations. Shaded area at pH 4–4.5 represents dissociation range of COOH. Shaded area at pH \sim 9 represents the i.e.p. of alumina.

the other slips; the slips with PVA at pH 4.4 and the slips with Na-PMAA and low electrolyte concentration, the solids accumulated on the substrate surface and the calculated solid content of absorbed slip corresponded with the original slip solid content.

The dip-coated layer porosity is compared with the particle size in Fig. 9. Larger particle sizes and higher amounts of polymer led to higher porosity. When the amount of PVA was increased from 0.5 to 2.15 wt.% the porosity of the layer increased at both pH values,

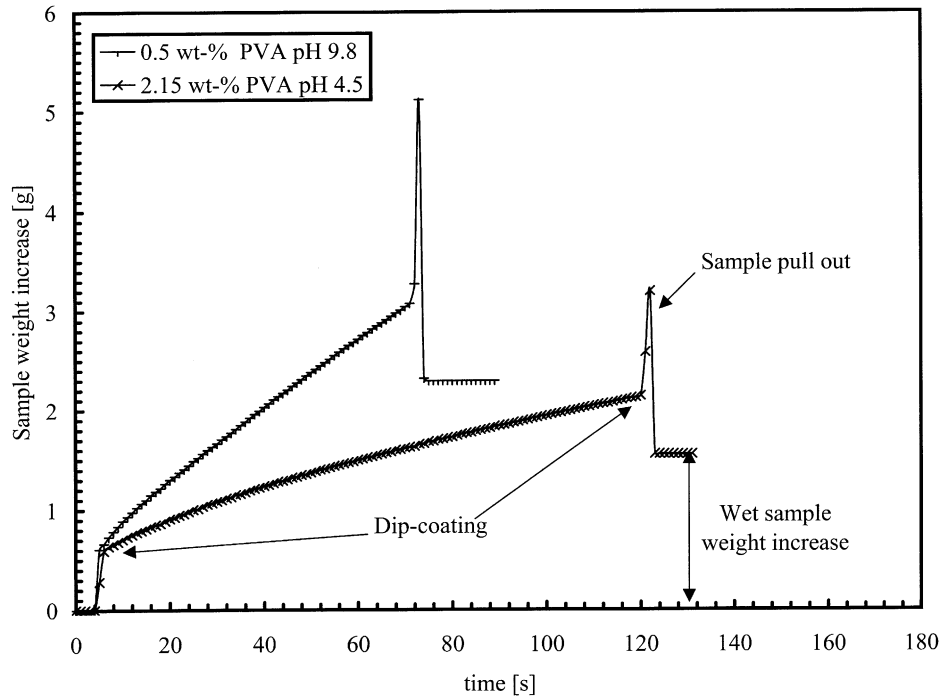


Fig. 8. Examples of the weight increase of the samples during dip-coating.

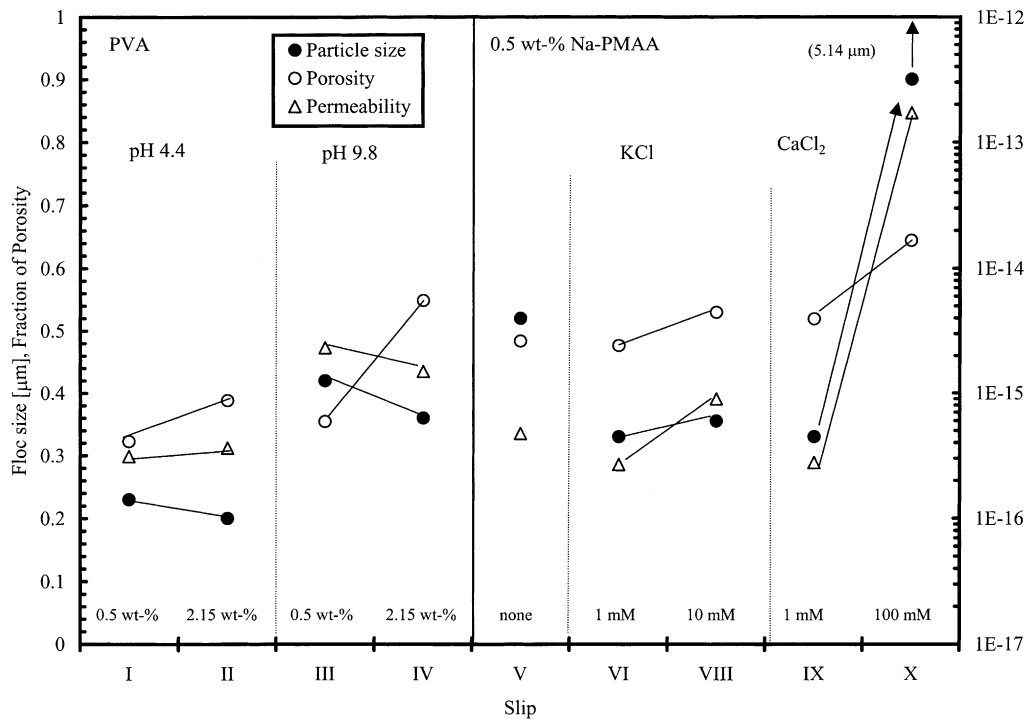


Fig. 9. The particle sizes of the slips with the porosities and the permeability of the dip-coated layers.

while the particle size decreased. The free PVA in solution may produce voids to the coated layer. Use of Na-PMAA led systematically to higher porosity compared to the slips with PVA addition. The porosity of the layers with Na-PMAA followed clearly the particle size. Small addition of electrolyte slightly decreased porosity

by compressing double layer, but higher concentration led to higher porosity due to flocculation. The floccled slip with 100 mM CaCl₂ had flock size of 5.14 μm and produced layer with porosity of 64%.

The properties of the solvent phase of the slips are presented in Table 2. The used additive amounts were

Table 2
Properties of the solutions at 25 °C

Solution	Kinematic viscosity (mm ² /s)	Density (g/cm ³)	Dynamic viscosity (mPas)	Surface tension (mN/m)
I and III	0.912	0.997	0.909	56.6
II and IV	0.982	0.998	0.979	52.2
V	0.963	0.997	0.961	70.8
VI	0.940	0.997	0.937	71.3
VII	0.909	0.998	0.907	70.7
VIII	0.896	1.002	0.898	68.2
IX	0.921	0.998	0.918	72.3
X	0.911	1.006	0.917	71.9
DI-H ₂ O	0.888	0.997	0.886	71.5

so small that their effect on density and viscosity was negligible. The PVA addition strongly reduced the surface tension and therefore also the capillary pressure, whereas the Na-PMAA had no effect on the surface tension.

The permeability calculated from the layer growth data followed also clearly the particle size as shown in Fig. 9. The layers coated from the deflocculated PVA slips gave the lowest permeability values, which agrees with the low porosity and the smallest particle sizes. The layers from the flocculated PVA slips had very high permeability suggesting large flow channels between large flocks. Anyhow the voids caused by excess PVA cannot be clearly observed in permeability values especially in the case of flocculated slip having 2.15 wt.% PVA. The permeability of the layers prepared from the slips with Na-PMAA followed clearly the particle or flock size of the respective slip. This suggests that the flock size does not change during the layer growth by capillary compaction pressure and the flow channels between flocks are related to the floc size. At the low electrolyte concentrations the permeability of the coated layer varied within one decade being almost the same as the permeability of the deflocculated PVA slips. At the high electrolyte concentration, 100 mM CaCl₂, the permeability was three decades higher than that of the deflocculated slips. The flocculated slip had very large particle size leading to high porosity and very high permeability of the coated layer.

4. Summary

A correlation between colloidal state, particle size, porosity and permeability was observed. The pH, the amount and the type of the polymeric additive and electrolyte concentration had strong effect on the zeta potential and the particle size in the slip. The particle size of the slip governs the layer buildup rate during dip-coating and affects on the porosity and permeability of the final layer.

Small particle or flock size was obtained by using electrostatic stabilization and nonionic PVA as additive. The small amount of adsorbed PVA might have some steric stabilization effect. During dip-coating the high amount of excess PVA increased porosity by causing voids in the layer, which is not always desired. PVA significantly reduces surface tension, and therefore the capillary pressure, which allows more accurate control of the layer thickness. The pH value near the isoelectric point of alumina resulted in easily settling flocculated slip. The PVA addition had only small deflocculation effect near the isoelectric point. The flocculated PVA slips gave layers having high porosity and high permeability suggesting large flow channels in the layer.

The use of Na-PMAA resulted in high negative zeta potential values. Increase of ionic strength reduced the zeta potential by compression of double layer. Further increase of ionic strength compressed the double layer and resulted in flocculation of the slip since repulsive charges diminished. The divalent electrolyte had a stronger effect on the ionic strength and it compressed the electrical double layer more effectively than the monovalent electrolyte. Despite the high absolute zeta potential values the Na-PMAA deflocculation resulted in larger particle size than electrosteric stabilization with PVA addition. The increase of the floc size also resulted in higher porosity and permeability of the dip-coated layer.

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