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The effect of anionic polyelectrolytes on the properties of aqueous silicon nitride suspensions

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Abstract

The effect of anionic polyelectrolytes on the electrokinetic and rheological properties of concentrated Si_3N_4 suspensions was investigated experimentally. We found that polyelectrolyte adsorption and, thus, colloidal stability at $pH > pH_{iep}^{Si_3N_4}$ is mainly governed by the surface charge density of the solid phase. Comparing anionic methacrylic acid comb copolymer modifications with grafted poly(ethylene oxide) chains (PMMA-PEO), with poly(acrylic acid) (PAA) showed that the grafted PEO chains have a minor influence on the colloidal stability. The common viscosity minimum for all the anionic polyelectrolytes around pH 7 suggests that the suspensions are electrosterically stabilized. The polyacrylic backbone attains an extended conformation perpendicular to the surface. The effect of excess addition of polyelectrolyte was also discussed; we attribute the significant increase in suspension viscosity to the increased ionic strength caused by the release of associated counterions of the polymer functional groups. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolytes; Rheology; Si_3N_4; Surfaces; Suspensions

1. Introduction

Polyelectrolytes are usually the dispersant of choice when preparing aqueous ceramic powder suspensions. The popularity of polyelectrolytes stems from their low cost and high efficiency in dispersing many different kinds of powders in aqueous media. Accordingly, a large number of studies have also been devoted to investigating the effect of polyelectrolytes on the properties of aqueous silicon nitride suspensions.[1–11] The effect of polyelectrolyte addition on the colloidal stability and rheological behavior is determined by a complex interplay between the polyelectrolyte, the powder surface and the solution phase. In order to understand the adsorption behavior of polyeletrolytes and the nature of the induced interparticle forces, we have to consider the surface chemistry of the solid phase as well as the solution properties of the polyelectrolyte.

Previous studies have shown that pH is a very important parameter in controlling polyelectrolyte adsorption. Hackley, for example, concluded that the effectiveness of polyelectrolytes as dispersants depends strongly on pH in relation to the acid-base properties of the particulate phase and the dispersant.[10] Hence, it is useful to distinguish between pH regimes where the particle surface and the polyelectrolyte carry net charges of either the same or opposite sign. If the segment–surface interaction is purely electrostatic, adsorption will only take place if the polyelectrolyte bears a net charge of opposite sign. However, high electrolyte concentrations can obstruct such a purely electrostatically controlled adsorption process by means of competitive ion adsorption or screening effects. In the case where the charges on surface and polymer have the same sign, adsorption is only possible if the segment–surface interaction also has a “specific” or “chemical” contribution which overcompensates the repulsive electrostatic part. For such conditions we expect that an increasing ionic strength should promote adsorption since the electrostatic repulsion is screened. The electrostatically dominated adsorption should also be more pH dependent than the specific adsorption since the surface charge density and the charged segment fraction is a function of pH. At a pH where the polyelectrolyte is uncharged

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and/or in a solution at very high ionic strength, water might become a poor solvent for the polymer which may eventually precipitate on the particle surfaces.

Adsorption of polyelectrolyte at the solid–liquid interface induces interparticle forces whose nature is strongly dependent on the charge density and segment density profile.[12] Since the stabilization mechanism may be of electrostatic and steric origin, the term "electrosteric" stabilization is often used to describe how polyelectrolytes act as dispersants. If the polyelectrolyte adsorbs in a flat conformation, the steric repulsion is short-range, and the stabilization mechanism is mainly electrostatic. This is usually the case when the polyelectrolyte is highly charged, having an extended conformation, and the particle surface is oppositely charged.[13] With thicker adsorbed layers, having chains protruding into the solution, the polymeric contribution will become more important. However, there is always an electrostatic contribution since the adsorption of a highly charged polyelectrolyte on a weakly charged, amphoteric oxide surface usually results in an increase of the net surface charge density. If no polyelectrolyte adsorption takes place it is only the electrostatic forces between the charged particle surfaces that counteract agglomeration induced by attractive van der Waals forces. At adsorption densities below full coverage polymer bridging may occur and lead to strong flocculation.

This study deals with the effect of polyelectrolyte adsorption on the rheological and electrokinetic properties of concentrated aqueous silicon nitride suspensions. We have studied two types of anionic acrylic-based polyelectrolytes; poly(acrylic acid) (PAA), perhaps the most commonly used dispersant in ceramic applications, and an anionic methacrylic comb copolymer with grafted poly(ethylene oxide) side chains (PMAA-PEO). PMAA-PEO was introduced to elucidate the effect of nonionic side chains on the balance between electrostatic and steric stabilizing mechanisms in concentrated suspensions. The adsorption of the polyelectrolytes at neutral and basic conditions was correlated to the electroacoustic zeta potential measurements and theological behavior. We have attempted to interpret the complex rheological behavior based on conceptual considerations of the induced interparticle forces.

2. Experimental

2.1. Materials

An α-silicon nitride powder (grade SN-E10) obtained from UBE Industries, Japan, was used in all experiments. It is characterized by a mean diameter of 500 nm and a specific surface area of 10.4 m^2/g. As dispersants we have used a commercial ammonium salt of poly(acrylic acid) (Dispex A40, Allied Colloids, UK) and two modifications of a commercial poly(methacrylic acid) comb copolymer (SSP 104N and SSP 168; Takemoto Oil & Fat Co., Ltd., Japan). In this paper the polyelectrolytes are denoted by the corresponding generic names PAA, PMAA-PEO 104N, and PMAA-PEO 168, respectively. The chemical structure of PAA and PMAA-PEO is depicted in Fig. 1. The chemical structure of the two PMAA-PEO modifications is identical, except for the length of the grafted poly(ethylene oxide) (PEO) chains and the ionic species used to neutralize acidic functional groups. The grafted PEO chains of PMAA-PEO 104N are shorter compared to PMAA-PEO 168. PMAA-PEO 168 is a sodium salt of a methacrylic acid polymer, whereas PMAA-PEO 104N is neutralized with ammonium. The average molecular weight of PAA is $M_w = 10\,000$ with a polydispersity of $M_w/M_n = 1.56$.[14] The average molecular weights and polydispersities of PMAA-PEO 104N and PMAA-PEO 168 according to the manufacturer data are: $M_w = 32\,700$ ($M_w/M_n = 3.5$) and $M_w = 43\,200$ ($M_w/M_n = 6.4$), respectively. All reagents used to adjust the pH (NaOH, HCl and the electrolyte concentration (NaCl) were of analytical grade and purchased from Merck KGaA, Germany. The deionized water was obtained from a Millipore Milli-Q plus unit (> 18.2 MΩ/cm resistivity, < 9 ppb TOC total organic carbon content).

2.2. Methods

All experiments were carried out in aqueous media with 0.01 M NaCl electrolyte concentration. All polymer concentrations are given in wt% with respect to the dry powder weight (dwb). Unless otherwise stated all of

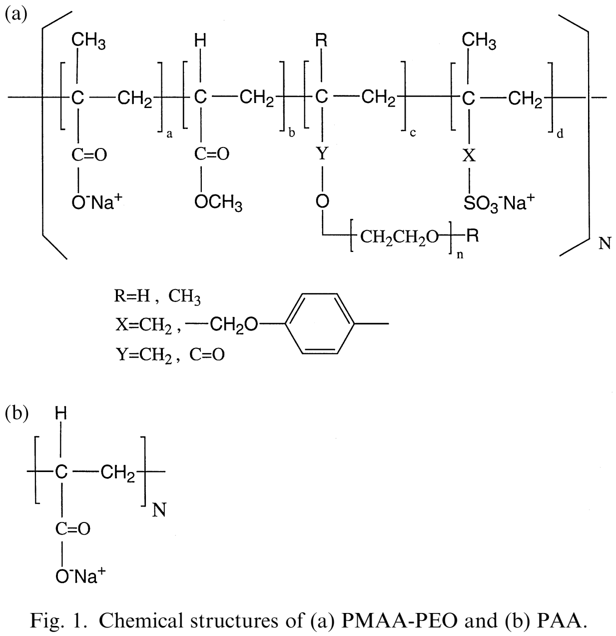

Fig. 1. Chemical structures of (a) PMAA-PEO and (b) PAA.

the experimental studies in this paper have been carried out at equilibrium conditions and kinetic aspects of adsorption/desorption processes are not considered in detail.

2.2.1. Adsorption isotherms

Adsorption isotherms were obtained using a depletion concentration method where suspensions were mixed and equilibrated, particles and supernatant separated by centrifugation and filtration and the remaining polyelectrolyte concentration in solution determined by potentiometric acid-base titration. Polyelectrolyte solutions (15 ml) were acidified to pH 3 and then titrated with 0.01 M NaOH to pH 11 using a Metrohm 670 Titroprocessor (Metrohm AG, Switzerland). During titration the sample temperature was kept constant at 22°C and CO_2 was stripped by continuous purging with pure nitrogen gas. The amount of polyelectrolyte in solution was determined by using calibration curves for PAA and PMAA-PEO 104N, respectively. The calibration curves were also used to determine the counter ion concentration associated with the ionization of the polyelectrolytes.

2.2.2. Electroacoustic measurements

The electroacoustic measurements on 10 vol% silicon nitride suspensions were carried out using the AcoustoSizer (Matec Applied Science, USA). Suspensions were prepared by mixing powder, electrolyte solution and required amount of polymer stock solution followed by ultrasonication and addition of base to reach pH 10. Samples were kept stirring for at least 12 h prior to measurement. During measurement, the 400 ml sample was titrated with 1 M HCl at 25°C using the built-in automatic titration device. The samples were continuously stirred and the equilibration time between two data points was approximately 3 min. The dynamic mobility of the particles was measured in a range of frequencies (0.3–11.2 MHz) of the applied electrical field. More details about the measuring technique and the underlying principles for acoustophoresis can be found in a recent review article.[15]

2.2.3. Rheological measurements

Steady shear measurements were performed using a controlled stress rheometer (UDS 200, Physica Messtechnik GmbH, Germany). A concentrical cylinder geometry with a cup (inner diameter 13.56 mm) and a sandblasted bob (diameter 12.5 mm, length 37.5 mm) was used for all measurements. The temperature was maintained at 25°C during each measurement. We prepared samples of 20 ml by mixing powder, electrolyte solution and required amount of polymer stock solution followed by ultrasonication and adjusting pH. All suspensions were kept stirring for at least 12 h and pH was readjusted if necessary. Prior to the steady shear measurement all samples were subjected to 3 min preshearing at 1000 s^{-1} followed by a rest period of 2 min. Flowcurves were obtained in the shear rate range 0.01–1000 s^{-1}. Data points at 50 s^{-1} were selected for the evaluation of the steady shear behavior.

3. Results and discussion

3.1. Adsorption isotherms

The adsorption of PAA and PMAA-PEO 104N on silicon nitride is displayed in Figs. 2 and 3, respectively. The adsorption isotherms represent the equilibrium state for the investigated systems at pH 7 and pH 9. All the adsorption isotherms are characterized by a saturation behavior and a corresponding adsorption plateau. At pH 7 plateau adsorption is observed at polyelectrolyte additions above 0.3 wt% PAA and 1.5 wt% PMAA-PEO, respectively. The adsorbed amount at pH 9, however, was very small or even below the detection limit of the titration method for both of the anionic polyelectrolytes. At pH 7 we find that the maximum adsorbed amounts are 0.05 mg/m^2 for PAA and 0.25 mg/m^2 for PMAA-PEO 104N.

Adsorption of anionic polyelectrolytes at high pH, where $pH > pH_{iep}$, is mainly dictated by the balance between the specific (non-electrostatic) affinity between segments and powder surface, and the electrostatic repulsion between the negatively charged solid/liquid interface and the strongly negatively charged polymer chains. The fact that anionic polyelectrolytes adsorb at $pH > H_{iep}$ implies that the specific segment–surface interactions are of significant magnitude.

Assuming that the pH dependence of the specific surface–segment interaction is negligible, we can relate the strong pH dependence of PAA adsorption to the variation in surface charge density. The surface charge density of silicon nitride is strongly pH-dependent in the investigated pH range;[16,17] the charged fraction, α, of PAA, however, is almost constant and equal to one.[18] Comparison of our data with previous studies of PAA adsorption at basic pH on oxide materials illustrates the pivotal role of the acid-base properties of the native solid for the adsorption behavior of the charged polyelectrolyte (Table 1). At a given pH the maximum adsorbed amount, Γ_M, is a strong function of the isoelectric point, pH_{iep}, of the powder; e.g. at pH≈9 the Γ_M of PAA on zirconia[14] and alumina[19] is much higher than on silicon nitride (Table 1). The data in Table 1 also implies that there are significant differences in magnitude of the specific PAA segment–surface affinity for the different materials. The work by Foissy et al.[20] on the adsorption of PAA on anatase (TiO_2) powder shows a PAA adsorption an order of magnitude higher compared to the adsorption on silicon nitride although the

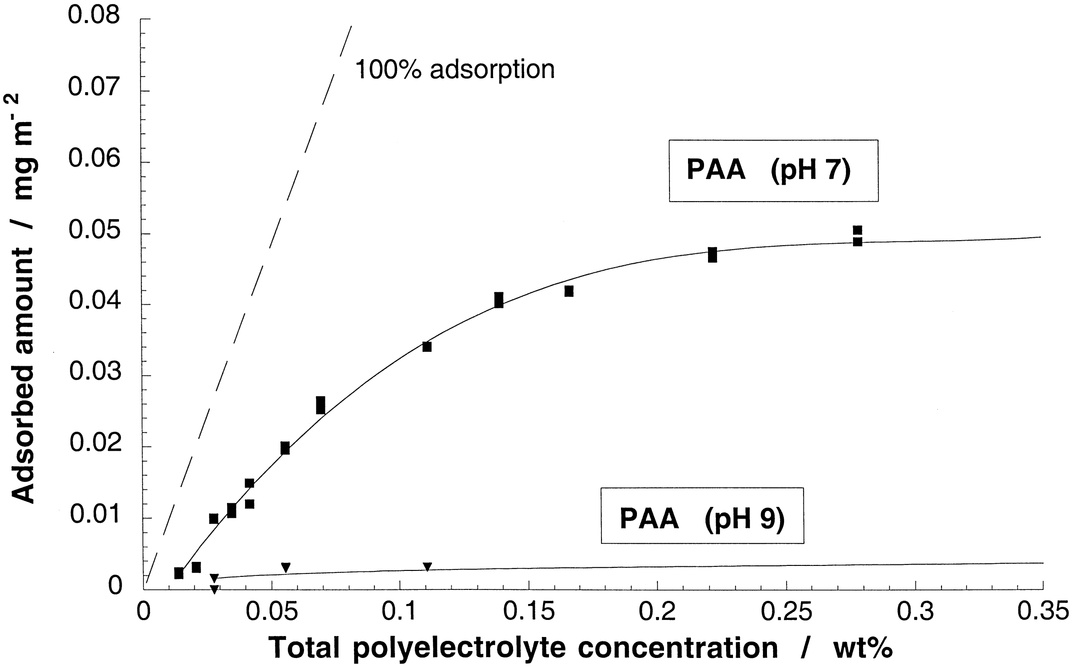

Fig. 2. Adsorbed amount PAA at pH 7 and 9 vs the total amount polymer added (10 vol% solids fraction, 0.01 M NaCl).

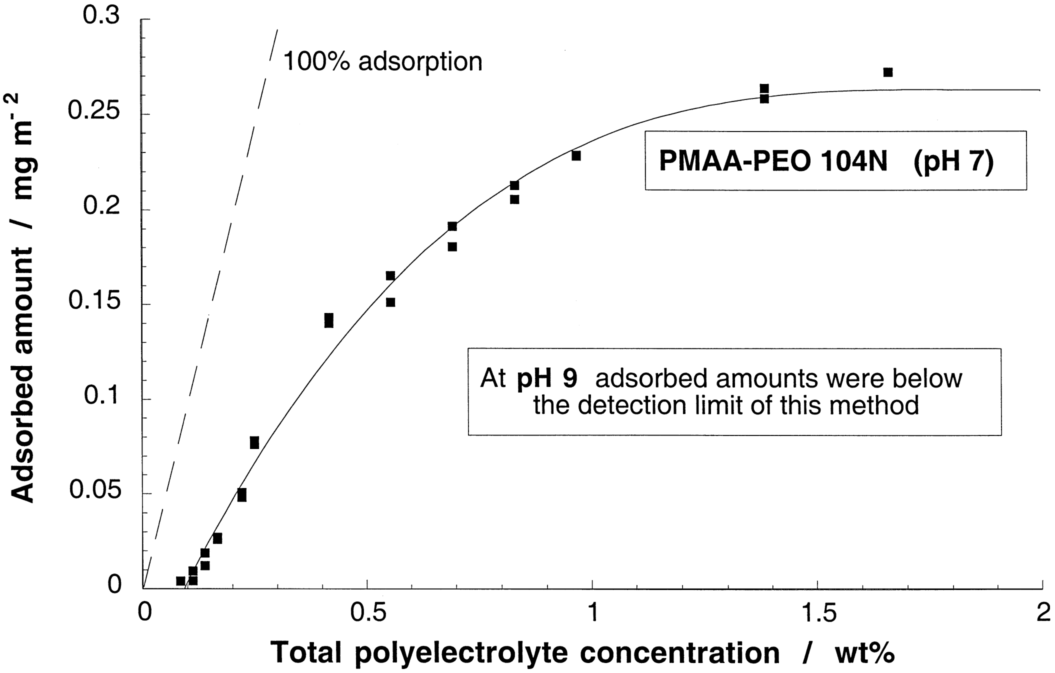

Fig. 3. Adsorbed amount PMAA-PEO 104N at pH 7 vs the total amount polymer added (10 vol% solids fraction, 0.01 MNaCl).

isoelectric points are nearly identical ($pH_{iep}^{TiO_2} = 6.2$, $pH_{iep}^{Si_3N_4} = 5.8$).

The much higher plateau adsorption value for PMAA-PEO 104N compared to PAA at pH 7 (Figs. 2 and 3) can be attributed to the significantly higher average molecular weight of PMAA-PEO 104N. Other reasons that may account for the higher adsorbed amounts are a higher flexibility of the PMAA-PEO polymer which would promote more densely adsorbed layers, and specific surface–PEO segment interactions. The higher flexibility of PMAA-PEO stems from the larger distance between the charged segments — i.e. weaker intermolecular repulsion — compared to PAA (see Fig. 1). Specific surface–segment interaction between PEO segments and undissociated Si–OH surface groups have been reported recently in the context of PEO

Table 1
Maximum adsorbed amount, Γ_M, of PAA on alumina,[19] zirconia,[14] titania,[20] and silicon nitride[a]

Material	M_w PAA	Ionic strength	pH_{iep}	pH	Γ_M (mg/m^2)
Al_2O_3	15 000	No electrolyte	8.0	9.2	≅0.45
Ce–ZrO_2	10 000	0.01 M NaCl	7.9	8.3, 9.5	⩾0.2
Si_3N_4	10 000	0.01 M NaCl	5.8	9.0	<0.004
TiO_2	4000	No electrolyte	6.2	9.8	≅0.1

[a] Additional data about the solid phase (pHi$_{iep}$), the polymer molecular weight (M_w) and the solution conditions (pH, ionic strength) are included.

homopolymer adsorption onto silica[21] and plasma-synthesized silicon nitride (pH_{iep}≅3.5).[22] However, in our adsorption studies at $pH > pH_{iep}$ a large fraction of the silanol groups are dissociated; hence, the effect on adsorption of possible hydrogen bonding between the PEO moieties of PMAA-PEO 104N and Si_3N_4 silanol groups is probably negligible.

3.2. Electroacoustic properties

Fig. 4 shows the effect of polyelectrolyte additions on the electrokinetic properties of moderately concentrated (10 vol%) silicon nitride suspensions. The polyelectrolytes were added in such amounts (0.4 wt% PAA and 1.5 wt% PMAA-PEO 104N) as to assure saturation surface coverage and to minimize the amount of free polymer in solution. The analytical expressions included in the Acoustosizer software were used to calculate zeta potential values from the dynamic mobility data. We expect these approximations to be applicable to our system since the particulate phase exhibits a thin electrical double layer ($\kappa a \approx 165$).

The electroacoustic measurements show that the isoelectric point is shifted from $pH_{iep} = 5.8$ for the native silicon nitride powder to a much more acidic value $pH_{iep} = 3.5$ for the polyelectrolyte containing systems. This shift in pH_{iep} is a consequence of the adsorption of the anionic polyelectrolytes; the charged polyelectrolytes are able to induce a substantial negative charge at the silicon nitride/solution interface over the pH-range $3.5 < pH < 8$. At pH-values above 8, the zeta potential for the polyelectrolyte containing systems is essentially identical to that of the native powder. This supports the conjecture that the polyelectrolyte adsorption is negligible at basic conditions, in agreement with the adsorption results dicussed above. The difference in zeta potential between the bare silicon nitride suspensions and the suspensions containing polyelectrolyte is progressively increasing when decreasing the pH from pH 8 down to pH 6. Again, this is in line with the adsorption isotherms that reveal significant polyelectrolyte adsorption at pH 7.

The PMAA-PEO 104N system displays lower absolute values of the zeta potential in the range $3.5 < pH < 8$ compared to the PAA system. We attribute this difference to variations in adsorbed layer thicknesses and segment density profiles which result in different hydrodynamic properties and, thus, different dynamic mobilities of the coated particles. A correlation between the magnitude of the measured dynamic mobility (or the related zeta potential) and the average molecular weight

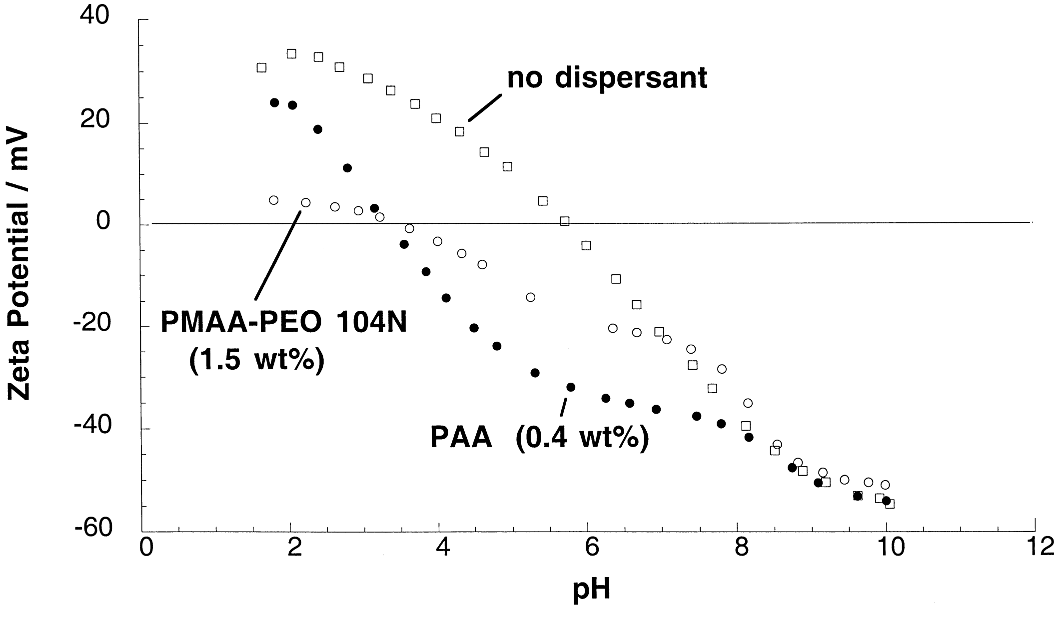

Fig. 4. Zeta potential vs pH for various polymeric additives at 10 vol% solids fraction: □, no polymer; ●, 0.4 wt% PAA; ○, 1.5 wt% PMAA-PEO 104N.

of the adsorbed polymer at constant pH has been reported for the adsorption of both PAA and PEO homopolymers onto silicon nitride by Hackley[10] and Eremenko et al.,[22] respectively. They found a lower absolute zeta potential or dynamic mobility for particles with adsorbed polymer of higher molecular weight (only at $pH > pH_{iep}^{Si_3N_4}$ in the case of PAA). For a thin, dense layer the hydrodynamic plane of shear is at the outer edge of the adsorbed layer. Thicker layers shift the plane of shear further away from the surface although the shear plane can be located somewhere within the adsorbed layer when the segment density is low. A lower absolute value of the zeta potential is the result of the shift further away from the surface since the electrostatic potential decays exponentially with distance.

The location of the shear plane depends on the layer thickness but in case of adsorbed polyelectrolytes the charge on the polymer chain complicates the interpretation. At constant pH the surface charge density and the charged fraction of the polyelectrolyte are practically unaffected by the molecular weight of the polymer. Yet, if the shear plane is positioned within the adsorbed layer, a fraction of the charged polymer segments will be located beyond the plane of shear. The larger the polyelectrolyte molecular weight the larger this fraction and the larger the decrease in absolute zeta potential.

3.3. Rheological behavior

The dependence of the steady shear viscosity on the polyelectrolyte concentration at pH 7 is given in Fig. 5. We find that anionic polyelectrolytes reduce the apparent viscosity drastically: already very low amounts of approximately 1 wt% or less polyelectrolyte result in a drop of the apparent viscosity by 2–3 orders of magnitude. Upon addition of approximately 0.3 wt% PAA a minimum in suspension viscosity of about 30 MPa s is reached. There are no significant differences in rheological response between the two PMAA-PEO modifications. Adding 1.3 wt% of a PMAA-PEO comb copolymer is sufficient to obtain a minimum suspension viscosity slightly lower than the minimum viscosity of the PAA system. The polyelectrolyte concentrations needed to achieve minimum suspension viscosity coincide very well with the plateau adsorption values of the adsorption isotherms, for both PMAA-PEO and PAA additions (Figs. 2 and 3).

There is a substantial difference in rheological response to excess addition of PMAA-PEO compared to PAA. While the viscosity increase is rather pronounced upon increasing the excess concentration of PAA, addition of excess PMAA-PEO has a negligible effect. For example, upon 2 wt% PAA and PMAA-PEO addition the suspension viscosity increases by 100 and 10%, respectively, compared to the minimum value. With regard to industrial applications this can be an important issue since the choice of dispersant affects the allowed margin in polyelectrolyte dosage and, hence, determines the risk of overdosage with its detrimental effect on suspension properties.

What is the cause of the increase in viscosity upon excess addition of polyelectrolytes? Polymer bridging effects can be excluded because in this concentration regime all particle surfaces are saturated with adsorbed

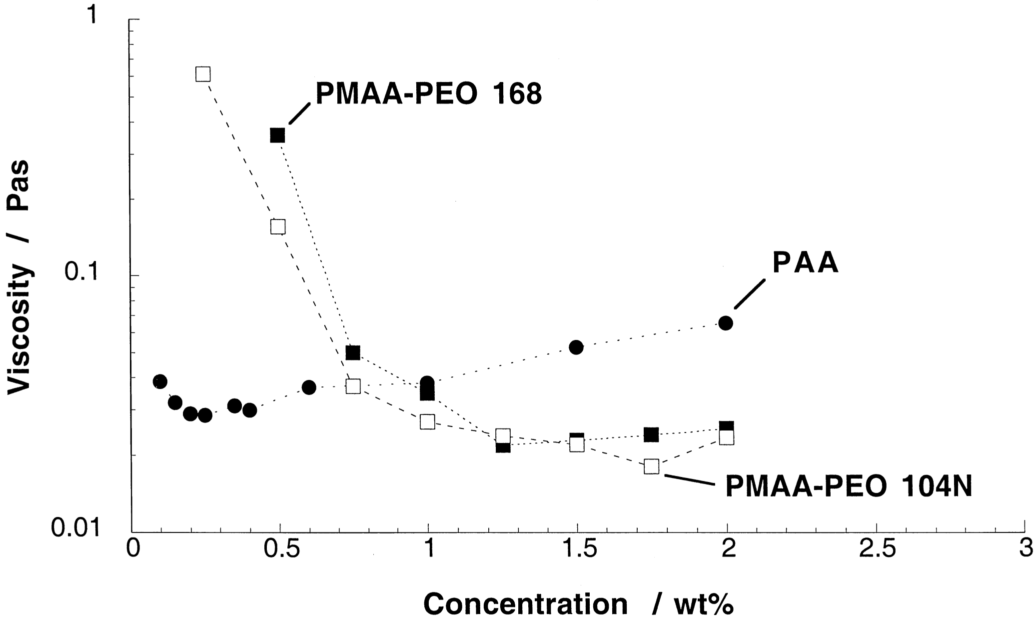

Fig. 5. Steady shear viscosity at a shear rate of 50 s^{-1} of 20 vol% suspensions at pH 7 as a function of polymer concentration: ■, PMAA-PEO 168; □, PMAA-PEO 104N; ●, PAA.

polymer. The addition of the polyelectrolytes in the corresponding concentration range results in a neglible increase in the viscosity of the continuous phase; hence, relative viscosity effects can be ruled out. It is unlikely that the increase in viscosity is related to an increasing thickness of the adsorbed layer with added amount. Such an effective volume effect is not likely to occur for fully covered surfaces. The fact that the systems containing polyelectrolytes with higher molecular weights, PMAA-PEO 168 ($M_w = 43\,200$) and PMAA-PEO 104N ($M_w = 32\,700$), actually display the lowest viscosities (Fig. 5) is a strong indication that effective volume effects are neglible.

Moving our focus to the associated counter ions of the polyelectrolyte provides a plausible explanation for the observed viscosity increase. Excess addition of polyelectrolyte gives rise to an increased counter ion concentration in solution. This change in ionic strength, however, can significantly affect the colloidal stability. Gourmand[23] concluded in a previous study that the poor stability of alumina suspensions upon excess addition of PAA at pH 9 was related to the increase in ionic strength. With increasing ionic strength we expect the electrostatic double layer forces to become very short range and the extended polyelectrolyte layer will collapse due to the screening of the electrostatic repulsion between charged sites of adjacent polyelectrolyte chains. Hence, the repulsive, electrosteric forces may become too short range to prohibit flocculation. In order to test this hypothesis, we rescaled the viscosity data in Fig. 5 to show the counterion concentration in the solution instead of the polyelectrolyte concentration (based on dry weight of the powder). The rescaling (Fig. 6) could be achieved by using data from the potentiometric acid-base titration of the respective polyelectrolytes.

We find that the marked increase in viscosity corresponds to a background electrolyte concentration of more than 50 mM. Fig. 6 also shows that the excess addition of PMAA-PEO resulted in counter ion concentrations below 30 mM. Hence, the relatively small increase in viscosity upon addition of relatively high amounts of PMAA-PEO 104N (in wt% dwb) is due to the low release of associated cations. This result also implies that the number of chargeable groups per unit mass of polymer is lower for PMAA-PEO 104N compared to PAA. In the light of these results, we find the previously proposed hydrodynamic coupling between particles and free polymer with extended conformation as an explanation to the observed viscosity increase[10] less likely.

Fig. 7 displays the steady shear viscosities of the investigated polyelectrolytes as a function of suspension pH. The lowest viscosity is obtained at pH 10 where the suspension is electrostatically stabilized. When the pH is decreased, a viscosity maximum around pH 8.5 and a minimum around pH 7 is observed. All polyelectrolytes exhibit a qualitatively similar behavior irrespective of the length of the grafted PEO chains. The higher viscosities at pH > 8.5 of the suspensions with PMAA-PEO 168 suggest bridging flocculation. Weak adsorption in combination with a high polymer chain length provide good conditions for polymer bridging between particle surfaces.[24]

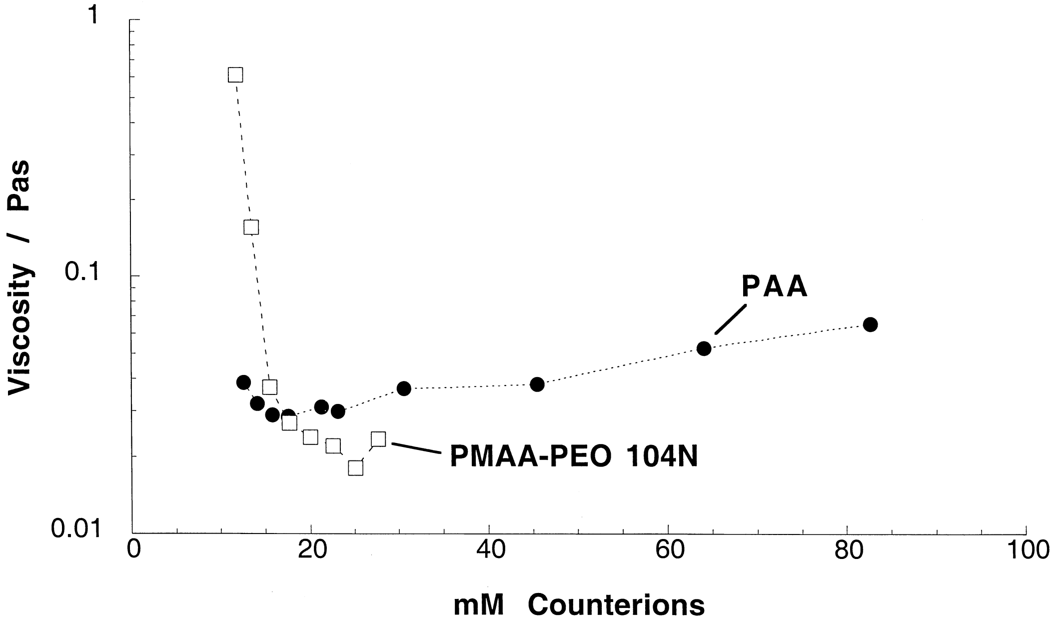

Fig. 6. Steady shear viscosity at a shear rate of 50 s^{-1} of 20 vol% suspensions at pH 7 as a function of counterion concentration: ●, PAA; □, PMAA-PEO 104N.

The experimental results for the systems with PMAA-PEO 104N and PAA suggest that the carboxylic functional groups dominate the electrostatic and specific interactions between the polyelectrolytes and the silicon nitride surface. A scheme of four different pH regimes can be used to summarize the general behavior of these systems as shown in Fig. 8. At pH > 9 both the polyelectrolyte and the silicon nitride surface are strongly negatively charged and the system is well dispersed due to electrostatic particle–particle repulsion. No adsorption

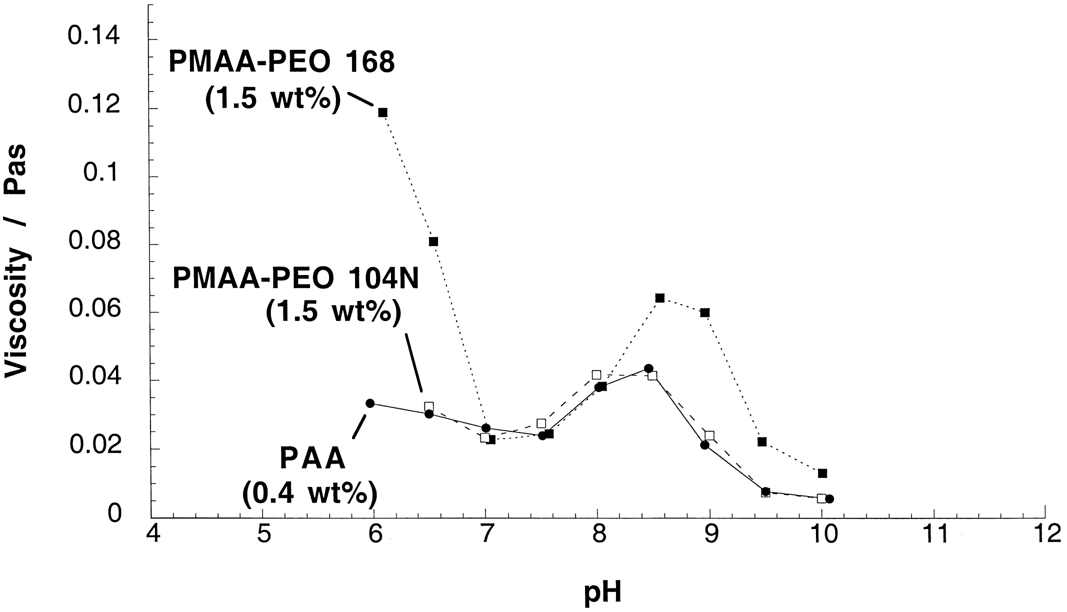

Fig. 7. Steady shear viscosity at a shear rate of 50 s^{-1} of 20 vol% suspensions containing: ●, 0.4 wt% PAA; ■, 1.5 wt% PMAA-PEO 168; □, 1.5 wt% PMAA-PEO 104N as a function of suspension pH.

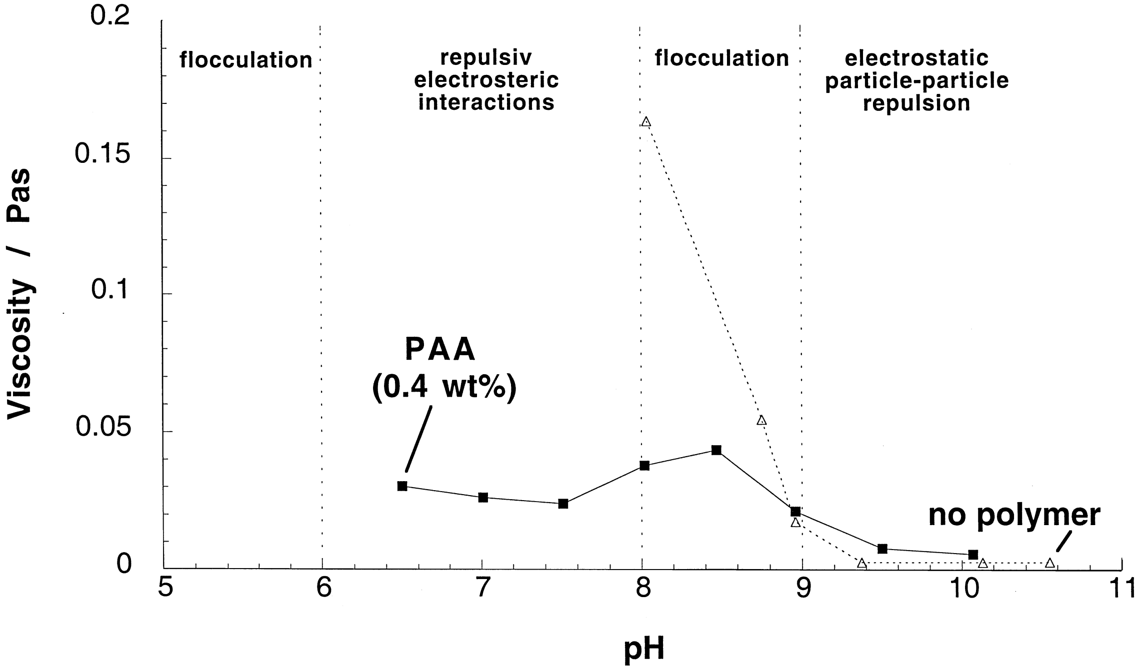

Fig. 8. Schematic presentation of different regimes in the pH dependent rheological response of silicon nitride suspensions. The data for the system with PAA is taken to be representative for all investigated systems. Data for a system without polymer additions is taken as a reference; △, no polymer; ■, 0.4 wt% PAA.

occurs because of highly repulsive electrostatic segment–surface interactions. At $pH < 9$ a regime with suspension flocculation is entered. Here, the magnitude of the surface charge decreases to a level where electrostatic particle–particle interaction is no longer sufficient for stabilization. At some point in this regime specific interactions between functional polymer groups and the surface sites overcome the electrostatic repulsion and adsorption commences. At low surface coverages polymer bridging occurs and enhances the electrostatically driven flocculation resulting in an increase in viscosity. Decreasing the pH further results in a higher surface coverage and a decreasing probability for polymer bridging; hence we observe a maximum in viscosity. The suspension becomes electrosterically stabilized when enough polyelectrolyte for surface saturation has adsorbed; this is characterized by the minimum in viscosity.

The charging and solution conditions in that regime are comparable to the system investigated recently by Guldberg Pedersen and Bergström.[12] They measured the interparticle forces between ZrO_2 surfaces with adsorbed PAA layers in aqueous 0.01 M NaCl solutions and showed that at alkaline pH conditions long-range steric forces are active additional to the electrostatic double layer forces. The electrosteric interparticle forces were observed at basic pH slightly above the pH_{iep} of zirconia where both surface and polyelectrolyte are negatively charged and a stretched conformation of the adsorbed polymer chains is promoted, similar to our silicon nitride system at pH 6–8. Because the steady shear viscosity in this pH range is practically identical for all investigated anionic polyelectrolytes (Fig. 7) it can be concluded that the grafted PEO chains do not impart an enhanced steric repulsion to the system. That means that the PEO chains do not extend further into solution than loops or tails of the polyacrylic backbone, as schematically illustrated in Fig. 9.

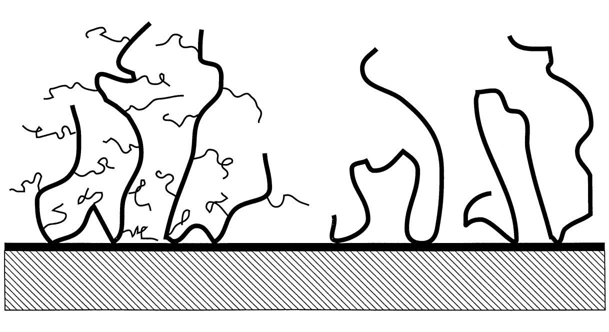

Fig. 9. Schematic illustration of the polymer conformation of anionic polyelectrolytes (PAA and PMAA-PEO) adsorbed on the silicon nitride surface in aqueous medium at basic pH ($pH_{iep}^{Si_3N_4} < pH < 8$).

4. Conclusions

The addition of anionic acrylic-type polyelectrolytes in aqueous silicon nitride suspensions results in a rheological response that is strongly dependent on pH and amount added. Comparing the two polymers, we find that the adsorption of the simple PAA and PMAA-PEO comb copolymer modifications on silicon nitride at $pH > pH_{iep}$ are governed by the same mechanisms. Surface–segment interactions of non-electrostatic nature account for the driving force of adsorption, counteracted by repulsive electrostatic forces between the charged sites of the polyelectrolyte and the surface. At $pH > pH_{iep}^{Si_3N_4}$ the charged fraction of the polyelectrolyte segments and the magnitude of the specific surface–segment interactions are practically independent pf pH. Consequently, the suspension stability is controlled solely by the silicon nitride surface charge density. At $pH > 9$ the adsorption is negligible due to highly repulsive electrostatic surface–segment interactions; a stable suspension is obtained, however, due to electrostatic interparticle repulsion originating from the dissociated surface groups.

Decreasing the suspension pH below pH 9 reduces the surface charge density of the silicon nitride which results in flocculation. As a consequence of the reduced electrostatic segment–surface repulsion, polyelectrolyte adsorption is observed at $pH_{iep}^{Si_3N_4} < pH < 9$. The amount of adsorbed polyelectrolyte increases with decreasing pH values until surface saturation is reached where the combination of electrostatic and steric particle interactions results in a viscosity minimum at pH 7. Grafted PEO side chains of varying length did not affect the general stabilization characteristics which indicates that the polyacrylic backbone attained an extended conformation perpendicular to the solid surface. At $pH < pH_{iep}^{Si_3N_4}$ incipient flocculation due to insufficient dissociation of the adsorbed polyelectrolytes results in a strong increase in viscosity. We were able to relate the viscosity increase at excess addition of polyelectrolyte to the ionization of free polymer in solution. Dissociation of the functional groups of the polymer leads to a release of cations. This increases the counterion concentration, thus inducing electrostatic screening effects and the resulting weak flocculation of the suspension.

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