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Surface charge and rheological properties of raw porcelain gres suspension with acrylic copolymers bearing carboxylic groups

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Abstract

The continuous demand of porcelain gres as a raw material for many ceramic applications is requiring a particular attention to the green body properties. The fluidity of these suspensions must be appropriate and their solid content must be as high as possible in order to minimize the drying cost. To circumvent this problem, incorporation of polyelectrolytes to get a high state of dispersion could be a solution. In this contribution, the effect of copolymers bearing carboxylate during the preparation of aqueous porcelain gres suspensions was investigated using adsorption isotherms, electrokinetic properties and rheology. The trends by the adsorption isotherms suggest the formation of a monolayer according to the Langmuir model. Moreover, the density of charge of the surface of porcelain gres particle was found to depend on the quantity of adsorbed carboxylic groups. The ability of the acrylic copolymer to stabilize porcelain gres suspension was found to be greatly affected by the content of carboxylic groups contained in the macromolecular chain. Moreover, we analyzed the relation between polymer adsorption and flow properties of concentrated suspension.

Keywords: Powders-chemical preparation; Suspensions; Chemical properties; Porcelain; Silicate

1. Introduction

Within the great range of products offered by the ceramic industry, developments in porcelain tile commonly referred to as porcelain gres, have been outstanding. Some processing techniques, for example slip casting or injection moulding, use ceramic suspensions with high solid volume and proper stability to improve its economics.[1] However, with increasing solid loading, processing of a suspension becomes increasingly difficult. Since its flow characteristics are usually of crucial importance, they have to be controlled in order to yield a final product with the best properties as well as to improve the economics of the process to optimize energy requirements.[2]

In preparation of raw porcelain gres systems, solids are dispersed in the suspending fluid as fine particulates and remain separated from each other through electrostatic, steric, or electrosteric stabilization. Control of the range of interparticle interactions is of significant importance in terms of stability and flow properties. In order to improve the material properties, interparticle forces in the suspension should be manipulated during processing and forming.[3] These interactions are: Van deer Waals attractive forces, electrostatic repulsive forces, steric (due to the adsorbed polymer) and electrosteric (polyelectrolytes) forces, depletion forces (due to the presence of free polymers), and structural (hydration) forces (short range). Fine particles tend to attract each other due to Van der Waals attractive forces. Brownian motion of the particles resists this force tending to keep the particles in the dispersed state. However, if the former dominates, particles will aggregate into flocs and trap the suspending fluid, leading to a high viscosity. Van der Waals attractive forces can be neutralized through the addition of like charges, and adsorbing or grafting polymer molecules onto the surface of the particles. In the first case, stabilization occurs due to electrostatic repulsion, while in the second case, stabilization occurs due to steric repulsive forces.

Quite often, minor quantities of polyelectrolytes are added in a classical deflocculating mixture with sodium silicate to get a homogenous dispersion of the powder in the liquid phase, thus leading to both high solid loadings and low viscosities.[4] After adsorption onto the surface of the particle, polyelectrolytes

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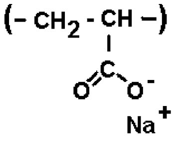
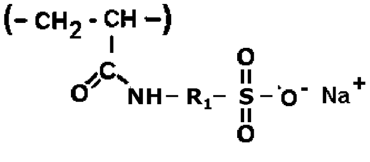
create an excess of charge which results in the formation of an electrical double layer around each particle. Interactions between double layers result in net repulsive electrostatic and steric forces, which prevent the particles coming physically close enough for the attractive force.[5]

Polyacrylic acids are frequently used to disperse oxide particles.[6–9] The adsorption of polyacrylic acids on these particles was found to be responsible for the dispersion. It was shown that polyacrylic acid strongly adsorbed on positively charge particle surfaces.[10] At a pH of around 8, as used in this study, the density of positive charges on the surface of porcelain gres particle (pH lower than $\mathrm{pH_{IEP}}$[11]) was large enough to allow electrostatic interactions with COO^- groups of the copolymer chain.[12,13] Moreover, the effect of copolymer molecular weight had been found to affect suspension stability.[4,5,12]

The purpose of this paper was to investigate the stability of concentrated suspensions of raw porcelain particles in the presence of different acrylic copolymers in the classical and economical deflocculating mixture with sodium silicate,[14,15] in order to find the more effective dispersing agents for maximizing the solid loading of the suspension. In this study, four different polyelectrolytes were evaluated: (1) a linear homopolymer of sodium acrylate (SA), carrying hydrophilic weak acid carboxylate as an ionized main group (Table 1); (2) two random linear copolymer comprised of 90% of sodium acrylate (SA) and 10% of sodium alkyl sulfonated (SS) a hydrophilic strong acid group, one with a high molecular weight and another with a low molecular weight (Table 1); (3) copolymer with 77% of sodium acrylate (SA) and 23% of sodium alkyl sulfonated (SS) (Table 1).

The adsorption of polyelectrolytes at interfaces was discussed by Lyklema.[16] The presence of several polyelectrolytes in the same system may induce a competitive adsorption, which can in turn affect rheological properties and dispersion stability.[17,18] Different studies suggest that the adsorption mechanism of polymer contained a weak acid carboxylate group, as sodium acrylate (SA), with the ceramic particle proceeds via electrostatic interactions.[13]

Table 1
Chemical structure and properties of polyelectrolytes

Polymer	Chemical Structure
Sodium acrylate homopolymer (SA) MW (SA) = 2000 Max. polymer charge density (pH $\sim$8) = 984 C g^{-1}	
Sodium alkyl sulfonate (SS) SS$_1$: 10 wt.% SS MW(SA/SS$_1$) = 4000 Max. polymer charge density (pH $\sim$8) = 859 C g^{-1} SS$_2$: 10 wt.% SS MW(SA/SS$_2$) = 9800 Max. polymer charge density (pH $\sim$8) = 859 C g^{-1} SS$_3$: 23 wt.% SS MW(SA/SS$_3$) = 2000 Max. polymer charge density (pH $\sim$8) = 742 C g^{-1}	

In this work, we also examined the relationship between the specific electrical charge of the polyelectrolyte and the range of repulsive forces between particles. The density charge on the polyion depends on the number of ionisable groups in the polymer and on the degree of dissociation.[19] Thus, it can be expected that the electrical double layer of a particle will be altered due to the adsorption of charge polymer onto the particle surface.

Rheological measurements have been used for the evaluation of the fluidity of powder suspensions.[20] A rheological test was established to obtain the rheological behaviour of porcelain gres suspensions.[21]

From the experimental results, it is possible to analyze qualitatively the relation between polymer adsorption onto the particle, specific polymer electrical charge and stability of concentrated suspensions.

2. Experimental procedure

2.1. Materials

The basic composition of the raw porcelain gres material was a synthetic mixture supplied by ECESA (Lugo, Spain) whose mineralogical composition was 45 wt.% feldspar, as flux, 40 wt.% plastic clay, as plasticizing agent, and 15 wt.% kaolin, as whiting agent. The mean diameter of the raw porcelain gres particles, measured by laser diffraction (LD), was 2.5 μm and with about 100% of the material below 3–4 μm and the 50% of the ceramic particles were larger than 1 μm. The specific surface area for this powder was 16.9 $m^2\,g^{-1}$, determined by nitrogen adsorption (BET). The isoelectric point (IEP) was at pH 9.0, determined by acid–base titration.[22] Rohm and Hass supplied all tested polyelectrolytes. The linear homopolymer of sodium acrylate (SA) is used in the ceramic industry as a classical mixture with sodium silicate. The three random linear copolymers, SA/SS, are used as paint additive to improve the paint flows, to make it stick better and to limit mildew growth. The SA/SS copolymers have a higher acidity than the typical sodium polyacrylate due to the terminal acid sulfonate group. A series of three different copolymers, SA/SS$_1$, SA/SS$_2$ and SA/SS$_3$, have been tested in order to study the effect of the chemical composition and the molecular weight on the stabilization. Some physical properties and the chemical structures of these dispersants are given in Table 1.

All tested deflocculant mixtures contained 25 wt.% of commercial polymer with a solid content of 50 wt.% and a 75 wt.% of sodium silicate ($SiO_2/Na_2O = 1$) supplied by FMC Foret Corporation. This is a typical formulation used by ceramic suspension manufacturers where the polyelectrolyte is the main ingredient and sodium silicate acts as coadjuvant,[23] an electrolyte which not modifies the action of the principal ingredient and improves the electrostatic stabilization.

2.2. Methods

2.2.1. Adsorption isotherms

Ceramic dispersions were prepared by mixing 1 g of the raw material with 50 mL of polymeric solution, without sodium silicate. A total of 24 different dispersions were prepared by adding the four different polymers at six different concentrations: 0, 2, 10, 20, 30 and 40 mg L^{-1}. The natural pH of the solutions was around 8. The mixture was stirred overnight. After equilibration took place, the mixture was centrifuged. The settled dispersion was filtrated with a 0.2-μm cellulose microfilter. The polymer concentration in the filtered solution was determined by the nephelometric method using a UV/VIS Lambda 20 (PerkinElmer, United States) spectrophotometer.

The amount of polymer adsorbed on the particles was evaluated from the difference between the initial polymer concentration and the polymer concentration in the supernatant.

2.2.2. Electrophoretic measurements

The specific polymeric electrical charge was determined from the measurement of zeta potential. This measure was evaluated by electrophoresis. A diluted porcelain gres suspension was prepared by dispersing 0.1 g of porcelain gres in 100 mL of solution. A total of 20 different polymer solutions were prepared by adding the four different polymers at five different concentrations: 0, 50, 100, 200 and 250 mg L^{-1}. A ZetaSizer instrument (ZetaSizer Nano ZS, Malvern Instruments Inc., United Kingdom) was used to evaluate the dynamic mobility.[24] The zeta potential, ζ, was calculated from the dynamic mobility according to the Smoluchowski theory.[24]

2.2.3. Rheological measurements

The slurry was prepared by mixing the raw porcelain material, water and deflocculant mixture, followed by ultrasonication (Ultrasonic Bandelin Sonoplus, Germany) for 10 min in order to homogenize the suspension. Polymer adsorption takes several hours to reach equilibrium. Therefore, the obtained suspension was kept in a sealed flask for a day at 25 °C before testing. The final pH of the suspensions was around 8. All suspensions were prepared with 35% (w/w) of water. A total of four different suspensions were prepared by adding the different polyelectrolyte mixtures at 0.057% (w/w), on the basis of dry material. This is a common composition used for the preparation of ceramic concentrated suspensions.

The rheological experiments were carried out in a rotational rheometer, HAAKE CV20 at 25 °C. The measuring device was the ME31 bob/cup sensor system (inner cylinder diameter 28.93 mm, beaker diameter 30.0 mm, length 24.0 mm and sample volume 1.80 cm^3). The rheological test consisted of the following steps: (1) leaving the dispersion undisturbed in the rheometer sensor system for 15 min, (2) linearly increasing the shear rate from 0 s^{-1} to maximum shear rate within 5 min (LS-HS), (3) shearing at the maximum shear rate for 5 min to attain the steady state viscosity at this shear rate and (4) linearly decreasing of the shear rate from maximum to 0 s^{-1} within 5 min (HS-LS). Three maximum shear rates were tested: 20, 100 and 500 s^{-1}.

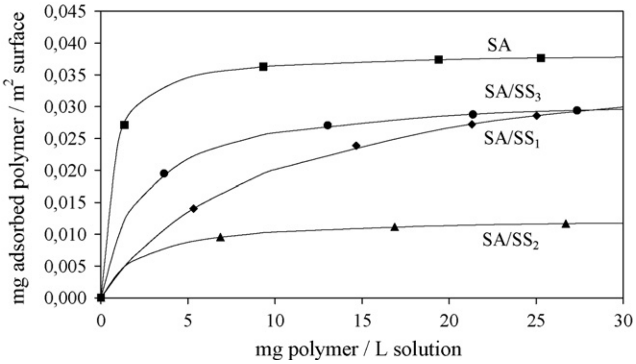


Fig. 1. Adsorption isotherms: SA (■), SA/SS$_1$ (♦), SA/SS$_2$ (▲) and SA/SS$_3$ (●).

3. Results and discussion

3.1. Adsorption isotherms

The isotherms for each polymer at different polymeric concentration are shown in Fig. 1.

In all cases, the adsorbed amount increased as the polymer concentration increases, until a plateau was reached. The plateau observed in the isotherms indicated a monolayer adsorption of the polymers, independently of their composition.[1,25,26]

At pH below the IEP of the raw porcelain gres the positive charge of the particles anchors negatively charged dispersants[23,26–29] (remember that pK_a of acrylic acid is 6.0 and pK_a of sulfonic acid is below 1).[30,31] After the adsorption, the interactions between electrical double layers result in repulsion among the particles and electrostatic stabilization takes place.

Results given in Fig. 1 indicated that the adsorption density in the presence of SA polymer was larger than with copolymers. Therefore, the acrylic content seems to control the adsorption process. Within the range of SA/SS concentrations investigated, some difference on the adsorption isotherms was observed. It is apparent from the results that copolymer with a low molecular weight and a high acrylic content (SA/SS$_3$) was more effective than the two others copolymers, SA/SS$_1$ and SA/SS$_2$.

For these systems, the Langmuir model was a good predictor of polymer adsorption onto porcelain gres particles.[32,33]

The constant K, as well as the adsorbed polymer concentration at plateau, C_m^S, was evaluated from the Langmuir equation and the data obtained are reported in Table 2.

The amounts of SA/SS adsorbed were smaller than the amount of SA adsorbed. Large values of C_m^S and lower values of K confirmed the high affinity of SA to porcelain particles.

Table 2
Langmuir adsorption parameters

Polymer	Adsorption K (L mol^{-1})	Parameters C_m^S (mg m^{-2})
SA	0.567 ± 0.30	0.039 ± 0.20
SA/SS$_1$	2.316 ± 0.09	0.032 ± 0.09
SA/SS$_2$	9.687 ± 0.10	0.013 ± 0.10
SA/SS$_3$	2.233 ± 0.10	0.040 ± 0.09

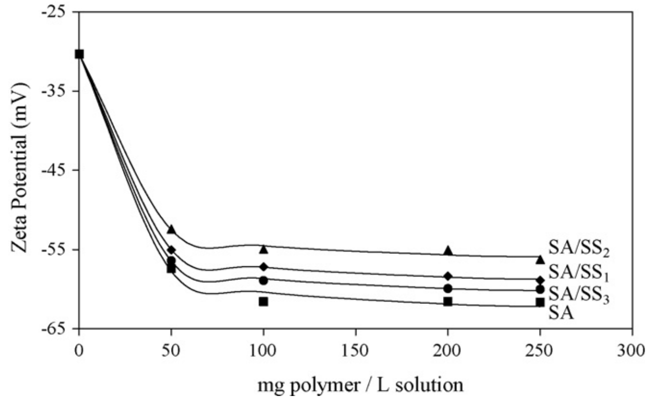


Fig. 2. Zeta potential of porcelain gres particles in the presence of SA (■), SA/SS$_1$ (♦), SA/SS$_2$ (▲) and SA/SS$_3$ (●).

As mentioned before, this behaviour may be explained by the stronger interaction of carboxyl groups with the ceramic particles.

3.2. Zeta potential

The Smoluchowski zeta potential of porcelain gres particles for each adsorbed polymer at different polymer concentration is shown in Fig. 2.

It can be observed from this figure that over the entire range of polymer dosage the zeta potential values indicate a negative charge on the surface of the particles. The magnitude of the zeta potential increased significantly as the polymer gradually covered the surface of the particles and reached a plateau corresponding to the value of saturation adsorption density. This fact suggests that the anionic polyelectrolytes adsorb to the positive sites on the particles.

In order to investigate the effect of the polymer electrical charge, the experimental values of zeta potential were adjusted by the following equation:

$$\frac{\zeta-\zeta_0}{\zeta_{\min}-\zeta_0}=\frac{C^{\mathrm{L}}}{b+C^{\mathrm{L}}} \qquad (1)$$

where ζ is the zeta potential in mV, ζ_0 is the zeta potential value in absence of polymer in mV, $\zeta_{\min}$ is the minimum zeta potential in mV, and b is fit parameter in mg L^{-1}.

In addition, we calculated the specific polymer electrical charge, θ (F g^{-1}) dividing the electrical charge between the polymer molecular weight, considering that all ionic group are completely ionisable. The data obtained are reported in Table 3.

Table 3
Electrophoretic parameters of ($\zeta_{\min}-\zeta_0$), b and specific polymer charge, θ

Polymer	Electrophoretic	Parameters	
	($\zeta_{\min}-\zeta_0$) (mV)	b (mg L^{-1})	θ (F g^{-1})
SA	33.2 ± 0.08	8.7 ± 0.05	0.011
SA/SS$_1$	29.5 ± 0.10	9.8 ± 0.09	0.009
SA/SS$_2$	26.6 ± 0.30	10.0 ± 0.20	0.009
SA/SS$_3$	31.0 ± 0.10	9.2 ± 0.09	0.008

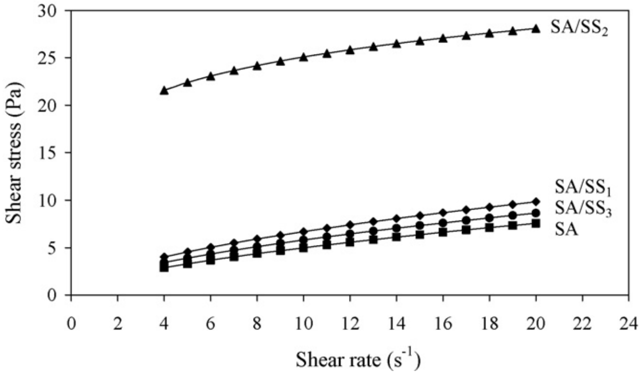


Fig. 3. Shear stress (Pa) versus shear rate (s^{-1}) particle concentration 0.057% (w/w) SA (■), SA/SS$_1$ (♦), SA/SS$_2$ (▲) and SA/SS$_3$ (●), when a linear increasing of shear rate up to 20 s^{-1} for 5 min is carried out.

The zeta potential, ζ, correlated with the specific polymer electrical charge and the adsorption amount. Therefore, both characteristics may affect the final particle electrical charge.

Addition of SA produced the highest negative zeta potential at the lowest dispersant addition (Fig. 2). All results indicated that the amount of carboxylic groups adsorbed controls the effective charge density of the particle surface and therefore, the electrostatic repulsion.[34,35]

Within the range of concentrations investigated, differences on the zeta potential were observed. This behaviour is agreement with the adsorption studies which indicated that interaction between the carboxyl group and the particle surface was higher than the one obtained with the sulfonic group. Moreover, SA/SS$_2$ showed the lowest zeta potential magnitude which is due to the compression of the double layer around the particles with increasing molecular weight.[36]

3.3. Rheological parameters

Figs. 3–5 show the plots of the shear stress versus shear rate as a function of different maximum shear rates (20, 100 and 500 s^{-1}) for the tested polymers. Moreover, Fig. 6 shows the steady state viscosity values for the same maximum shear rates.

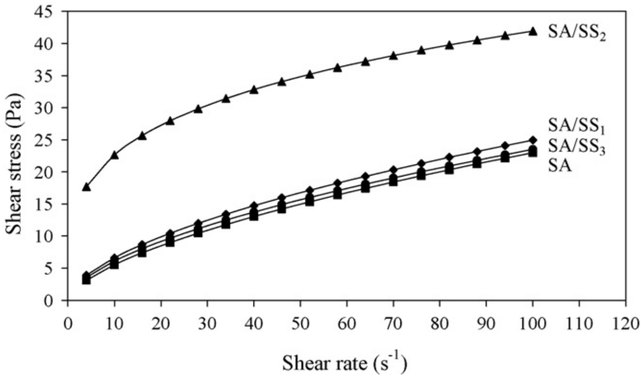


Fig. 4. Shear stress (Pa) versus shear rate (s^{-1}) particle concentration 0.057% (w/w) SA (■), SA/SS$_1$ (♦), SA/SS$_2$ (▲) and SA/SS$_3$ (●), when a linear increasing of shear rate up to 100 s^{-1} for 5 min is carried out.

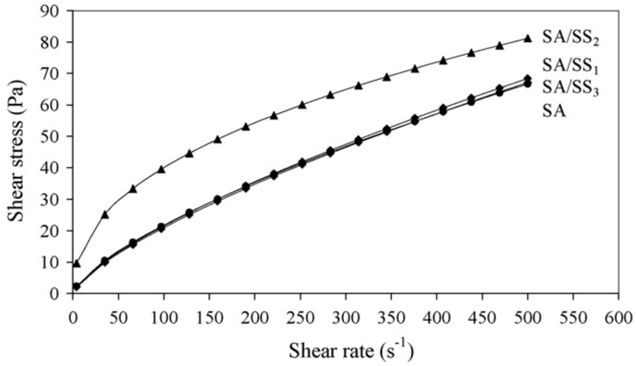


Fig. 5. Shear stress (Pa) versus shear rate (s^{-1}) particle concentration 0.057% (w/w) SA (■), SA/SS$_1$ (♦), SA/SS$_2$ (▲) and SA/SS$_3$ (●), when a linear increasing of shear rate up to 500 s^{-1} for 5 min is carried out.

The rheological behaviour of raw porcelain gres suspensions is strongly dependent on both nature of deflocculant and maximum shear rate applied. All the porcelain dispersions display a shear-thinning behaviour.[37] It can be seen that SA polymer produced the lowest shear stress.

To compare the rheological properties, we apply a simplified version of a rheological model presented elsewhere.[19,38] The model assumes that the shear stress, σ, is a function of the shear rate, $\dot{\gamma}$ and the structural viscosity, $\eta(\dot{\gamma})$, which depends on the shear rate. For these concentrated ceramic suspensions, the relationship between the steady state shear stress and the shear rate can be described as a power-law function,[39] $\sigma = k\,\dot{\gamma}^n$, where k is the consistency index and n is the flow behaviour index. A lower value for the consistency index for an identical flow behaviour index denotes lower viscosity. The adjusted rheological parameters are collected in Table 4.

From rheological parameters values, the most effective polyelectrolyte was SA and the least effective was SA/SS$_3$. This means that the viscosity is lowered in a more effective way when the polyelectrolyte has charged groups derived from strong acids. Furthermore, in the explaining the lowest viscosity in the presence of SA, the smaller number of anionic groups ($SO_3{}^-$) in SA/SS copolymers in comparison with COO^- groups in the SA, should be taken into account.

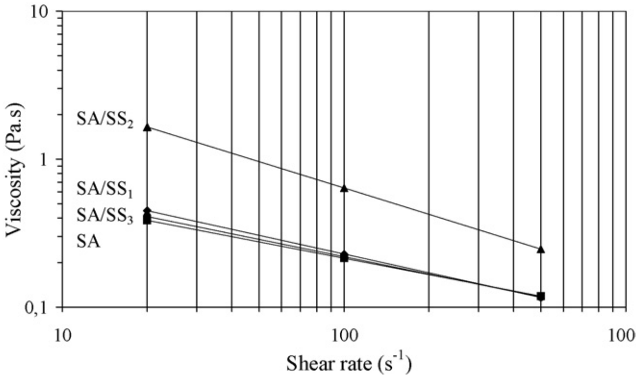


Fig. 6. Steady state viscosities at particle concentration 0.057% (w/w) SA (■), SA/SS$_1$ (♦), SA/SS$_2$ (▲) and SA/SS$_3$ (●) for the three maximum shear rates tested (20, 100 and 500 s^{-1}).

Table 4
Rheological parameters k, n and values of steady state viscosities

Polymer	Rheological parameters				
	k (Pa s^n)	n (−)	Viscosity (Pa s)		
			γ_{20} (s^{-1})	γ_{100} (s^{-1})	γ_{500} (s^{-1})
SA	1.16	0.63	0.698	0.386	0.214
SA/SS$_1$	1.58	0.58	0.884	0.450	0.229
SA/SS$_2$	9.67	0.41	1.666	0.648	0.252
SA/SS$_3$	1.32	0.61	0.772	0.414	0.222

Experimental results showed that there was a direct relation between the rheology of the suspensions, the adsorption density of the adsorbed polymer and the zeta potential.[5] Based on the results shown in Figs. 2–6, the increase in the amount of adsorbed anionic polymer increased the absolute value of the zeta potential which suggests improved suspension fluidity. As a consequence, it can be concluded that the colloidal stability is controlled by an electrical effect than a steric effect.

4. Conclusions

The stability of suspensions of raw material for porcelain gres deflocculated with four polymers (SA, SA/SS$_1$, SA/SS$_2$, SA/SS$_3$) was studied by adsorption experiments, electrophoretic and rheological measurements. The electrical charge densities of the tested polymers indicated that electrical repulsion was stronger in the presence of a high content of acrylic monomer and low molecular weight. This suggests that the influence of electrical repulsion forces seems to be more significant than the influence of steric forces in stabilizing concentrated raw porcelain gres suspensions.

SA/SS copolymers with low molecular weight (SA/SS$_3$ and SA/SS$_1$) were effective in reducing the viscosities of concentrated raw porcelain suspensions, although the efficiency of these deflocculant mixtures was slightly lower than that of SA alone.

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