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Effect of copolymer dispersant structure on the properties of alumina suspensions

Samir Baklouti[a,*], Mohamed Ramzi Ben Romdhane[a], Sami Boufi[b], Cécile Pagnoux[c], Thierry Chartier[c], Jean François Baumard[c]

[a]*Laboratoire de Chimie Industrielle, Equipe Céramique, E.N.I.S., B.P. W, 3038 Sfax, Tunisia*
[b]*Faculté des Sciences de Sfax, Tunisia*
[c]*SPCTS UMR CNRS 6638, E.N.S.C.I., 87065 Limoges, France*

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Abstract

The effects of the molecular structure of sulfonic copolymer dispersants on the interaction with alumina particle surfaces in water and on the rheological properties of alumina suspensions are studied. Sulfonic copolymers with various contents of sulfonate groups were synthetised. The polyelectrolyte-solid surface interactions were investigated through electrokinetic properties and adsorption measurements. The optimum conditions to ensure the stability of the alumina suspension, estimated through particle size distribution and rheology behavior, were obtained for the maximum electrostatic repulsive force with the highest SO_3^- group fraction. Changes in the configuration of the adsorbed polymer versus the fraction of SO_3^- group was also discussed.

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1. Introduction

Polyelectrolytes are widely used in colloidal processing of ceramic powders to improve characteristics of suspensions such as, powder concentration homogeneity, rheology and state of dispersion. These characteristics are necessary to obtain high density green parts with a homogeneous microstructure.[1–4]

The dispersion of colloidal ceramic particles in an aqueous media using a charged homopolymer has been investigated extensively.[5–8] Most often, such a dispersion is obtained by an electrosteric mechanism. The stabilizing forces that result from electrical double layer repulsion and/or steric interaction must be sufficiently large in magnitude to provide an energy barrier against aggregation. Several factors, such as pH, temperature and ionic strength, nature, structure and molecular weight of the polyelectrolyte and its degree of dissociation can affect the respective contribution of electrostatic and steric interactions.[9–12]

The interactions of copolymers with ceramic powders have received little attention.[13] Compared to homopolymers, copolymers present the advantage to have different functional groups, which can play different roles in ceramic processing and then can reduce the number of additives. In this respect, the copolymer used in this study, denoted AMPS(n), presents two functional groups, sulfonic group and hydroxyl group. The first charged group is known to be responsible for ceramic powder dispersion[14] whereas the second group could be the basis of a binder in ceramic green products [15].

The aim of the present work is to study the effect of this charged copolymer [AMPS(n)] structure on the properties of a ceramic suspension. Specifically, the objective was to provide a clearer understanding of the basic mechanisms of interaction between the copolymer and the alumina particles, and of the effects on suspension behavior. The interactions of these copolymers with alumina surface were analysed using a combination of adsorption and electrokinetic measurements.

The effect of these copolymers on the mechanical properties of the green products will be presented in a next paper.

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[*] Corresponding author.
E-mail address: samir.baklouti@fss.rnu.tn (S. Baklouti).

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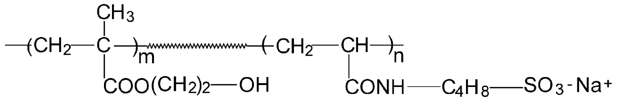

$$-(CH_2-\overset{CH_3}{\underset{COO(CH_2)_2-OH}{C}}-)_m \sim\sim (CH_2-\underset{CONH-C_4H_8-SO_3^-Na^+}{CH}-)_n$$

Fig. 1. The structure of the copolymer model compound: AMPS(n).

2. Experimental

2.1. Copolymer dispersants

The molecular structure of the dispersants used in this study is shown in Fig. 1. They are copolymers of sodium salt of a sulfonic acid and hydroxy ethyl methacrylate with different SO_3^- group fractions (n%) (Table 1). Each copolymer was prepared by radical copolymerisation of the sodium salt of 2-acrylamido-2-methyl propane sulfonic acid and hydroxy ethyl methacrylate monomers. The reaction was carried out in an aqueous medium at 60 °C during 2 h with persulfate ($K_2S_2O_8$) as initiator and thiosulfate ($K_2S_2O_3$) as activator. After precipitation in acetone, the copolymer is isolated, then dried under a nitrogen atmosphere. The amount of SO_3^- groups in the copolymer was determined by colloidal titration with a cationic polyelectrolyte. The average molecular weight of each polymer was estimated by intrinsic viscosity measurements using the Mark Houwink equation:[16]

$$[\eta] = KM_W^a$$

where $[\eta]$ is the intrinsic viscosity and K and a are constants ($K = 3.6\times10^{-5}$ and $a = 0.77$). These copolymers remain totally ionised in a large pH domain ($3 < pH < 12$).

2.2. Powder characterisation and suspension preparation

An α-Al_2O_3 powder (P172SB, Pechiney-France) was used in all experiments. This powder is characterised by a mean diameter of 0.34 μm and a specific surface area (BET) of 10 $m^2\ g^{-1}$.

The alumina suspensions were prepared with volume fractions in the range of 2.7–27.4%, depending on the experiment. The required amount of copolymer AMPS(n) was first dissolved in deionised water, then the alumina powder was added to the solution. The suspensions obtained were subjected to ultrasonic treatment ($P = 200$ W for 15 min) to break down agglomerates. In order to establish equilibrium, the suspensions were aged for 24 h at room temperature using a magnetic stirrer. In order to determine the amount of copolymer adsorbed onto alumina particles, the amount of free, non adsorbed, polymer in solution was measured. For this purpose, alumina suspensions, prepared with a variable amount of polymer, were centrifugated at speed of 3000 rpm for 1 h and the concentration of free polymer in the supernatant was determined by colloidal titration technique using poly(trimethyl ammonium ethyl acrylate chloride) solution and orthotoluidine blue as indicator[17] To adjust the pH of suspensions, reagents as HCl (0.1 M) and NaOH (0.1 M) were used.

Table 1
Characteristics of the various copolymer dispersants

Polyelectrolyte	SO_3^- group fraction n (%)	Estimated average molecular weight M_w (g mol^{-1})
AMPS(100)	100	16 000
AMPS(80)	80	17 000
AMPS(55)	55	18 000
AMPS(20)	20	17 000

The electrokinetic behavior of alumina suspensions was characterised by using an electroacoustic technique (Model ESA800, Matec, Northborough, MA, USA). The measured electrokinetic sonic amplitude (ESA) is the acoustic wave amplitude that is generated by the ceramic suspension per unit electric-field strength and that is directly proportional to the dynamic electrophoretic mobility, which in turn is a function of the particle zeta potential (shear plane).[18]

The rheological behavior of the alumina suspensions was measured at 25 °C by a controlled-stress rheometer (Stress Tech, Rheologia, Sweeden) using a plane-cone geometry. The particle size distribution of alumina powder in suspension was measured by X-ray gravitational sedimentation analysis (Sedigraph 5100, Micromeritics).

3. Result and discussion

3.1. Adsorption isotherms

The adsorption of AMPS(n) with different anionic group (SO_3^-) contents (n) onto the surface of alumina powder at pH 8.5–9 is displayed in Fig. 2. For all

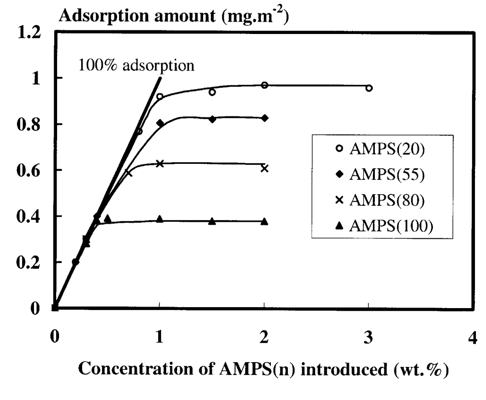

Fig. 2. Adsorption isotherms for AMPS(n) copolymers on alumina surface as a function of the amount of AMPS(n) introduced.

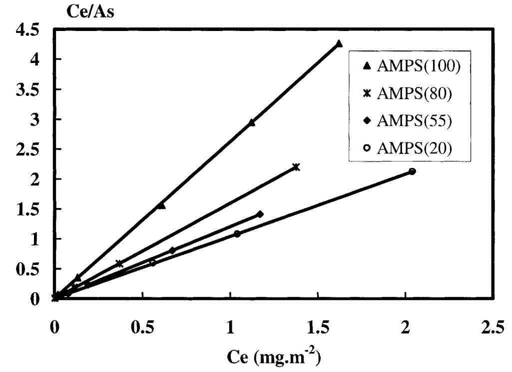

Fig. 3. Replot of Fig. 2 according to the Langmuir equation.

polymers, the adsorption curves present a characteristic plateau, which corresponds to the amount of AMPS(n) C_m required for a monolayer coverage (adsorbance). With increasing SO_3^- group content, the relative amount of polymer adsorbed on the surface decreases. To determine the monolayer AMPS(n) adsorbance C_m quantitatively, the data in Fig. 3 is analyzed using the Langmuir monolayer adsorption equation:[19]

$$C_e/A_s = C_e/C_m + 1/(K.C_m) \quad (1)$$

where C_e is the equilibrium concentration of AMPS(n) in solution expressed in mg m^{-2} with respect to alumina, C_m the monolayer adsorbance of AMPS(n) expressed in mg m^{-2}, A_s the adsorbance of AMPS(n) polymer and K an adsorption constant. A linear variation of C_e/A_s in function of C_e was observed (Fig. 3) that indicates that these isotherms are of Langmuir monolayer-type adsorption. The slopes of the lines represent the reciprocal of the monolayer adsorbance of AMPS(n). The amount of monolayer AMPS(n) adsorption decreases as the SO_3^- group fraction increases (Table 2). At low polymer additions, the total adsorption of the polymer implies a high affinity between the polymer and the alumina surface.

The adsorption of polymer is mainly dictated by all the interactions between alumina surface and the different polymer functional groups. At pH 8.5–9, around pH corresponding to the isoelectric point of alumina ($pH_{IEP} = 8.5$), the particle surface carries not only AlOH groups but also locally negative and positive charged groups, respectively AlO^- and $AlOH_2^+$. Such sites promote interactions with SO_3^- and OH groups of the polymer by electrostatic interactions and hydrogen bonding.

The decrease of adsorption when the SO_3^- group fraction in polymer increases suggests that the alumina-polymer interactions in suspension mainly occur by SO_3^- groups and that the interactions with hydroxyl groups are negligible. According to the work of Hidber et al.,[20] the maximum adsorbed amount of poly(vinyl alcohol) (PVA) onto alumina particles decreases when citric acid (CA) is added as dispersant. The introduction of 0.1 wt.% of CA in the alumina suspension lowers the amount of PVA adsorbed from 0.08 to 0.02 mg m^{-2} at pH 8.5. This behavior was explained by a low affinity of the alumina surface for the OH groups of PVA at $pH = 8.5$. The decrease of the pH by adding of CA may also result in a further decrease of PVA adsorption. In our case, all the adsorption isotherms of AMPS(n) onto alumina particles are of high affinity type (Fig. 2). These results suggest also that adsorption of AMPS(n) is mainly driven by the interaction of alumina surface with SO_3^- groups, the interaction with hydroxyl groups being negligible.

As far as the pH of the suspension is considered, the adsorption of AMPS(n) capacity increases as the pH is decreasing whatever the sulfonic group fraction in copolymer (Fig. 4). Whatever the pH and the sulfonic group fraction, the adsorption can be described as a high affinity type. The surfacic concentration of $AlOH_2^+$ sites increases when the pH decreases. These results may confirm that adsorption of AMPS(n) is dominated by electrostatic interactions between SO_3^- groups on the copolymer and the charged surface sites.

As the SO_3^- group fraction increases in the macromolecule, the repulsion between ionized groups results in a more expanded molecule configuration, which leads to a reduced adsorption onto the alumina surface.[12] In this case, AMPS(100) adsorption onto alumina surface is presumed to occur in a relatively flat configuration as it was observed for polyacrylate molecules when they are totally ionised,[6,21,22] whereas AMPS(80), AMPS(55) and AMPS(20) adsorption occurs in a coiled structure onto the alumina surface. Then the adsorbed layer thickness increases when the SO_3^- groups fraction decreases. A schematic illustration of the conformation of AMPS(n) adsorbed onto alumina surface is presented in Fig. 5.

Table 2
Adsorption results

Polyelectrolyte	Adsorption amount C_m (experimental) mg m^{-2}	Adsorption amount C_m (calculated from Langmuir equation) mg m^{-2}
AMPS(100)	0.39	0.38
AMPS(80)	0.63	0.62
AMPS(55)	0.83	0.83
AMPS(20)	0.97	0.96

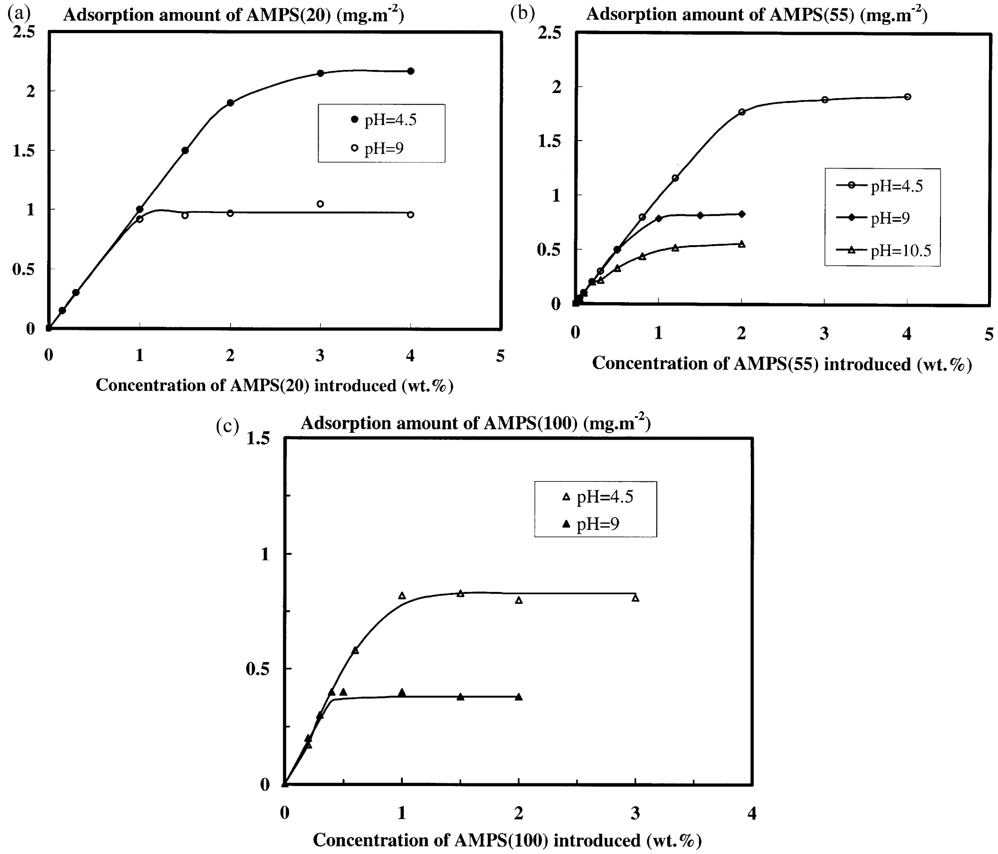

Fig. 4. Adsorption isotherms for AMPS(n) copolymers on alumina surface as a function of suspension pH. (a) AMPS(20), (b) AMPS(55) and (c) AMPS(100).

In the present study we assume that the contribution of hydrogen bonding in the adsorption of AMPS(n) onto alumina is negligible and that the hydroxyl ethyl methacrylate segment emerges in solution.

3.2. Electrokinetic properties

The electrokinetic behavior of alumina suspension prepared with copolymers as a function of pH is shown in Figs. 6 and 7. The ESA signal amplitude is strongly dependent on the suspension pH and on the copolymer [AMPS(55)] concentration (Fig. 6). The isoelectric point (pH_{PIE}) of P172SB alumina is at pH = 8.5. Above this pH, the particles carry a net negative charge because of the formation of $Al–O^-$, and below this pH the alumina surface carries a net positive charge because of the formation of $Al–OH_2^+$, that results from the dissociation of Al–OH groups.[23] Adsorption of the copolymer onto alumina surface shifts the pH_{PIE} of alumina towards acidic pH, with a decrease of the ESA signal amplitude. For copolymer concentrations larger than 0.8 wt.%, the ESA signal amplitude is rather constant and negative due to the saturation of alumina surface with AMPS(55) copolymer.

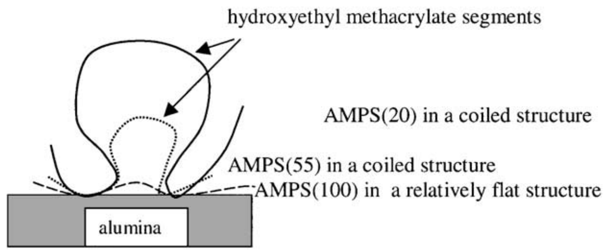

Fig. 5. Schematics of the effect of anionic group fraction in copolymer on the structure of adsorbed AMPS(n) on alumina surface.

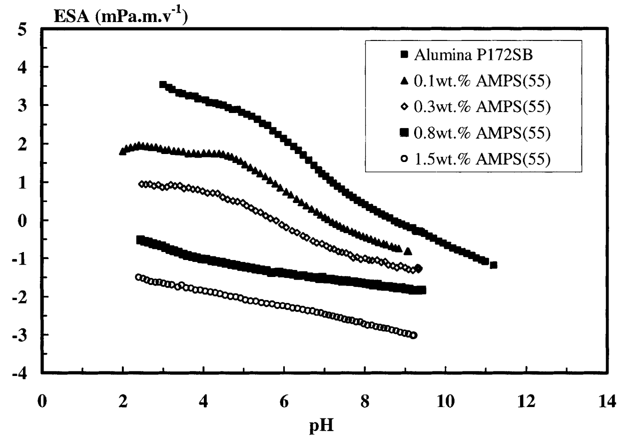

Fig. 6. Electrokinetic curves of alumina suspensions after addition of different amounts of AMPS(55).

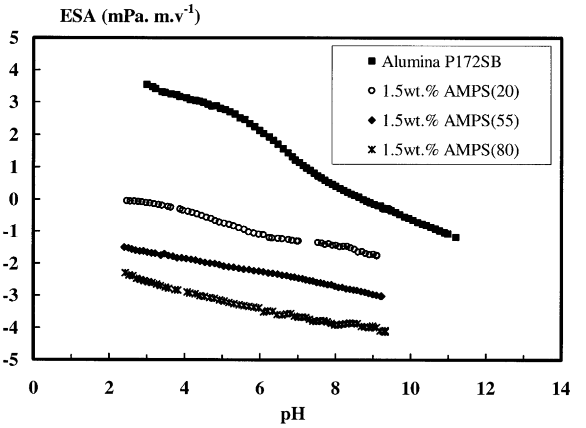

Fig. 7. Electrokinetic curves of alumina suspensions after addition of 1.5 wt.% of AMPS(n).

The effect of SO_3^- group content in the copolymer on the electrokinetic behavior for a concentration of 1.5 wt.% is shown in Fig. 7. The increase of the SO_3^- group content in the polymeric chain results in an increase of the absolute of the ESA signal amplitude and then, of the zeta potential (Fig. 7). The increase of the SO_3^- group content in the polymeric chain, leads to the neutralization of the Al–OH_2^+ site on the alumina surface and then to a negatively charged surface. We have also to consider the distance of the shear plane from the particle surface. The presence of coiled polymer chains at the interface solid-liquid may disturb the hydrodynamic plane of shear, shifting it further out from the particle surface. The magnitude of this phenomena increases when the SO_3^- group in the polymeric chain decreases (Fig. 5).

AMPS(n) polymer adsorbed onto alumina can exert two repulsive contributions for alumina powder dispersion. An electrostatic repulsive force due to the electric double layer surrounding the particle and a steric repulsive interaction due to adsorbed polymer ($M_w > 16{,}000$). The dispersant with the highest ionised SO_3^- group content (100%) leads to the largest electric repulsive force.

3.3. Rheological properties

The rheological flow curves for alumina suspensions (27.4 vol.%) as a function of polymer dispersant concentration and SO_3^- groups content at pH = 8.5–9 are

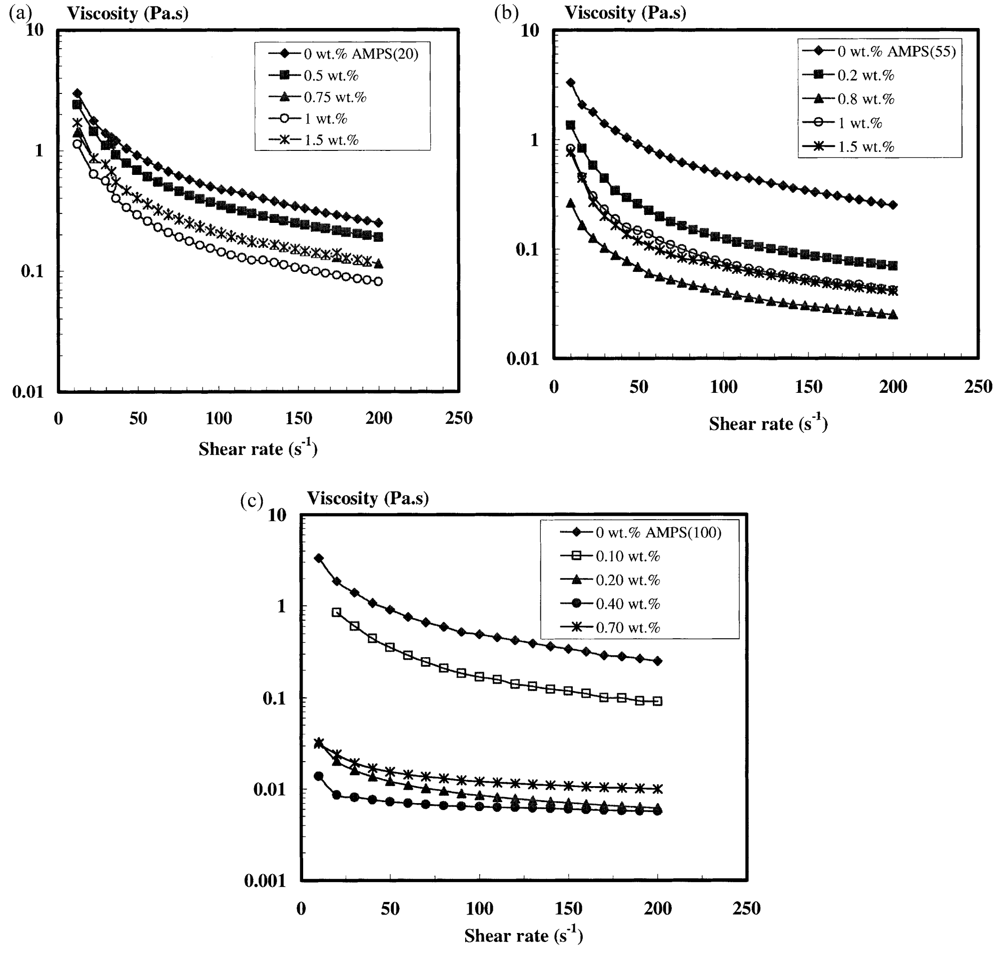

Fig. 8. Influence of copolymer dispersant concentration on the viscosity of alumina Suspensions (vol.% alumina = 27.4 and pH = 8.5–9). (a) AMPS(20), (b) AMPS(55) and (c) AMPS(100).

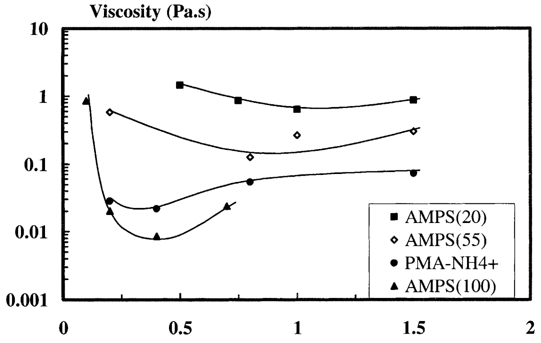

Fig. 9. Viscosity of alumina suspensions as a function of dispersant concentration at a shear rate 95 s^{-1}.

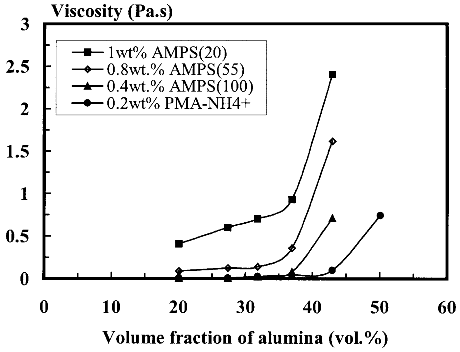

Fig. 10. Effect of AMPS(n) copolymers and PMA-NH_4^+ on the viscosity of suspensions containing different alumina volume fractions at a shear rate 22 s^{-1}.

shown in Fig. 8a–c. At pH 8.5–9, close to the alumina pH_{PIE}, the suspension without polymer dispersant exhibits a high viscosity in the range of shear rate tested, with a significant shear thinning behavior due to the structure breakdown at high shear rate. The addition of AMPS(n) decreases the viscosity of the alumina suspension. That suggests that the degree of flocculation decreases and that adsorbed polymer enhances repulsive forces between particles. The viscosity reaches a minimum for a critical addition of polymer dispersant. A further addition of polymer dispersant increases viscosity due to bridging effect which develops a network between particles and due to the compression of the double electric layer. The optimum concentration decreases as the SO_3^- groups number increases that strengthen the hypothesis of a flat conformation of AMPS(100) onto the surface. A lower concentration leads to the surface saturation.

Fig. 9 illustrates the viscosity of alumina suspensions (27.4 vol.%) for various dispersant concentrations of different copolymers compared to that of alumina suspensions containing the ammonium salt of polymethacrylate acid (PMA-NH_4^+) dispersant at a shear rate 95 s^{-1}. The optimum concentrations of dispersant are about 1, 0.8, 0.35–0.4 and 0.2 wt.%, for AMPS(20) AMPS(55), AMPS(100) and PMA-NH_4^+ respectively, that correspond to a respective adsorption of about 1, 0.8, 0.4 and 0.2 mg m^{-2}. According to the adsorption results, (Fig. 2) these amounts correspond to the saturation conditions.

The rheological behavior of alumina suspensions containing AMPS(n) copolymer dispersants is then mainly controlled by the polymer structure and by the polymer configuration at the alumina-liquid interface. The viscosity of suspensions prepared with the optimum concentration is decreasing with increasing SO_3^- group content in polymer. This result indicates that under these conditions and for alumina concentration of 27.4 vol.%, colloidal stability is mainly controlled by electrostatic mechanism. Steric effects probably play a lower role for this low alumina suspension concentration. Steric repulsion acts at short distance, then for a more concentrated suspension. The presence of loops and trains adsorbed onto alumina surface may increase the interaction between moving particles, this phenomena resulting in an increase of viscosity. The magnitude of these interactions increases when the thickness of the polymeric monolayer increases i.e. when the SO_3^- group content decreases.

The effect of AMPS(n) copolymers on the dispersion of suspensions containing different alumina volume fractions is studied by measuring the suspension viscosity at a shear rate 22 s^{-1} and compared to that of PMA-NH_4^+. According to the obtained results (Fig. 10), the viscosity of suspensions prepared with the optimum concentrations of AMPS(n) is decreasing when the SO_3^- group fraction in the polymeric chain increases. Viscosity of suspension prepared with the optimum concentration of AMPS(100) remains similar to that measured with 0.2 wt.% PMA-NH_4^+ up to a solid concentration of 37 vol.%. For higher solid contents, PMA-NH_4^+ disperses more efficiently than AMPS(100). But, the synthesized copolymers AMPS(n), especially those with high SO_3^- group content, show a satisfactory effect on the dispersion of concentrated alumina suspension. A maximum volume fraction of 43 vol% leads to a suspension able for process applications.

The AMPS(55) efficiency in dispersing alumina particle in aqueous suspension was compared to that obtained with the ammonium salt of polymethacrylate acid (PMA-NH_4^+),[15] by measuring particles size distribution. Suspensions containing 2.7 vol.% of alumina were prepared with various amounts of AMPS(55) and with 0.2 wt.% of PMA-NH_4^+ at pH 8.5–9. The samples were ultrasonicated for 3 min at 300 W prior to the measurement of the particle size distribution. The variation of the mean size of alumina versus amount of dispersant is plotted in Fig. 11. The dispersion state of alumina with addition of 0.8 wt.% of AMPS(55) is almost the same as that obtained with 0.2 wt.% of PMA-NH_4^+. Then, AMPS(n) copolymer can be used as a dispersant for alumina powder.

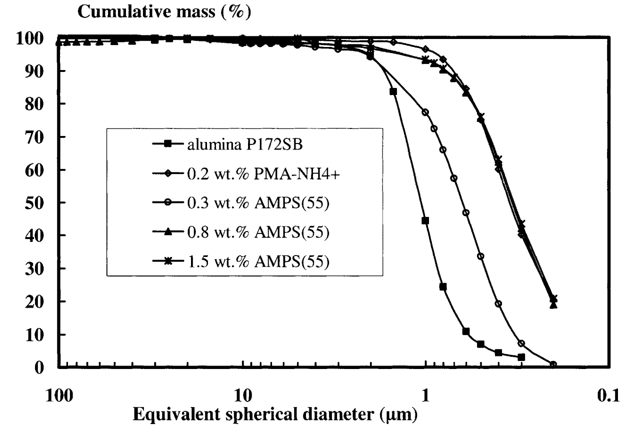

Fig. 11. Alumina particle size distribution in suspensions as a function of AMPS(55) concentration, compared to that obtained with 0.2 wt.% PMA-NH_4^+.

4. Conclusion

Sulfonic copolymers (AMPS(n)) have proved to be efficient dispersants for aqueous alumina suspensions (similar to classical polyacrylates). The interaction of these copolymer dispersants with alumina surface is a high affinity type and is mainly dictated by SO_3^- groups. The thickness of adsorbed polymer layer decreases when SO_3^- group content increases and fully ionised, AMPS(100) adsorption onto alumina surface is presumed to occur in a relatively flat configuration. The optimum concentration of dispersant to obtain the minimum viscosity corresponds to the saturation conditions of the surface and to the maximum of charge density at the particle surface. Polymer with the highest SO_3^- group content (AMPS(100)) leads to the lowest viscosity that indicates that electrostatic repulsive forces control alumina particle dispersion for the powder concentration tested, i.e. 27.4 vol.%.

The effect of these copolymers on the cohesion and on the mechanical properties of alumina green products will be presented in a next paper.

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