

Dispersion of Al₂O₃ concentrated suspensions with new molecules able to act as binder

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Abstract

The objective is to define and synthesise molecules with a double function of dispersant and of binder. New acrylic copolymer molecules containing both carboxylic groups expected to bring a dispersant contribution and hydroxyl vinyl groups expected to bring a binder contribution were synthesised. The fraction of these two types of groups can be adjusted to balance the dispersion and the binder contributions. In a first step, the effect of these acrylic copolymer molecules on the interactions between alumina particles in aqueous suspension and on the rheology of concentrated suspensions was studied. Carboxylic groups allow adsorption of acrylic copolymers onto the alumina surface and can promote sufficient electrostatic repulsive forces to obtain a good state of dispersion. The amount of carboxylic groups controls the density of charge of the particle surface and hence, the ability of the copolymer to act as a dispersant. A low amount (0.6 wt.%) of a copolymer containing 35% of carboxylic groups, leads to stable suspensions with a critical powder loading of 80 wt.% corresponding to 50 vol.%.

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1. Introduction

Numerous polymeric additives are used in colloidal processing such as: wastewater treatment, paper products, paints and ceramics. In all of them, the mechanisms of action are closely connected with adsorption phenomena which have therefore been much studied.^{1–11}

Among these macromolecules, charged ones are commonly used as dispersants to enhance suspension stability and to impede particle flocculation, thus leading to both high solid loadings and low viscosities.^{12–22} The adsorption of a polyelectrolyte onto the surface of the powder creates an excess of charge, which results in the formation of a double electrostatic layer that surrounds each particle. The interaction of these double layers

provides an electrostatic repulsive force between particles.²³

In addition to polymer dispersing agents, water-soluble non-ionic polymeric binders (PVA, PEG...) are commonly added to confer strength to the green parts.^{24–27} Most often, the binders are non-ionic polymers and the interaction with the oxide powder surfaces mainly proceeds via dispersive forces and hydrogen bonding. Such interactions are very weak compared to the electrostatic interactions typically encountered for polyelectrolytes.²⁸ The consequences of this difference in affinity between dispersant and binder for the powder surfaces is, (1) an increase of the viscosity of the suspension due to a large amount of binder remaining in solution and, (2) a non homogeneous distribution of the organic binder in the granule after spray-drying and then, in the green part.^{29–30} To overcome these problems, the use of a polyelectrolyte which plays both the dispersing and binding role could constitute an attractive solution.³¹

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In this work, a set of copolymers has been prepared to study the interactions between these copolymers and Al_2O_3 powder in aqueous medium and to explore the suspension stability and the rheological properties.

2. Experimental

2.1. Starting materials

An $\alpha\text{-Al}_2\text{O}_3$ powder (P172SB, P echiney-France) with a mean particle size of 0.35 μm and a specific surface area (BET) of 10 $\text{m}^2\cdot\text{g}^{-1}$ was used. Three polyelectrolytes (PV20, PV35 and PV55), which are copolymers of sodium acrylate and of vinyl hydroxide, were synthesised. A commercial ammonium salt of poly-methacrylic acid (Darvan-C[®], Vanderbilt, UK) was used for comparison. The structure of the various polyelectrolytes used in the present work and the corresponding molecular weights are given in Table 1.

2.2. Copolymer synthesis

The PVX copolymers (X being the molar fraction of carboxylic groups) were prepared by radical copolymerisation of sodium acrylate and of vinyl acetate. Copolymerisation was carried out in a backward flow in methanol in the presence of benzoyl peroxide as an initiator during 5 h. The PVX copolymer was then obtained by hydrolysing the acetate fraction of the previously synthesised copolymer. The hydrolysis was carried out by methanolysis in the presence of NaOH as catalyst. Once hydrolysed, the formed polymer precipitated instantaneously in methanol. After filtration, the polymer was washed twice with acetone, dried under nitrogen atmosphere and dissolved in water to obtain a concentrated solution. The content of carboxylate groups -COO^- in the polymer was determined by col-

loidal titration with a cationic polyelectrolyte [poly (chloride N,N,N-trimethyl ammonium ethyl acrylate) ‘‘PAD-Cl⁻’] studied in earlier work.^{32,33}

2.3. Adsorption isotherms

Experiments concerning the adsorption of polymers were performed by adding given amounts of the polymer solution, at the pH required, to a 10 wt.% aqueous Al_2O_3 suspension. The pH adjustments were made using NaOH or HCl solutions. Then suspensions were sonicated for 15 mn under an output power of 200 W. Samples were then shaken for 24 h to reach adsorption equilibrium.

The suspensions were centrifuged at 3000 rpm for 1 h. The supernatant was removed, and the amount of free polyelectrolyte in the solution was determined by a colloid titration technique using the cationic PAD-Cl⁻ polymer and orthotoluidine blue as indicator.³⁴ This colloidal titration is based on the fact that oppositely charged polyelectrolytes form 1:1 complexes in a low ionic strength medium. The point of charge equivalence is determined by colour change of an appropriate indicator, as orthotoluidine blue in the present case. In cationic systems, this indicator becomes pink due to the formation of a complex with the anionic polymer.

All titrations were here carried out under conditions of low ionic strength (lower than 10^{-3}), obtained by dilution of the supernatant sample with distilled water. Blank tests conducted on PMA-NH₄⁺ and other commercial acrylic copolymers, made of acrylamide and N,N,N trimethyl ammonium ethyl acrylate chloride, have confirmed the validity of the method with a sensitivity of the titration up to 1 ppm.³³

2.4. Electrokinetic measurements

The electrokinetic behaviour of the powder suspension was characterised by Electrokinetic Sonic Amplitude

Table 1
The three polyelectrolytes, PV20, PV35 and PV55, are synthesised^a

Polymer	Structure	COO ⁻ %	M_w	Dispersant function	Binder function
PMA-NH ₄ ⁺		100	15,000	-COO-NH ₄ ⁺	—
PV20		20	13,000	-COO-Na ⁺	-OH
PV35		35	17,000		
PV55		55	15,000		

^a PMA-NH₄⁺ is a commercial polymer (Darvan-C[®], Vanderbilt, UK). COO⁻% is the molar fraction of carboxylic groups in the copolymer.

(ESA) measurements (Model ESA-8000, Matec, Northborough, MA, USA).

This technique is based upon the acoustic wave that is generated by the respective motion of the particles and of their diffuse electrical double layers, submitted to a high-frequency electric field. The amplitude of the acoustic wave is proportional to the electrostatic potential at the shear plane where the zeta potential is defined.³⁵ The ultrasonic signal is detected and converted into a voltage (ESA) by a piezoelectric transducer. The ESA signal being directly proportional to the zeta potential, the curves describing variations of the electrokinetic properties in terms of pH or polyelectrolyte amount will be presented with the ESA values as the Y axis.

3. Results and discussion

3.1. Adsorption isotherms

For the four copolymers tested, the amount of PVX adsorbed onto the alumina particles at pH=8.5–9 increases as the polymer concentration increases, until a plateau is reached (Fig. 1). The shape of these isotherms suggests a monolayer adsorption of the polyelectrolyte, independent of the polymer composition. The adsorption is complete for concentrations smaller than 0.3 wt.% of PMA–NH₄⁺, PV55 and PV35, and than 0.7 wt.% of PV20 as no polymer was detected in the supernatant until these values were reached. Such an observation indicates a rather significant affinity type adsorption. The amount of adsorbed polyelectrolyte on the plateau decreases as the content of carboxylic

groups in the polymer increases. The quantities adsorbed are about 0.36 mg.m⁻², 0.58 mg.m⁻², 0.67 mg.m⁻², and 1.17 mg.m⁻² for PMA–NH₄⁺, PV55, PV35 and PV20 respectively. Such values correspond to respective adsorbed surface molar amounts of 4.27 10⁻⁶ mol. m⁻², 8.11 10⁻⁶ mol. m⁻², 10.89 10⁻⁶ mol. m⁻² and 21.66 10⁻⁶ mol. m⁻² of polymer.

The quantity of PMA–NH₄⁺ adsorbed on the plateau (pH=9), i.e. 0.36 mg.m⁻², is in agreement with that reported by Cesarano.¹⁵ At pH=9, PMA–NH₄⁺ is fully ionised, and its adsorption on the surface of alumina proceeds in a relatively flat configuration.¹⁵ The increase of the adsorbed amount of copolymer on the plateau as the carboxyl fraction group was reduced may be explained by a lower repulsion between ionisable groups that allows a denser packing of the macromolecular chains on the alumina surface, but particularly by an expected formation of loops in the adsorbed configuration as the fraction of hydroxyl vinyl units increases. Then, more chains, with a lower surface covering are required to get a saturated monolayer.

According to Hidber,²⁸ polymers bearing hydroxyl groups such as PVA are weakly adsorbed on the surface of alumina. Adsorption on the surface comes from hydrogen bonding, which is weak compared to the strong interaction taking place with –COO⁻ carboxyl groups. Moreover, co-adsorption studies in binary systems containing polyacrylic acid and PVA revealed that the adsorption of PVA was significantly reduced by the presence of poly(acrylic acid). In the pH range between 8 and 9, carboxylic groups are responsible for the chemisorption resulting from an exchange process with surface hydroxyl groups, that leads to the formation of Al–OOC complexes.³⁶

According to this discussion, in the loop-like configuration of copolymer PV20, PV35 and PV55, loops are mainly formed of non-ionic hydroxyl vinyl units, whereas carboxylic units act as anchoring groups (Fig. 2).

The Langmuir model was applied to the polyelectrolyte adsorption onto the alumina particles. The amount of adsorbed polymer (C_{ads}) is expressed by:³⁷

$$C_{\text{ads}} = \frac{K \cdot C_{\text{max}} \cdot C_{\text{sol}}}{1 + K \cdot C_{\text{sol}}} \quad (1)$$

where C_{sol} is the equilibrium concentration of the polymer in the solution (mol. l⁻¹), C_{max} the amount of adsorbed polymer for a monolayer coverage (mg. m⁻²) and K a constant (l. mol⁻¹).

This equation may be rewritten in a linearized form:

$$\frac{C_{\text{sol}}}{C_{\text{ads}}} = \frac{C_{\text{sol}}}{C_{\text{max}}} + \frac{1}{K \cdot C_{\text{max}}} \quad (2)$$

The linearity of the variation of $C_{\text{sol}}/C_{\text{ads}}$ as a function of the added polymer for PMA–NH₄⁺, PV20, PV35, and PV55, shown in Fig. 3, confirms that the Langmuir

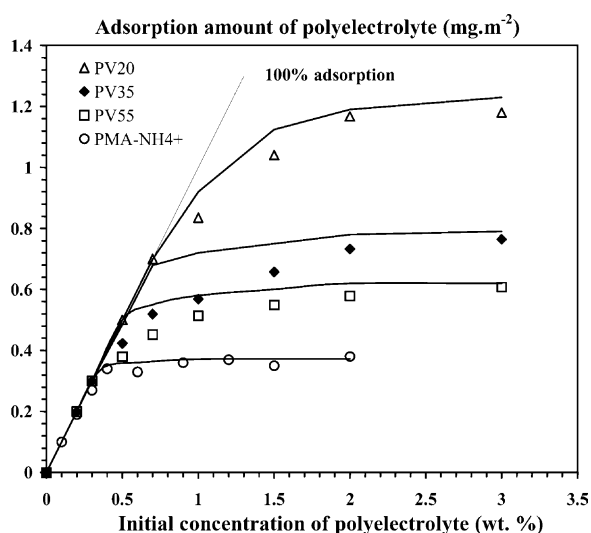


Fig. 1. Adsorption isotherms of the various polyelectrolytes onto P172SB alumina as a function of initial amount of polyelectrolyte. The solid lines are fits based on the Langmuir adsorption model as explained in the text (pH ≈ 8.5–9).

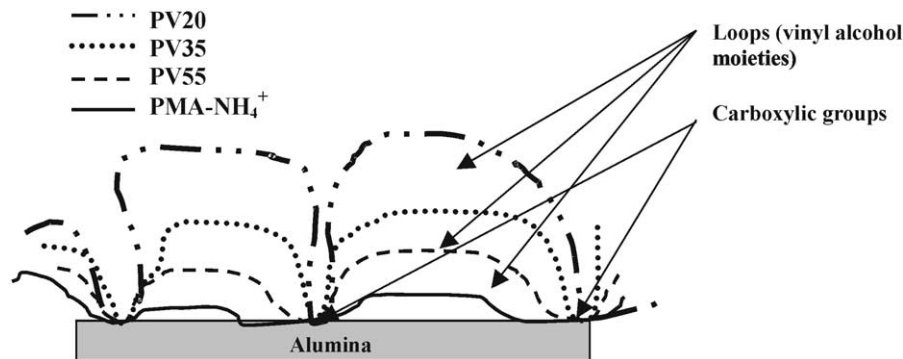


Fig. 2. Schematics of the effect of COO^- group fraction in copolymer on adsorbed structure of PVX on alumina surface.

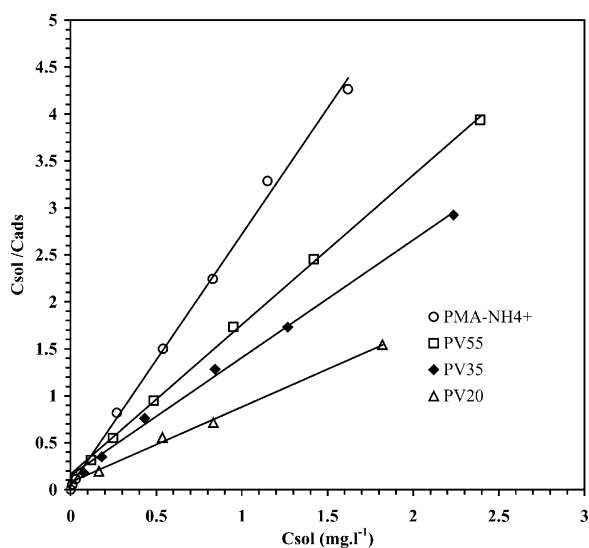


Fig. 3. Langmuir adsorption isotherms of PMA-NH_4^+ , PV 55, PV35 and PV 20 polymers onto alumina particles.

model is an adequate choice. The adsorption constants K , as well as the concentrations of polymer adsorbed on the plateau, were calculated (Table 2). Large values of K confirm again the high affinity of polyelectrolytes with respect to the alumina particle surface. Agreement of the adsorption characteristics with predictions made from the Langmuir model gives evidence for a monolayer polymer adsorption.

As the pH is reduced, a significant increase in the amount adsorbed was observed regardless of the carboxyl fraction in the polymer (Fig. 4). This phenomenon probably results from two effects when the pH is

decreasing, viz (1) a larger density of positive surface charges that contributes to anchor more carboxylic groups and, (2) a lower fraction of dissociated carboxyl groups that reduces the global charge of the polyelectrolyte chain, and thus favors adsorption in a more looped conformation.

3.2. Electrokinetic behavior

The effect of the addition of PMA-NH_4^+ , PV20 and PV35 on the electrokinetic properties of alumina suspensions is shown on Figs. 5–7. Addition of PMA-NH_4^+ shifts the IEP towards acidic pH. Beyond contents of 0.35 wt.%, the IEP stabilises close to 2.6 and no more evolution is observed, in agreement with the results of other studies.^{38–41} A similar behaviour was observed with the addition of polymers PV20 or PV35. However the asymptotic value of the IEP value is larger, i.e. 2.8 and 3.6 for an addition of 2 wt.% of PV35 and PV20, respectively.

Below the IEP, the adsorption of the polymer, bringing negative charges, contributes to neutralise positive sites on the surfaces of the particles, and then to decrease the net positive surface charge (Figs. 5–7).⁴² On the other hand, beyond the IEP, negative ESA values result from the effect of both AlO^- negative surface sites and adsorbed carboxylic groups of the polymer, which are dissociated to a large extent in this range of pH.

At $\text{pH} \approx 8.5\text{--}9$, no more evolution of the ESA signal amplitude was observed, after a threshold of polymer addition (about 0.35 wt.%, 0.5 wt.% and 1 wt.% of

Table 2

Maximum values of adsorption (C_{max} determined from adsorption isotherm and C_{max}^* determined from the Langmuir model) and adsorption equilibrium constant K for PMA-NH_4^+ and the three PVX copolymers

Polymer	C_{max} (mg.m^{-2})	C_{max}^* (mg.m^{-2})	K (l.mg^{-1})	$K \cdot 10^{-3}$ (l.mol^{-1})
PMA-NH_4^+	0.38	0.37	11,545	112
PV55	0.61	0.63	8637	14.2
PV35	0.76	0.8	8190	13.3
PV20	1.18	1.23	7727	12.1

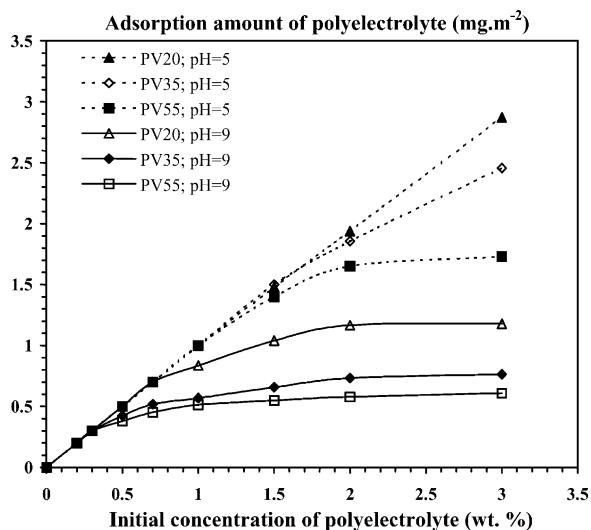


Fig. 4. Adsorption isotherms for PVX copolymers onto alumina for two pH of the suspension (5 and 9).

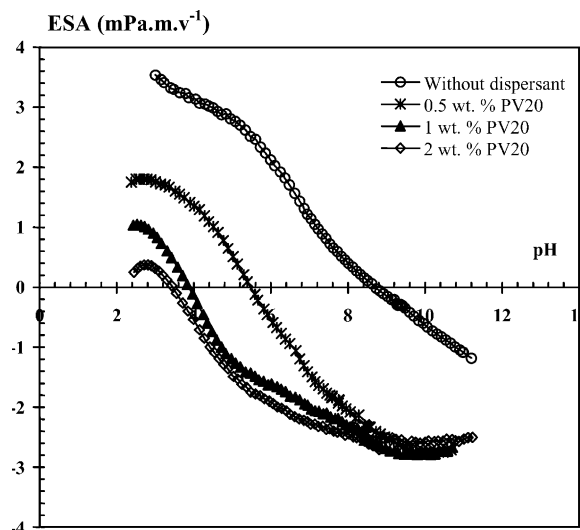


Fig. 6. Electrokinetic properties of the suspension after addition of PV20.

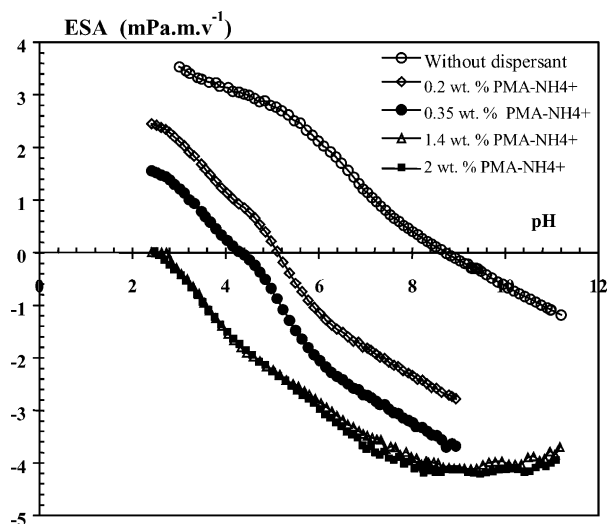


Fig. 5. Electrokinetic properties of the suspension after addition of PMA-NH₄⁺.

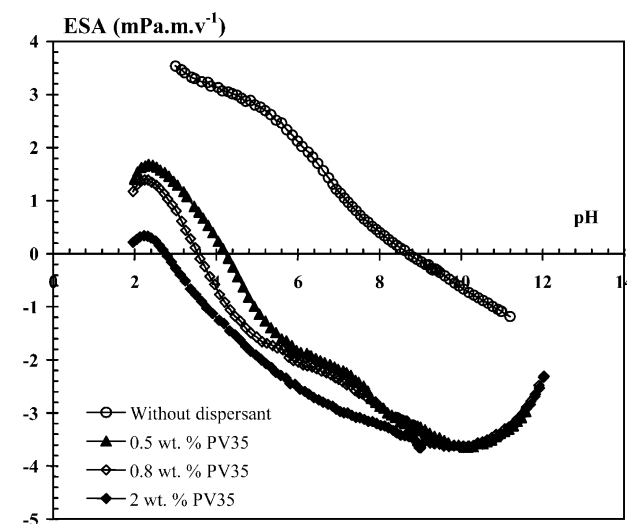


Fig. 7. Electrokinetic properties of the suspension after addition of PV35.

PMA-NH₄⁺, PV35 and PV20), suggesting that the surface of the alumina particles becomes saturated. These threshold values were in agreement with the maximum values of adsorption reported in Table 2. Above this threshold, the absolute value of the ESA signal on the plateau is increasing from PV20, PV35 to PMA-NH₄⁺, then as the fraction of carboxylic groups of adsorbed polymers is increasing, as shown by the evolution of the ESA signal at pH \approx 8.5–9 in function of the introduced amount of polyelectrolyte (Fig. 8). If the polymer conformation is not taken into account, almost the same ESA value is expected as the amount of carboxylic groups bound to the surface does not change. Nevertheless, the ESA amplitude decreases significantly as the fraction of hydroxyl vinyl units raises. This suggests

that the loops of a polymer, with a low fraction of carboxylic groups, extend in the liquid and result in the outward movement of the shear plane, and hence in a lower potential. The modification of the shear plane, corresponding to a decrease of the fraction of carboxylic groups on the adsorbed polymer, will be enhanced if the thickness of the adsorbed layer increases. This result reinforces the hypothesis of a loop-like conformation of the polymer adsorbed on the surface of alumina in the pH range 8.5–9.

3.3. Particle size distribution

In order to evaluate the effect of polyelectrolyte addition on Al₂O₃ powder dispersion, the particle size

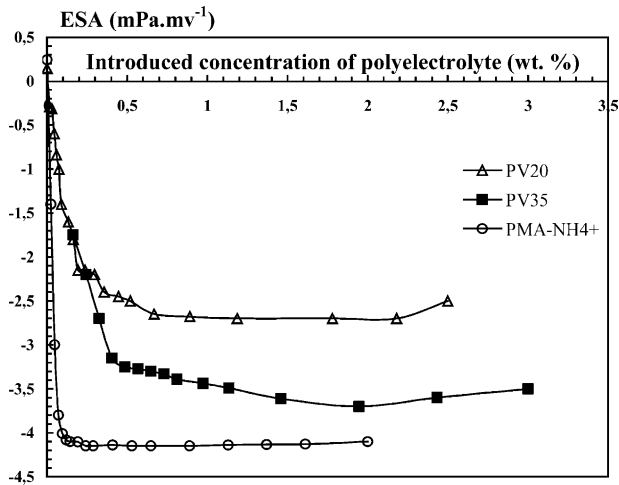


Fig. 8. Evolution of the ESA signal as a function of the introduced concentration of polyelectrolyte at pH \approx 8.5–9.

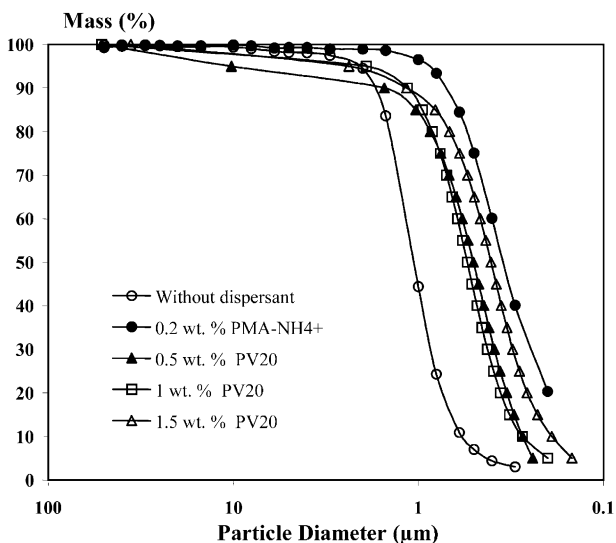


Fig. 9. Particle size distribution of alumina after addition of PV20 copolymer.

distribution in suspensions containing the synthesised dispersants was determined by X-ray sedimentation technique (Figs. 9 and 10).

The best state of dispersion for P172 SB alumina was obtained after addition of an amount of 0.2 wt.%, with respect to the dry powder, of the classically used PMA-NH₄⁺ dispersant.³¹ In the absence of polymer, Al₂O₃ particles are agglomerated, as the natural pH of the suspension, e.g. 8.5, is close to the IEP. Addition of PV20 improves the dispersion state of the suspension but remains lower than for an addition of 0.2 wt.% PMA-NH₄⁺ even for an addition of 1.5 wt% PV20 polymer (Fig. 9). In agreement with ESA measurements (Fig. 6), the PV20 polymer does not generate a sufficient surface charge density to prevent solid particles from agglomeration.

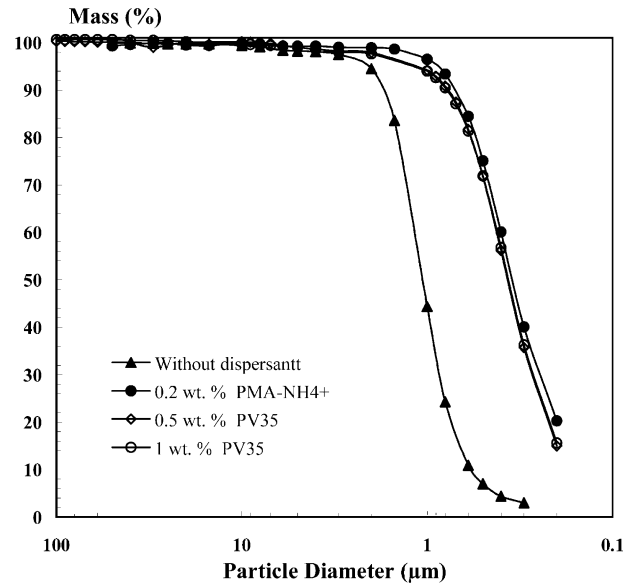


Fig. 10. Particle size distribution of alumina after addition of PV35 copolymer.

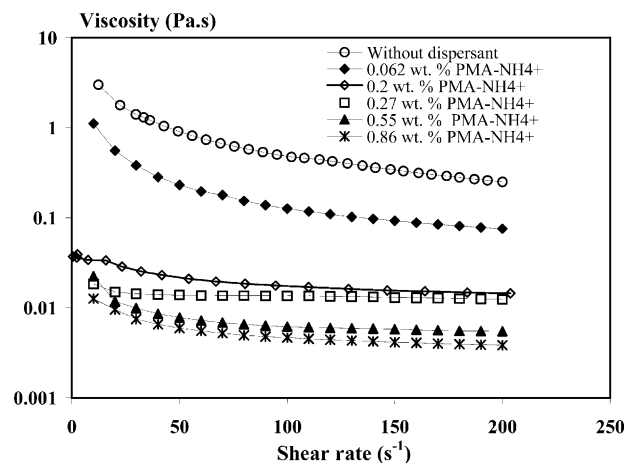


Fig. 11. Influence of the concentration of the PMA-NH₄⁺ dispersant on the viscosity of alumina suspensions (27 vol.%, pH = 8.5–9).

PV35 generating a larger charge density (Fig. 7) is a more efficient dispersant with a state of dispersion similar to that obtained with 0.2 wt.% PMA-NH₄⁺, obtained after an addition of about 0.5 wt.% (Fig. 10). This indicates that an optimum content of carboxylic groups in the copolymer PVX, close to 35%, is required to get a good state of dispersion and to prevent alumina flocculation.

3.4. Rheological properties

Viscosity measurements were performed to evaluate the state of dispersion of the suspensions prepared with the various copolymers. Figs. 11–13 report the flow curves for slurries containing 27 vol.% Al₂O₃ after addition of various quantities of polymer. In the absence of any polyelectrolyte, entrapped liquid within

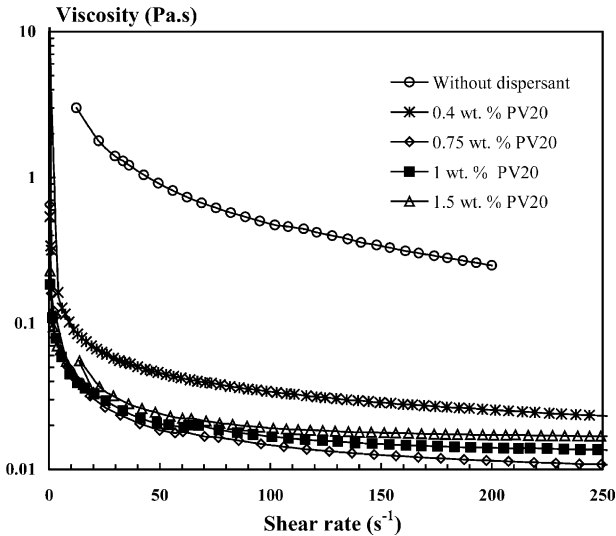


Fig. 12. Influence of the concentration of the PV20 dispersant on the viscosity of alumina suspensions (27 vol.%, pH = 8.5–9).

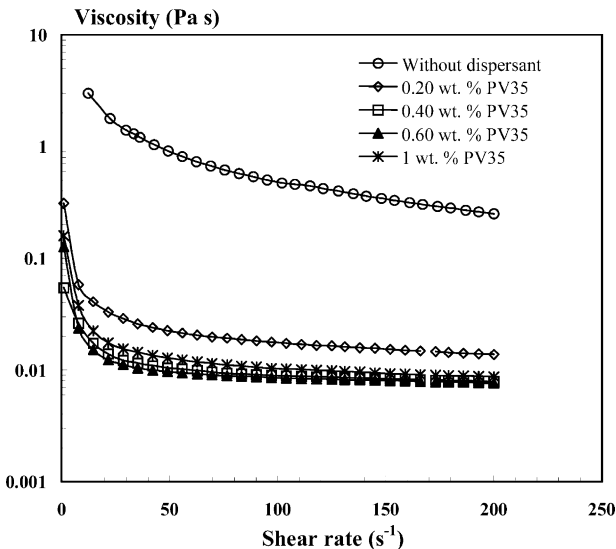


Fig. 13. Influence of the concentration of the PV35 dispersant on the viscosity of alumina suspensions (27 vol.%, pH = 8.5–9).

the agglomerates results in a larger apparent volume fraction of solid, that is responsible for the large viscosity of the suspension.^{43–46} An addition of 0.2 wt.% PMA-NH₄⁺ drastically decreases the viscosity ($\eta = 30$ MPa.s at 22 s⁻¹) which becomes almost independent of the shear rate (Newtonian). In the presence of PV20 and PV35, a significant decrease of viscosity was observed for an addition of 0.75 and 0.6 wt.%, respectively (Figs. 12 and 13).

The quasi-Newtonian behaviour of suspensions prepared with addition of PMA-NH₄⁺ and PV35 is characteristics of a stable system, already suggested by the large negative zeta potential resulting from the polymer adsorption, that allows the particles in the suspension to move independently. Using the copolymer containing a

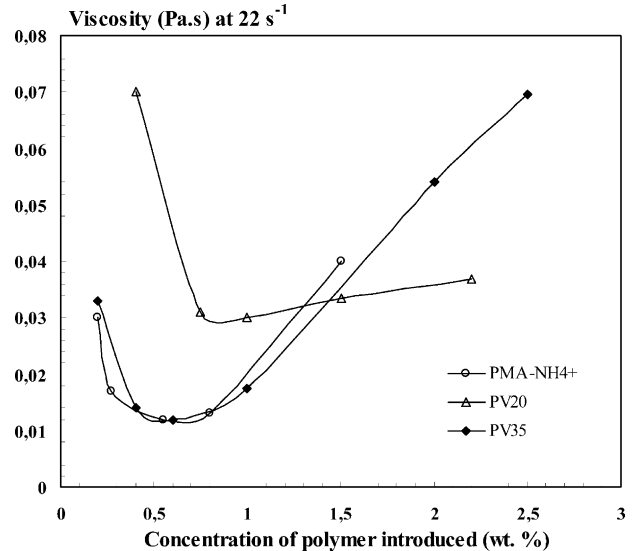


Fig. 14. Variation of the viscosity of the alumina suspensions in function of the concentration of the copolymer dispersant at a shear rate of 22 s⁻¹.

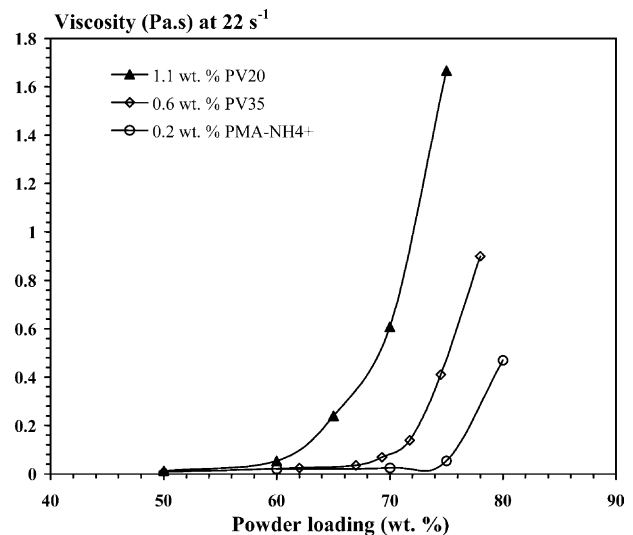


Fig. 15. Variation of the viscosity of alumina suspension in function of the powder loading for 1.1% wt.% PV20, 0.6 wt.% PV35 and 0.2 wt.% PMA-NH₄⁺.

large content of hydroxyl vinyl units (PV20), the suspension exhibits a significant shear thinning behaviour with a yield stress whatever the amount of added PV20 (Fig. 12), this results from flocculation of the alumina particles. In this case, the charge density on the surface of the alumina is not large enough, even at pH 9, to maintain a sufficient repulsion (Figs. 6 and 7) that is in agreement with evolution of the particle size distribution (Fig. 9).

The viscosity first decreases with the addition of polymer to reach a minimum at a given amount of dispersant (Fig. 14). The optimum concentrations are about 0.5–0.6 wt.% for PMA-NH₄⁺ and PV35, and 0.9 wt.% for PV20. These concentration values are in

agreement with the adsorption data (Fig. 1) corresponding to the saturation of the particle surface, i.e. 0.36, 0.67 and 1.17 for PMA–NH₄⁺, PV35 and PV20, respectively. The minimum of viscosity is shifted towards larger polymer concentrations for fractions of carboxylic groups larger than 35% and, as a general rule, as the fraction of hydroxyl vinyl groups is increasing or as the fraction of carboxylic groups is decreasing. This can be attributed to, (1) the loop-tail conformation of polymers containing a low fraction of carboxylic groups, that must be compensated by a larger polymer content for an equivalent surface coverage and/or, (2) to a lower negative charge brought by carboxylic groups. Indeed, carboxylic groups are responsible for the decrease of viscosity by an electrostatic contribution to the dispersion. In the same respect, the minimum value of the viscosity decreases from PV20 to PV35 and PMA–NH₄⁺, PV20 bringing too low a density of charge.

The evolution of the viscosity according to the weight fraction of the alumina in the suspensions (Fig. 15) shows a rather satisfactory effectiveness of the synthesized polyelectrolytes and especially of the PV35. Copolymers bearing 35% carboxylate groups are efficient dispersants with a critical powder loading of 80 wt.% corresponding to 50 vol.% of alumina in the suspension.

4. Conclusion

Synthesized copolymers have proved to be efficient dispersants for aqueous suspensions of alumina when the fraction of carboxylic groups is larger than 35% within the macromolecular chain. Adsorption of acrylic copolymers takes place due to carboxylic groups that anchor the polymer chain on specific surface sites, namely Al–(OH)₂⁺. The amount of carboxylic groups controls the effective charge density of the particle surface and the copolymer aptitude to be used as a dispersant. In another hand, the hydroxyl vinyl groups promote a loop-like adsorbed configuration, the thickness of loops increasing with the content of such groups.

Addition of a copolymer containing 35% of carboxylic groups, at an optimum amount of 0.6 wt.%, leads to stable suspensions with a critical powder loading of 80 wt.% corresponding to 50 vol.%.

Hydroxyl groups in the copolymer are expected to act as a binder after forming of alumina by dry-pressing. The effect of these copolymers on the cohesion and mechanical properties of green products is under investigation.

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