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Degradation of Dispersant During Milling

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Abstract

Deterioration of the ammonium salt of poly(methacrylic acid) ($PMAA\text{-}NH_3$), used as a dispersant during wet ball-milling of an alumina, has been investigated. Rheological behaviour, sedimentation tests, adsorption isotherms, pH and isoelectric point measurements, and infra-red analysis have allowed us to conclude that degradation of the dispersant takes place in two stages: (i) decrease of the charge by dehydration and (ii) complete neutralization of the dispersant by the formation of monodentate COOX groups, which can lead to desorption of the polymer from the alumina surface. This second phenomenon involves a strong increase of viscosity. A low viscosity can be recovered by a subsequent addition of $PMAA\text{-}NH_3$ at the end of milling.

1 Introduction

Ceramic processing includes many operations to transform raw materials into ultimate products. Milling, and more particularly wet ball-milling, is often used to break aggregates and to reduce the average particle size, as well as to add and mix some organic additives such as binders and plasticizers.

In order to achieve high solid contents, suspensions must contain an amount of water and organic additives that is as low as possible. Nevertheless, the slurry viscosity should be kept low enough during milling to confer efficiency to the milling media. It has been observed that viscosity increases a lot during ball-milling, thus reducing the efficiency and leading to rheological properties that are not fully compatible with the following stage of the process.[1,2]

Many factors can affect the state of dispersion during milling: (i) change in the specific surface area of the powder, (ii) change of the nature of surfaces of particles, (iii) change in pH of the solution and (iv) degradation of the dispersant.

The tumbling media in a rotating mill produce a grinding action by impacting and shearing the particles on their surfaces.[3] Polymer chains of dispersants are adsorbed on particle surfaces and are also present in water surrounding the particles. Impacts between particles and media can affect the polymer structure and possibly lead to desorption from the particle surfaces.

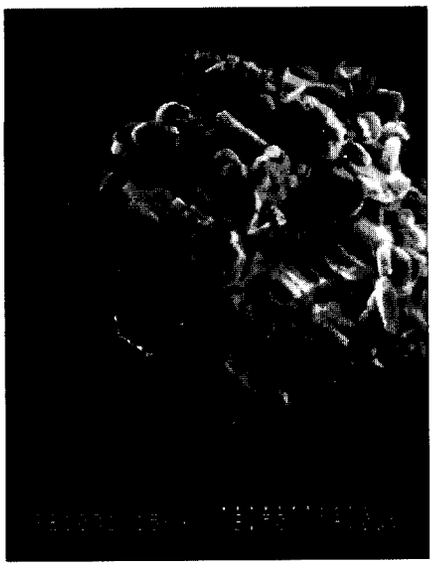
The aim of this study was to follow the efficiency of a common polyelectrolyte, an ammonium salt of poly(methacrylic acid), used for this purpose. Sedimentation tests, viscosity, pH and isoelectric point (IEP) measurements, adsorption isotherms and infra-red observations (FTIR) were used to follow the evolution of the dispersion state of alumina slurries during milling.

2 Experimental

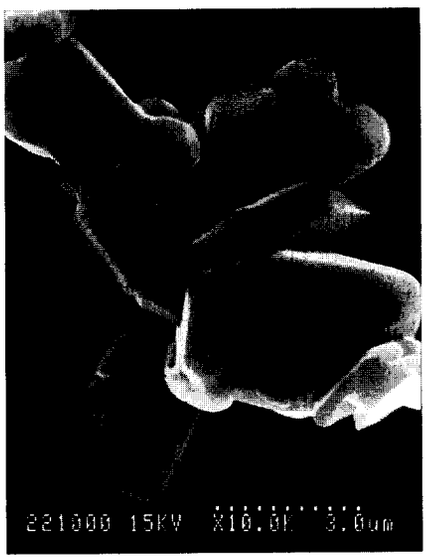
2.1 Powder and dispersant

The ceramic powder used in this study was a calcined α-alumina formed from the Bayer process (P122, Aluminium Péchiney, France). This powder consists of ~35 μm mean diameter aggregates containing ~3 μm mean diameter elementary particles (Fig. 1). The specific surface area of the starting powder was 0·7 $m^2\ g^{-1}$. The major impurities, located mainly, on the surface of particles, are SiO_2, CaO, Fe_2O_3 and Na_2O with respective concentrations of 1050, 600, 300 and 150 ppm.

Polyelectrolytes are generally used as dispersants for ceramic powders. Polyelectrolytes are macromolecules delivering a large number of ionic charges in solution, with small inorganic counterions. The dispersant used here was an ammonium salt of poly(methacrylic acid) ($PMAA\text{-}NH_3$), which, as received, contains 25 wt% active species and 75 wt% water (Darvan C, R. T. Vanderbilt Company, Inc., USA). This polyelectrolyte has been used extensively to deagglomerate and disperse alumina powders in aqueous media.[4,5] Depending on the charge, and then on the



(a)



(b)

Fig. 1. Aggregate of P122 alumina (a) containing 3 μm mean diameter elementary particles as shown on a smaller aggregate (b).

repulsion between the segments of the chains, these polymeric dispersants may adsorb in trains on the powder surface, in extended tails in the solution or in loops.[1,6] Thus stabilization of suspensions, using PMAA-NH_3 as dispersant, is due to an electrostatic repulsion combined with steric interactions, the global effect being called electrosteric stabilization. Figure 2 shows that the functional groups of PMAA-NH_3 are carboxylic acid groups, COO-, which can be protonated when the pH decreases.

2.2 Slurry preparation

The concentration of alumina in the slurries was 10 vol% (30·7 wt%) and the concentration of PMAA-NH_3 was 0·6 wt% with respect to alumina.

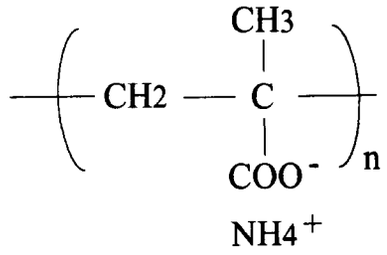


Fig. 2. Chemical structure of PMAA-NH_3.

The water used was deionized. Ball-milling was performed using a load factor (mass of alumina balls/mass of powder) equal to 8. Slurries were prepared by milling for several durations, i.e. 2, 8, 15, 18, 21 and 24 h.

2.3 Characterization

2.3.1 Grain size distribution and specific surface area

After each milling time, grain size distribution (SediGraph 5100, Micromeritics, USA) and specific surface area (DeSorb/FlowSorb II 2300A, Micromeritics, USA) were measured.

2.3.2 Agglomeration of particles

The amount of dispersant adsorbed on the particle surfaces, the configuration of the adsorbed molecules and the electric surface charge on the particles, developed by the polymeric chains, govern the agglomeration state and the stability of the dispersion. Ball milling may alter all these parameters by damaging (scission), desorbing or decreasing the charge of the polymeric dispersant. The efficiency of the PMAA-NH_3 during ball-milling was evaluated in terms of the agglomeration state of particles in the suspensions by sedimentation tests and viscosity measurements.

2.3.2.1 Sedimentation tests. Sedimentation tests were performed in order to follow the evolution of the particle agglomeration in the slurry. The average porosity of a sediment bed has been shown to be mainly a function of the size and shape of particles and of the state of agglomeration.[7-9] Thus the specific sediment volume and the average volume fraction of solid allowed us to determine the state of particle agglomeration in a suspension.

A part of each slurry (15 ml) was poured in a closed test tube. After agitation, the end of which determines the reference time, the mixture was allowed to settle until the sediment reached, a constant volume. The upward movement of the sediment/suspension interface, as well as the downward movement of the suspension/clear liquid interface, were reported on sedimentation curves.

A classification of suspensions may be made on the basis of the settling behaviour as proposed by Scott[10] and Hasset.[11]

In an infinite medium, a large number of identical particles settles down more rapidly than a single one, because the surrounding liquid is dragged down by the movement of falling particles. On the other hand, when the suspension settles in a tube, the liquid flow is disturbed because of friction effects at the wall, and the particles settle down more slowly.[12] Their velocity decreases as the powder concentration increases.

Figure 3, from Tiller and Khatib,[8] shows a typical settling curve for a non-flocculated suspension with a uniform concentration. The settling rate and build-up of the sediment are constant, until the particle velocity decreases when they reach the bottom of the tube, due to an upward flow of liquid passing up through the suspension. When all particles come to contact, compression point C is reached. Then, compression of the sediment occurs as liquid flows out of the sedimentation zone, until the structure stabilizes and the sediment reaches its ultimate volume.

For a flocculated suspension, particles are already in contact and settle very rapidly. The sediment was formed at the beginning of the test, and the sedimentation curve began at compression point C (Fig. 3).

2.3.2.2 Viscosity measurements. The evolution of the efficiency of the PMAA-NH_3 during ball-milling was also evaluated by viscosity measurements. A low viscosity, at a high powder loading, is representative of a good dispersion of non-agglomerated particles. Flow curves were obtained with a controlled stress rheometer (Carri-Med CLS 100, UK).

2.3.3 IEP determination

The isoelectric points of as-received alumina and alumina ball-milled for 24 h were measured using an acoustophorometer (ESA 8000, Matec Applied Sciences, Hopkinton, MA, USA).

2.3.4 Adsorption isotherms

In order to determine the influence of milling on the adsorption of dispersant, adsorption isotherms were plotted for (i) the as-received alumina and (ii) the alumina wet ball-milled without addition of dispersant and dried. The milling conditions were adjusted to obtain similar characteristics (grain size distribution and specific surface area) as for a 24 h wet ball-milling in the presence of 0·6 wt% of PMAA-NH_3. Slurries were centrifuged after 24 h of equilibrium. The resulting supernatants were dried at 110°C. The drying temperature was chosen according to a thermogravimetric analysis, in order to remove water and to avoid the thermal degradation of the PMAA-NH_3. Then, the residual amounts of dispersant were weighed, and therefore the adsorbed amounts were determined.

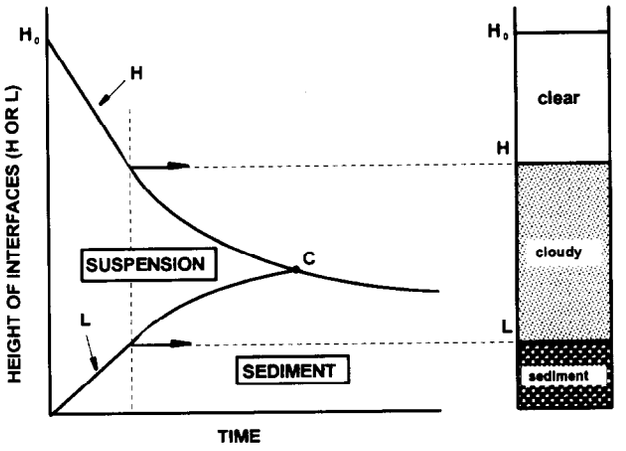


Fig. 3. Typical settling curve for a non-flocculated suspension with uniform concentration, from Tiller and Khatib.[8]

2.3.5 Infra-red study

Infra-red spectroscopy has commonly been used to investigate the adsorption of polymers. For instance, Joppien and Hamman[13] studied the adsorption of polyester resin on silica, alumina, titania and iron oxide powders, and gave spectroscopic evidence of loop formation by the polymers. Fontana and Thomas[14] reported the adsorption of poly(alkyl methacrylate) on silica surfaces. They noted that the C=O stretching mode at ~1710 cm^{-1} shifted to lower wavenumber (22–30 cm^{-1}) when the polymer was adsorbed on the silica surface by hydrogen bonding. These studies were mainly performed on high surface-area powders, using transmission spectroscopy.

In this work, transmission spectroscopy was used to detect eventual desorption of PMAA-NH_3 from the alumina surface and/or changes of the PMAA-NH_3 structure due to degradation by ball-milling. The slurries, prepared for each milling time, were centrifuged. Both the centrifuged alumina and the supernatant were dried at 110°C in order to analyse the alumina with the species adsorbed on its surface, as well as organic species dissolved in the supernatant, respectively. In the infra-red analysis we neglect the PMAA-NH_3 present in the water contained in the sediment, which can deposit on the surface of alumina during drying. The KBr pellet method was used for spectral analysis, using thoroughly mixed and pressed pellets containing 1 mg of the investigated sample in 100 mg of KBr.

Spectra of dried alumina and of supernatant were collected after each milling time; they were also obtained for a water solution of PMAA-NH_3 and for the dried, as-received, alumina to get spectral references.

Table 1. Evolution of particle size and specific surface area

Milling time (h)	*Average particle size (μm)*	*Surface area ($m^2 g^{-1}$)*
0	35·00	0·7
2	4·53	0·8
8	3·18	2·1
13·5	2·61	2·7
15	2·58	3·2
18	2·42	3·3
21	2·20	4·3
24	1·19	4·9

3. Results and Discussion

3.1 Evolution of particle size and specific surface area

Average particle size decreases and surface area increases with milling time (Table 1). Whereas the observed viscosity became high for milling times longer than 18 h, the particle size continues to decrease. Figure 4 shows that the particle size decreases rapidly at the beginning of the milling (from 35 to 4·5 μm after 2 h), with no significant evolution of the specific surface area. During the first stage of the milling, brittle aggregates are broken down [Fig. 5(a)]. For longer times of treatment, the particle size continues to decrease slowly (from 4·5 to 1·2 μm after 22 h) with a rather linear increase of the specific surface area, suggesting that deaggregated particles are now milled during this second stage [Fig. 5(b)].

3.2 Rheological study

The rheological behaviour of the slurry obtained after ball-milling for 24 h is represented by curve 1 in Fig. 6. A subsequent addition of 0·6 wt% PMAA-NH_3 to this slurry resulted in a marked decrease of the viscosity (Fig. 6, curve 2). This suggests that the initial amount of dispersant (0·6 wt%) used for ball-milling was too low to prevent the agglomeration of alumina particles with a sevenfold increase in surface area (from 0·7 to 4·9 $m^2 g^{-1}$ or conversely that the efficiency of the dispersant decreased during milling.

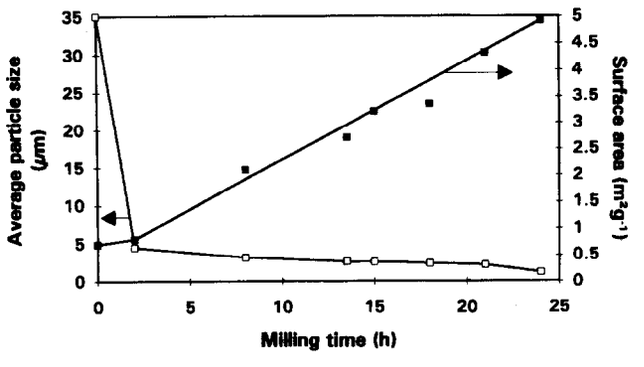
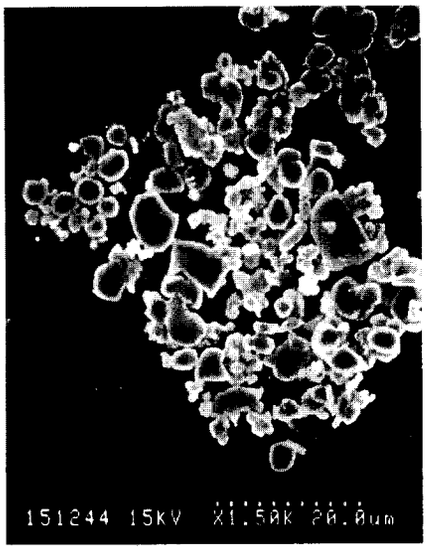
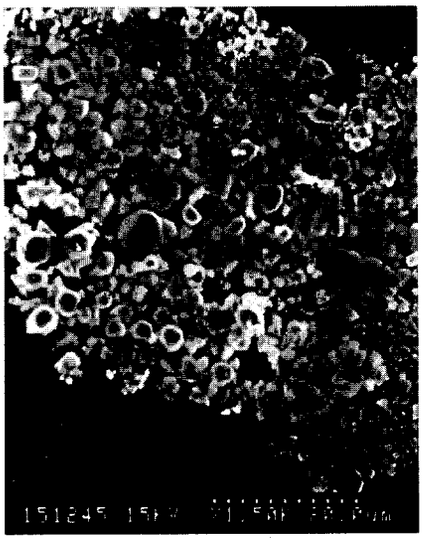


Fig. 4. Evolution of particle size and surface area during ball-milling.



(a)



(b)

Fig. 5. Alumina particles after ball-milling for 2 h (a) and 24 h (b)

In order to elucidate this point, the alumina slurry containing 0·6 wt% PMAA-NH_3 was ball-milled for 24 h and the suspension was then centrifuged. The clear supernatant was removed and the solid phase calcined at 600°C for 1 h to eliminate organic species contained in the sediment. The powder obtained was redispersed under the same conditions as previously with 0·6 wt% dispersant (Fig. 6, curve 3). Curves 2 and 3 being quite similar, one can safely conclude that an amount of 0·6 wt% of fresh PMAA-NH_3 is large enough to provide good dispersion of the alumina powder when the specific surface area reaches 4·9 $m^2 g^{-1}$.

3.3 Sedimentation tests

During sedimentation tests, two behaviours were observed depending on the milling time. After

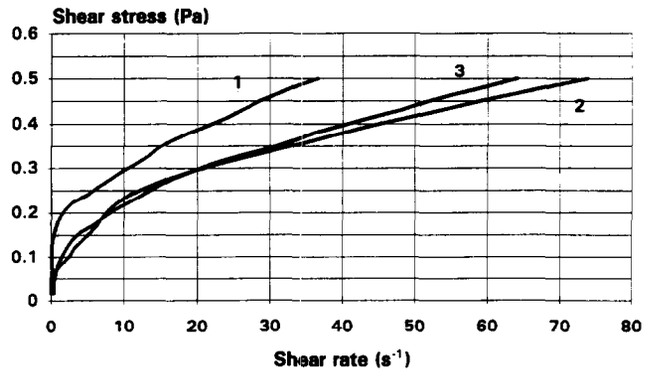


Fig. 6. Influence of PMAA-NH_3 degradation on the rheological properties of alumina suspensions: (1) ball-milled for 24 hours with 0·6 wt% PMAA-NH_3; (2) same as (1), but 0·6 wt% PMAA-NH_3 was added just before the end of ball-milling, and (3) same as (1), the powder was then centrifuged, dried and pyrolysed before redispersion with 0·6 wt% PMAA-NH_3.

milling times shorter than 15 h, three zones were observed in the tubes during the test, corresponding to a sediment bed, a cloudy liquid zone and a clear liquid zone. Slurries behave as non-flocculated suspensions. The sediment volume increased with time (Fig. 7). No compression of sediments was observed. For milling times longer than 15 h, only two zones were observed, i.e. a clear liquid zone and a sediment bed. The sediments formed rapidly and their volume decreased with time, an observation which is typical of flocculated slurries (Fig. 8).

The heights of the final equilibrium sediments obtained after various milling time, are shown in Fig. 9. The equilibrium height of sediment (H_{eq}) was the smallest after 13·5 h of milling. After 15 h H_{eq} is slightly higher, but particles in suspension always form a cloudy zone. For milling times longer than 18 h, H_{eq} increases continuously with milling time. Equilibrium height of sediment is reached more rapidly for slurries milled for long times, i.e. 90 min for a 18 h milling and 300 min for a 13·5 h milling. After 13·5 h of milling, particles reagglomerated and the stability of the slurries decreased.

Sedimentation tests confirm that the dispersant lost its efficiency during ball-milling.

Figure 10 shows the difference between the equilibrium sediment volumes of the slurries milled for 24 h with and without a subsequent addition of 0·6 wt% PMAA-NH_3 at the end of milling. The addition of PMAA-NH_3 allowed an

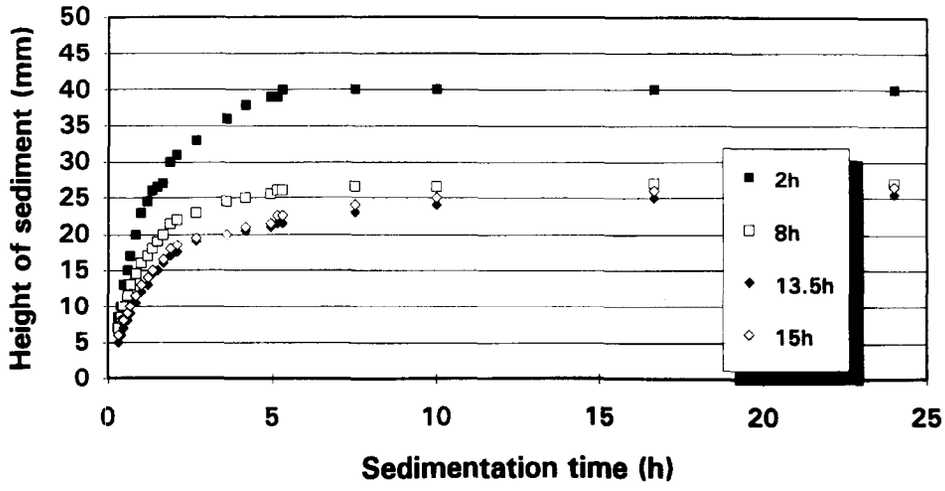


Fig. 7. Settling of alumina suspensions ball-milled for 2, 8, 13·5 and 15 h.

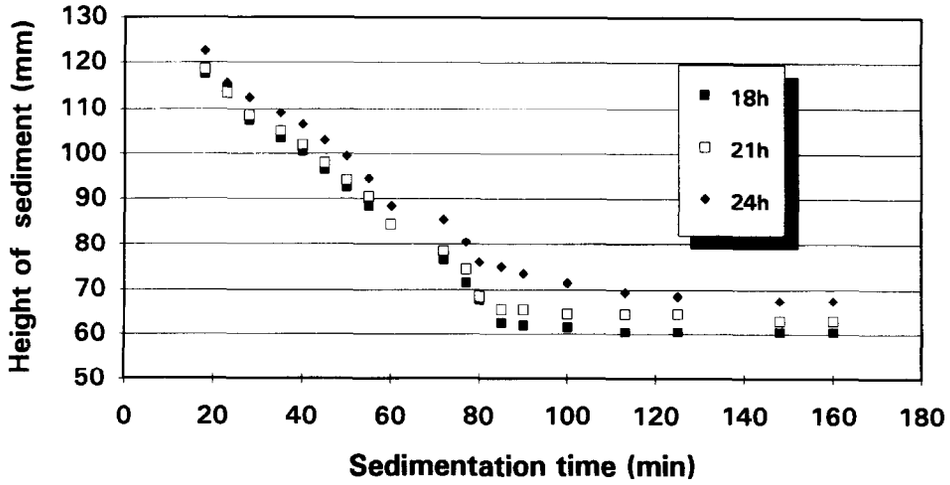


Fig. 8. Settling of alumina suspensions ball-milled for 18, 21 and 24 h.

important decrease of the sediment volume, while changing drastically the settling behaviour. Thus, additional PMAA-NH_3 redispersed the agglomerated particles.

Many factors can decrease the efficiency of the dispersant and then deteriorate the state of the dispersion during milling: (i) change in the specific surface area of the powder, then modification of the amount of adsorbed dispersant, (ii) change of the nature of surfaces of particles, then modification of the zeta potentiel and adsorption of the dispersant onto these particles, (iii) change in pH, then the degree of dissociation of PMAA-NH_3 and the charge on the particles and (iv) degradation of the dispersant.

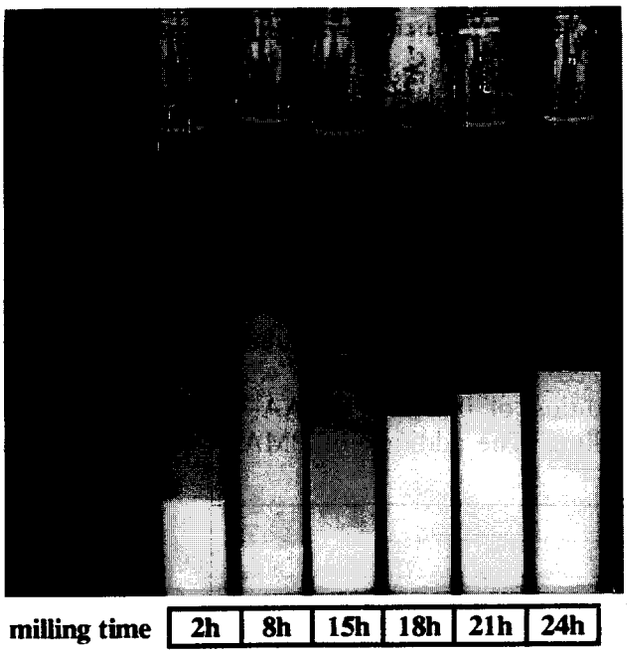


Fig. 9. Influence of milling time on the equilibrium height of the alumina sediment.

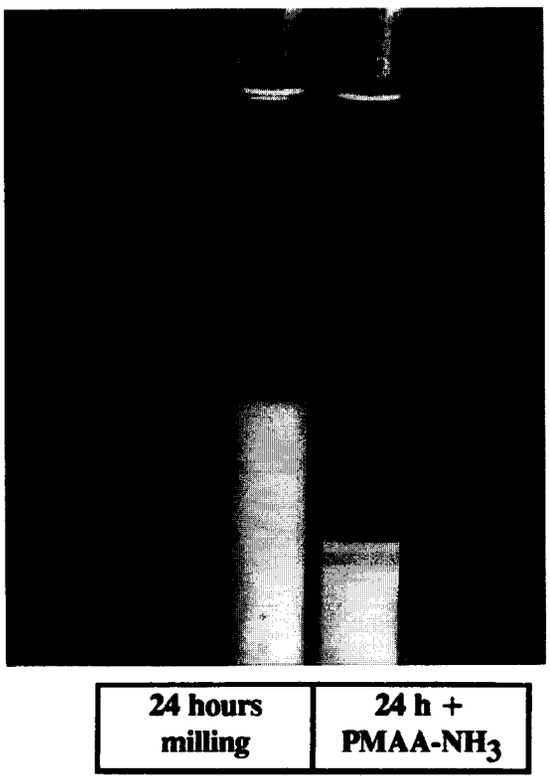


Fig. 10. Influence of an addition of PMAA-NH_3 on the equilibrium height of the alumina sediment.

The rheological measurements suggested that the initial amount of dispersant (0·6 wt%) used for ball-milling was sufficient to provide a good dispersion of the alumina powder when the specific surface area increased up to 4·9 $m^2 g^{-1}$.

The IEP value of the P122 alumina increased from 7·8 for the as-received powder to 8·8 after a 24 h of wet milling. On the other hand, the pH of the slurry varied from 8·5 for the as-received powder to 9·6 after a 24 h of wet milling (Fig. 11). Perrin[15] reported an amorphization of the surface of particles of a similar alumina during dry ball-milling, associated with a decrease of the number of acidic sites, then with an increase of the IEP. The same behaviour was reported in the case of wet ball-milling of an alumina powder.[16] The evolution of the pH during milling may be attributed to the passage in solution of cations (Ca^{2+}, Mg^{2+}, Na^+) contained as impurities in the as-received alumina powder. These impurities are mainly located on the surface of alumina particles. For pH values higher than the IEP of alumina, divalent ions adsorbed onto the negative surface of alumina particles increased the affinity of the negatively charged PMAA-NH_3 with alumina.[16]

The milling modified both the nature of the alumina surface and the adsorption/desorption of cations. These parameters may greatly affect the adsorption of the dispersant. Figure 12 shows adsorption isotherms of PMAA-NH_3 on as-received alumina and alumina previously ball-milled without addition of dispersant and dried. The adsorption of PMAA-NH_3 onto ball-milled alumina was three times less than for unmilled powder.

During milling, the basic pH of the solution was maintained higher than the IEP, so the surface of the alumina particles remained weakly

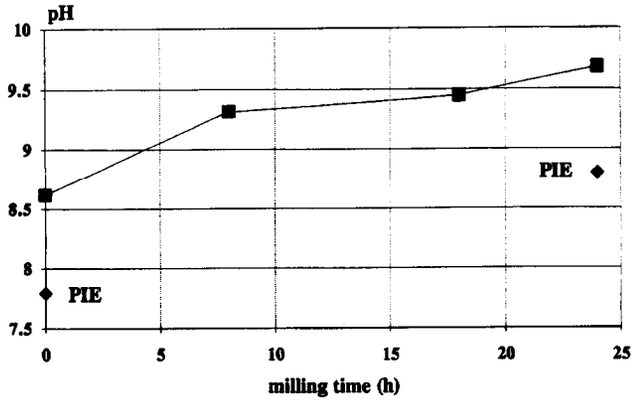


Fig. 11. Variation of pH and the IEP of alumina during wet ball-milling.

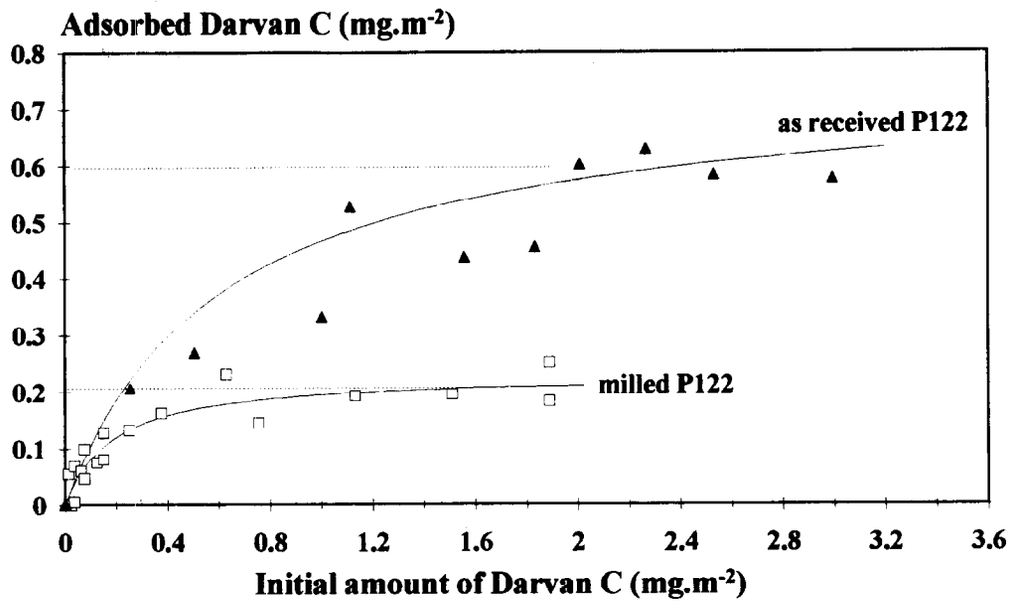


Fig. 12. Adsorption isotherms of PMAA-NH_3 on as-received alumina and alumina previously ball-milled without addition of dispersant and dried. The milling conditions were adjusted to obtain similar characteristics (particle size distribution and specific surface area) as for a 24 h wet ball-milling in the presence of 0·6 wt% of PMAA-NH_3.

negative and the PMAA-NH_3 entirely dissociated.[4] This suggests that variations of the IEP and pH did not significantly influence the adsorption of the dispersant.

The deterioration of the state of dispersion cannot be attributed to the lower adsorption of the PMAA-NH_3 onto the ball-milled alumina particles (i.e. to a lower charge of particles) because a viscosity as low as 25 mPa s was achieved for a 70 wt% suspension of milled particles (24 h) with an addition of 0·6 wt% (i.e. 1·2 mg m^{-2}) PMAA-NH_3, corresponding to the beginning of saturation of the surface (Fig. 12).

To summarize, the evolution of the specific surface area, the modification of the surface of particles and the change in pH seem to be not sufficient to explain the decrease of the efficiency of the dispersant during wet ball-milling of alumina. Thus, the degradation of the dispersant during milling remains the most probable factor which can affect the state of dispersion.

3.4 Infra-red analysis

Figure 13 shows IR spectra of dried pure PMAA-NH_3 and of the dried supernatant after milling times of 8, 18 and 24 h.

The bands at 1534 and 1415 cm^{-1} in Darvan C can be assigned to antisymmetrical and symmetrical vibrations of $-COO^-$ groups while the band at 1444 cm^{-1} can be assigned to the NH_4^+ deformation mode.

After 8 h of milling, a change of the dispersant was observed with the appearance of bands at 3525, 3450, 1688 and 1621 cm^{-1}. These bands may be attributed to amide functions ($-CO-NH_2$). According to this assumption, one explanation

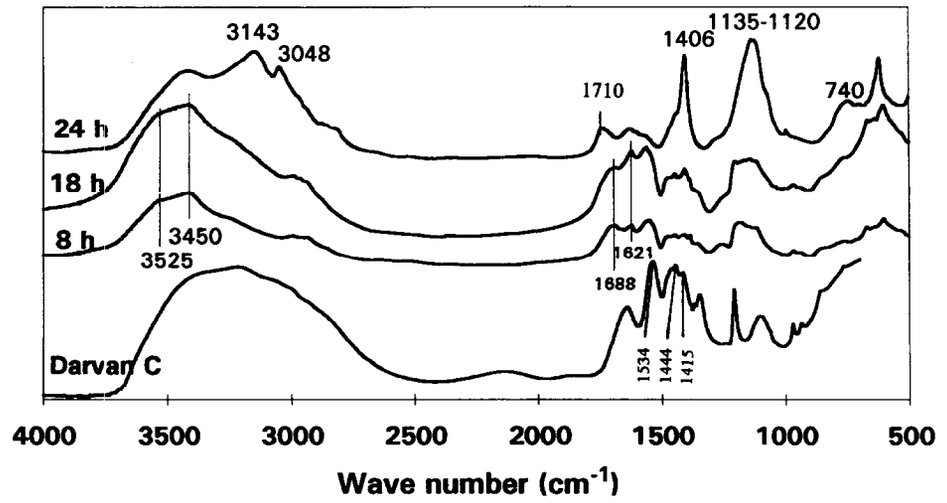


Fig. 13. Infra-red spectra of dried pure PMAA-NH_3 and of dried supernatant after milling times of 8, 18 and 24 h.

could be dehydration of the PMAA-NH_3 adsorbed on the alumina surface according to the global reaction:[17]

$$R\text{–}COO^-, NH_4^+ \rightarrow R\text{–}CO\text{–}NH_2 + H_2O$$

Bands near 1550 and 1400 cm^{-1} illustrate the presence of $-COO^-$ groups and indicate that dehydration is not complete. The $-COO^-$ groups can bind to the Al^{3+} on the surface of fine alumina particles remaining in suspension, in spite of centrifugation. Bands near 600 cm^{-1} illustrate the presence of alumina in the supernatant. The degradation of the dispersant observed with sedimentation tests between 13·5 and 18 h seems to result from a decrease of the polymer charge due to dehydration. Thus the increase of sediment volume after 13·5 h of milling, relative to some reagglomeration, can be attributed to a reduced electrostatic repulsion.

After 18 hours of milling, the IR spectrum is drastically different. Bands which appear at 3143, 3048, 1406, 1135, 1120 and 740 cm^{-1} are difficult to attribute. The appearance of the 1710 cm^{-1} band, which is characteristic of the C=O stretching vibration of monodentate COOX group,[18] is coincident with the disappearance of the $-COO^-$ groups. PMAA-NH_3 seems to be fully degraded, which can possibly in turn affect adsorption of the polymer onto the alumina surface.

The decrease of the efficiency of the PMAA-NH_3 dispersant, during milling, involved two stages. The first, at the beginning of milling, may be attributed to reduced electrostatic repulsion due to decrease of the charge by dehydration. The second stage, after longer milling times, may be due to complete neutralization of the dispersant by the formation of COOX groups. In addition, the results obtained suggest that the dispersant has been irreversibly altered during milling.

4 Conclusion

Results of this study showed that the ammonium salt of poly(methacrylic acid), generally used as dispersant of alumina, was degraded during wet ball-milling. Degradation takes place in two stages:

(1) the decrease of the charge by dehydration induced a small agglomeration of alumina particles, but the rheological behaviour of the slurry was not affected; and
(2) the complete neutralization of the dispersant by the formation of monodentate COOX groups, which can lead to a desorption of the polymer from the alumina surface, involved a significant agglomeration.

The deterioration of the dispersant certainly depends on experimental conditions: size and velocity of the mill, size of the media relative to size of the feed material, loading of the mill, relative volumes of media and feed material, and viscosity of the slurry. Our results were obtained for slurries containing a low concentration of alumina (30 wt%). Industrial slurries contain up to 70–80 wt% of powder, for a capacity up to several tons. In this case, deterioration of dispersant involves a strong increase in viscosity and media could be hindered in their rotating movement. Then, milling could be less efficient as expected, and would require additional time, and energy, to produce the desired distribution of particle size.

A simple solution should be to add a determined amount of dispersant during milling, or just before the end, to balance its deterioration.

Acknowledgements

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