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A new processing aid for dry-pressing: A copolymer acting as dispersant and binder

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Abstract

PV*X* copolymers containing both carboxylate ($-COO^-$) and hydroxyl groups (vinyl alcohol) are synthesized with the objective to ensure the double function of dispersant and of binder for dry-pressed green parts.

Carboxylate groups are responsible for strong adsorption of copolymers onto alumina surface and can promote sufficient electrostatic repulsive forces to achieve a good state of dispersion, similar to that obtained with a classical ammonium polymethacrylate ($PMA-NH_4^+$) for a proportion of carboxylic groups in the copolymer larger than 35%. On the other hand, hydroxyl groups confer higher mechanical strength than PVA to the green pressed parts (4.2 MPa for 1.5 wt.% PV35 (35% $-COO^-$) versus 1.8 MPa for 1.5 wt.% PVA, with and without PEG as plasticizer, in the case of samples pressed at 120 MPa).

The high density of the green parts obtained with soft PV35 copolymer and the good adsorption of this compound onto alumina surface lead to a high mechanical strength of the pressed compacts. After addition of 1.5 wt.% PV35, the amount adsorbed (0.7 wt.%) confers a high cohesion to the spray-dried granules and the non-adsorbed copolymer (0.8 wt.%) reinforces adhesion between granules through interdiffusion of the low T_g polymeric films.

Then, synthesized PV*X* copolymers have proved to be efficient dispersants for aqueous suspensions of alumina and also efficient binders for dry-pressing, even for concentrations as low as 1.5 wt.%.

Keyword: Binder

1. Introduction

The forming of advanced ceramics generally requires the use of organic additives, in order to confer to the system desired properties of flow and cohesion.[1–5] In aqueous systems, charged polyelectrolytes are commonly used as dispersants to enhance suspension stability and to impede particle flocculation, thus leading to both high solid loadings and low viscosities.[6–10] The adsorption of polyelectrolyte molecules onto the surface of the powder results in the formation of a double electrostatic layer that surrounds each particle and leads to electrostatic repulsive forces between particles.[11,12] Ammonium or sodium polyacrylates are currently used for dispersion of concentrated alumina suspensions.[13,14]

Binders are often introduced in ceramic processing to confer additional cohesion to the green parts.[15,16] In the spray-drying and dry-pressing process, the addition of these organic binders in the starting suspension is required, first to confer adequate cohesive strength and free flowing properties to the sprayed granules, and, secondly to improve the mechanical strength of the green compacts. The binder must satisfy a compromise since it should be "soft" enough to allow granules to deform during pressing, and at the same time "hard" enough to confer cohesion to the spay-dried granules and mechanical strength to pressed green bodies.[17] Polyvinyl alcohol (PVA) is largely used as a binder in dry-pressing of ceramics.[18,19] But the adsorption of the binder is

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generally considered as weak in comparison to that of the dispersant. This generates an heterogeneous distribution of the organic phase in the ceramic green part.[20] Indeed, during water removal from the droplets in the spray-dryer, the non-adsorbed, soluble, PVA tends to migrate with water to the surface of granules. Baklouti investigated the binder distribution in spray-dried alumina agglomerates and in the pressed green parts.[20] He showed the great influence of the heterogeneous binder distribution on the mechanical properties of the pressed samples.

Moreover, the use of various organic additives in a suspension often involves interactions not only between the additives and the ceramic powder but also between the additives themselves. For instance, one can observe a competitive adsorption of these additives onto the surface of the ceramic particles, which can result in a decrease of the dispersant and/or the binder efficiency.[21]

In order to avoid, or at least to minimize, these problems, a solution consists in using copolymers which can adsorb onto the grain surface and which can play the simultaneous role of dispersant and binder. In this context, the aim of the present work was to evaluate the dispersant and the binder efficiency of synthesized copolymers bearing two different groups, i.e. one ionized function which facilitates adsorption on alumina particles and provides a sufficient density of charge to disperse particles in water as well as one neutral function, which provides cohesion to the spray-dried granules and to the pressed green parts.

2. Experimental procedure

2.1. Starting materials

An α-Al_2O_3 powder (P172SB, Pechiney-France) with a mean particle size of 0.4 μm and a specific surface area (BET) of $10\,m^2\,g^{-1}$ was used.

Polyelectrolyte copolymers of sodium acrylate and of vinyl hydroxide, were synthesized (PV*X* copolymers, *X* being the molar proportion of functional carboxylic groups). PV*X* copolymers, with $X = 20$, 35 and 55, were prepared by radical copolymerisation of acrylic acid and of vinyl acetate. Copolymerisation was carried out in methanol in presence of benzoyl peroxide as initiator during 5 h in a backward flow. The PV*X* copolymer was then obtained after hydrolysis of the acetate fraction of the previously synthesized copolymer. The hydrolysis was carried out by methanolysis using NaOH as catalyst. Once hydrolyzed, the formed copolymer precipitated instantaneously in methanol. After filtration, the copolymer 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 colloidal titration with a cationic polyelectrolyte (PAD-Cl^-, poly(chloride *N*,*N*,*N*-trimethyl ammonium ethyl acrylate)) studied in earlier work and alternating moieties in polymeric chains were confirmed by differential scanning calorimetry (DSC).[22,23]

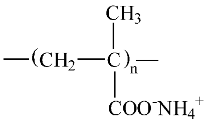
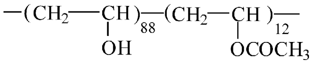
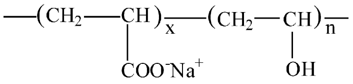
A commercial ammonium salt of polymethacrylic acid as dispersant (PMA-NH_4^+, Darvan-C, Vanderbilt, UK), a commercial polyvinyl alcohol as binder (PVA 4-88, $M_w = 31{,}000$, $T_g = 70\,°C$ (dry PVA), Mowiol, Hoechst, D) and polyethylene glycol as classical plasticizer (PEG400, $M_w = 400$, Union Carbide, USA) were used for comparison. The structure of the various polymers used in the present work and the corresponding molecular weights are given in Table 1.

The glass transition temperature T_g of synthesized polymers was determined by differential scanning calorimetry. The average molar masses (M_w) of synthesized copolymers were estimated from intrinsic viscosity measurements (Ubbelhode viscometer) using Mark–Houwink relation[24] $[\eta] = KM_w^{\alpha}$, where parameters K and α are characteristics of each polymer/solvent couple.

2.2. Adsorption isotherms

Experiments concerning the adsorption of polymers were performed by adding given amounts of the copolymer solution,

Table 1
The copolymers PV*X* are synthesized (*X* corresponds to the COO^- molar fraction (%) of carboxylic groups in the copolymer)

Organic additives	Structures	T_g (°C)	M_w
PMA-NH4+	 $-(CH_2-C(CH_3)(COO^-NH_4^+))_n-$	–	15,000
PVA	 $-(CH_2-CH(OH))_{88}-(CH_2-CH(OCOCH_3))_{12}-$	70 “dry PVA”	31,000
PV*X*	 $-(CH_2-CH(COO^-Na^+))_x-(CH_2-CH(OH))_n-$	$X = 20$	
		46	20,000
		$X = 35$	
		35	20,000
		$X = 55$	
		27	17,000

PMA-NH_4^+ (Darvan-C®, Vanderbilt, UK) and PVA (PVA 4-88, $M_w = 31{,}000$, Mowiol, Hoechst, D) are commercial polymers. The copolymers PVX are synthetised (*X* corresponds to the COO molar fraction (%) of carboxylic groups in the copolymer).

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 min under an output power of 200 W and shaken for 24 h to reach equilibrium. Then they 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 a cationic PAD-Cl^- polymer and orthotoluidine blue as indicator. 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 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-NH_4^+ 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 down to 1 ppm.

2.3. Powder processing and characterisation

Spray-drying of suspensions containing 50 wt.% alumina (20 vol.%) was performed with a laboratory spray-dryer (Büchi 190). The inlet temperature of the spray-drier was fixed at 200 °C, which in the present experimental conditions leads to an exit temperature of 104 °C.

The copolymer was first dissolved in distilled water, the alumina powder added, and the dispersion was deagglomerated by ultrasonic treatment with a power of 300 W applied during 2 min. Then, the dispersion was submitted to mechanical stirring during 2 h. The preparation of the alumina suspensions containing the PMA-NH_4^+ dispersant and the PVA binder, with and without addition plasticizer (PEG), was performed in two steps. The alumina powder was first deagglomerated in water by ultrasonic treatment with the dispersant, then the binder and the plasticizer were added and the suspension was submitted to agitation during 2 h.

The average diameter of the granules obtained is relatively small (10–20 μm), which leads to a poor flowability of the powder. However, the use of this laboratory equipment makes possible the evaluation of the efficiency of additives.

The spray-dried alumina powders were pressed uniaxially. The spray-dried alumina containing organic additives was previously dried at 100 °C for 1 h before pressing to be sure of the value of T_g. Indeed, the T_g of polymer will depend on the water content, water being a plasticizer of PVA. The powder morphology and the fracture surfaces of green pressed samples were observed by SEM (Cambridge S260). The size distribution of spray-dried granules was measured by laser light diffusion (Malvern 2000). The strength of the green samples was measured immediately after pressing by the diametral compression test (Brasilian test) performed with a universal testing machine at a loading rate of 0.5 mm mn^{-1}. The strength was calculated according to the following expression:

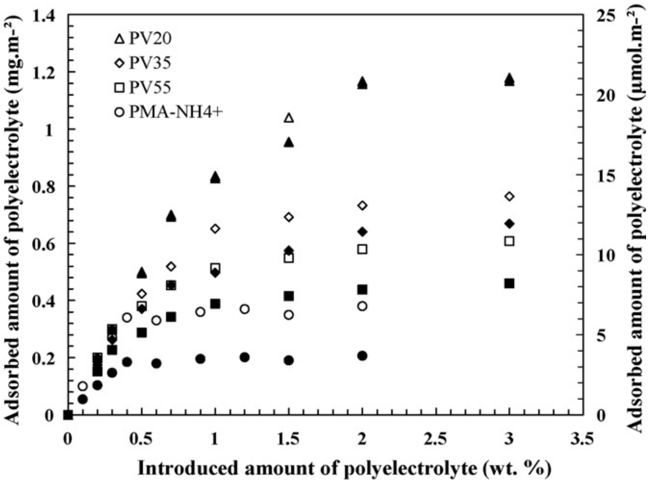


Fig. 1. Adsorption isotherms of the polyelectrolytes onto P172SB alumina (pH 8.5–9). Open and black symbols are related to mg m^{-2} and μmol m^{-2} scales, respectively.

$$\sigma_r = \frac{2F}{\pi D l} \tag{1}$$

where F is the load applied at fracture, D and l are the diameter and the thickness of the sample, respectively. These mechanical measurements were performed immediately after forming because the strength may vary with time after ejection.[15] The reported values of strength correspond to the average of three tests.

3. Results and discussion

3.1. Adsorption isotherms

For the three synthesized copolymers and for the PMA-NH_4^+, the amount adsorbed onto the alumina surface at pH 8.5–9 increases as the quantity added increases, until a plateau is reached (Fig. 1). The shape of these isotherms suggests a monolayer adsorption of the polyelectrolyte, whatever the polymer composition. The adsorption is complete for additions lower than 0.3 wt.% in the case of PMA-NH_4^+, PV55 and PV35, and lower than 0.7 wt.% of PV20. No polymer was detected in the supernatant until these values were reached. Such an observation indicates a rather high affinity type adsorption. The amount adsorbed on the plateau decreases as the content of carboxylic groups in the polymer increases. The corresponding quantities adsorbed are about 0.36, 0.58, 0.67 and 1.17 mg m^{-2} for PMA-NH_4^+, PV55, PV35 and PV20, respectively. Such values correspond to respective adsorbed surface molar amounts of 4.27×10^{-6}, 8.11×10^{-6}, 10.89×10^{-6} and 21.66×10^{-6} mol m^{-2}.

The quantity of PMA-NH_4^+ adsorbed on the plateau (pH 9), i.e. 0.36 mg m^{-2}, is in agreement with that reported by Cesarano et al.[25] At pH 9, PMA-NH_4^+ is fully ionized, and its adsorption on the surface of alumina proceeds in a relatively flat configuration. The adsorption increase on the plateau as the fraction of carboxyl groups is reduced may be explained by a lower repulsion between ionisable groups inside the polymer chain. That allows a denser packing of the macromolecular chains on the alumina surface and an expected formation of loops in the adsorbed configuration as the fraction of hydroxy vinyl units increases. Then, more chains with a lower surface covering are required to get a saturated monolayer.

3.2. *Stability of the suspension*

When plotted versus the quantity of polymer added, the viscosity of the alumina suspension first decreases to reach a minimum at a given amount of dispersant. The optimum concentrations are about 0.4 wt.% for PMA-NH_4^+, 0.55 wt.% for PV55, 0.6 wt.% for PV35 and 0.9 wt.% for PV20 (Fig. 2). These values are in fair agreement with the adsorption data corresponding to the saturation of the solid surface, i.e. 0.36, 0.58, 0.67 and 1.17 wt.% for PMA-NH_4^+, PV55, PV35 and PV20, respectively. The minimum of viscosity is shifted towards larger polymer concentrations as the fraction of hydroxyl vinyl groups is increasing or as the fraction of carboxylic groups is decreasing. This can be attributed to: (i) 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 (ii) 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, PV55 and PMA-NH_4^+, PV20 bringing a too low density of charge. The evolution of the viscosity according to the weight fraction of the alumina in the suspension suggests a good efficiency of the synthesized polyelectrolytes and especially of the PV35 and PV55 (Fig. 3). Copolymers bearing 35% or 55% of carboxylate groups are efficient dispersants with a critical powder loading of 80 wt.% corresponding to 50 vol.% of alumina in the suspension.

3.3. *Spray-dried alumina powder*

One must keep in mind that the objective is to conjugate a dispersing effect brought by carboxylate groups and a binding one brought by vinyl groups in the PV*X* copolymers. On one hand, the state of dispersion obtained with 0.6 wt.% PV35 and with 0.55 wt.% PV55 (Figs. 2 and 3) is similar to that obtained with 0.4 wt.% of PMA-NH_4^+. On other hand, the expected binding effect of PV55 is likely lower than that of PV35 due to its lower concentration of hydroxyl vinyl groups. This is the reason why the PV35 copolymer, which represents a good compromise between the dispersing and binding effects, will be considered only in the following. In order to evaluate the aptitude of this PV35 copolymer to improve cohesion of the pressed parts, the alumina powder was spray-dried with different amounts of PV35, dry PVA and PVA with plasticizer (PEG400).

Besides the size, one of the parameters governing the flow properties of a spray-dried powder is the morphology, which should be spherical. The morphology of granules is conferred by the surface tension, which is exerted on the suspension droplets once formed at the exit of the nozzle in the spray-dryer. Fig. 4 shows granules of alumina spray-dried with 0.4 wt.% PMA-NH_4^+ + 3 wt.% PVA and with 1.5 wt.% PV35. An addition of 1.5 wt.% PV35 copolymer allows the formation of more spherical granules than those obtained with 3 wt.% of PVA, that will facilitate the flow of the granules. In both cases, the granules present a marked depression (donut shape). During spray-drying, the fine fraction of the powder in suspension and water soluble additives migrated towards the external surface of the granule where evaporation takes place and form an impermeable polymeric film. Once this layer was formed in the early stage of drying, the vapour pressure in the heart of the droplets creates a hole in this impermeable layer to allow the water to escape. The donut shape, observed after addition of 1.5 wt.% PV35 suggests that some polymer has migrated during spray-drying.

It is worthwhile to mention at this stage that one of the objectives of this work was to avoid, or at least to minimize, the

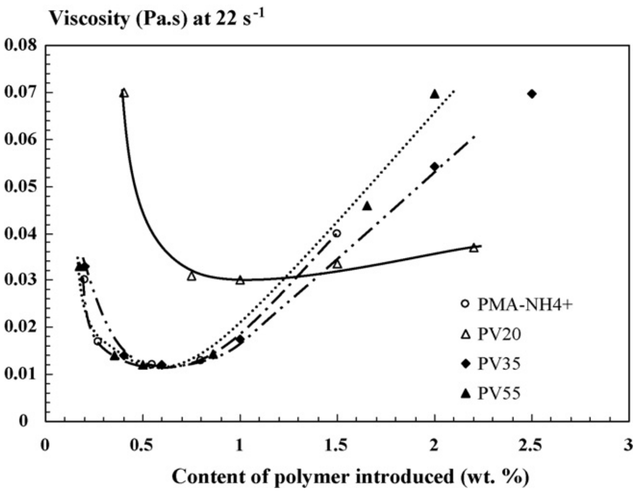


Fig. 2. Variation of the viscosity of the alumina suspensions in function of the concentration in PV20, PV35, PV55 and PMA-NH_4^+ (60 wt.% Al_2O_3, 22 s^{-1}).

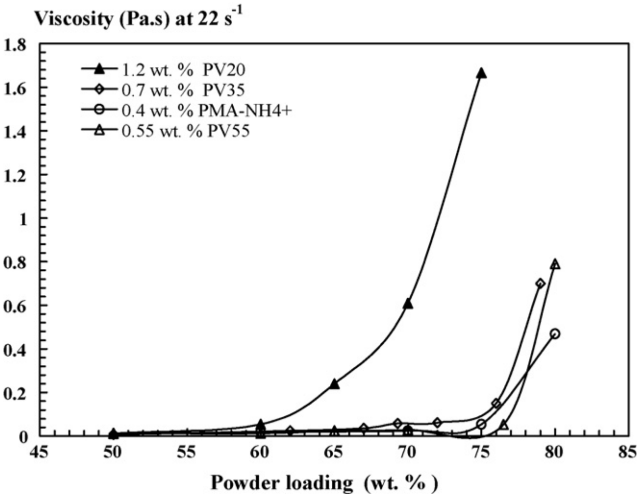


Fig. 3. Variation of the viscosity of alumina suspensions in function of the powder concentration for 1.2 wt.% PV20, 0.7 wt.% PV35, 0.55 wt.% PV55 and 0.4 wt.% PMA-NH_4^+.

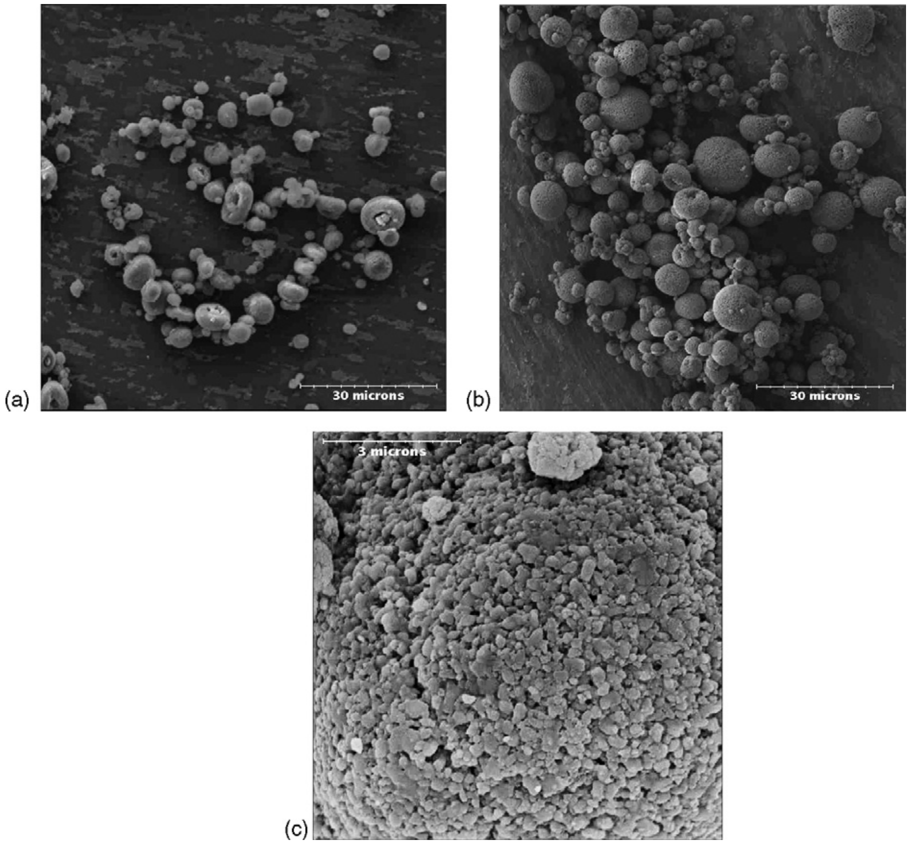


Fig. 4. Morphology of alumina spray-dried granules with (a) 0.4 wt.% PMA-NH_4^+ + 3 wt.% PVA, (b) and (c) 1.5 wt.% PV35.

binder migration onto the surface of the granules by adsorption of copolymer on the surface of the alumina grains. The acidic groups present on the chains of the macromolecules of PV35 strongly attach to surface alumina and avoid the migration. Nevertheless, the quantity in excess, not adsorbed, will be able to follow the departure of water during spray-drying. The saturation of the alumina surface is obtained for 10.89×10^{-6} mol m^{-2} of PV35, corresponding to 0.67 wt.%. Then, with and addition of 1.5 wt.% PV35, about 0.8 wt.% is non-adsorbed and is expected to migrate during drying. A precaution has to be taken concerning these values. Indeed, adsorption isotherms were measured at room temperature and the temperature inside the granules during spray drying is close to 100 °C. The adsorbed amount of polymer can slightly vary with temperature. A compact arrangement of the alumina grains in spherical granules were obtained with an addition of 1.5 wt.% of PV35 (Fig. 4c). The spherical and cohesive aspect of the granules can be attributed to the hydrogen bonds with the vinyl alcohol sequences of the PV*X* copolymer. A tangle of the chains adsorbed on the powder can also contribute to the cohesion of the granules.

The size distribution of granules (laser granulometer) prepared with 0.9 wt.% PV35 is given in Fig. 5. The size distributions obtained with 0.3 wt.% of PMA-NH_4^+ + 3 wt.% PVA and with 0.9 wt.% of PMA-NH_4^+ dispersant only are plotted for comparison. The average diameter of the granules increases when the fraction of carboxylic groups decreases, then when the fraction of vinyl binding groups increases. The smallest diameters were logically obtained with the PMA-NH_4^+ dispersant which does not contain any group able to act as binder.

The average diameter of the granules is increasing versus the quantity of PV35 copolymer introduced (Fig. 6). Introduction of 1.5 wt.% PV35 leads to granules having a similar size distribution to those obtained with 0.3 wt.% PMA-NH_4^+ + 3 wt.% PVA. The difference between the size distributions of the granules con-

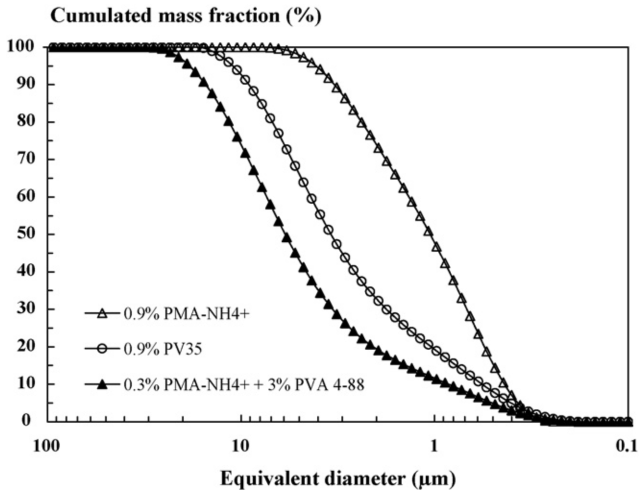


Fig. 5. Size distribution of alumina granules spray-dried with 0.9 wt.% of PV35 copolymer, 0.9 wt.% of PMA-NH_4^+ and 0.4 wt.% PMA-NH_4^+ wt.% + 3 wt.% PVA.

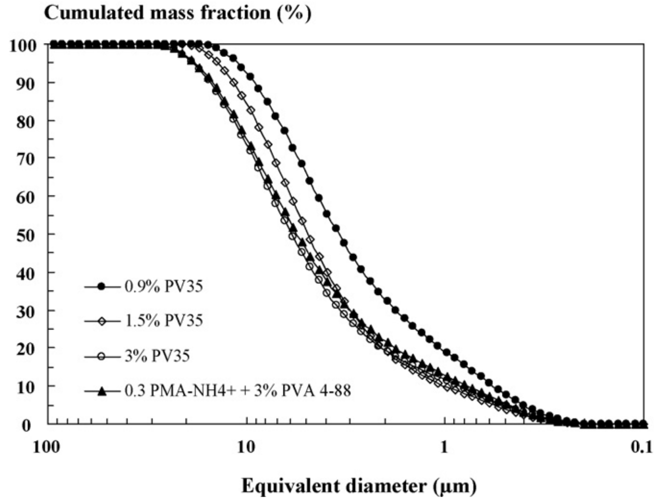


Fig. 6. Evolution of the size distribution of alumina granules spray-dried with different concentrations of PV35.

taining 1.5 and 3 wt.% PV35 remains small. PV35 is efficient to form granules by spray-drying, even at low concentration. This can be due to a more significant quantity of PV35 copolymer adsorbed on the surface of the alumina powder compared to PVA.

3.4. Pressed samples containing PV35

The variation of the relative density of green samples prepared from the spray-dried powder containing PV35, dry PVA and PVA + PEG follows a linear law versus logarithm of applied pressure (Fig. 7). For a given forming pressure, the density of pressed samples decreases as the content of PV35 is increasing (Fig. 8). This behaviour, observed for other commercial binders such as PVA, is due to increasing granule hardness, which makes them less deformable. The glass transition temperature (T_g) of PV35 is 35 °C and is slightly above the working temperature. Pressing is thus carried out with a more or less ductile copolymer. In the case of dry PVA used, with a T_g of about 70 °C, the granules are less deformable and the intergranular macroporosity is more difficult to resorb. The addition of a plasticizer (PEG) softens the PVA binder and improves the density of the green samples.

3.5. Mechanical properties

3.5.1. Mechanical strength of green parts

In absence of organic binder, a green part of P172SB alumina pressed under 120 MPa has a strength which does not exceed 0.1 MPa.[26] Introduction of 1.5 wt.% PV35 or PVA with

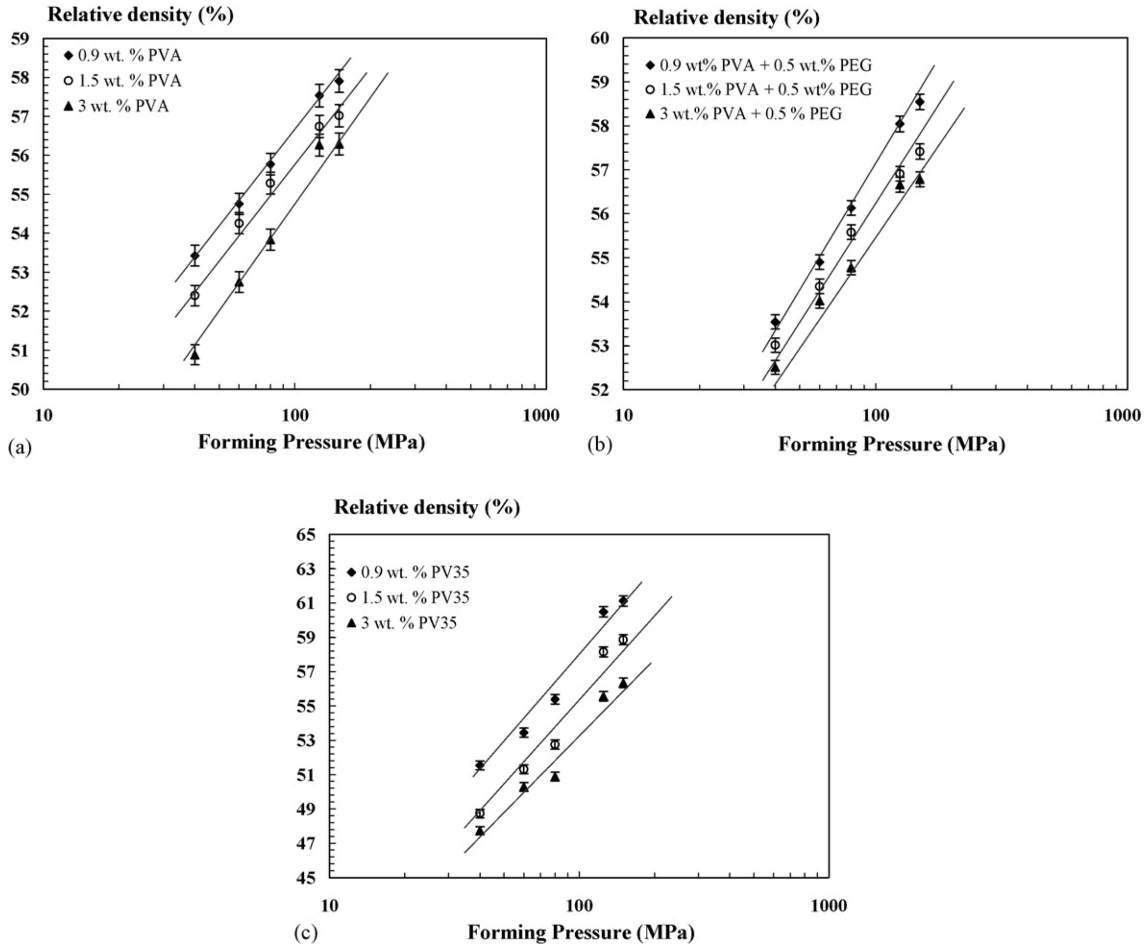


Fig. 7. Variation of density for alumina samples containing (a) PVA, (b) PVA + PEG and (c) PV35 in function of logarithm of the applied pressure.

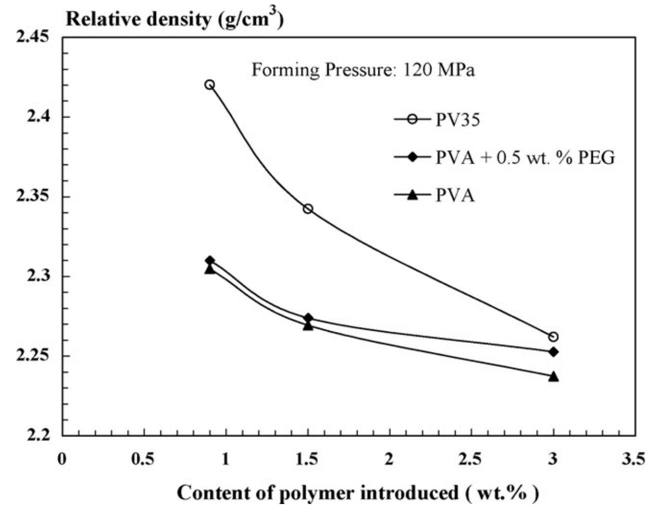


Fig. 8. Variation of density for alumina samples in function of the content of PV35, PVA and PVA with PEG after forming at 120 MPa.

and without PEG (Fig. 9) greatly improves the mechanical resistance of the green parts. This result confirms the binding effect of water-soluble polymers such as PVA or PV35 once introduced in the alumina suspensions. The evolution of the strength for green parts prepared from granules containing PV35 copolymer versus pressure is similar to that observed for polyvinyl alcohol with or without PEG, added in the same concentration, i.e. 1.5 wt.%. The strength is increasing with the forming pressure before more or less reaching a plateau. The strength of the green parts containing 1.5 wt.% PV35 copolymer is more than twice larger than that measured on parts containing the same quantity of dry or plasticized PVA, whatever the pressure applied (4.2 MPa after forming at 120 MPa, instead of 1.8 MPa for the dry PVA and 2 MPa for the PVA + PEG). These values confirm the good binding efficiency of the PV*X* synthesized copolymer. A first contribution to the increase of mechanical resistance can be the higher density of the green parts containing PV35 than those containing PVA, even plasticized, under the same pressure (2.35, 2.27 and 2.29 g cm^{-3} for PV35, PVA and PVA + PEG at 120 MPa, respectively). PV35 copolymer, with a T_g of 35 °C presents an almost ductile behaviour, with more deformable granules during pressing at room temperature, than fragile dry PVA with a T_g of 70 °C and even than PVA softened with PEG. The improvement of the mechanical properties of pressed parts containing PV35 can also be attributed to: (i) a more significant adsorption on the surface of the alumina particles (0.7 wt.% adsorbed) than in the case of the PMA-NH_4^+/PVA system, that will increase the resistance of the granules themselves and (ii) the formation of a polymeric film on the surface of the granules due to the migration of polymers in excess in the suspensions (about 0.8 wt.% for an addition of 1.5 wt.% PV35), that will increase the adhesion between granules.

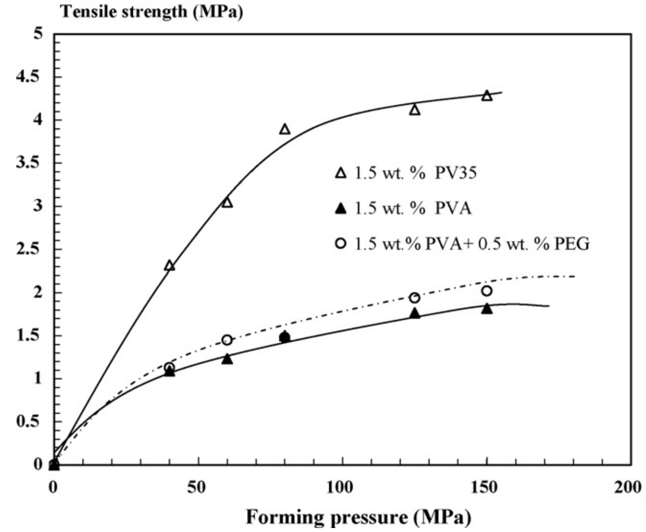
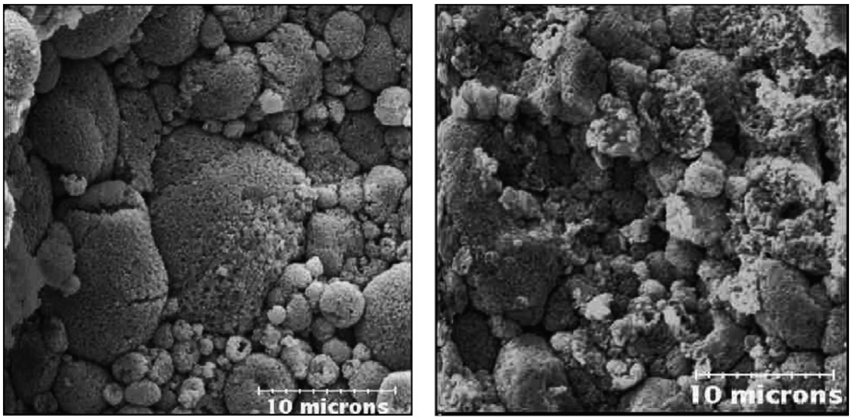


Fig. 9. Variation of strength for samples containing 1.5 wt.% PVA, 1.5 wt.% PVA + 0.5 wt.% PEG and 1.5 wt.% PV35 in function of the forming pressure.

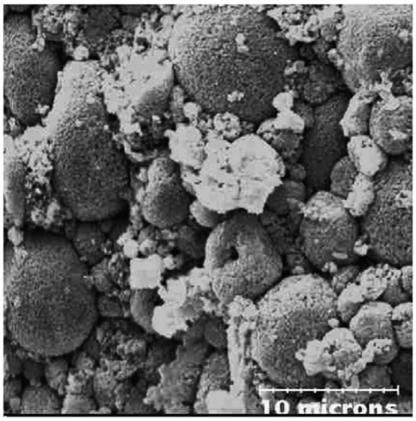
3.5.2. Mode of rupture of the green parts

The fracture surfaces of pressed green parts were observed by SEM (Fig. 10). Two modes of fracture were observed. The rupture can occur between the deformed granules (intergranular fracture) or the rupture is propagated inside the granules (intragranular fracture). The mode of fracture will depend on the relative mechanical resistance of the granule (link between the grains within the granule itself) and of the polymeric phase coating the granules (link between the granules). In the case of dry polyvinyl alcohol, the fracture of pressed samples pressed under 80 MPa is totally intergranular (separation of the deformed shells). The T_g of dry PVA (70 °C) forming the polymeric layer surrounding the granules due to the migration during spray-drying, is higher than the temperature of pressing, then the interdiffusion of polymer chains between organic shells surrounding the granules remains limited. The movements of the molecular chains of a polymer are very limited below the glass transition temperature. Adhesion between granules remains weak and the fracture propagates preferentially between the granules. In this case, one can consider that rupture is adhesive-type. In addition, micro-cracks are generated at the granule boundaries, during their deformation, because of the hardness of dry PVA.

The rupture of the alumina green parts containing 1.5 wt.% PV35 copolymer, pressed under 80 MPa, is mostly intragranular with a higher rupture strength than in the case of PVA. This suggests that the adhesion between granules is higher than the cohesion of granules themselves (intragranular rupture) and that the cohesion of granules is higher than in the case of PVA (higher rupture strength). The stronger adhesion between the granules can be due to the excess, non-adsorbed (about 0.8 wt.%) copolymer in the suspension, which is able to migrate to the surface of the granules during drying. In addition, the low T_g of PV35 is beneficial for the interdiffusion of polymeric films located at the surface of granules. The higher cohesion of granules obtained with PV35 can be attributed to a conjugate effect of higher adsorption of the PV35 on alumina surface and of a better compaction of the granules due to the low T_g of the PV35 copolymer. This leads to a larger content of binder, and a better spatial distribution, inside the granules.



(a) 1.5 wt.% dry PVA (b) 1.5 wt.% PV35



(c) 1.5 wt.% PVA + 0.5 wt. % PEG

Fig. 10. Fracture surfaces of samples containing 1.5 wt.% PVA, 1.5 wt.% PVA + 0.5 wt.% PEG and 1.5 wt.% PV35 (applied pressure = 80 MPa).

An addition of PEG as plasticizer of PVA confers similar mechanical properties than dry PVA (Fig. 9) for a concentration of 1.5 wt.% PVA, that is lower than concentrations generally used of about 3 wt.%. In presence of PEG, the fraction of intragranular fracture remains limited compared to that in the presence of soft PV35 (Fig. 10).

To summarize, advantages of the PV35 copolymer has been demonstrated with a better compaction ability of granulated powder and better mechanical properties of green parts than classical plasticized PVA, for a concentration as low as 1.5 wt.%. In addition, this copolymer, bearing carboxylic groups, ensure a good dispersion of the powder and does not require the addition of a dispersant.

4. Conclusion

Synthesized PV*X* copolymers, bringing both charged carboxylic and neutral vinyl hydroxyl groups have proven to be efficient dispersants for aqueous suspensions of alumina and efficient binders for dry-pressing, even for low contents introduced, as low as 1.5 wt.%.

Adsorption of PV*X* copolymers takes place by charged groups that anchor the polymer chain on specific surface sites of alumina, namely Al-$(OH_2)^+$. The amount of charged groups controls the effective charge density of the particle surface and the copolymer aptitude to be used as a dispersant. Addition of 0.6 wt.% PV35 (35% COO^- + vinyl alcohol groups) leads to a similar state of dispersion, with a low value of viscosity (about 10 mPa s for 28 vol.% alumina suspensions), to that obtained with 0.4 wt.% of the classical ammonium polymethacrylate (PMA-NH_4^+) dispersant.

The addition of the PV35 copolymer significantly improves the compaction ability and the mechanical properties of the green samples, with larger strength values than those conferred by classical PVA softened with PEG, for a concentration as low as 1.5 wt.% (4.2 and 2 MPa, respectively for samples pressed under 120 MPa). Generally, an addition of 3 wt.% of classical organic binder is required to confer a sufficient mechanical cohesion to the green pressed part.

The increase in mechanical resistance is attributed first to the higher density of the green parts containing ductile PV35 leading to more deformable granules during pressing than in the case of PVA and, secondly, to the larger adsorption of the PV35 on alumina surface which confers a high resistance to the granules. For an addition of 1.5 wt.% PV35, the adsorbed copolymer (about 0.7 wt.%), confers a good cohesion to the granules themselves and the non-adsorbed part (about 0.8 wt.%), allows the formation of a ductile polymeric film on the surface of the granules, that increases the adhesion between granules by interdiffusion of the low T_g polymeric films, also contributing to the mechanical strength of the compact.

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